

Statistical Mechanics

E0415

Fall 2021, lecture 7

Entropy

Take home... on snowflakes

"The fact that no two snowflakes can be identical boils down to statistical fluctuations in the environment during the snowflakes' forming. As the snowflake falls from the sky, initially as a tiny sphere of ice, the primary six dendrites, a feature shared by all snowflakes, form due to the six-fold symmetry of ice-crystals. However, the snowflake is exposed to external conditions that fluctuate violently; the effect which ultimately gives the snowflake its unique shape: Thermal fluctuations and collisions with dust particles in the air generate completely random nucleation sites. The varying temperature and humidity affect the rate of growth at different ends of the snowflake, etc. Considering that the snowflake experiences several such random events that configure its ultimate shape during its fall, it is highly unlikely that two identical snowflakes will form. "

"There have been attempts of creating identical snow crystals in very controlled conditions, with temperature, humidity, positioning and air flow control. Although the resulting snow crystals look very similar to one another, they are not precisely identical."

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

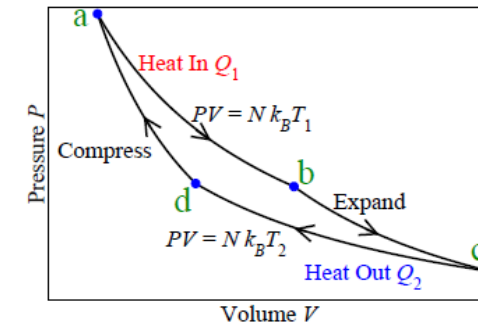
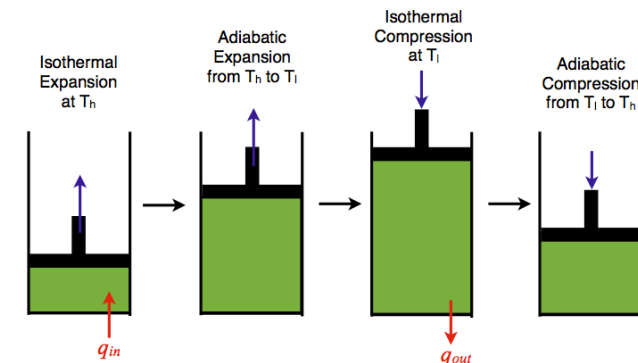


Fig. 5.3 Carnot cycle P - V diagram. The four steps in the Carnot cycle: $a \rightarrow b$, heat in Q_1 at constant temperature T_1 ; $b \rightarrow c$, expansion without heat flow; $c \rightarrow d$, heat out Q_2 at constant temperature T_2 ; and $d \rightarrow a$, compression without heat flow to the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

Entropy, arrow of time (and irreversible heat machines)

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

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



Mixing entropy

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

“Counting entropy”

Maxwell’s demon and entropy – and information.

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

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

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

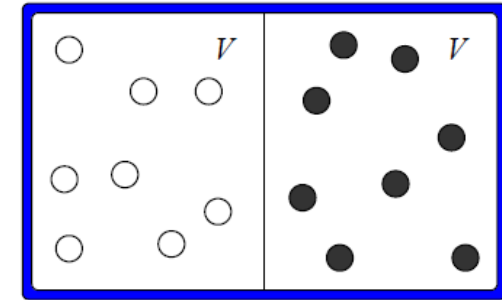


Fig. 5.4 Unmixed atoms. The pre-mixed state: $N/2$ white atoms on one side, $N/2$ black atoms on the other.

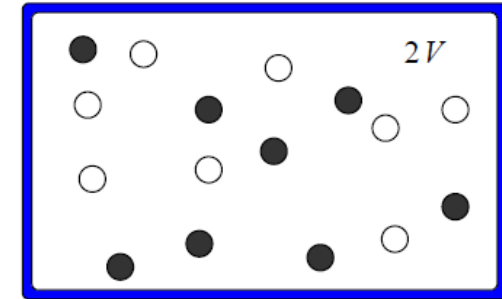


Fig. 5.5 Mixed atoms. The mixed state: $N/2$ white atoms and $N/2$ black atoms scattered through the volume $2V$.

