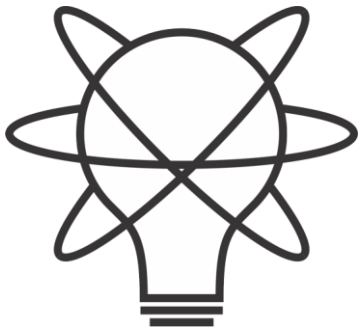


# Counting evolutions: a simple foundation for thermodynamics

Gabriele Carcassi



Assumptions  
of  
Physics

# Assumptions of Physics

- This talk is part of a broader project called Assumptions of Physics (see <http://assumptionsofphysics.org/>)
- The aim of the project is to find a handful of physical principles and assumptions from which the basic laws of physics can be derived

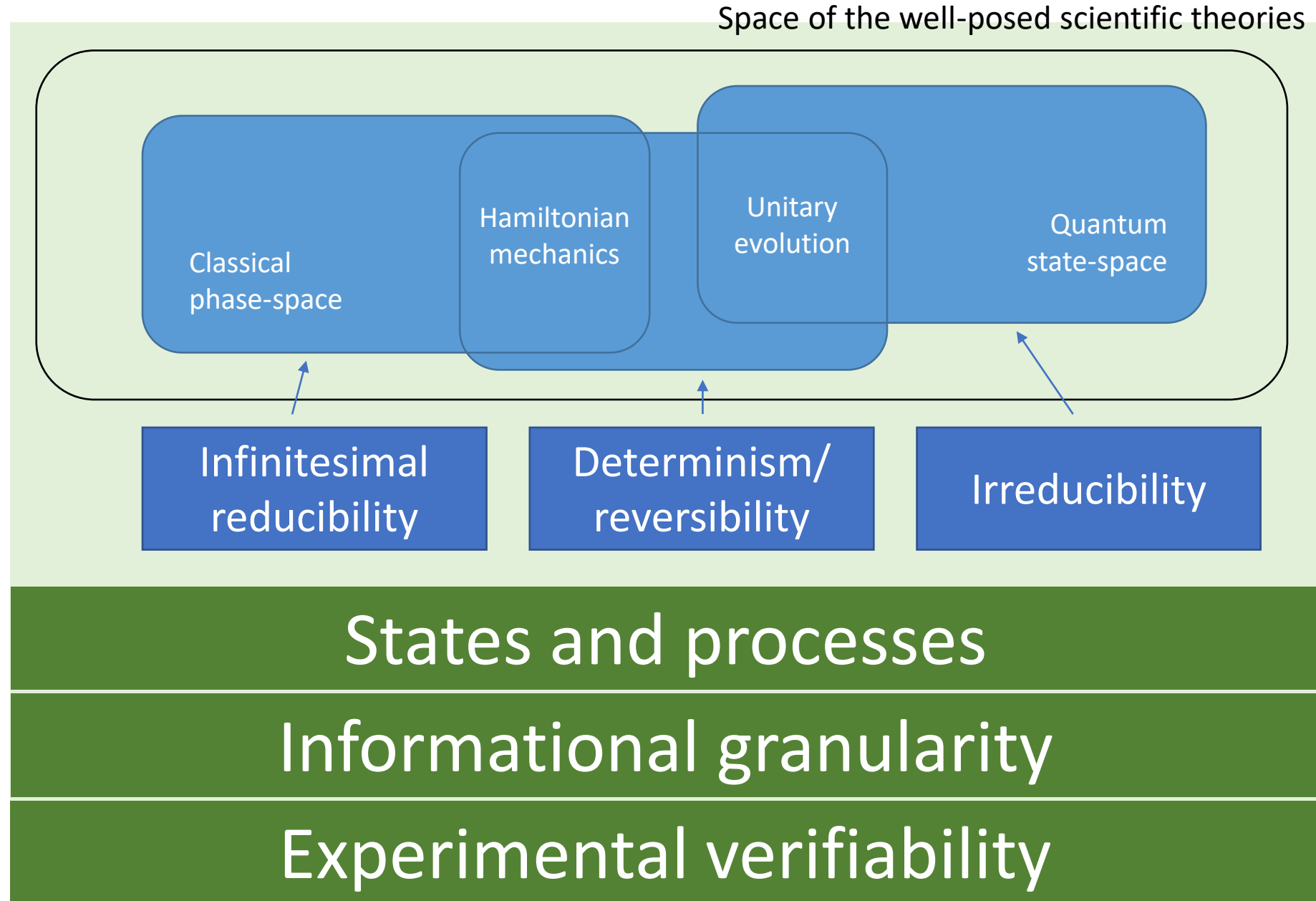
# Physical theories

Specializations of the general theory under the different assumptions

# Assumptions

# General theory

Basic requirements and definitions valid in all theories



# Assumptions of Physics

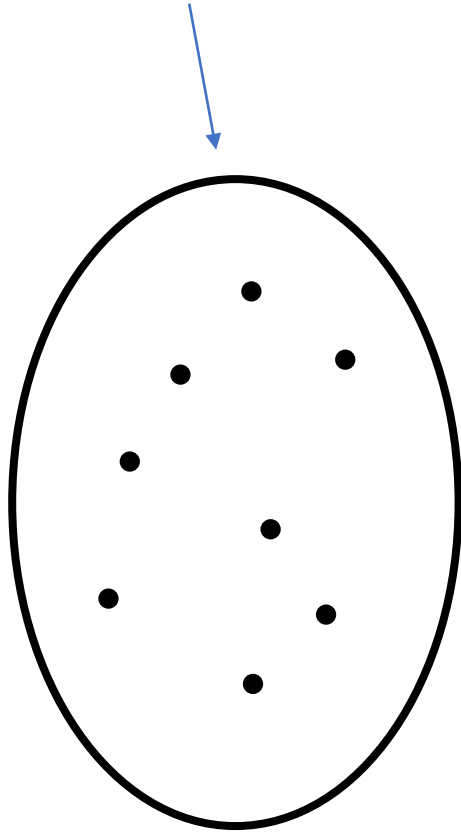
- Currently working on extending the framework to include non-deterministic and/or non-reversible processes
  - Required to make the theory general
- Thermodynamics is a good test case

# Outline

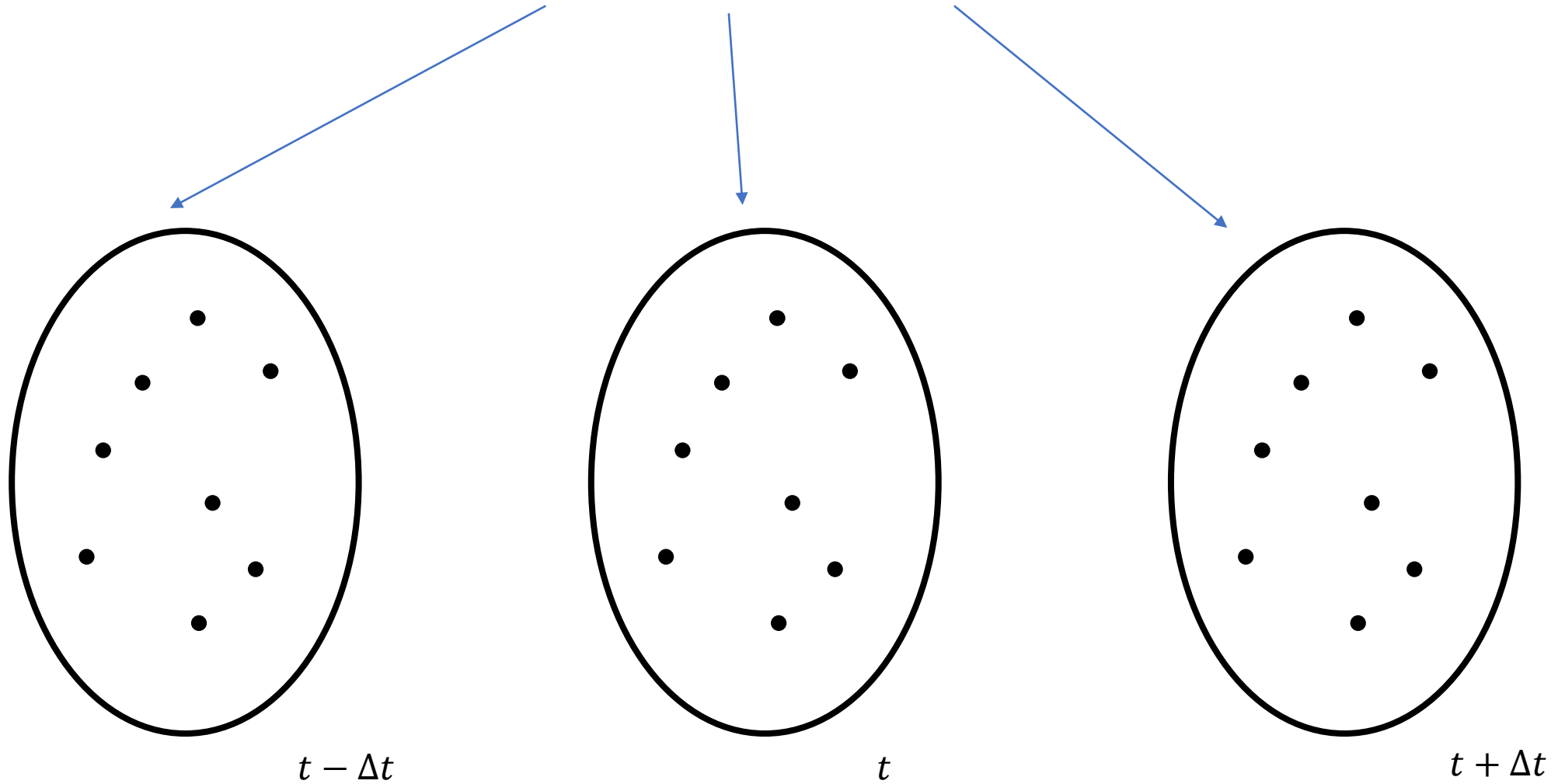
- Draft a simple general approach to describing processes
  - Define (process) entropy in very general terms and derive its fundamental link to irreversibility
- With a few extra assumptions, recover thermodynamics
  - Recover the thermodynamic laws
  - Show that the above entropy corresponds to the thermodynamic entropy for thermodynamic process
- Extend the discussion to other theories
  - Show that the above notion of entropy is already embedded in classical/quantum/statistical mechanics
  - Argue that the concepts we introduced are intrinsic requirements to properly define systems and states

