The Postulates

Equilibrium states of a macroscopic system are *completely described* by the values of its *extensive* coordinates (U, V, N_1 … N_m, …).

There exists a function of the *extensive coordinates* of a macroscopic system and its environment (called *the entropy* **S**) that is maximized by the equilibrium values of unconstrained extensive coordinates.

The entropy is *extensive*. It is a *continuous, differentiable and monotonically increasing* function of the internal energy.

$S = 0$ if $(\partial U/\partial S)_{V,N1\ldots Nm} = 0$.

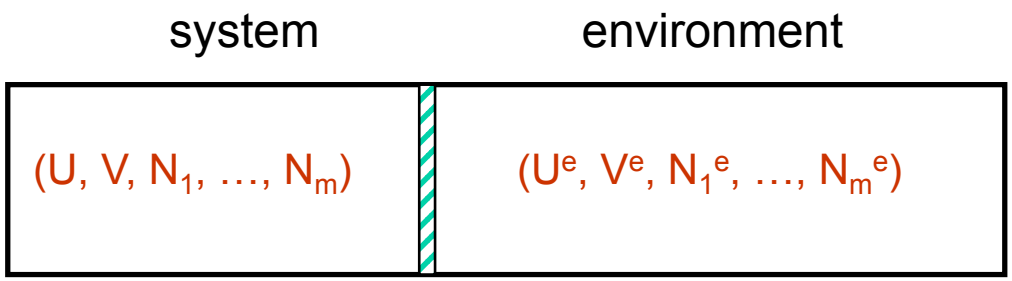
\+ the conservation of energy: $dU = \delta W + \delta Q$

Entropy of a system and its environment

On one hand, entropy is a maximum in equilibrium. On the other hand, entropy is a monotonically increasing function of the internal energy.

Does not this mean that the internal energy should be infinite in equilibrium? No!

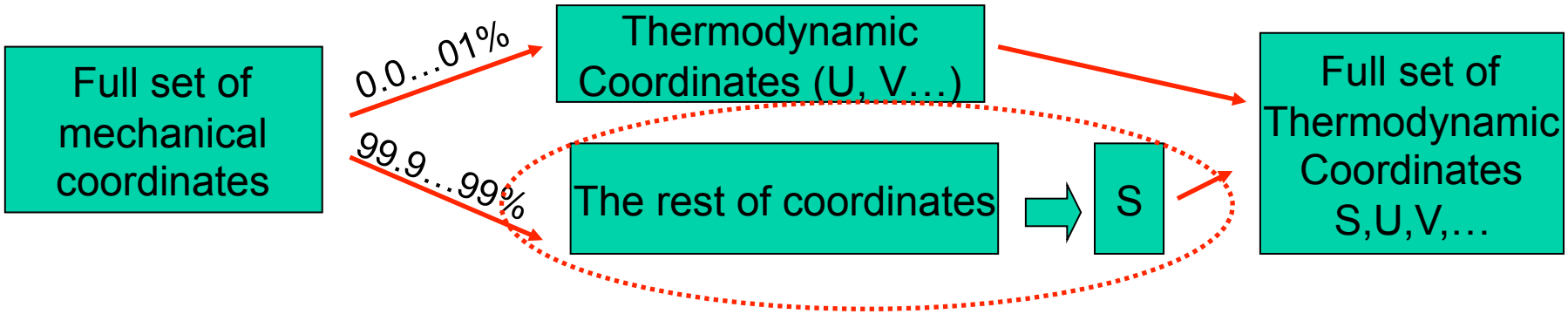
$$S_{comp.\,sys}(U, V, N_1, \ldots, N_m; U^e, V^e, N_1^e, \ldots, N_m^e) = S_{sys}(U, V, N_1, \ldots, N_m) + S_{env}(U^e, V^e, N_1^e, \ldots, N_m^e)$$



Since the composite system is isolated, its total internal energy is conserved: $U + U^e = U_0 = \text{const}$
Therefore $U^e = U_0 - U$.

If the energy of the system of interest increases, its entropy also increases
$dU>0$, $dS>0$
At the same time the energy and the entropy of the environment decrease
$dU^e<0$, $dS^e<0$
Entropy of the isolated composite system has a maximum for fixed value of U_0.