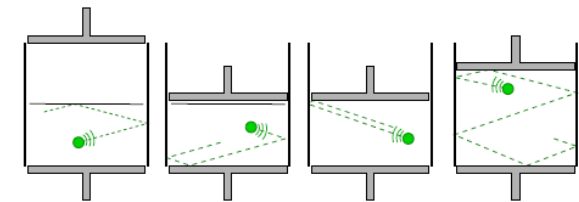
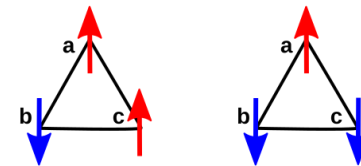
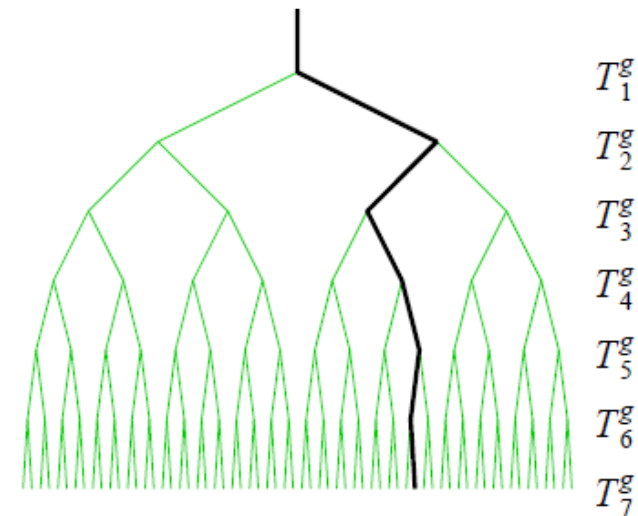


Fig. 5.11 Expanding piston. Extracting energy from a known bit is a three-step process: compress the empty half of the box, remove the partition, and retract the piston and extract $P dV$ work out of the ideal gas atom. (One may then restore the partition to return to an equivalent, but more ignorant,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

$$S_{\text{residual}} = S_{\text{liquid}}(T_\ell) - \int \frac{1}{T} \frac{dQ}{dt} dt = S_{\text{liquid}}(T_\ell) - \int_0^{T_\ell} \frac{1}{T} \frac{dQ}{dT} dT \quad ($$



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).

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

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

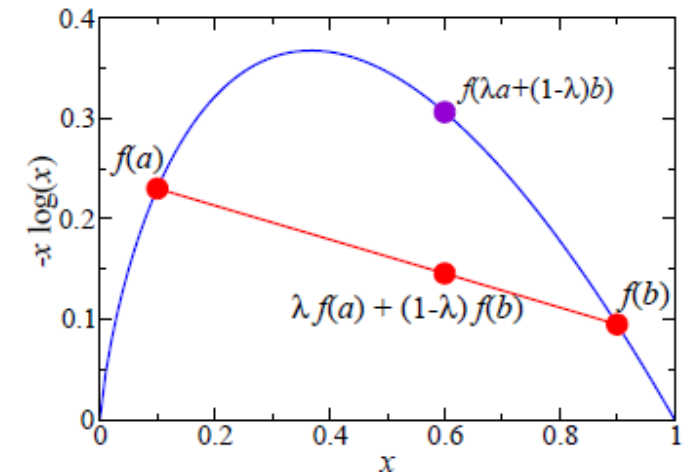
$$S_{\text{quantum}} = -k_B \text{Tr}(\rho \log \rho).$$

