# Lesson 3- Microcanonical ensemble

- In Stat Mech we use ensembles to relate the microscopic description of a system in equilibrium with its macroscopic *observables* because it is impossible to track the trajectories of N particles simultaneously.

- Statistical Mechanics does not describe how a system approaches equilibrium, it describes the thermodynamical relationships that hold at equilibrium starting from a microscopic description of the system.

- To do that, in statistical mechanics we define the so called ensembles, which are determined by how the system is set up. There are three main ensembles we will learn about: **microcanonical, canonical, and gran canonical**

- In each ensemble, the details of the connection with thermodynamics is different but each ensemble yields equivalent conclusions in the *thermodynamic limit* $N, V \rightarrow \infty$

- In the microcanonical ensemble the systems is *isolated:* **N, V** and **E** *(total energy)* are **fixed.** $N, V \to \infty$ but $V/N$ is well-defined.

- Particles in our system follow the canonical equations of motion:
$$\frac{\partial \mathcal{H}(p,q)}{\partial p_i} = \dot{q}_i \qquad \frac{\partial \mathcal{H}(p,q)}{\partial q_i} = -\dot{p}_i$$

- Having constant $E$ is then equivalent to a system with a Hamiltonian $H$ that is independent of time $\dfrac{d\mathcal{H}}{dt} = 0 \qquad \mathcal{H}(\mathbf{Q}, \mathbf{P}) = \sum_i \dfrac{p_i^2}{2m} + V = E = \text{const}$

- NOTE: This might look like a limiting assumption, but as we will see, this approach is enormously powerful as in the long-time equilibrium behaviour of a system is precisely the behaviour of all systems with the same value of conserved quantities (regression to the mean).

- In the microcanonical ensemble the systems is *isolated:* **N** *(number of particles)* , **V** (volume) and **E** *(total energy)* are **fixed.** The energy is all we need to describe our system.

- **Assumption of equal priori probability:** All *microstates* in *phase space* compatible with the same equilibrium state are **equiprobable.**

- Phase space: all the possible states of the *N* particles compatible with the macro state of a system (E,N). Each state is a microstate.

  - in a gas: $\mathbf{P} = (\vec{p}_1, \ldots, \vec{p}_N), \mathbf{Q} = (\vec{q}_1, \ldots, \vec{q}_n)$ (6N-dimensional space)

  - in a discrete system - e.g.quantum dices - discrete variables $\mathbf{D} = (d_1, \ldots, d_N)$ (N-dimensional space)

Energy shell

$E$

$E + \delta E$
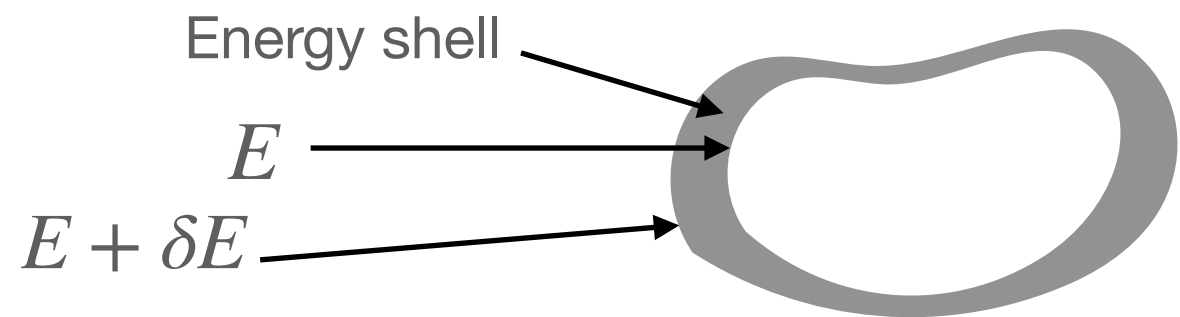
How does this ensemble work? Macro properties are the results of the averages over configurations with energies $\in [E, E + \delta E]$ and taking the limit $\delta E \to 0$.