States, processes and evolutions

State space of a system

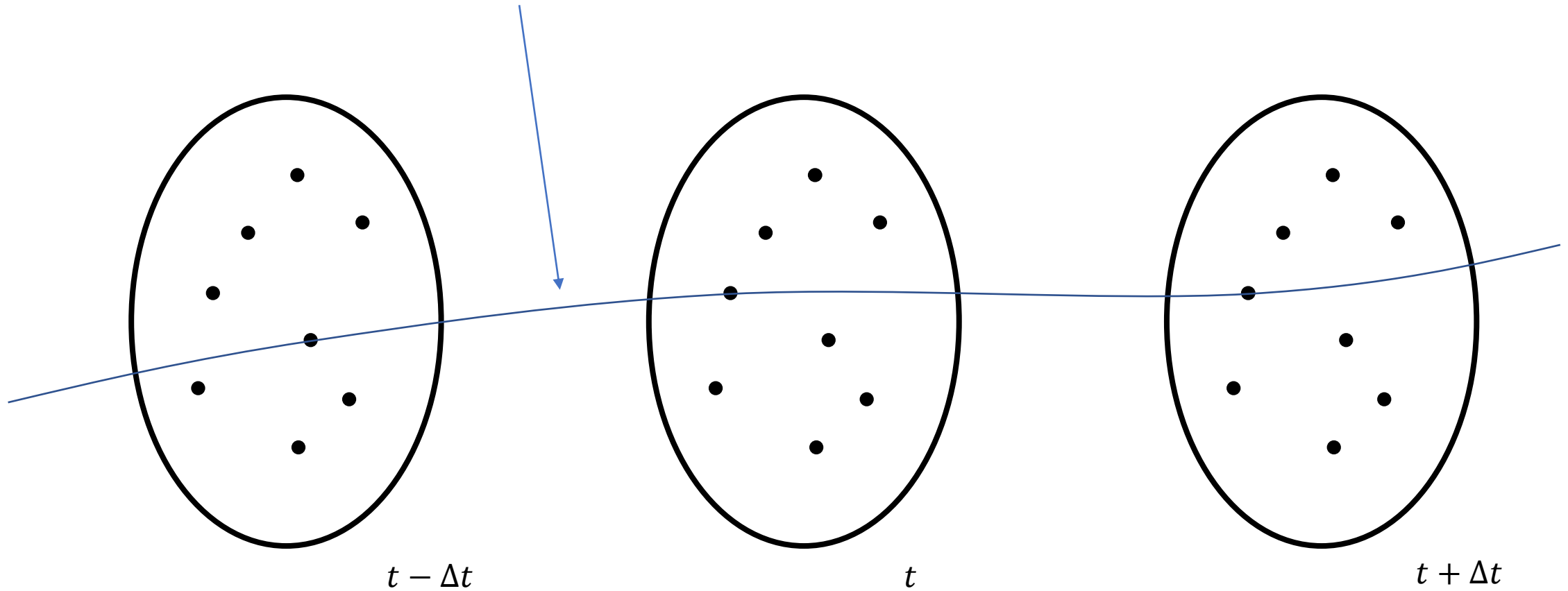


# State space of a system at different times

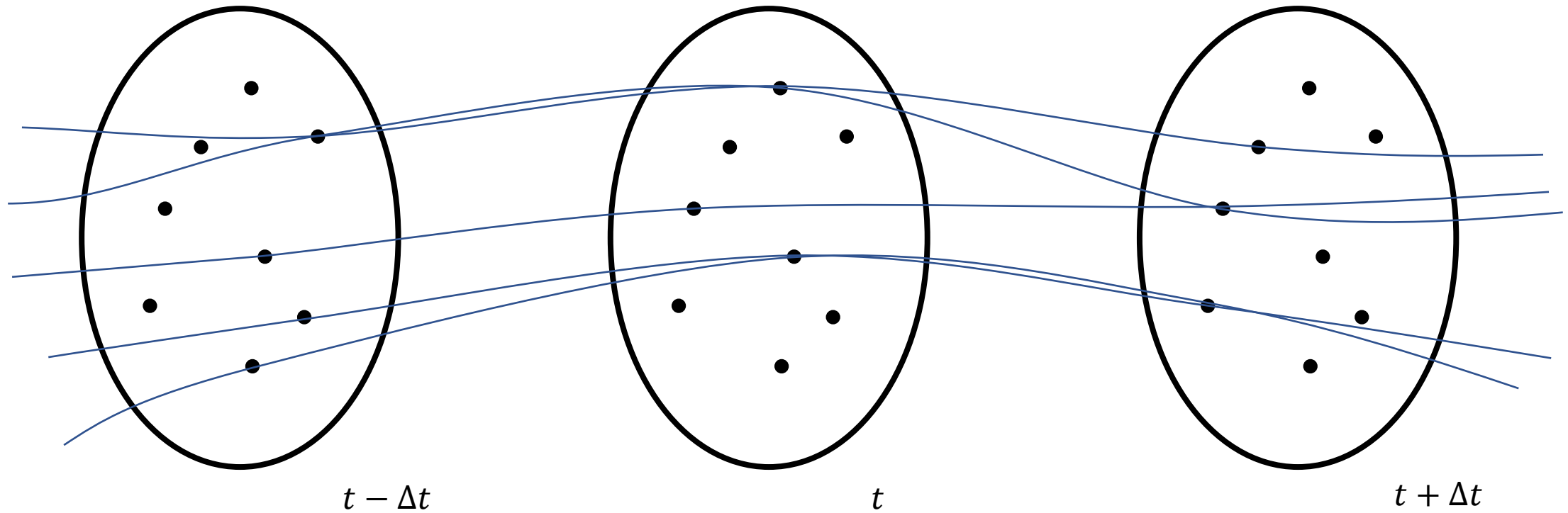




Evolution: complete description of the system at all times

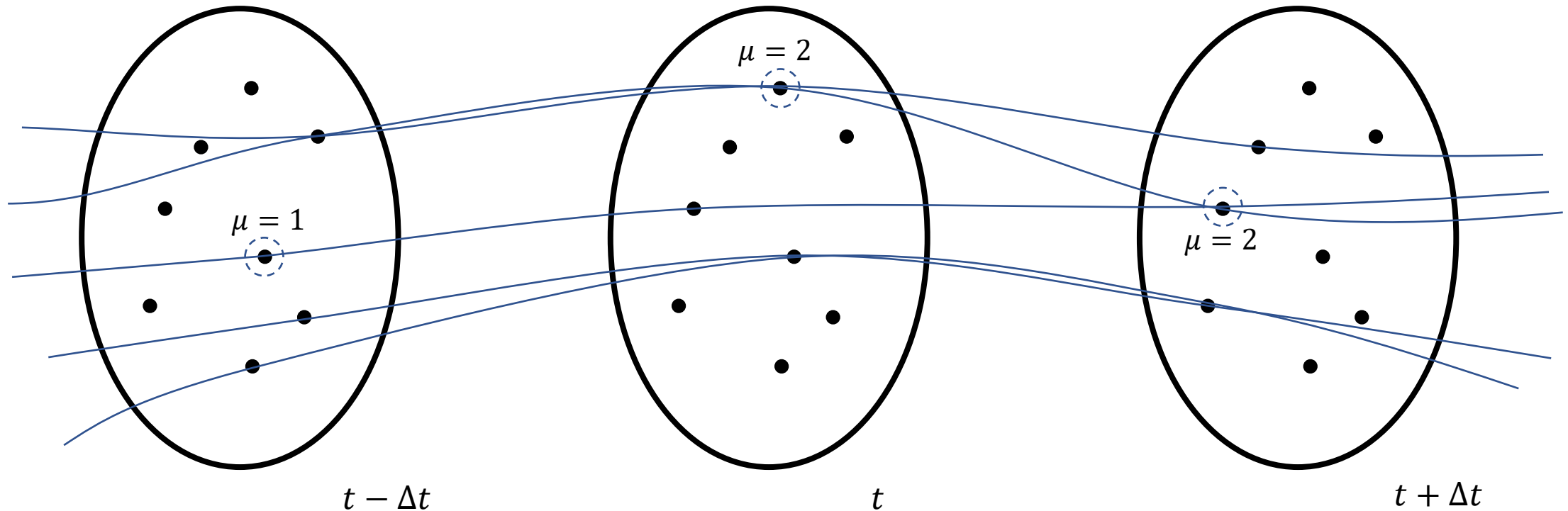


A process defines the set of all possible evolutions



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

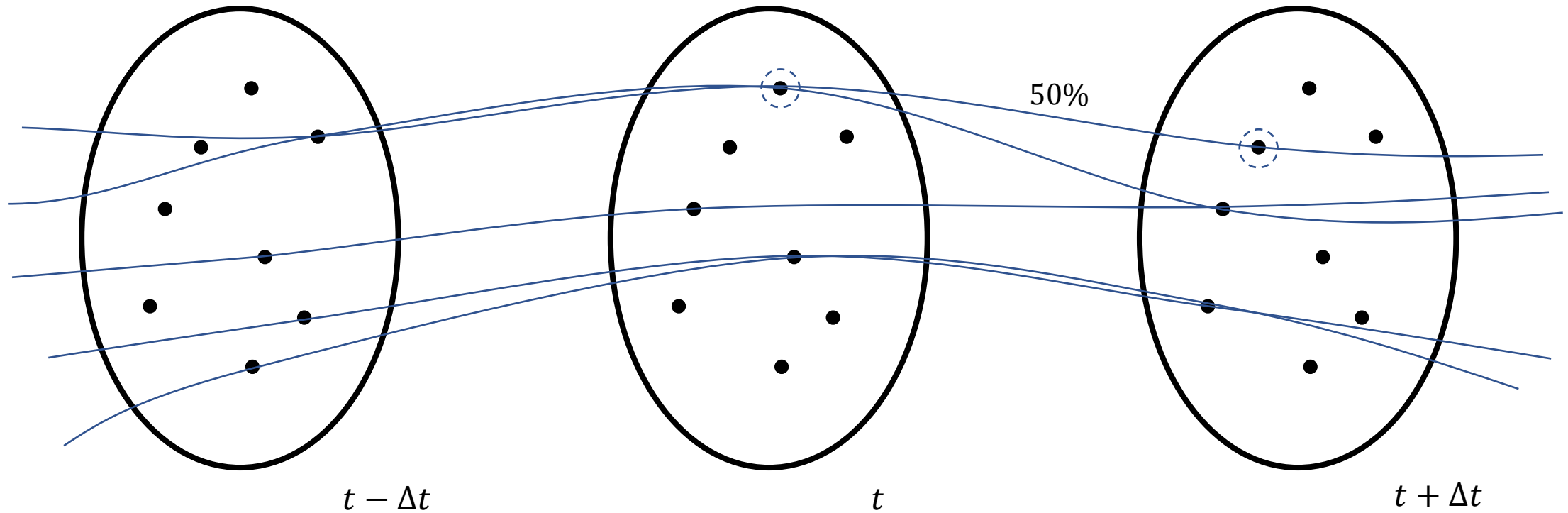
We can count the number of evolutions for a particular state  $s$  at a particular time with a measure\*  $\mu(s)$  since  $s$  identifies a set of evolutions.



\* The full mathematical characterization is a bit more complicated (i.e. preorder that leads to a family of measures)... but conceptually it is like that

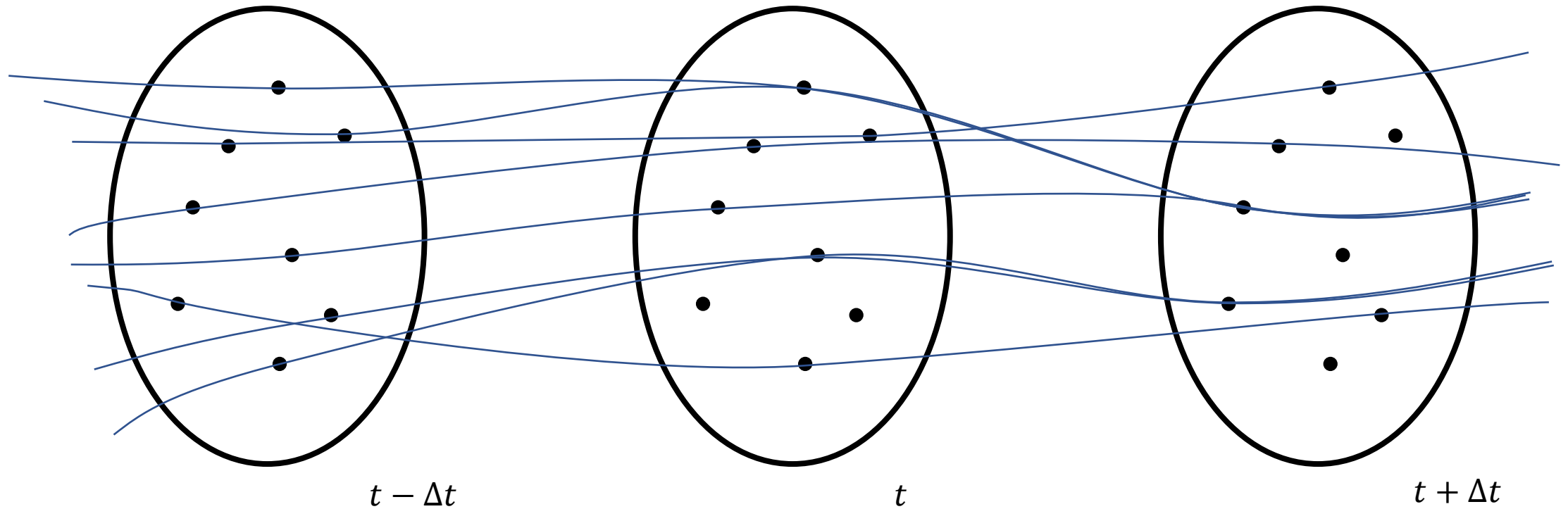
The probability  $P(s_1 | s_0)$  of having  $s_1$  given  $s_0$  corresponds to the fraction of evolutions that go from state  $s_0$  to state  $s_1$

$$\text{That is, } P(s_1 | s_0) = \frac{\mu(s_0 \cap s_1)}{\mu(s_0)}$$



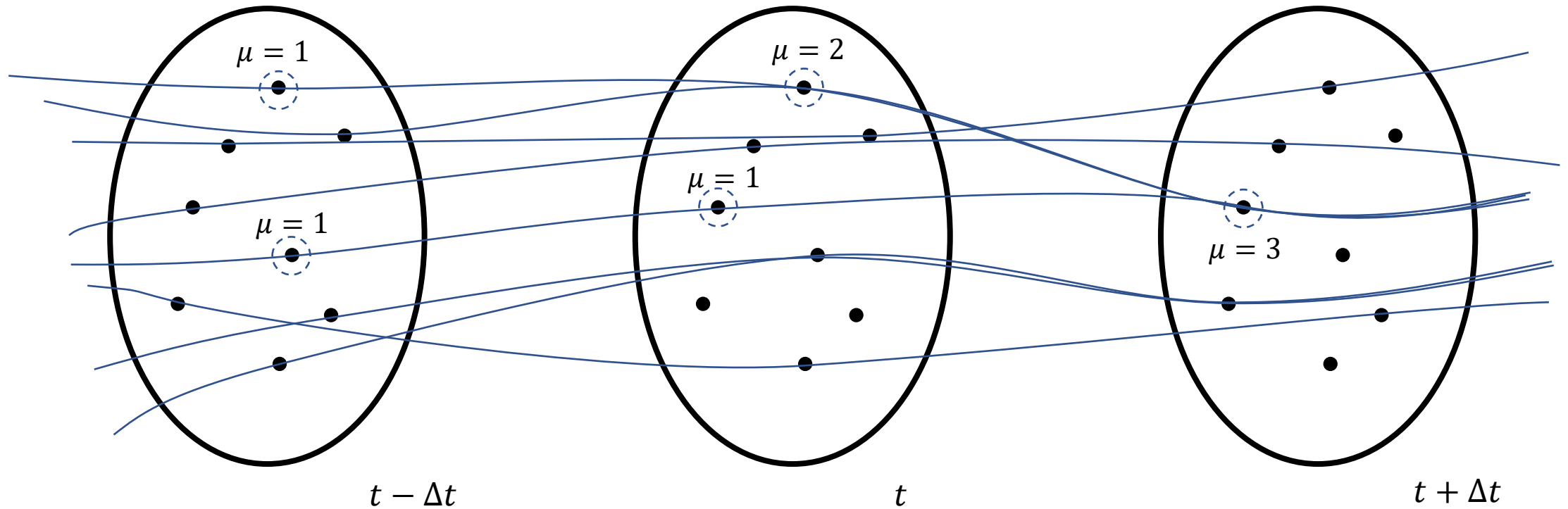
A process is deterministic if knowing the state at a time allows us to predict the state at a future time

