Statistical Mechanics E0415

Fall 2023, lecture 7 Entropy

Take home… on snowflakes

"There are multiple reasons for snowflakes having a close to zero chance to have the same appearance.

Once of them could be that the water is not homogeneous. Some of the hydrogen atoms are replaced by deuterium and some oxygen atoms are O^18, therefore the crystallization is different.

Another explanation could be the differences in crystallization conditions, crystallization is a very sensitive process and slight fluctuations in temperature, medium, and pressure can cause very different outcomes.

Then, some of the snow crystals can grow from a seed which again changes the crystallization conditions. So that there is a difference in seeded and not seeded crystallization but also which type of seed. .”

Why bother?

Says Sethna:

We shall see in this chapter that entropy has three related interpretations.[1] *Entropy measures the disorder in a system;* in Section 5.2 we will see this using the entropy of mixing and the residual entropy of glasses. *Entropy measures our ignorance about a system;* in Section 5.3 we will give examples from non-equilibrium systems and information theory. But we will start in Section 5.1 with the original interpretation, that grew out of the nineteenth century study of engines, refrigerators, and the end of the Universe. *Entropy measures the irreversible changes in a system.*

Irreversibility and the Carnot cycle

Four steps:

(ab): heat flow at T_1

(bc): expansion without heat transfer

(cd): gas compressed, heat flow at T_2

(da): compression, warm the gas back without heat transfer

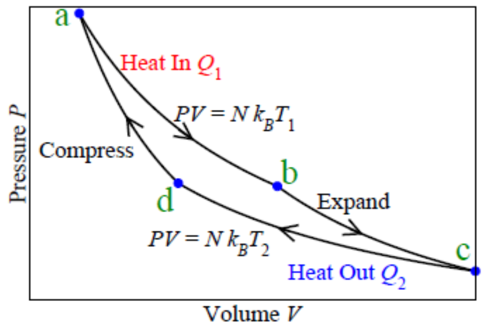
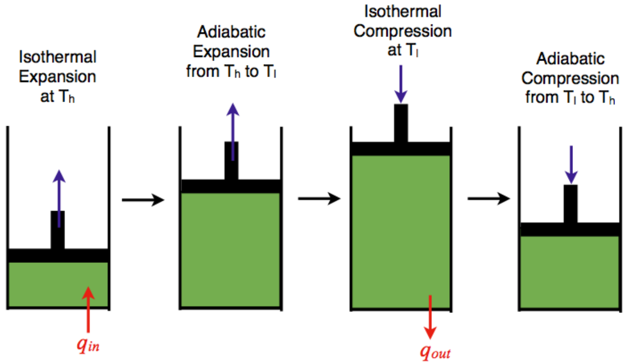


Fig. 5.3 Carnot cycle P–V diagram. The four steps in the Carnot cycle: a→b, heat in Q_1 at constant temperature T_1; b→c, expansion without heat flow; c→d, heat out Q_2 at constant temperature T_2; and d→a, compression without heat flow to the original volume and temperature.

$$\Delta S_{\text{thermo}} = \frac{Q}{T}.$$

Entropy, arrow of time (and irreversible heat machines)

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}.$$



Mixing entropy

Information and entropy via mixing: how much information there is in a configuration?

“Counting entropy”

Maxwell’s demon and entropy – and information.

$$S_{\text{unmixed}} = 2\,k_B \log[V^{N/2}/(N/2)!], \qquad S_{\text{mixed}} = 2k_B \log[(2V)^{N/2}/(N/2)!],$$

$$\Delta S_{\text{mixing}} = S_{\text{mixed}} - S_{\text{unmixed}} = k_B \log 2^N = N k_B \log 2.$$

$$S_{\text{counting}} = k_B \log(\text{number of configurations})$$

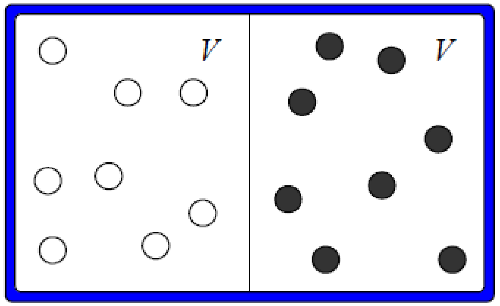


Fig. 5.4 Unmixed atoms. The premixed state: $N/2$ white atoms on one side, $N/2$ black atoms on the other.