1. Need to count the number of possible microstates of N particles with a fixed energy:

$$\Omega(E) = \frac{1}{\delta E} \int_{E < \mathscr{H} < E + \delta E} d\mathbf{P}\, d\mathbf{Q} = \frac{1}{\delta E} \int d\mathbf{P}\, d\mathbf{Q} \left[\Theta(E + \delta E - \mathscr{H}) - \Theta(E - \mathscr{H})\right] = \int d\mathbf{P}\, d\mathbf{Q}\, \delta\left(E - \mathscr{H}(\mathbf{Q}, \mathbf{P})\right)$$

We have used that $\delta(x) = \frac{d}{dx}\Theta(x)$

Observables as averages $\langle O \rangle = \frac{1}{\Omega(E)} \int d\mathbf{P}\, d\mathbf{Q}\, O(\mathbf{Q}, \mathbf{P})\, \delta\left(E - \mathscr{H}(\mathbf{Q}, \mathbf{P})\right)$

2. Compute thermodynamic quantities from the entropy $S = K_B \ln \Omega$ using thermodynamic relationships (we will talk more about this later)!!!

Liouville's theorem states that: '*For a Hamiltonian system the density of states $\rho$ in an ensemble of many identical states with different initial conditions is constant along every trajectory in phase space.*' Or in mathematical terms $\dfrac{d\rho}{dt} = 0$.

Implication I: flows in phase space are incompressible. The volume occupied by the initial states remains unchanged.

Implication II: There are no attractors in phase space, i.e. there are no specific configurations from which the system cannot escape.

Implication III: Microcanonical ensembles are time independent. Specifically, if the density of initial conditions is uniform in phase space, it will remain uniform as the identical copies of the system evolve (the same argument with micro states with energies $\in [E, E + \delta E]$ ).

This property is a necessary condition for the microcanonical ensemble to describe the time-independent equilibrium state.

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By averaging over the surface of energy $E$, we are assuming that all the states in the surface are being visited during the time evolution of the system. This is equal to assuming that a system is *ergodic*

(Def 1. Acc Boltzmann) *In an ergodic system, the trajectory of almost every point in phase space eventually passes arbitrarily close to every other point on the surface of constant energy.*

Def 2. *A time evolution in a set $S$ if ergodic iff all the ergodic components $R$ in $S$ either have zero volume or the same volume as $S$.*

If we let a system evolve for a long time, the time spent by a system in some region of the phase space of microstates with the same energy is proportional to the volume of this region, which means that all accessible microstates are equiprobable over a long period of time.

The **implications** of this is that <u>temporal averages over trajectories can be equated to averages over all microstates in phase space</u>.

$$\langle O \rangle_S = \lim_{T \to \infty} \frac{1}{T} \int_0^T \langle O(t) \rangle_S \, dt = \left\langle \lim_{T \to \infty} \frac{1}{T} \int_0^T O(t) \, dt \right\rangle_S = \langle \overline{O} \rangle_S \quad \text{ensemble and time averages are equal.}$$

CAVEATS: Ergodicity has been mathematically proven for very few systems. However, many of the theoretical gaps are academic and do not apply for real systems for which Statistical Physics approaches have been extremely successful.

IDEAL GAS:

**N** non-interacting particles in a closed, fixed volume **V**.

Energy given by the Hamiltonian: $H = \sum_{i=1}^{N} \frac{p_i^2}{2m}$

It is impossible to track all the trajectories of the N particles!!! However, after al long time we can measure conserved quantities such as the energy, E. The microcanonical ensemble gives us a way to find macroscopic observables and the equation of state by counting configurations compatible with E.

$\Omega(E) \rightarrow$ microstates given by the set of coordinates **Q** and moments **P** of **N** particles that satisfy the constraints of the ensemble.

Positions and velocities (momenta) are independent so that:

$$\Omega_{\text{ideal gas}}(E) = \Omega(\mathbf{Q}) \times \Omega(\mathbf{P})$$

Positions: They are independent of the energy. Particles are 'points' (no excluded volume) that can occupy any position within the volume V with equal probability: $\Omega(\mathbf{Q}) = V^N$

Conversely, the probability density of a position configuration $\rho(\mathbf{Q}) = \dfrac{1}{V^N}$

Problem: consider two gas particles in a cube of length L: what is the prob that the two of them are on the right? What is the difference between prob density and probability?

Worked example: If there are 2N non-interacting particles in the box: what is the probability $P_m$ that $N+m$ particles are on the right half?