From Mechanics to Thermodynamics

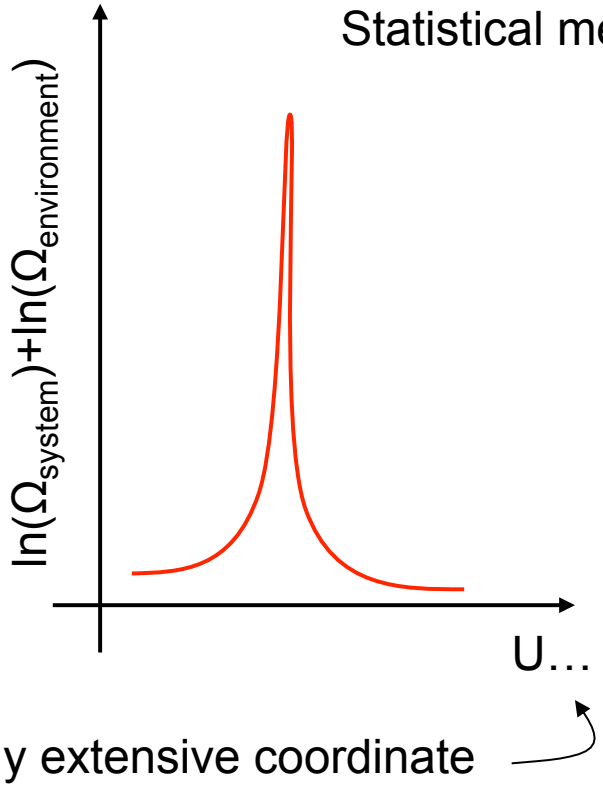


The recipe for reduction of microscopic mechanical coordinates to a single thermodynamic coordinate, entropy, is given by statistical mechanics:

1. Fix the values of all macroscopic thermodynamic coordinates U,V, …
2. Determine the phase space volume Ω(U,V,…) of the microscopic coordinates
3. Calculate entropy as: S(U,V,…) = const*Log[Ω(U,V,…)]

Quantum mechanics tells that the number of quantum states of a system is proportional to the volume of its phase space $n_{states} = \Omega / h^{3N}$, so $S \sim \mathrm{Ln}(n_{states})$

Physical meaning of entropy: a detour to statistical physics



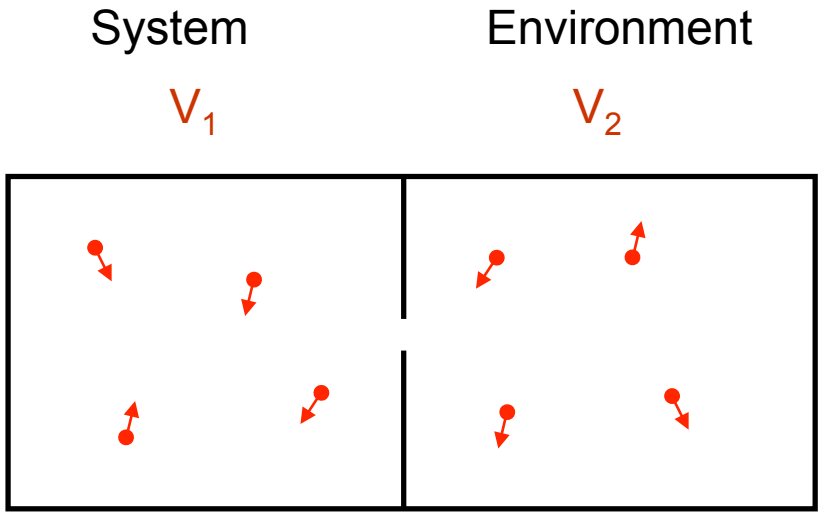
Statistical mechanics results:

- The number of microscopic states of the system + environment as a function of extensive coordinates of the system of interest exhibits a sharp peak

- Basic postulate of statistical physics: An isolated system is equally likely to be in any of its accessible microstates.