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

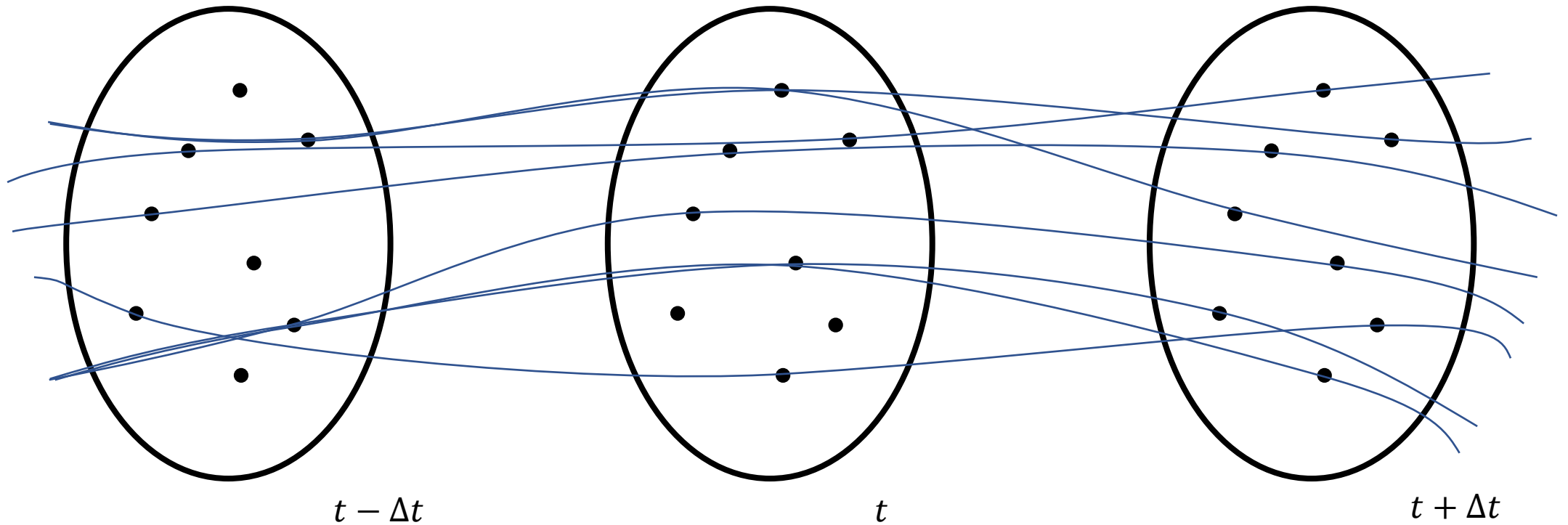


In a deterministic process, the evolutions can never split, only merge

$$\text{That is, } \mu(s(t + \Delta t)) \geq \mu(s(t))$$

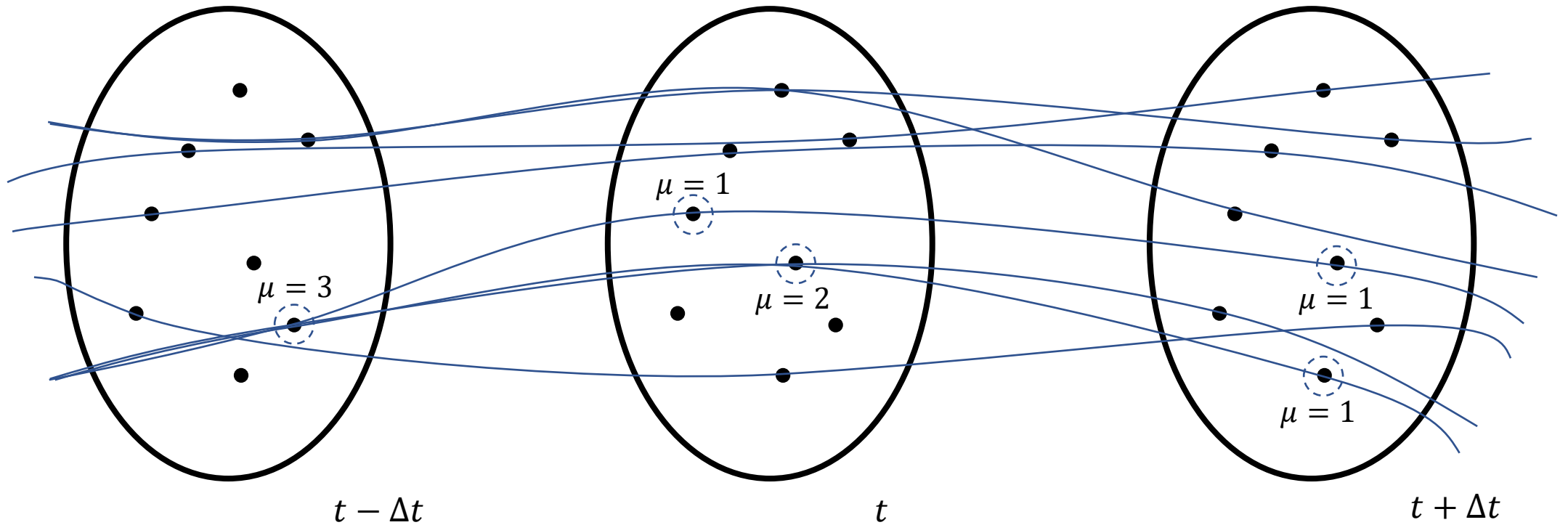


A process is reversible if knowing the state at a time allows us to reconstruct the state at a past time



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

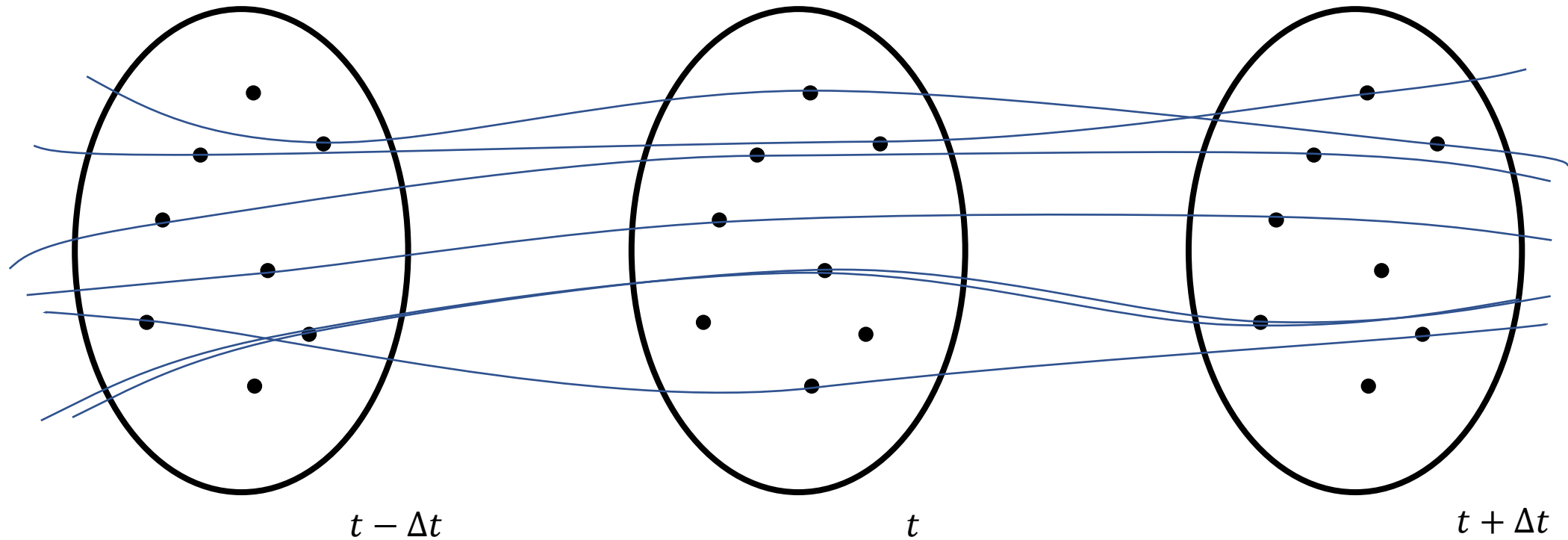
$$\text{That is, } \mu(s(t + \Delta t)) \leq \mu(s(t))$$