# of ways to divide 2N particles into either half of the box: $2^{2N}$

# of combinations of $N+m$ in one side $\binom{2N}{N+m}$

$$P_m = 2^{-2N} \binom{2N}{N+m}$$

Using Stirling's formula ($n! \sim (n/e)^n$ - forgoing the $\sqrt{2\pi N}$ factor)  and some algebra

$$P_m \approx P_0 \exp\left( -\frac{m^2}{N} \right) \longrightarrow \text{Gaussian entered at 0 with } \sigma = \sqrt{N/2} \text{ (relative}$$

fluctuations $\sigma/N$ go to zero as $N \to \infty$, as is typical in Stat Phys).

Moments are related to the Energy so $\Omega(\mathbf{P}) = \dfrac{1}{\delta E} \displaystyle\int_{E<\mathscr{H}<E+\delta E} d\mathbf{P} = \int d\mathbf{P}\, \delta\left(\mathscr{H}(\mathbf{P}) - E\right)$

$\mathscr{H} = \displaystyle\sum_i \frac{p_i^2}{2m} = \frac{\mathbf{P}^2}{2m} = E \rightarrow$ Moments in 3D such that the kinetic energy is E, lie on a hypersphere in 3N

dimensions with radius $\;R = \sqrt{2mE}$

We know how to compute the volume of this sphere (a 3N-1 sphere $S_R^{3N-1}$ in Mathematics) as

$$V(S_R^{3N-1}) = \frac{\left(\sqrt{\pi}\right)^{3N} R^{3N}}{(3N/2)!}$$

To obtain the volume of a thin shell between two spheres of $R = \sqrt{2mE}$ and $R' = \sqrt{2m(E + \delta E)}\;\rightarrow$

$$\Omega(\mathbf{P}) = \frac{V(S_{R'}^{3N-1}) - V(S_R^{3N-1})}{\delta E} = \frac{dV(S_R^{3N-1})}{dE} = \frac{3N}{2E}\frac{\pi^{3N/2}\,(2mE)^{3N/2}}{(3N/2)!}$$

In this ensemble, then the probability density of any configuration of moments $\mathbf{P}$ is $1/\Omega(\mathbf{P})$.

Worked example: What is the probability density that a given particle has $p_x = p_1$, $\rho(p_1)$?

$$\rho(p_1) = \frac{\int dP\, \delta(\mathcal{H} - E - \frac{p_1^2}{2m})}{\Omega(\mathbf{P})}$$

$$\mathcal{H} = \frac{p_1^2}{2m} + \sum_{p_1 \notin p_i} \frac{p_i^2}{2m} = E \rightarrow$$ All other moment components subject to this constraint lie on a hypersphere in 3N-1

dimensions with radius $R_{p_1} = \sqrt{2mE - p_1^2}$ whose volume is $V(S_R^{3N-2}) = \dfrac{(\pi)^{(3N-1)/2}\, R^{3N-1}}{\big((3N-1)/2\big)!}$

As before $\displaystyle \int dP\, \delta\left(\mathcal{H} - E - \frac{p_1^2}{2m}\right) = \frac{d}{dE} V(S_{R_{p_1}}^{3N-2})$

Putting everything together we get that

$$\rho(p_1) \propto \frac{R^2}{R_{p_1}^2}\left(1 - \frac{p_1^2}{2mE}\right)^{3N} \lim_{p_1 \ll 2mE} \rightarrow \rho(p_1) = \frac{1}{\sqrt{2\pi m(2E/3N)}} \exp\left(-\frac{p_1^2}{2m}\frac{3N}{2E}\right).$$

<u>Worked example:</u> What is the probability density that a given particle has $p_x = p_1$, $\rho(p_1)$?

$$\rho(p_1) = \frac{1}{\sqrt{2\pi m(2E/3N)}} \exp\left(-\frac{p_1^2}{2m}\frac{3N}{2E}\right).$$

Note that:

1. This is independent from the component or the particle.

2. This is a Boltzmann distribution (your first example), as we will see later.

3. Most of the area of the hypersphere surface is close to the equator of the hypersphere. This is 'to be expected' in statistical physics: if there is symmetry among the N particles, energy should be more or less equally distributed among them. Configurations in which a particle has most of the energy are very unlikely.

How do we go from counting states to thermodynamic quantities?