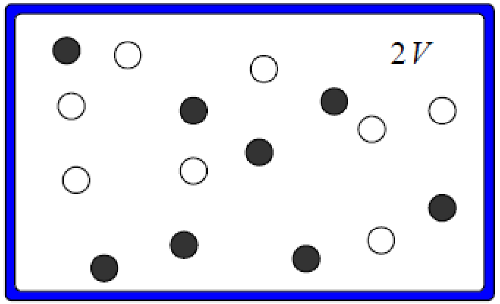


Fig. 5.5 Mixed atoms. The mixed state: $N/2$ white atoms and $N/2$ black atoms scattered through the volume $2V$.

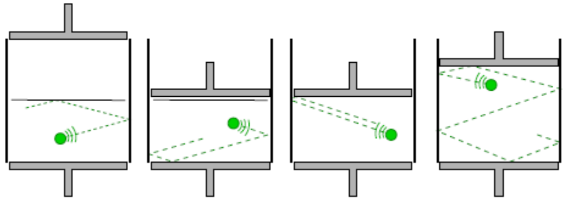
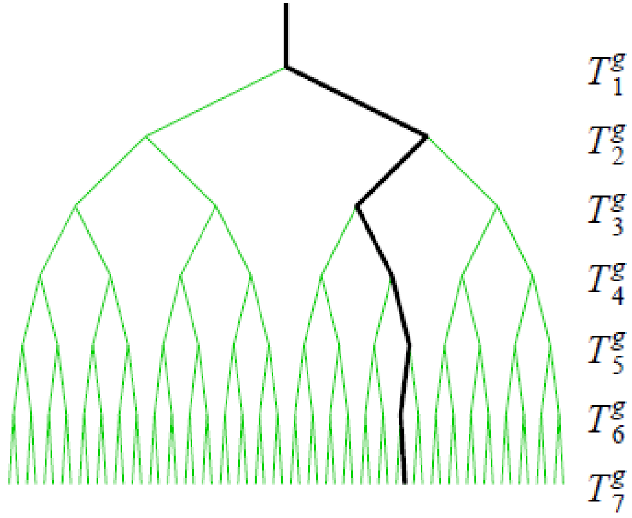


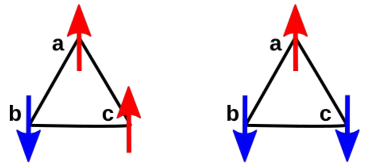
Fig. 5.11 Expanding piston. Extracting energy from a known bit is a three-step process: compress the empty half of the box, remove the partition, and retract the piston and extract $P\,dV$ work out of the ideal gas atom. (One may then restore the partition to return to an equivalent, but more ignorant, state.) In the process, one loses one bit of information (which side of the the partition is occupied).

Residual entropy of glasses

Argument: locally glasses are two-state systems (position of an atom in an amorphous system). Cool a glass from a liquid: freezing will lead to a random configuration, with a lot of frozen, metastable two-state configurations (extensive).

$$S_{\text{residual}} = S_{\text{liquid}}(T_\ell) - \int \frac{1}{T}\frac{\mathrm{d}Q}{\mathrm{d}t}\mathrm{d}t = S_{\text{liquid}}(T_\ell) - \int_0^{T_\ell} \frac{1}{T}\frac{\mathrm{d}Q}{\mathrm{d}T}\mathrm{d}T$$





Compare: Triangular Ising Antiferromagnet (Residual T=0 entropy known)

Entropy: information, non-equilibrium

Various ways of considering the question, how random is a probability distribution (discrete, continuous, quantum statistical mechanics [density matrix – based], information theoretic).