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

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



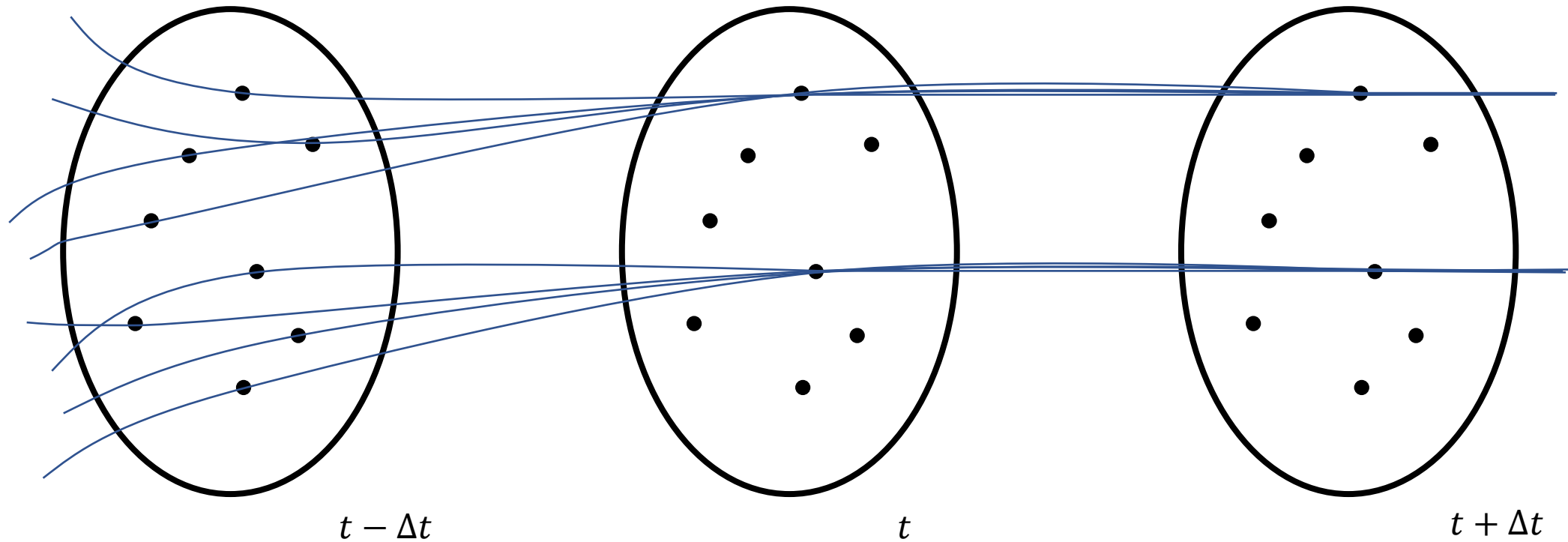
For a deterministic process

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

(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



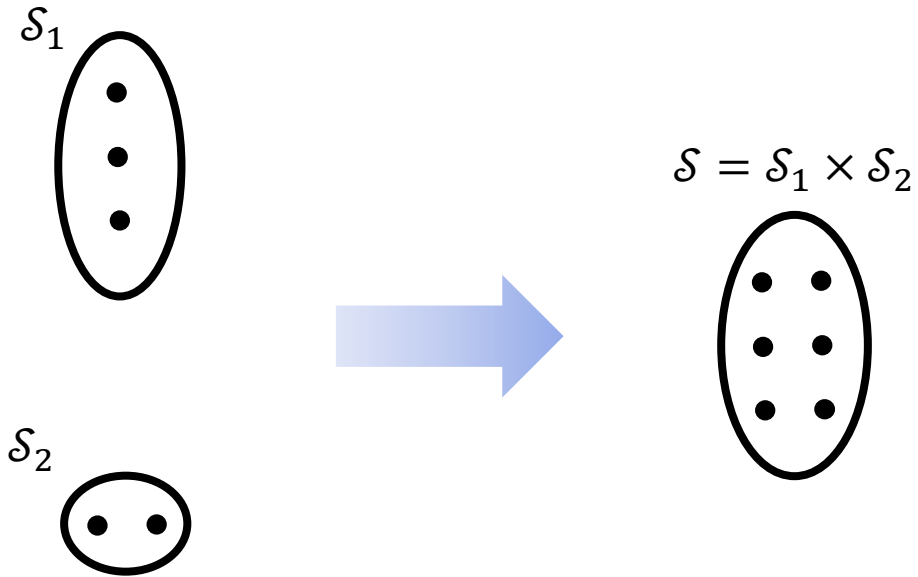
For a deterministic process

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

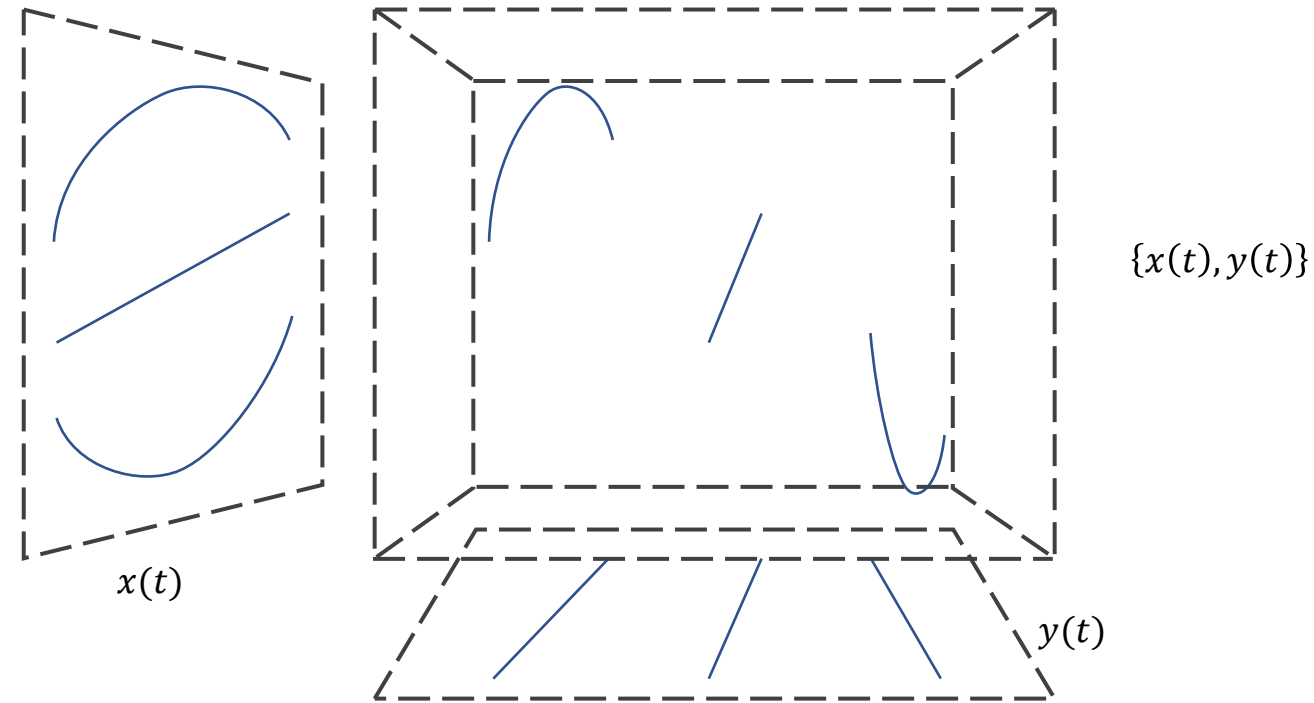
(equal if reversible)

(maximum at equilibrium)

Suppose we have a composite of two systems



State space is the product



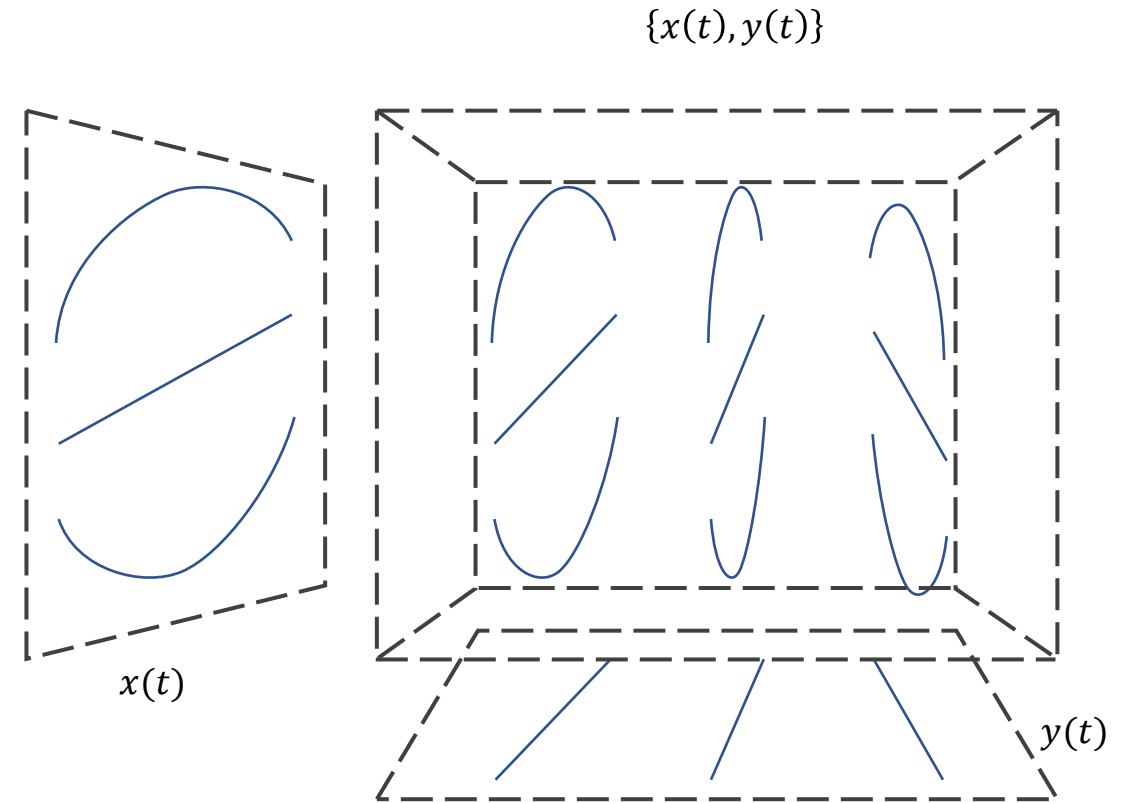
Evolutions, in general, are not the product: there may be correlations between the evolutions

Suppose we have a composite of two systems

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:  $\#(\mathcal{S}) = \#(\mathcal{S}_1)\#(\mathcal{S}_2)$

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

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

(equal if reversible)

(maximum at equilibrium)

# 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)

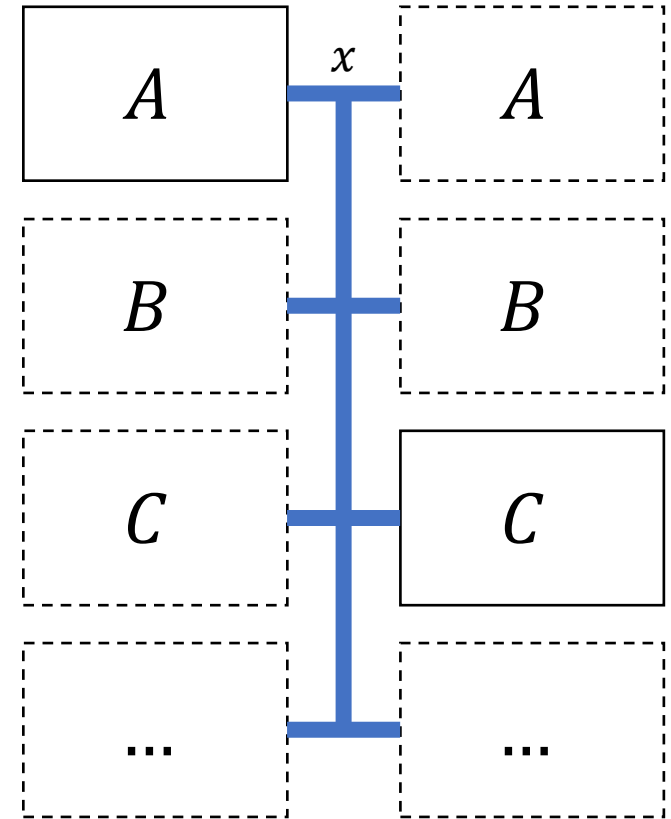


# Process entropy

- The main difference is that process entropy is process dependent
  - The same state in different processes (or in the same process at different times) will yield a different process entropy
- We typically think of entropy as state dependent
  - I.e. it is a state variable
- In what circumstances can process entropy be associated to the state? And why?

Note: if we want to “switch” processes, the evolution count at the junction must be uniquely defined

This is at least one reason why we would want to have a well defined entropy at the states at the junction points



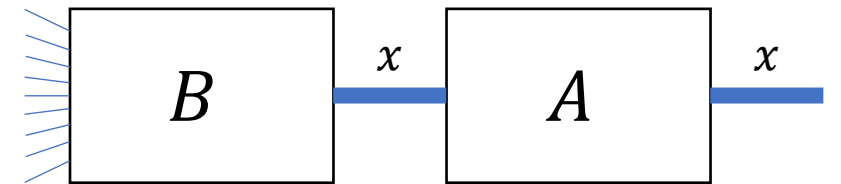
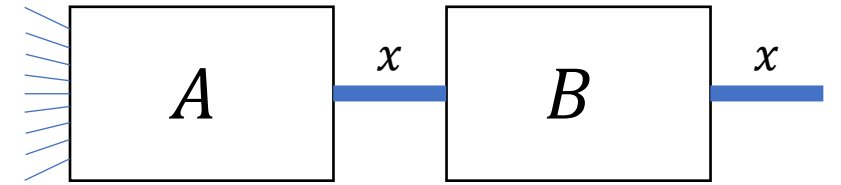
# Equilibria can be assigned a unique entropy