Boltzmann found the solution to this by defining entropy in the micro canonical ensemble as

$$S = k_B \ln \Omega(E) \qquad k_B = 1.380649 \times 10^{-23} m^2 kg/s^2 K (= J/K)$$

**S** is a thermodynamic potential which is a function of E, N, V. (We will see more about $k_B$ later.)

Through this definition we can make connections between the properties of configurations compatible with a certain energy and thermodynamic quantities.
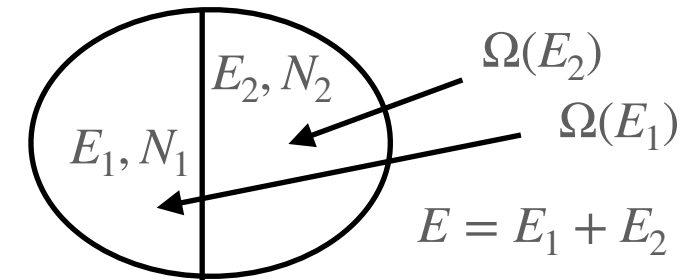
Let's see an example of why this definition of entropy 'works'.

Let's assume we divide our system into two parts of volumes $V_1, V_2$ with $N_1, N_2$ particles:

These two subparts are in equilibrium.

$$\Omega(E) = \int dE_1 \, dE_2 \, \Omega(E_1) \, \Omega(E_2) \, \delta \left( E - (E_1 + E_2) \right) = \int dE_1 \, \Omega_1(E_1) \, \Omega_2(E - E_1)$$

So that the density of states $\rho(E_1) = \dfrac{\Omega_1(E_1)\Omega_2(E - E_1)}{\Omega(E)}$

Note that $\rho(E_1) \propto \Omega_2(E - E_1)$

The largest contributions to the integral come from those values of $E_1$ such that the number of configurations compatible in both subsystems are the largest.

If we use the definition of entropy $\Omega(E_1) = e^{S_1(E_1)/K_B}$ and $\Omega(E_2) = e^{S_2(E_2)/K_B}$.

Around such maximum $S_1(E_1) = S_1(E_1^\star) + \dfrac{\partial S_1}{\partial E_1}(E_1 - E_1^\star) + \dfrac{1}{2}\dfrac{\partial^2 S_1}{\partial E_1^2}(E_1 - E_1^\star)^2$ and

$$S_2(E_2) = S_2(E - E_1) = S_2(E - E_1^\star) - \frac{\partial S_2}{\partial E_2}(E_1 - E_1^\star) + \frac{1}{2}\frac{\partial^2 S_2}{\partial E_2^2}(E_1 - E_1^\star)^2 \qquad \frac{\partial S_2}{\partial E_1} = \frac{\partial S_2}{\partial E_2}\frac{dE_2}{dE_1} = -\frac{\partial S_2}{\partial E_2}$$

So that $\Omega(E) = \displaystyle\int dE_1 \exp\left[ S_1(E_1^\star) + S_2(E - E_1^\star) + \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right)(E_1 - E_1^\star) + \left(\frac{1}{2}\frac{\partial^2 S_1}{\partial E_1^2} + \frac{1}{2}\frac{\partial^2 S_2}{\partial E_2^2}\right)(E_1 - E_1^\star)^2 \right]/k_B$

Because the condition of maximum is that the first derivative equals zero, we have that $\left(\dfrac{\partial S_1}{\partial E_1}\right)_{N_1,V_1} = \left(\dfrac{\partial S_2}{\partial E_2}\right)_{N_2,V_2}$. Since the two subsystems are at equilibrium this condition is equivalent to the condition that the temperatures are equal, in particular, we have that $\left(\dfrac{\partial S_1}{\partial E_1}\right)_{N_1,V_1} = \left(\dfrac{\partial S_2}{\partial E_2}\right)_{N_2,V_2} = \dfrac{1}{T}$

So that $\Omega(E) = \displaystyle\int dE_1\, \Omega(E_1^\star)\Omega(E_2^\star)\, \exp\left[\left(\frac{1}{2}\frac{\partial^2 S_1}{\partial E_1^2} + \frac{1}{2}\frac{\partial^2 S_2}{\partial E_2^2}\right)(E_1 - E_1^\star)^2\right]/k_B$ - which is a Gaussian distribution of the energy fluctuations!

Note that this relationship $\left(\dfrac{\partial S_1}{\partial E_1}\right)_{N_1,V_1} = \left(\dfrac{\partial S_2}{\partial E_2}\right)_{N_2,V_2} = \dfrac{1}{T}$ is what we

obtain from thermodynamics equations that relate the different thermodynamic quantities $dU = -PdV + TdS + \mu dN$

In fact, once we obtain the entropy, we can obtain any thermodynamic quantity:

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E} \qquad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{V,E}$$

Important: The final proof that we are making sound definitions for **S** and sound assumptions for the ensemble is empirical, that is, if predictions match thermodynamical observations (and they do!!).