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

Properties of entropy

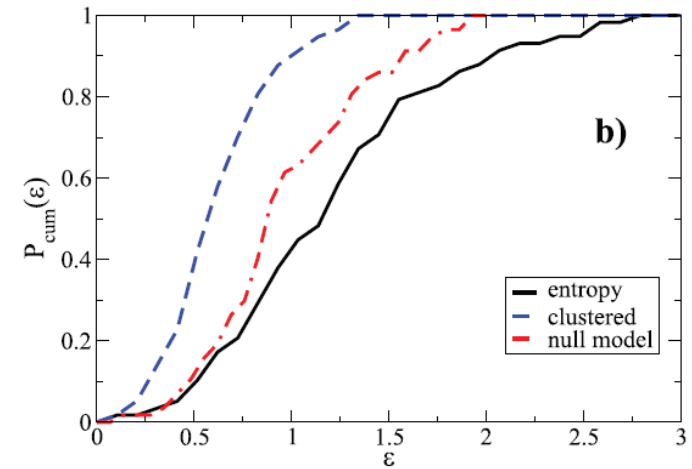
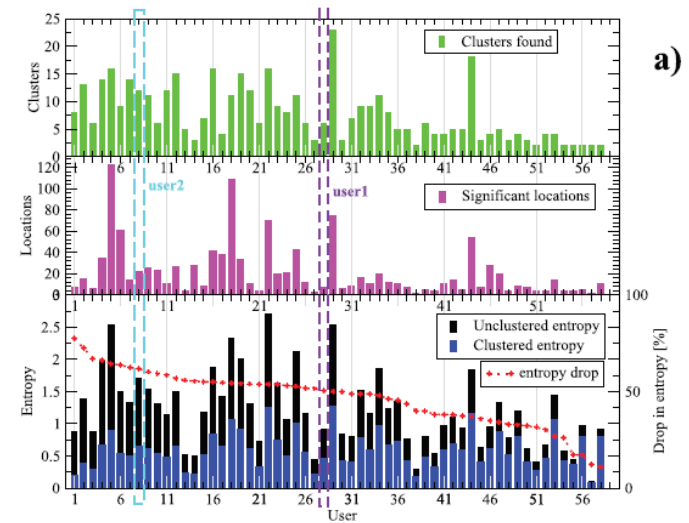
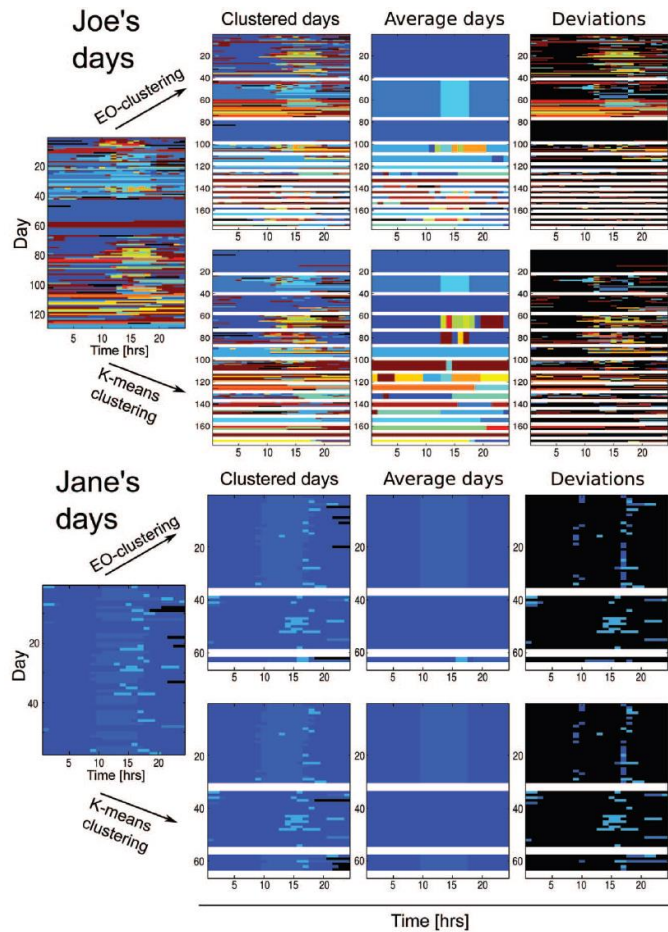
- 1) Maximum for equal probabilities.
- 2) Extra states with zero probability not important.
- 3) Entropy and conditional probabilities – ignorance is additive and entropy is extensive:

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



Entropy is concave!

Applications: human life



Patterns, Entropy, and Predictability of Human Mobility and Life

Shao-Meng Qin¹, Hannu Verkasalo^{2,3}, Mikael Mohtaschemi¹, Tuomo Hartonen¹, 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)