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  $A$



Number of evolutions of  $x$  must be independent of the process

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

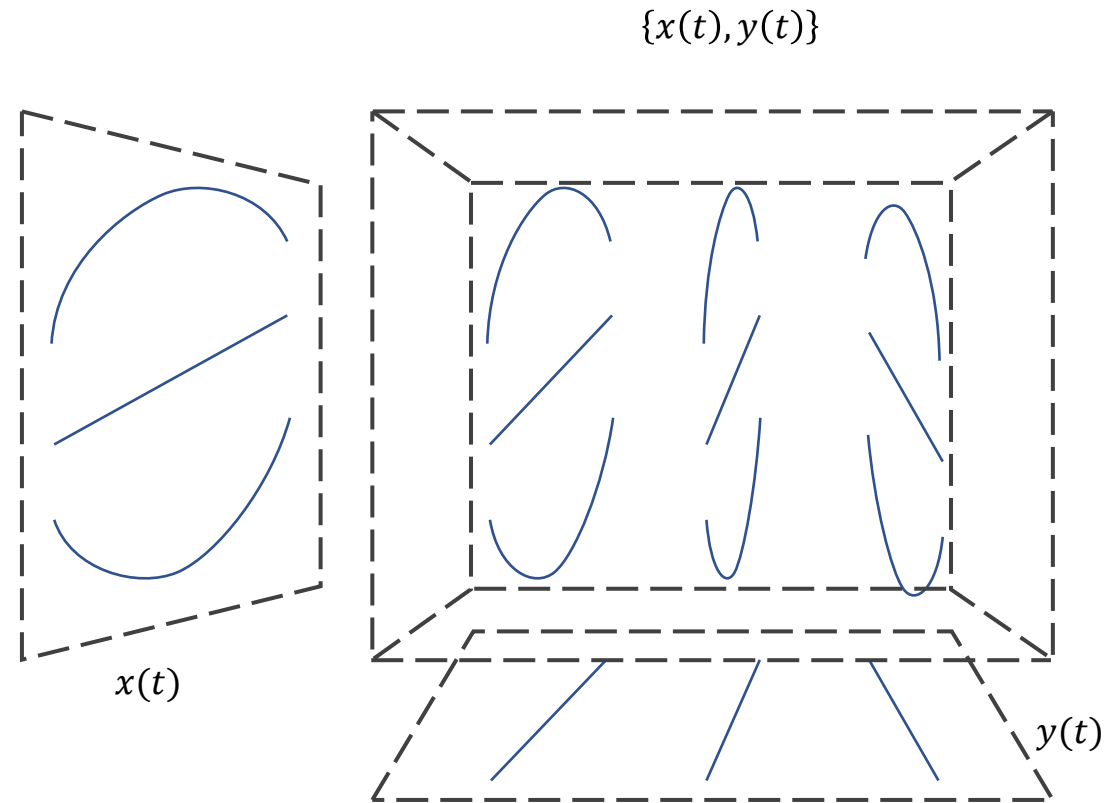
For composite systems, recall that in general the process entropy is not unique

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

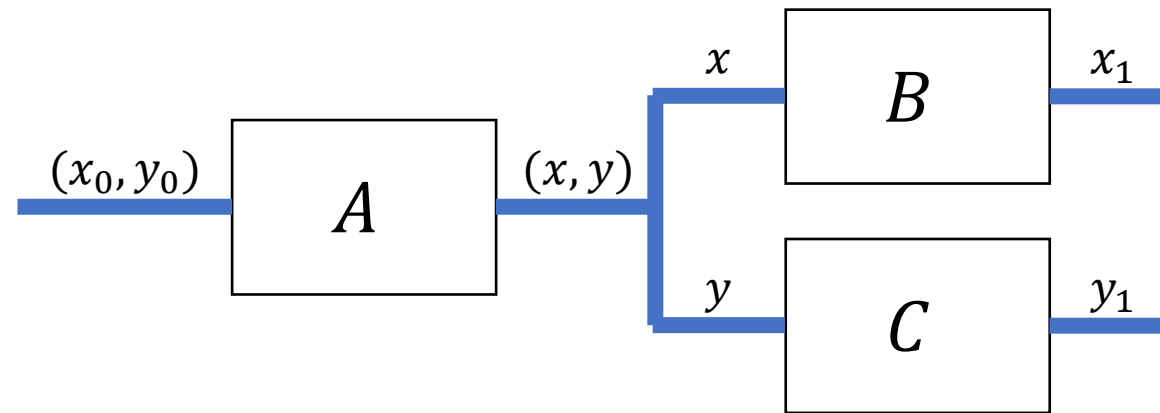


# State entropy

- We can assign a unique maximal process entropy to “states of independent equilibria” and 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  $S: X \rightarrow \mathbb{R}$  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

# Thermodynamics

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

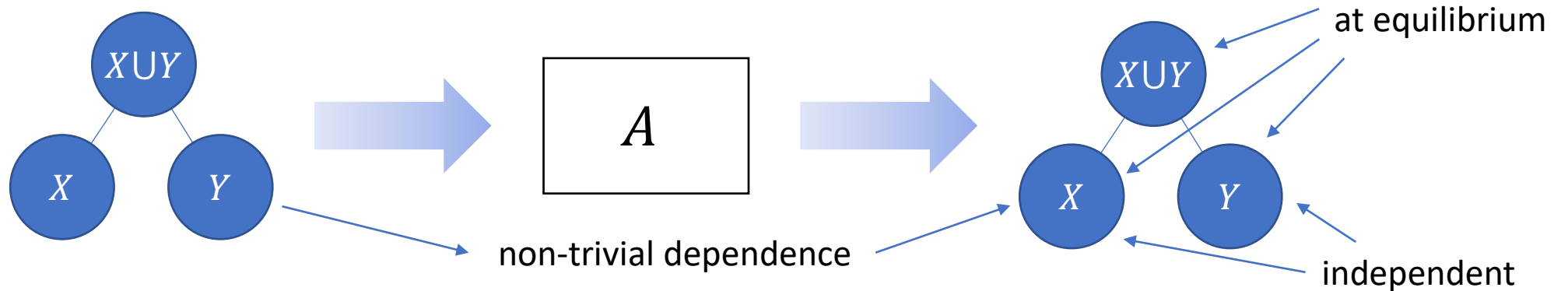


Not only we need a well defined evolution count for the composite, but also for each part

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

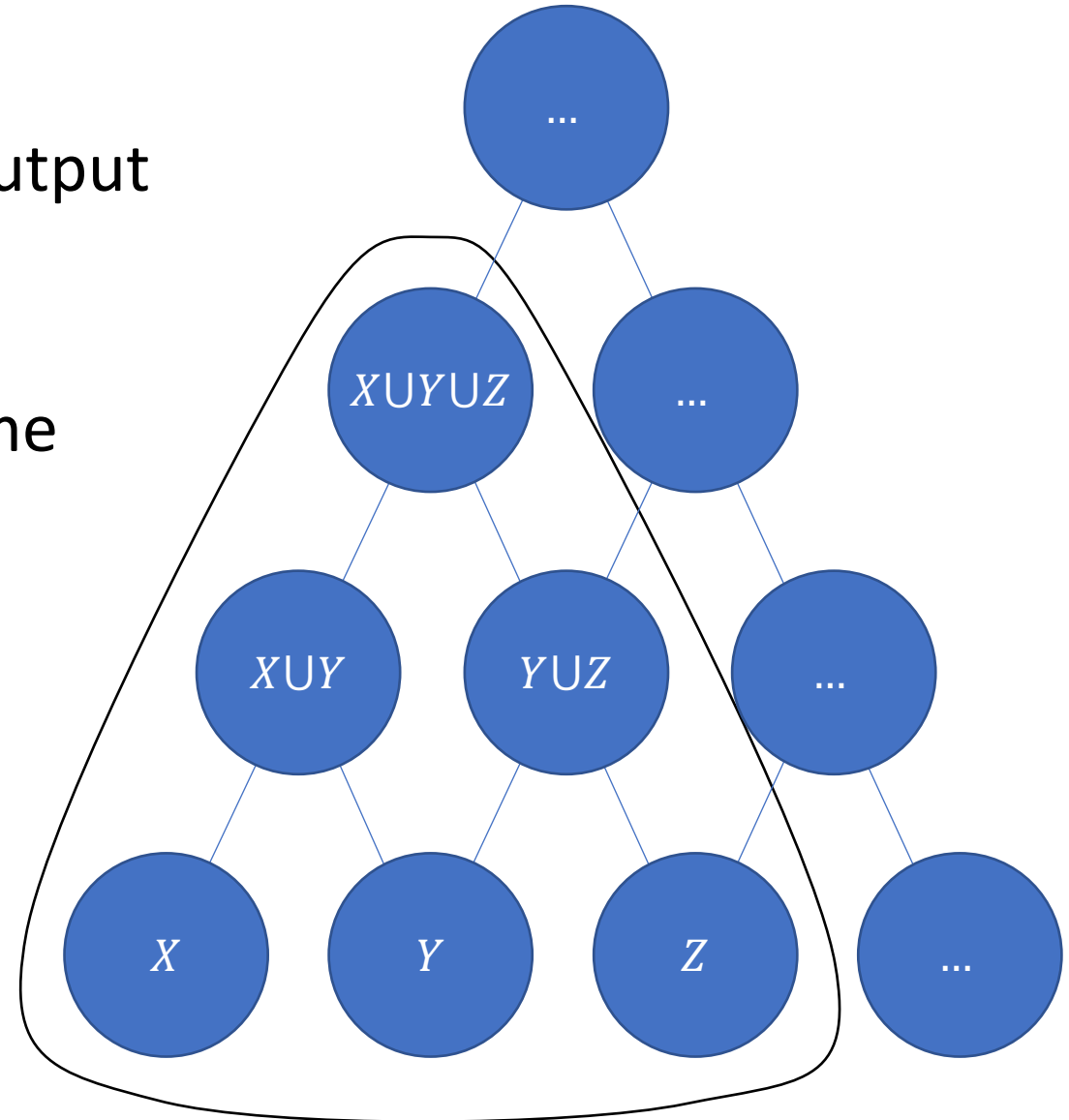




# Thermodynamic equilibrium

- 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

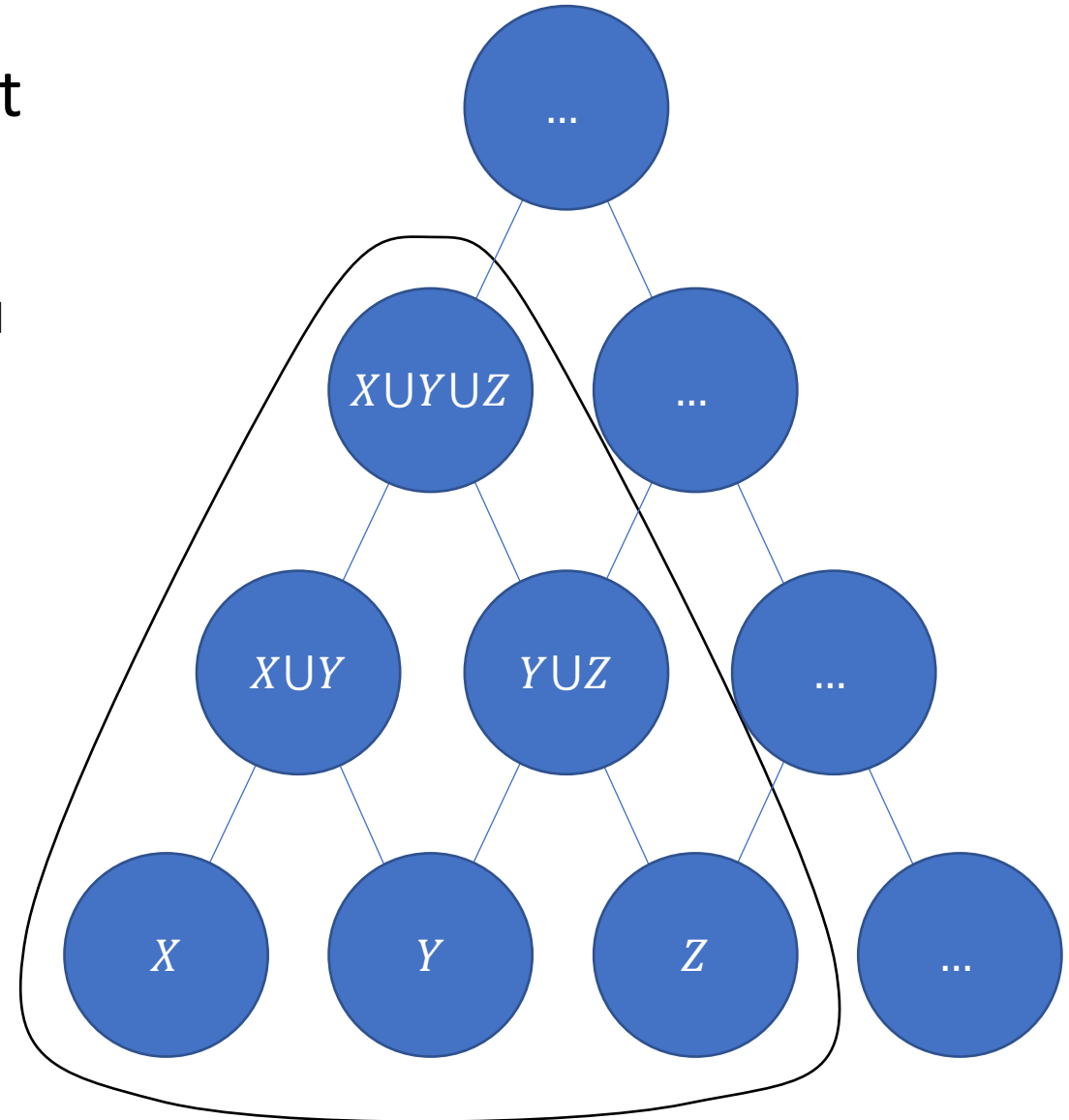
Based on the definitions, we can show that thermodynamic equilibrium is transitive

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*

# Existence of an equation of state

- Because the states are equilibria, we have a function  $S: \mathcal{S}_A \rightarrow \mathbb{R}$  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:

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

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

- Compare to  $dU = TdS_{Thermo} - pdV + \mu_i dN^i + \dots$
- $k_B dS$  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, 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  $\frac{\partial S_R}{\partial U_R} = \beta_R = \frac{1}{k_B T_R} = \text{const.}$   
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:  $S_M(U_M, x_M^i) = \text{const}$ . We call work  $W = \Delta U_M$  the energy acquired by a purely mechanical system during a transition.