Going back to our example, we had computed $\Omega(E) = \dfrac{V^N \left(\frac{3N}{2E}\right) \pi^{3N/2}(2mE)^{3N/2}}{(3N/2)!}$

(which as we will see shortly lack some small but relevant details)

Taking the leading terms in N:

$$S(E) = k_B \log\left(\frac{V^N \pi^{3N/2}(2mE)^{3N/2}}{(3N/2)!}\right) = N k_B \log V + \frac{3N k_B}{2}\log(2\pi mE) - \frac{3N k_B}{2}\left[\log\left(\frac{3N}{2}\right) - 1\right]$$

Using the thermodynamic relationships between S, T and P we get that:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3N k_B}{2E} \quad \text{so that } k_B T = \frac{2E}{3N}$$

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1. Note that this means that for the kinetic energy of one particle $K_1 = \dfrac{p_1^2}{2m}$

$$\rho(p_1) = \frac{1}{\sqrt{2\pi m(2E/3N)}} \exp\left(-\frac{p_1^2}{2m}\frac{3N}{2E}\right) \rightarrow \rho(K_1) \propto \exp\left(-\frac{K_1}{k_B T}\right)$$

This means that $k_B T$ is the typical kinetic energy assigned to one component of the momentum. Also, this is an example of a Boltzmann distribution $p(E) \sim \exp\left(-\dfrac{E}{k_B T}\right)$ as we will see in the canonical ensemble

2. Note that rearranging terms we obtain that $E = \displaystyle\sum_i \frac{p_i^2}{2m} = K = \frac{3}{2}k_B T N$ , since $k_B T$ is the typical energy assigned to each momentum component and each of the N particles had 3 components, this is an example of the **Equipartition theorem: each harmonic degree of freedom has a contribution to the kinetic energy** $1/2 k_B T$ **(as we will say in the canonical ensemble).**

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3Nk_B}{2E} \text{ so that } k_B T = \frac{2E}{3N}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E} = k_B \frac{N}{V} \qquad PV = k_B NT$$

which is the equation of state of the ideal gas:

$$PV = k_B NT \qquad PV = RnT \qquad \text{with} \qquad k_B N = Rn$$

(as promised!!)

Going back to our example, we had computed $\Omega(E) = \dfrac{V^N \left(\frac{3N}{2E}\right) \pi^{3N/2}(2mE)^{3N/2}}{(3N/2)!}$

But this needs some refinements:

1. Dimensions of length and momentum: Phase space has dimensions $([\text{length}][\text{momentum}])^{3N}$ However, as we will see later length x momentum are precisely the units of Planck's constant $h = 6.62607015\,10^{-34}\,\text{J} \cdot \text{Hz}^{-1}$ so it seems like a good option to use $h^{3N}$ as an 'adimensionalizing' factor. (We will see later that adding this factor is useful to get the correct zero temperature limits for the entropy!). $\Omega_{\text{new}}(E) = \Omega_{\text{rough}}(E)/h^{3N}$

2. Dimensions of energy: The volume of the energy shell depends on the choice of units as a multiplicative factor!! Most quantities depend only on derivatives of the entropy, so the overall constant (once you take the logarithm any multiplicative factor becomes a constant) is not important.

3. Identical particles: What about distinction between particles? We will see later about the difference between fermions and bosons in quantum systems (remember the quantum dice example!). Classical mechanics also identifies **undistinguished/undistinguishable** particles, i.e. those that are not identical copies, but are identical on terms of their contribution to the Hamiltonian or measuring instruments. Note that if this is the case, phase space has a permutation symmetry, we can exchange the positions and momenta of two particles and theHamiltonian would have exactly the same contributions. In that case, we have to divide $\Omega(E)$ by a factor $N!$ to account for this symmetry. This is usually called the Gibbs factor and has an effect in computing the chemical potential ($\mu = -T\,\partial S/\partial N\big|_{E,V}$).