- Since the peak is very sharp, the probability of finding the system very close to the peak position is very close to unity and one can introduce a well-defined value of the unconstrained coordinate in equilibrium

Entropy Example: Ideal Gas



$V_1 = V_2$

Constrained coordinate: V_1

Unconstrained coordinates: N_1, U_1

U_1 depends on velocities only

N_1 depends on coordinates only

Particle conservation law

Entropy Example: Ideal Gas

If we can measure a coordinate of a particle with precision λ, then there are $\Gamma = V/\lambda^3$ distinct position states for each particle of gas.

For each given particle of gas, $\Gamma/2$ of its position states are in V_1 and $\Gamma/2$ of its position states are in V_2 independent on the particle velocity.

We will group the position states of the composite system according to their value of N_1 – the number of particles in the left compartment. N_1 is an unconstrained macroscopic thermodynamic coordinate describing our system.

Entropy Example: Ideal Gas

Let us count microscopic states with a given value of N_1

Example: $N = N_1 + N_2 = 4$

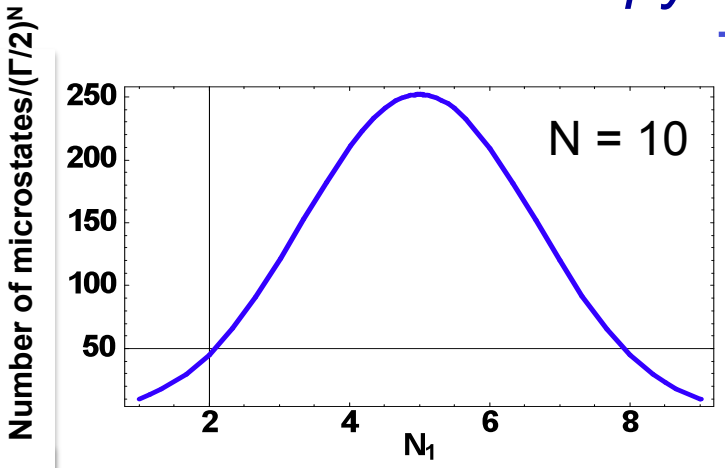
$N_1 = 0$:	(_ I 1,2,3,4)	$1*(\Gamma/2)^4$
$N_1 = 1$:	(1 I 2,3,4), (2 I 1,3,4), (3 I 1,2,4), (4 I 1,2,3)	$4*(\Gamma/2)^4$
$N_1 = 2$:	(1,2 I 3,4), (1,3 I 2,4), (1,4 I 2,3), (2,3 I 1,4) , (2,4 I 1,3), (3,4 I 1,2)	$6*(\Gamma/2)^4$
$N_1 = 3$:	(2,3,4 I 1), (1,3,4 I 2), (1,2,4 I 3), (1,2,3 I 4)	$4*(\Gamma/2)^4$
$N_1 = 4$:	(1,2,3,4 I _)	$1*(\Gamma/2)^4$

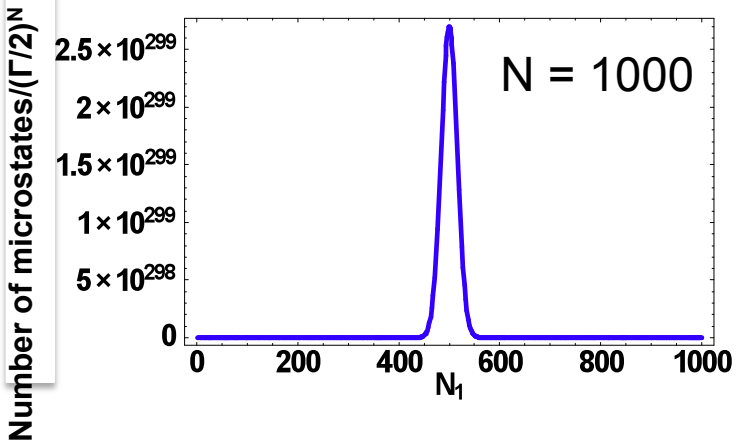
Macroscopic coordinate — Microscopic states — Number of microscopic states