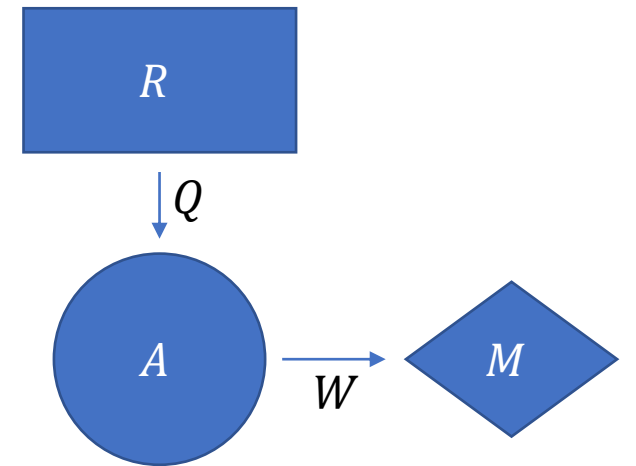
$$dS_M = 0 = \beta_M dU_M - \beta_M X_{Mi} dx_M^i$$
$$dU_M = X_{Mi} dx_M^i$$

- 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 later retrieved.



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



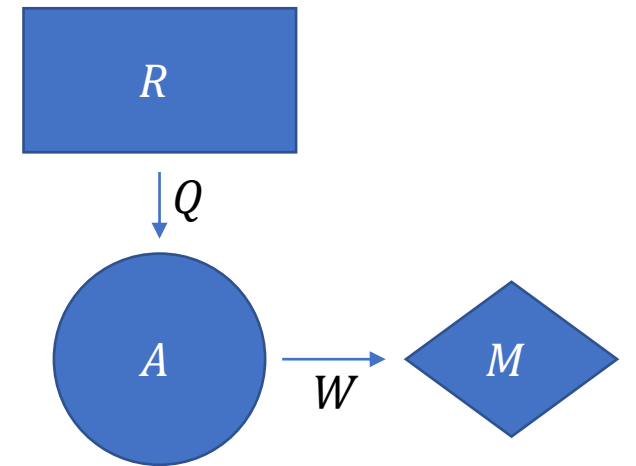
This recovers the  
first law of thermodynamics

# 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:

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

- $k_B \Delta S_A \geq \frac{Q}{T_R}$

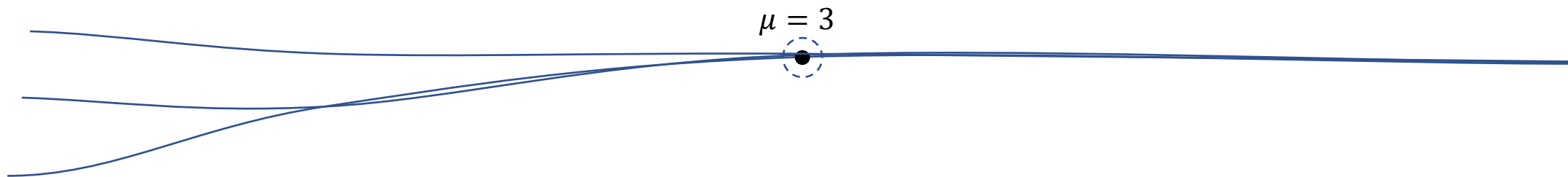


This recovers the second law of thermodynamics

Recall the definition of state entropy

$$S = \log \mu(x)$$

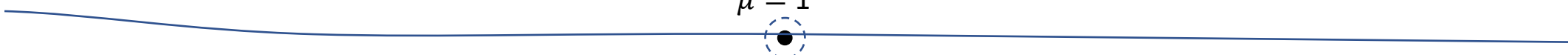
Count of evolutions



Recall the definition of state entropy

$$S = \log \mu(x)$$

Count of evolutions



$\mu = 1$

The least we can have is a single evolution

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

$$S \geq \log 1 = 0$$

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

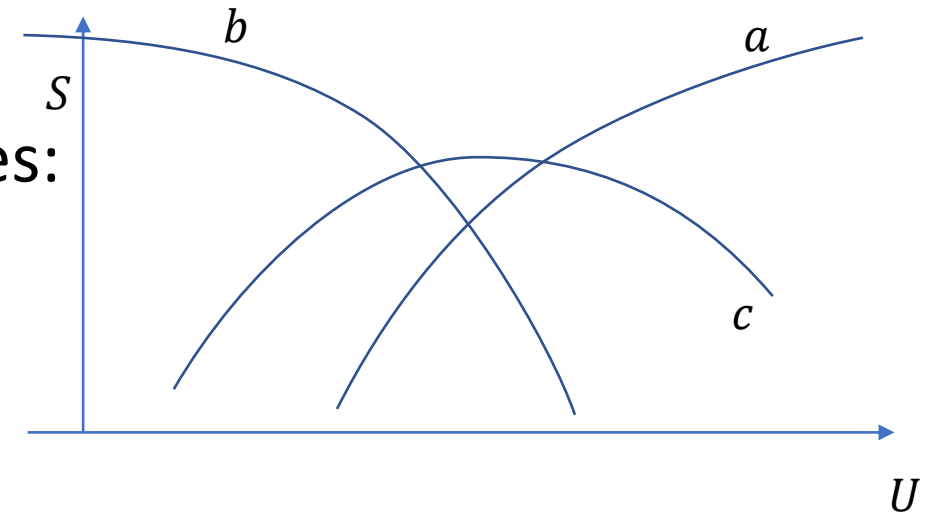
Evolution of a pure ground state fits into the  
single evolution case

This recovers part of the  
third law of thermodynamics

## 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 increasing
- b) No minimum energy, entropy monotonically decreasing
- c) 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.

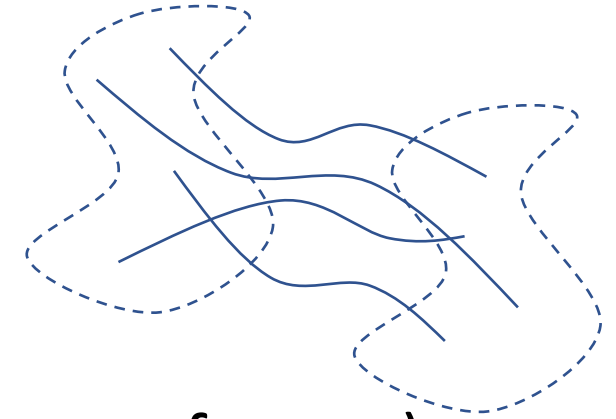
This recovers the remaining part of the third law of thermodynamics

# Thermodynamics recovered

- The laws of thermodynamics as we recovered them apply simply because of the properties of the processes we decide to focus on
  - 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, ...)

States, state entropy and  
equilibria

# Connection to statistical mechanics

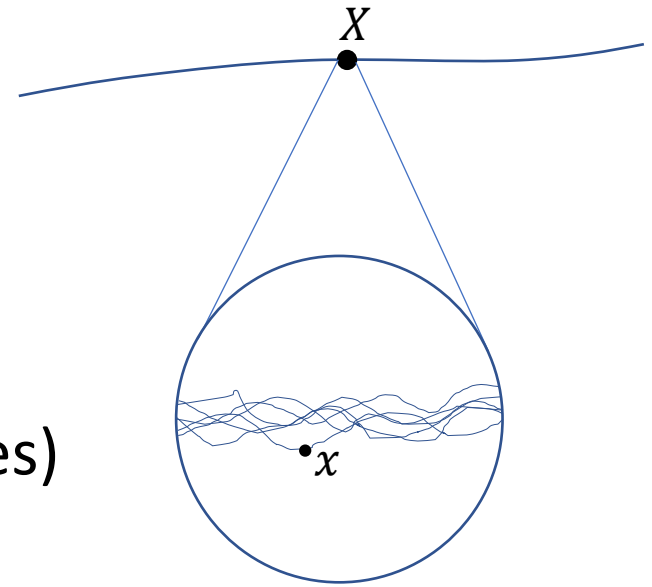


- One approach for entropy: fundamental postulate of statistical mechanics (entropy is the logarithm of the count of states)
- Can be recovered in the following way (not the only one)
  - Assume **macrostate** is fully defined by a **set of constraints** over the microstates
  - Assume **Hamiltonian evolution** that preserves **constraints** (i.e. macrostate variables are unchanged, we are at equilibrium)
  - Since each microstate provides a full description of the system, all **microstates** correspond to the **same number of evolutions**
  - **Process entropy** of the macrostate is, up to a constant, the **logarithm of the count of states that satisfy the constraint.**



# Connection to statistical mechanics

- Another approach for entropy: Gibbs and von Neumann entropies (Shannon entropy in classical and quantum cases)
- Can be recovered in the following way
  - Assume macroscopic equilibrium  $X$  is a **dynamical equilibrium** of microstate description
  - Then macroscopic equilibrium is a set of evolutions whose microscopic description can be characterized by a **stable probability distribution**  $\rho(x)$
  - An evolution  $\lambda(t)$  for the microstate is an dense sequence of infinitely many microstates whose **recurrence matches**  $\rho$
  - Since the state entropy is the maximal process entropy, we are counting **all possible evolutions** which means **all possible permutations**
  - **Shannon entropy** can be understood as the count of **all possible permutations** of an infinite sequence, of all possible evolutions

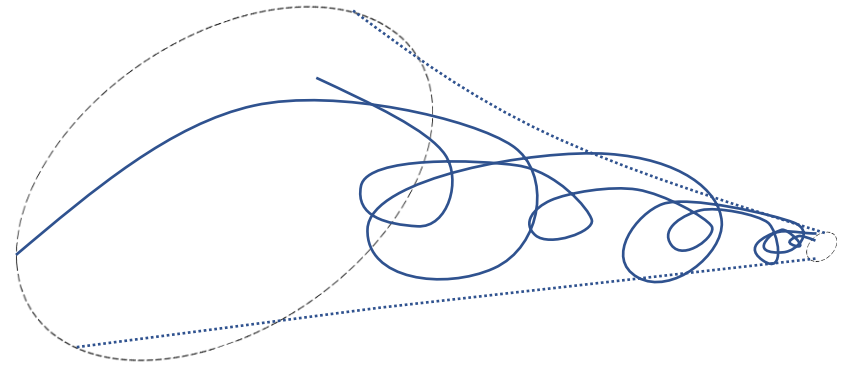


# Connection to mechanics

- Both classical and quantum systems are (implicitly) mechanical systems (i.e. entropy is the same for all states)
  - Von Neumann **entropy for all pure quantum states is zero**
  - Symplectic structure gives a uniform (i.e. translation invariant) measure: **all classical states have the same entropy**
  - Given any two states, we can (at least mathematically) find a deterministic/reversible evolution (i.e. symplectomorphisms and unitary transformations) that connects them

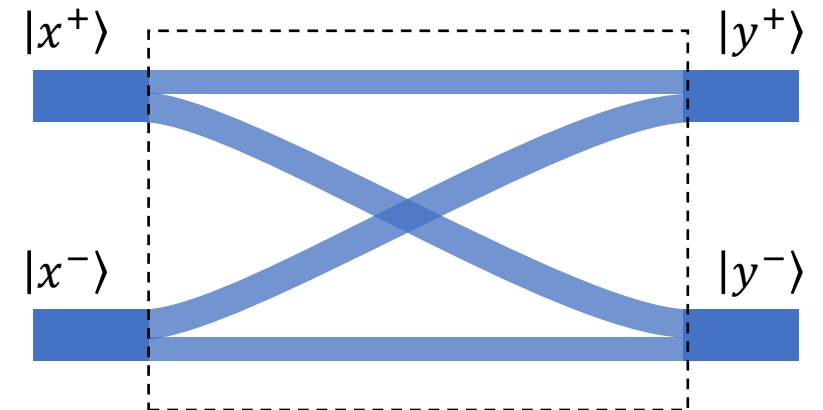
# Classical phase space

- The symplectic structure allows us to count evolution only under Hamiltonian evolution (i.e. isoentropic, deterministic and reversible evolution)
  - Count of states = count of evolutions
- This does not work in general
- Assume dissipative evolution (e.g. damped harmonic oscillator)
  - Evolution concentrate on fewer states
  - Count of states decreases
    - but entropy should increase for irreversible evolutions!
  - Count of evolutions per state increases
    - process entropy does increase