Putting everything together we obtain Maxwell-Boltzmann statistics

$$\Omega(E) = \int \frac{d\mathbb{Q}\,\mathbb{P}}{h^{3N}N!}\,\delta(\mathcal{H} - E)$$

For the ideal gas we have that $\Omega(E) = \dfrac{\left(\frac{V}{h^3}\right)^N \left(\frac{3N}{2E}\right)\pi^{3N/2}(2mE)^{3N/2}}{(3N/2)!}\dfrac{1}{N!}$

$$S(E) = \frac{5}{2}Nk_B + Nk_B \log\left[\frac{V}{h^3N}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right]$$

In class exercise: Microcanonical energy fluctuations

When considering two subsystems of $E_1, N_1, V_1$ and $E_2, N_2, V_2$, we had seen that the probability density of $E_1$

$$\Omega(E) = \int dE_1 \, \Omega(E_1^\star)\Omega(E_2^\star) \, \exp\left[\left(\frac{1}{2}\frac{\partial^2 S_1}{\partial E_1^2} + \frac{1}{2}\frac{\partial^2 S_2}{\partial E_2^2}\right)(E_1 - E_1^\star)^2\right]/k_B$$ is a Gaussian with

$$\sigma_{E_1}^2 = -\frac{1}{\frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2}}$$

a) Show that $\dfrac{1}{k_B}\dfrac{\partial^2 S}{\partial E^2} = -\dfrac{1}{k_B T}\dfrac{1}{Nc_v T}$ where $c_v = \dfrac{1}{N}\dfrac{\partial E}{\partial T}\bigg|_{V,N}$ - Hint: use that $\dfrac{\partial S}{\partial E} = \dfrac{1}{T}$

Note that this result implies that $\sigma \sim \sqrt{N}$ so that the fluctuations of energy per particle decrease as $1/\sqrt{N}$.

This expression is an example of a fluctuation-response relation: For system in equilibrium, the response to a perturbation (i.e. specific heat measures the change in temperature when we give energy -heat- to the system - our perturbation) is related to the equilibrium fluctuations in the variable that we are perturbing (i.e. the energy) — $c_v \sim \sigma_E^2/T^2$.

In class exercise: Microcanonical energy fluctuations

a) Show that $\dfrac{1}{k_B} \dfrac{\partial^2 S}{\partial E^2} = -\dfrac{1}{k_B T} \dfrac{1}{N c_v T}$ where $c_v = \dfrac{1}{N} \left.\dfrac{\partial E}{\partial T}\right|_{V,N}$

b) If $c_v^{(1)}, c_v^{(2)}$ are the specific heats per particle of two systems of $N$ particles each, show that: $\dfrac{1}{c_v^{(1)}} + \dfrac{1}{c_v^{(2)}} = \dfrac{N k_B T^2}{\sigma_{E_1}^2}$

c) Using the equipartition theorem for the kinetic energy, show that for a gas of non-interacting particles $c_v^{(1)} = \dfrac{3}{2} k_B$.

So far we have seen entropy as:

- a thermodynamic potential $S = \dfrac{\delta Q_{rev}}{T}$ from the heat changed in reversible

processes at constant temperature.

- a quantity that measures the number of microstates compatible with a given
energy $S = k_B \log \Omega(E)$

Interestingly entropy can also be interpreted as a measure of the ignorance we
have about our system, or the amount of disinformation in a distribution of a
random variable:

Claude Shannon defined (information) entropy as $S_S = -\, k_S \sum_i p_i \log(p_i)$ (for

discrete distributions) with $k_S = 1/\log(2)$ so that $S_S$ can be measured in bits. .

With this information-theoretic distribution, we can make many connections with statistical physics.

For instance, the most uninformative distribution is the uniform distribution.

Consider a discrete distribution $\{p_i\}$ with N states. We want to find the disturb that maximises $S_S$

$$\mathscr{L} = S_S - \lambda \left( \sum_i p_i - 1 \right) = - k_S \sum_i p_i \log(p_i) - \lambda \left( \sum_i p_i - 1 \right)$$

$$\frac{\partial \mathscr{L}}{\partial p_i} = - k_S \log p_i - k_s p_i \frac{1}{p_i} + \lambda = 0 \to p_i = \exp(\lambda/k_s + 1) = \text{const} = \frac{1}{N}$$

For the last step we have imposed the normalization condition.

Therefore: $S_S = - k_S \sum_i \frac{1}{N} \log \left( \frac{1}{N} \right) = k_S \log N$ (which is the expression for Boltzmann's

entropy. This result shows that the microcanonical ensemble, which assigns equal probability to all microstates, maximizes entropy!!! It is the distribution that is the least informative and is compatible with the information we have about the system (that energy is fixed, which sets N).