Shannon's entropy (base 2).

$$S_{\text{discrete}} = -k_B \langle \log p_i \rangle = -k_B \sum_i p_i \log p_i.$$

$$S_{\text{nonequil}} = -k_B \langle \log \rho \rangle = -k_B \int \rho \log \rho$$
$$= -k_B \int_{E<\mathcal{H}(\mathbb{P},\mathbb{Q})<E+\delta E} \frac{\mathrm{d}\mathbb{P}\,\mathrm{d}\mathbb{Q}}{h^{3N}} \rho(\mathbb{P},\mathbb{Q}) \log \rho(\mathbb{P},\mathbb{Q}).$$

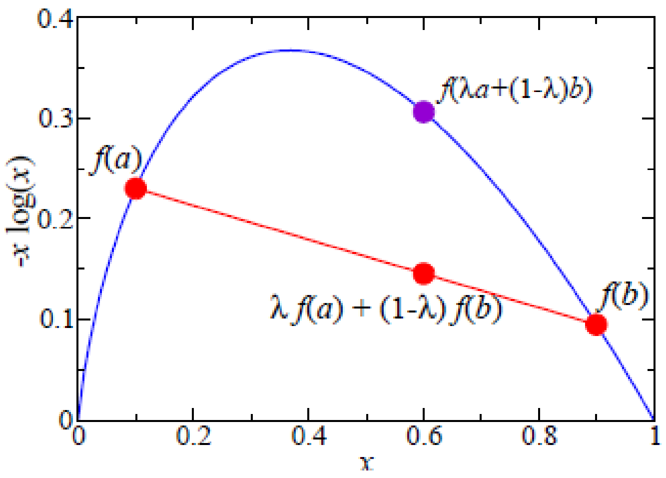
$$S_{\text{quantum}} = -k_B \mathrm{Tr}(\boldsymbol{\rho} \log \boldsymbol{\rho}).$$

$$S_S = -k_S \sum_i p_i \log p_i = -\sum_i p_i \log_2 p_i,$$

Properties of entropy

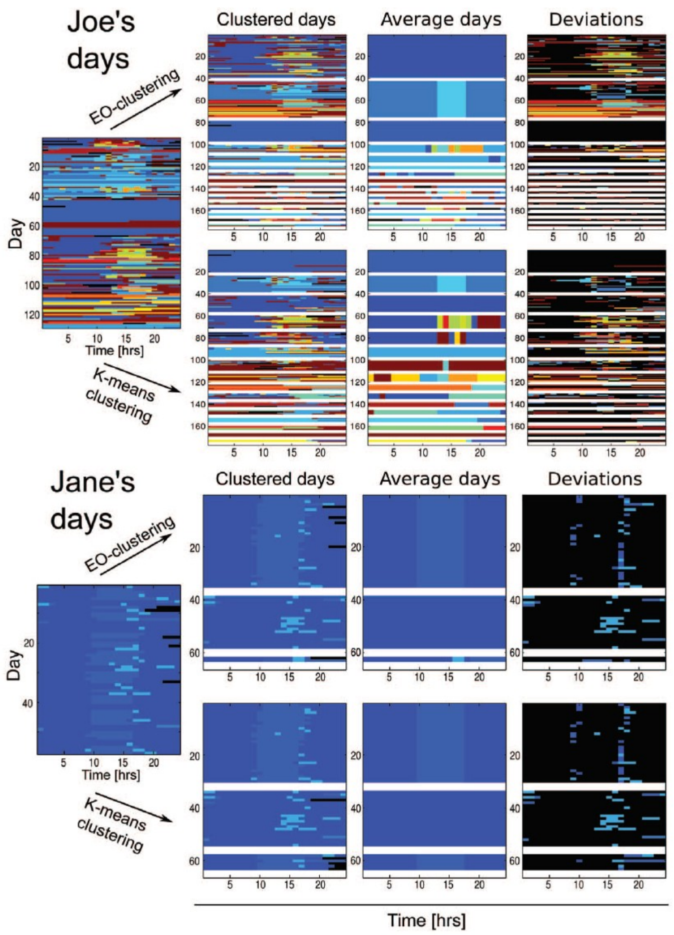
1) Maximum for equal probabilities.
2) Extra states with zero probability not important.
3) Entropy and conditional probabilities – ignorance is additive and entropy is extensive:

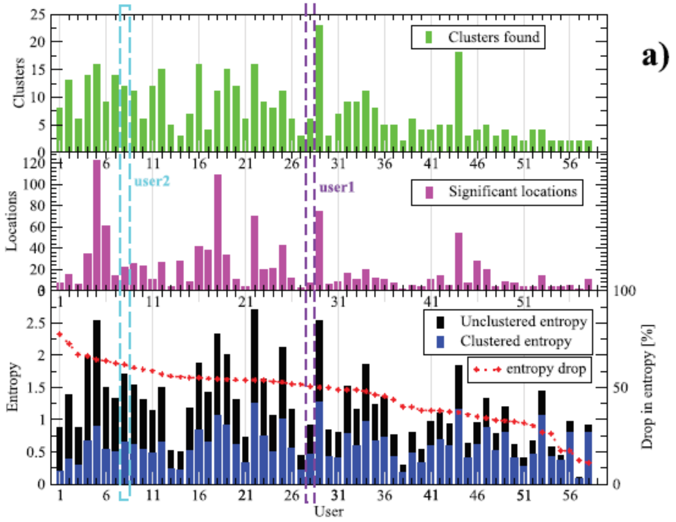
$$\langle S_I(A|B_\ell)\rangle_B = S_I(AB) - S_I(B).$$

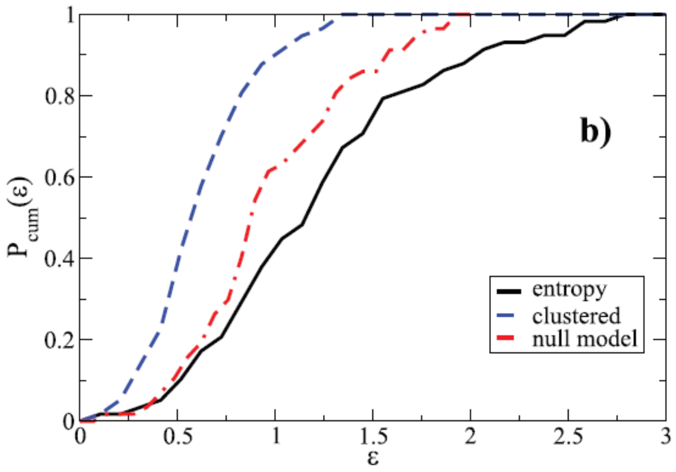


Entropy is concave!

Applications: human life







Patterns, Entropy, and Predictability of Human Mobility and Life

Shao-Meng Qin[1], Hannu Verkasalo[2,3], Mikael Mohtaschemi[1], Tuomo Hartonen[1], Mikko Alava[1]*

Take home…

We now concentrate on Ch. 5 of Sethna (Entropy). The argument splits into three main points: role of entropy in classical thermodynamics, it as a measure of disorder, and finally entropy as a way to quantify information whether the system is in equilibrium or not. Check that you get the Carnot engine argument, and - referring to the last of these - what the (Shannon) entropy must have as its fundamental properties.

The take home quiz splits into two parts. We have two applications, one of which has to do with glasses (and their entropy) and the other one refers to the use of entropy outside of physics - brain science. Your task is now to pick one of these. After that, justify why you wanted that particular one, and read the article in question and summarize it with a few sentences. A target max length for your take home is 2+8 sentences.

And, the choice is between:

https://journals.aps.org/prresearch/abstract/10.1103/PhysRevResearch.2.013202 (glasses)

https://journals.plos.org/plosone/article?id=10.1371/journal.pone.0089948 (brains and NMR)