# Quantum state space

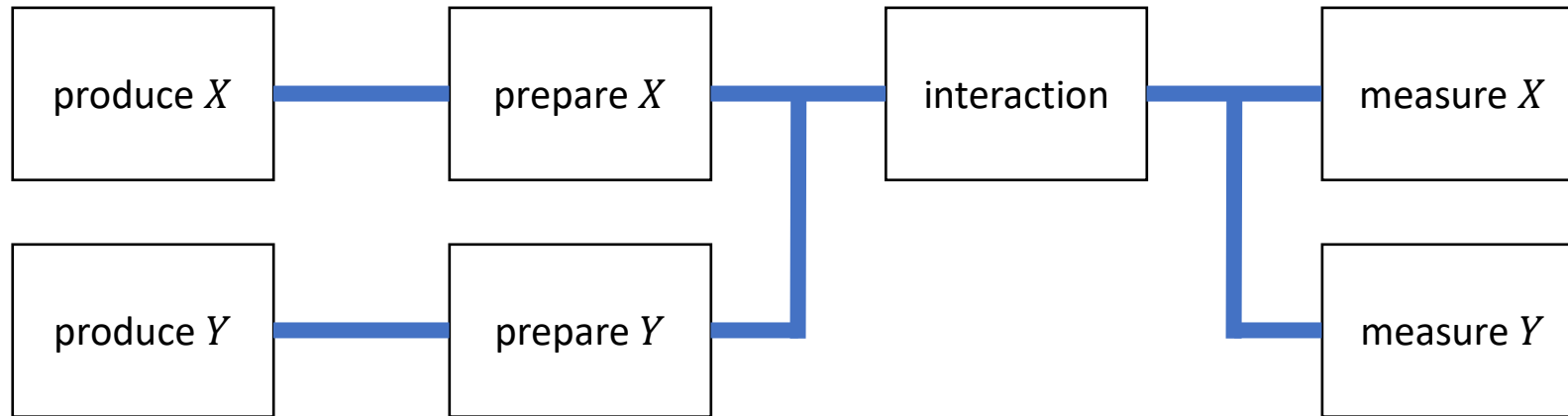
- The inner product of quantum mechanics characterizes probability of transitions for a “black box” process (i.e. measurement projection)
  - Probability are ratios of evolution counts
  - The geometrical structure of quantum mechanics can also be understood in terms of evolution counts
- Unitary evolution is deterministic and reversible
  - All evolutions from one state go to one and only one other state
- Projections are idempotent processes
  - The output consists of eigenstates, which are left unchanged by the process itself
  - Eigenstates are equilibria (i.e. symmetries of the process)
  - Each state is an eigenstate of some projection (Hilbert spaces are Banach spaces with projections)
  - In this sense, each quantum states is an (isoentropic) equilibria of some process



# Hints of a deeper connection

- Process entropy can recover the standard entropies of statistical mechanics
  - Just by applying the **same definition** in particular cases
- The ability to assign a unique process entropy to states is embedded in the state spaces of classical mechanics, quantum mechanics, thermodynamics and statistical mechanics
  - The geometrical structures can be fully understood in terms of evolution counts
- Is this a coincidence or a fundamental property state spaces must possess?

1) Process composition: we like to divide processes (including experiments) into a series of steps stitched together

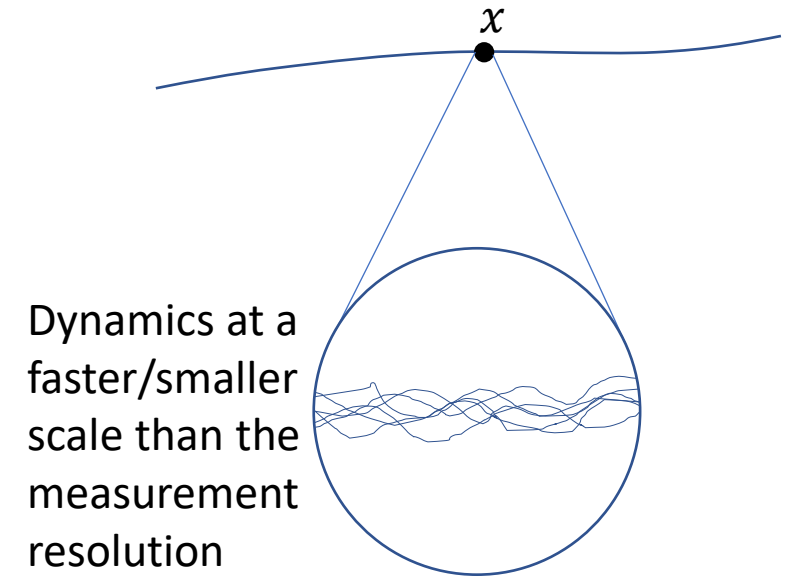


At the junction point, the evolution count from both processes for the same state has to match, physical theory must take that into account

**States are junction points**

2) Measurement finiteness:  
on closer inspection, measurements are not at an instant (or at a point); they are defined on a neighbourhood;  $x(t)$  is really  $x \left[ \left( t - \frac{dt}{2}, t + \frac{dt}{2} \right) \right]$

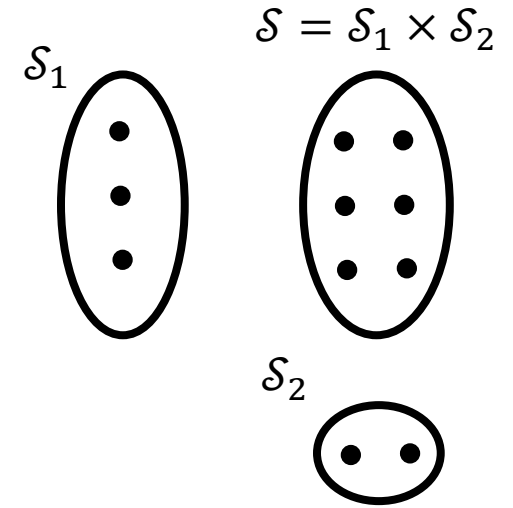
We can talk about a single state in the interval if all state variables are “stable” enough



States are equilibria of faster/smaller scale processes

3) Independent description:  
a state should describe the system and only  
the system (with minimal correlations)

A state is properly defined on an independent  
system, when all correlations have been  
removed



States are independent descriptions



- 1) States are junction points
- 2) States are equilibria of faster/smaller scale processes
- 3) States are independent descriptions



The very notion of state seems to be linked to equilibrium and state entropy (i.e. a unique, maximized evolution count)

These requirements are things we, maybe implicitly, look for when defining systems and states (epistemic desiderata); if they are not satisfied we change the system/state definition until they are; we look for sets of variables that “go together” in that way

How is unique maximized evolution count achieved?

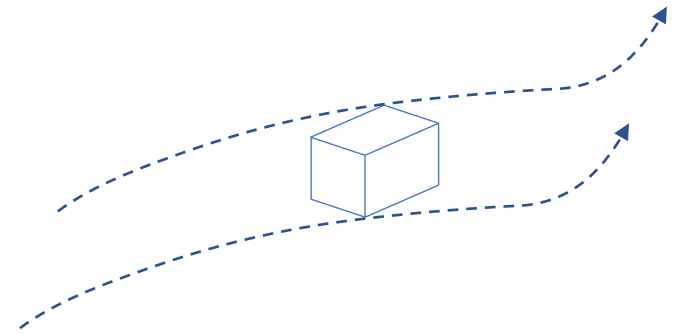
# Note: the notion of equilibrium as “nothing is changing” does not really work and needs to be amended

Take a volume of gas at equilibrium

It should be at equilibrium for every observer, yet only in the rest frame nothing is changing

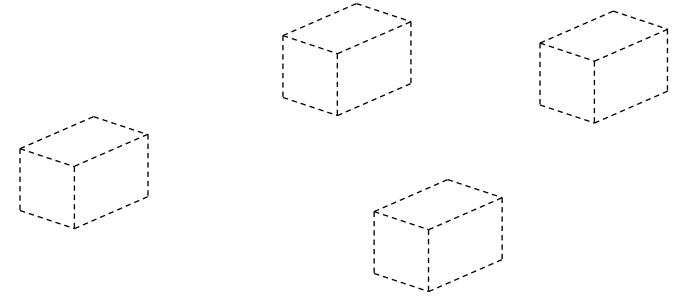
Moreover, in presence of gravity, gas at equilibrium must follow geodesics

Relativistically, “nothing is changing” makes no sense



So, let's try and find a way to put all these insights together in a consistent picture

# To define a system we must define a boundary and what happens at the boundary

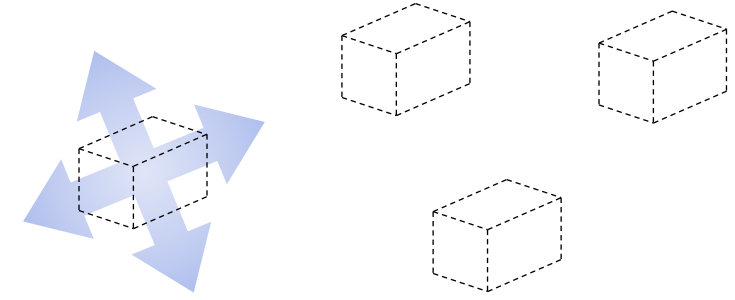


We need to say what is part of the system and what is not part of the system.

The interaction of the system at the boundary must be such that the system remains well defined. E.g. We can talk about a ball because we are on the surface of the earth at 20 Celsius. If we were on the surface of the sun, we would not be able to define a ball.

These processes must happen at a faster timescale than the one we are studying, so that we can consider the system well defined at all times.

To define a system we must define a boundary  
and what happens at the boundary

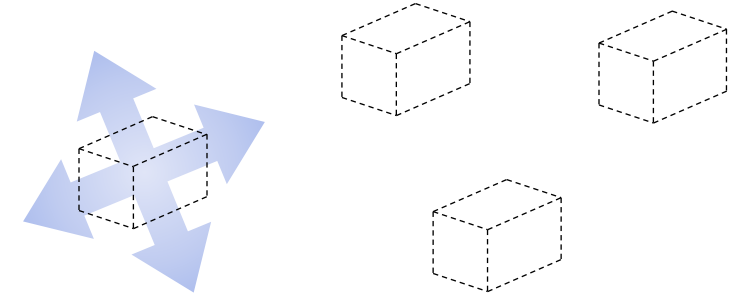


To characterize a system, we must have (at least in principle)  
processes at our disposal that render it independent

The state of the system should not tell us how the system came to be in that state, what process must act on it afterwards; it shouldn't tell us anything more about its subsystems and their internal dynamics, other systems or the environment than what the system strictly tells us. If the system is independent, its description gives us the least amount of information, it selects the biggest number of possible evolutions.

Historically, we have been grouping quantities (e.g. position/momentum, pressure/volume, electric/magnetic fields) in such a way to achieve that goal (e.g. form independent degrees of freedom). We don't define states by randomly putting quantities together.