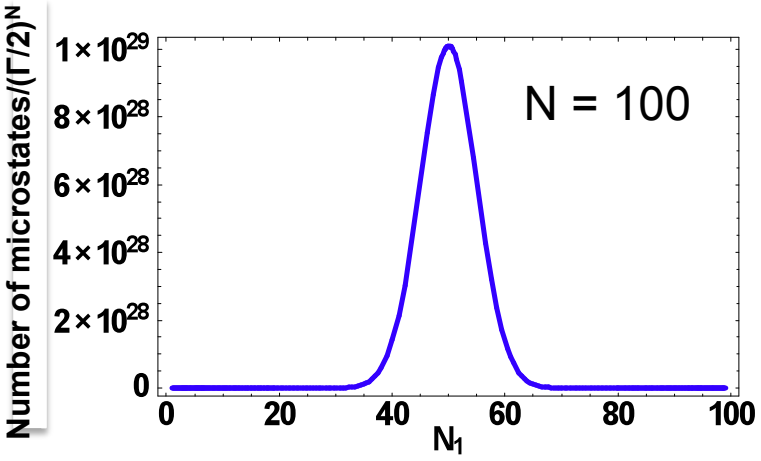
The number of microscopic realizations of the macroscopic state with a given value of N_1 :

$$\frac{N!}{N_1! * (N-N_1)!} (\Gamma/2)^N$$ (binomial coefficient)

Entropy Example: Ideal Gas





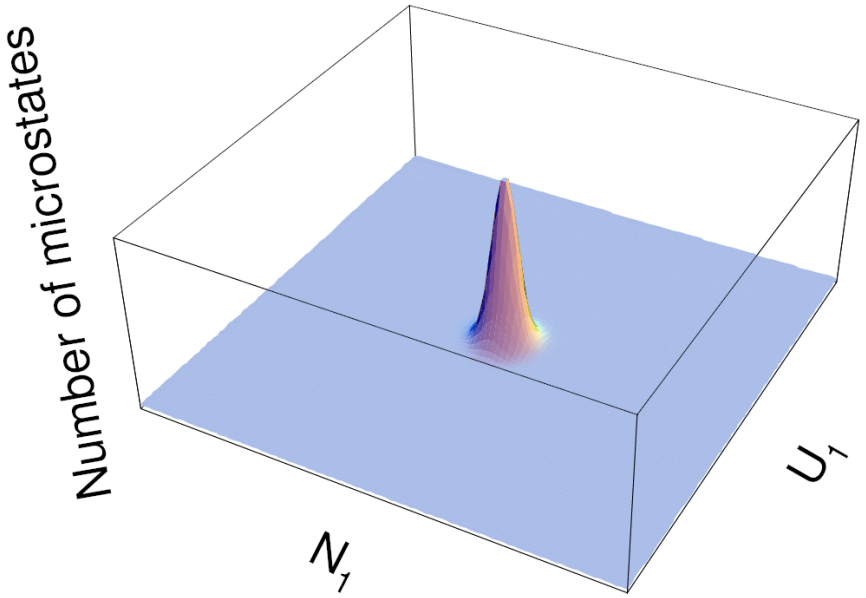


Peak width $\Delta N_1 \sim N_1^{1/2}$

Relative peak width $\Delta N_1/N_1 \sim N_1^{-1/2}$

For $N \sim 10^{24}$, the relative peak width is one part per trillion

Entropy Example: Ideal Gas

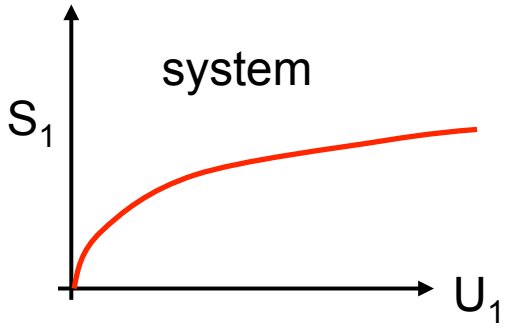


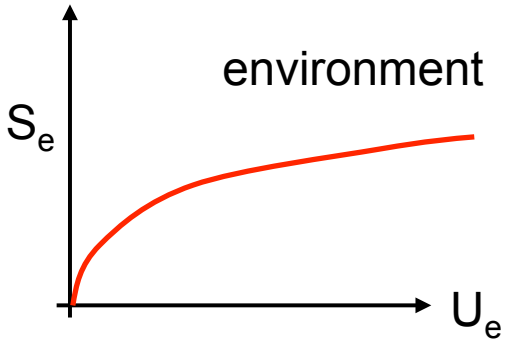
- Similarly we can consider all possible velocity states for the particles and calculate the number of velocity microstates as a function of U_1

- Since velocities and positions are independent from each other in ideal gas, the total number of microstates is just a product of the number of position and velocity microstates.

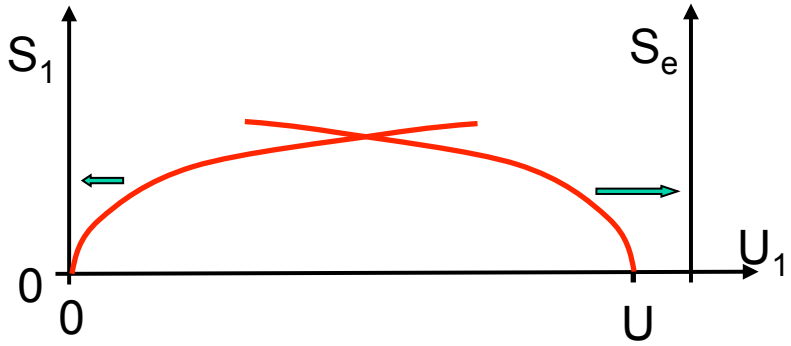
It is important to realize that any microstate with any value of unconstrained parameters is realized in the system with equal probability. For example, a microstate with N_1=0 and U_1=0 is realized with the same probability as a microstate with N_1=N/2 and U_1=U/2.

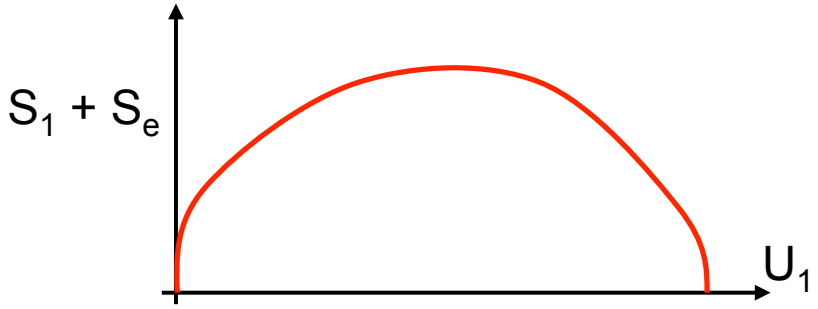
Why Entropy of a Composite System has a Peak





$U = U_1 + U_e$ ⇒ $U_e = U - U_1$





Irreversibility in Thermodynamics

A short description of thermodynamic processes:
If a constraint between system and its environment is removed, entropy of the system + environment increases: $dS = S_f - S_i > 0$ (Postulate II). This is because by removing a constraint we have increased the volume of phase space that the microscopic coordinates of the system + environment can explore.

This means that a process $S_i \rightarrow S_f$ is allowed while the opposite process $S_f \rightarrow S_i$ is prohibited because it decreases the entropy of the composite system.

Thus irreversibility is inherent in thermodynamics. In mechanics, all processes are inherently reversible. In mechanics, it is sufficient to reverse all velocities to return to a state of the system in the past (essentially to go backwards in time).

Origins of Irreversibility

Origins of irreversibility:

- Dynamic origins (tell you why reversing velocities does not get you to the initial state)
- Kinematic origin (the most fundamental one)

Dynamic origins:

1. Isolated macroscopic systems is an abstraction. A typical system with 10^{23} atoms has quantum energy spacing of ~ $10^{-10^{23}}$ Joules.

   For comparison, gravitational (weakest) interaction energy between two electrons at the opposite ends of observable universe is ~ 10^{-98} Joules. So a system as small as 100 particles cannot be truly isolated.

2. Even if we neglect interactions with the rest of the world, there are still interactions with fluctuations of the physical vacuum which are random in nature.

Kinematic Origin

The system evolves according to the reversible equations of mechanics.

According to these equations, the system goes through states with different values of unconstrained coordinates (e. g. U).

However, almost every time we look at the system (measure), we find it in a state with U close to U_0 because there are a lot of such states.