To define a system we must define a boundary  
and what happens at the boundary



To characterize a system, we must have (at least in principle)  
processes at our disposal that render it independent

If the system is well defined and independent, this “decoupling  
process” does nothing: states are equilibria of this process

Mathematically, states are symmetries (i.e. invariants, equilibria) of a group (i.e. a set of transformations, a set of processes). Properly defining a system, then, means giving not only a set of states, but a set of processes for which the states are equilibria that maximize the process entropy

# States

- All states are really “independence equilibria” of some process
  - At the boundary, the process is such to keep the system well defined
  - The process minimizes the correlation with the environment, removes all correlations with other systems, subsystems and their dynamics such that the system is allowed an independent description
    - A measurement at the level of the system tells us nothing about the rest
  - They can be used as junction points under process composition, as they are defined independently of past and future processes
- They are descriptions of the system when process entropy is maximized
  - They describe the evolution of the system and only of the system
  - State entropy is well-defined in these and only these conditions
- Outside these assumptions, we can still have processes but we are not going to have systems and states
  - For now, there doesn't seem to be a reason why would have to have group of descriptions that always form the same systems

Blueprint for a formal framework

Physical theories	Different assumptions depending on the system and processes at hand	Thermodynamics, classical Hamiltonian mechanics, Newtonian mechanics, quantum mechanics, ....
State spaces	Group descriptions that can be grouped into patterns of independent behavior	Systems, state space, state entropy, state variables, process composition
Processes	Algebra of descriptions that can be parametrized by time	Process entropy, determinism/reversibility, stochastic processes
Informational granularity	Ability to compare the granularity of the description provided by different statements (count possible cases)	Units, measures, geometry, probability, differentiability
Logical consistency + Experimental verification	Algebra of statements generated from a countable set of verifiable statements	Topologies, (Borel) $\sigma$ -algebras, continuous functions, properties and quantities





Extra material

Predictability and Retrodictability

# Predictability and Retrodictability

- Formally, the algebra of statements  $\bar{\mathcal{D}}$  is (at least) a Boolean algebra
- It comes with an order  $\preceq$  we call narrowness that tells us whether one statement is “more specific than”, “contained in”, another
  - “Socrates is in Athens”  $\preceq$  “Socrates is in Greece”
- Determinism and reversibility are defined using narrowness
  - Determinism:  $x(t) \preceq x(t + \Delta t)$
  - Reversibility:  $x(t + \Delta t) \preceq x(t)$
- Because we can only have one state at each time:
  - Determinism:  $x(t) \preceq f(x(t)) = x(t + \Delta t)$  Predictable
  - Reversibility:  $x(t + \Delta t) \preceq g(x(t + \Delta t)) = x(t)$  Retrodictable

# Predictability and Retrodictability

- Because we can only have one state at each time:
  - Determinism:  $x(t) \preceq f(x(t)) = x(t + \Delta t)$ 
    - All deterministic processes are predictable
  - Reversibility:  $x(t + \Delta t) \preceq g(x(t + \Delta t)) = x(t)$ 
    - All reversible processes are retrodictable
- If the state space is discrete,  $f$  and  $g$  are invertible if and only if the process is deterministic and reversible
  - In this case, only deterministic processes are predictable and only reversible processes are retrodictable

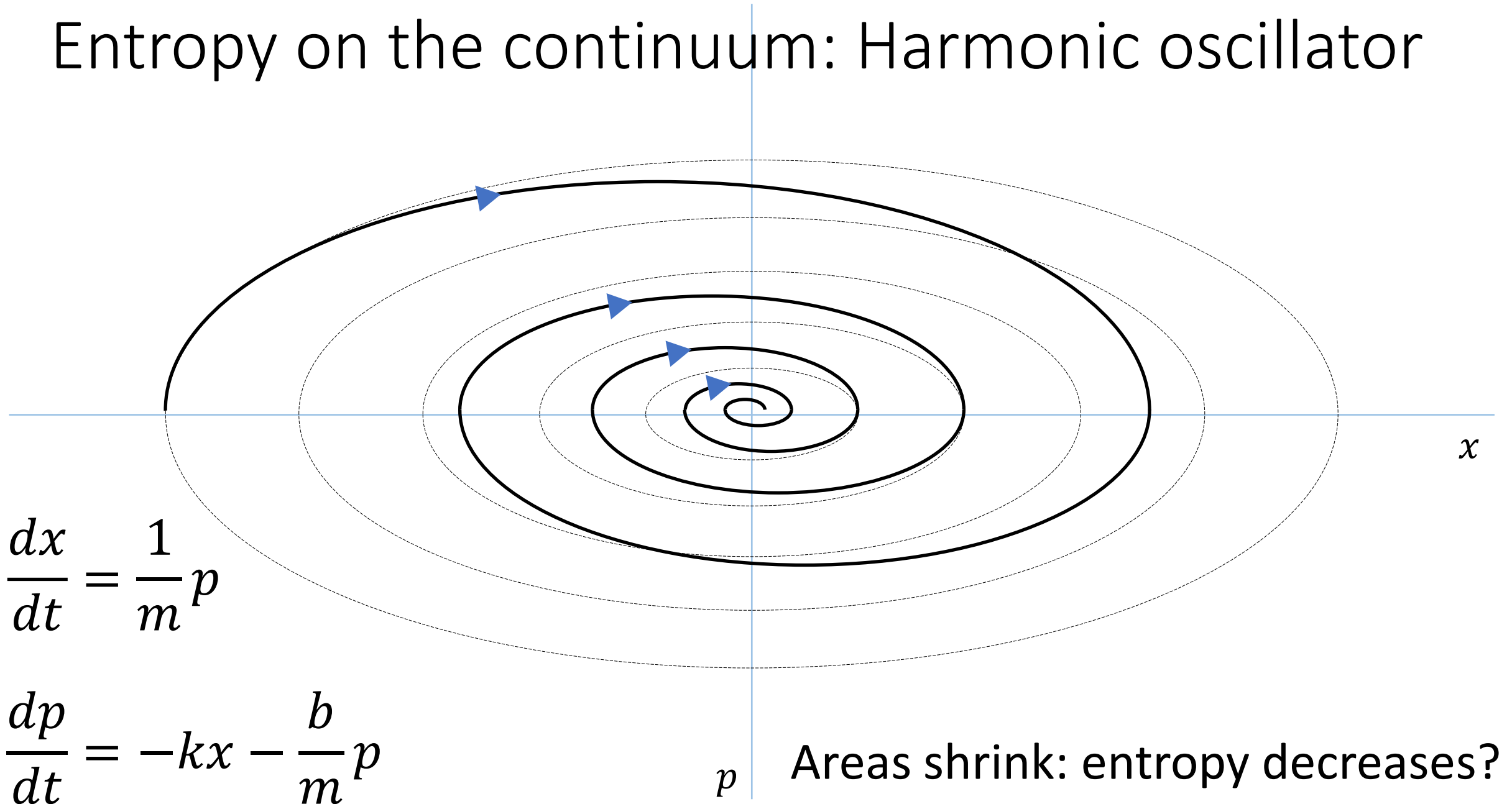
# Predictability and Retrodictability

- Because we can only have one state at each time:
  - Determinism:  $x(t) \preceq f(x(t)) = x(t + \Delta t)$
  - Reversibility:  $x(t + \Delta t) \preceq g(x(t + \Delta t)) = x(t)$
- If the space is continuous, there are non-reversible processes where  $f$  is invertible (and non-deterministic processes where  $g$  is invertible)
  - The evolutions concentrates (density increases) around a predictable average
- So we can have:
  - Determinism and retrodictability:  $x(t) = f^{-1}(x(t + \Delta t)) \preceq x(t + \Delta t)$
  - Reversibility and predictability:  $x(t + \Delta t) = g^{-1}(x(t)) \preceq x(t)$

# Entropy on the continuum

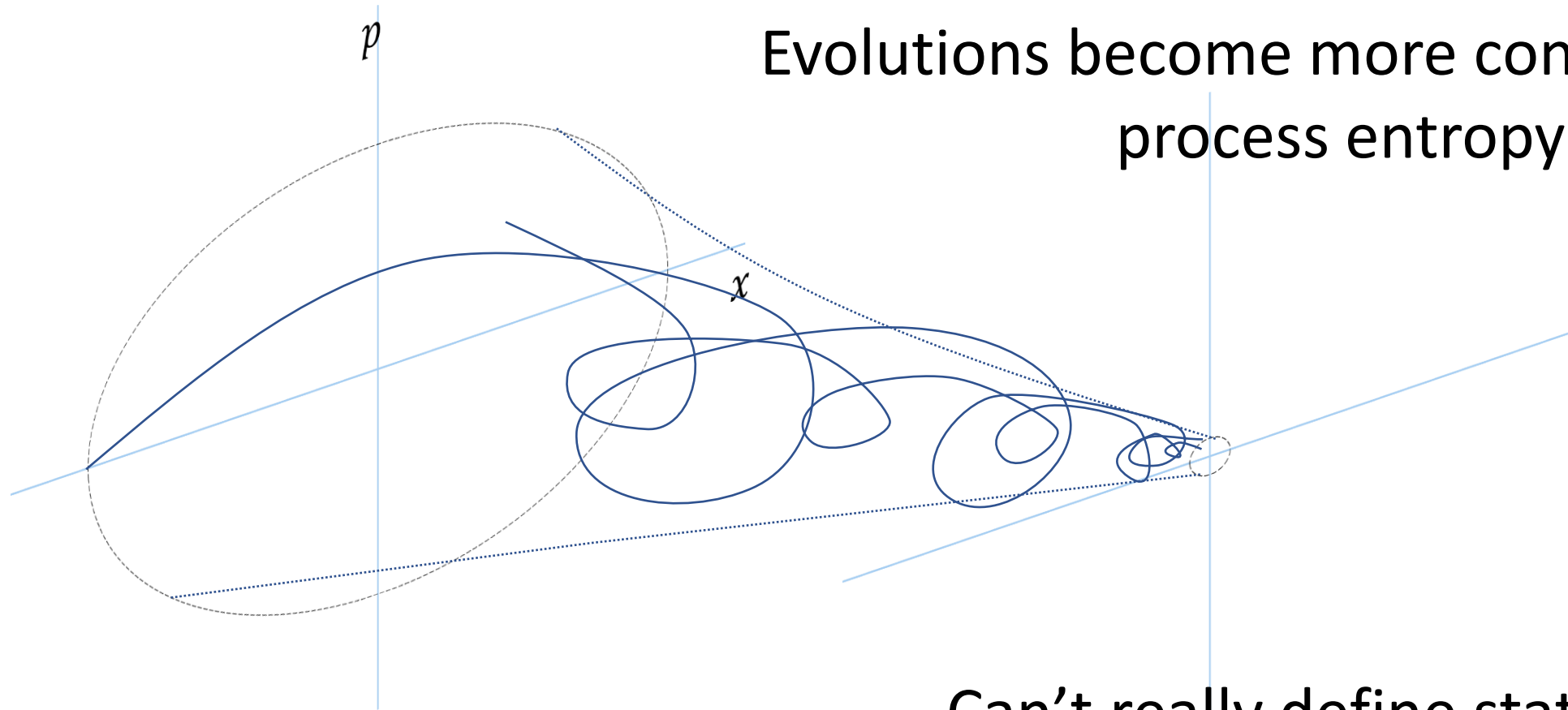
Counting states vs counting evolutions

# Entropy on the continuum: Harmonic oscillator





# Entropy on the continuum: Harmonic oscillator



Evolutions become more concentrated:  
process entropy increases!

Can't really define state entropy:  
system is not at equilibrium

Thermodynamics: open details

# Few open details

- Internal energy and Hamiltonian
  - All extensive quantities are absolute values because changing the zero breaks additivity
  - $U_A + U_B = U_{AUB} \Rightarrow \hat{U}_{AUB} = U_{AUB} + U_0 = U_A + U_B + U_0 = (U_A + U_0) + (U_B + U_0) - U_0 = \hat{U}_A + \hat{U}_B - U_0 \neq \hat{U}_A + \hat{U}_B$
  - What is the exact connection between the internal energy (absolute) and the Hamiltonian (not absolute)?

# Few open details

- Zero for extensive quantities
  - We saw extensive quantities must have a fixed zero
  - Note that the extensive quantities for the “null/empty” system must be zero (i.e. composition must yield no change); so it must be for the “null” state (i.e. the system is missing)
  - Are there actual states where some or all extensive quantities are zero? Or is zero reserved only for the “null” state? E.g. if volume or number of particles is zero, there is no system. Are there counter-examples?

# Few open details

- Non-negativity for extensive quantities
  - Are all extensive quantities always non-negative? It is the case for volume and number of particles. Are there counter-examples?
- If there are no counter-examples for non-negativity or zero value, is there an argument that can be made in line of principle?

# Few open details

- Reachability of arbitrarily small temperature for all systems
  - Is there an actual requirement that a system can reach an arbitrarily low temperature?
    - In principle, we only said that there is a minimum energy state and (since  $S(U)$  is concave) it will be reached at the lowest possible temperature – did not say that the lowest possible temperature is zero
    - Existence of equilibrium requires that the systems can reach the same temperature. So, existence one system with arbitrarily low temperature forces all systems that can be in equilibrium to have the same property.
  - Could we have a version of “thermodynamics” where the lowest temperature is small but not zero?
    - This should be excluded by statistical mechanics, but can we exclude it beforehand?

# Few open details

- Thermodynamic limit
  - The thermodynamic limit is typically taken to be when  $N \rightarrow \infty$  and  $V \rightarrow \infty$  with  $N/V$  constant, yet we derived the laws of thermodynamic with no mention of size: maybe there is a different (better?) way to characterize the thermodynamic limit?
  - A key assumption we made for thermodynamic equilibrium was that the parts are independent (i.e. entropy is additive)
    - When the system is “small”, boundary effects are non-negligible and entropy is not additive
  - Another (hidden) assumption is that equilibria of different processes yield exactly the same equilibria
    - Strictly not true: e.g. the equilibria when the system is closed will be characterized by a fixed  $N$  while when the system is open  $N$  will be a distribution
    - Since the particles are exchanged only at the boundary, when border effects are negligible  $N$  is sharply distributed

# “Fundamentality of thermodynamics”

- The existence of “thermodynamic-like” process that leave the parts independent and at equilibrium is a requirement for defining systems and states
  - What must fail is that the recursiveness (that all parts are independent or participate in the equilibrium) is something that must fail at the finest scale