Theo. 4. Statistical Physics.

Lecture 14.

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Last time: Calculating entropy, 2nd Law, Extensivity

Today: Shannon entropy

Third law; Gibbs entropy

From last time, we were considering the lack of extensivity of Boltzmann entropy, $S_B = -k_B H(t)$

$$H(t) = \int d^3\vec{p}\, d^3\vec{q}\; f_1(\vec{p},\vec{q},t) \ln f_1(\vec{p},\vec{q},t)$$

For a gas in equilibrium in a box of volume V, we can derive $f_1(\vec{p},\vec{q}) = n\left(\frac{1}{2\pi m k_B T}\right)^{3/2} \exp\left(\frac{-p^2}{2mk_BT}\right)$

with $n = \frac{N}{V}$.

Then $H = \int d^3\vec{p}\, d^3\vec{q}\; f_1(\vec{p},\vec{q}) \ln(\vec{p},\vec{q})$

Use $\int d^3\vec{q} = V$ since no $\vec{q}$ dep. in f_1

$$= V\int d^3\vec{p}\; n\left(\frac{1}{2\pi m k_B T}\right)^{3/2} \exp\left(\frac{-p^2}{2mk_BT}\right) \left(\ln\left[\frac{n}{(2\pi m k_B T)^{3/2}}\right] - \frac{p^2}{2mk_BT}\right)$$

$$H = N\left[\ln\left(\frac{n}{(2\pi m k_B T)^{3/2}}\right) - \frac{3}{2}\right]$$

(Note no time dependence since equilibrium.)

$$S_B = -k_B H = -k_B N\left(-\frac{3}{2} + \ln(n) - \frac{3}{2}\ln(2\pi m k_B T)\right)$$

$$= k_B N\left(\frac{3}{2} + \frac{3}{2}\ln(2\pi m k_B T) - \ln\left(\frac{N}{V}\right)\right)$$

Now, this is not properly extensive, since V scales.

It also violates the third law of thermodynamics.

Third law of thermodynamics.

The entropy of all systems at zero absolute temperature is a universal constant that can be taken to be zero.

Mathematically, this is $\lim_{T \to 0} S(\vec{X}, T) = 0$

Thus, beyond differences in entropy, we have a fundamental constant of entropy at $T=0$. This promotes $T=0K$ to be an absolute zero, and the limit $S(\vec{X},T)=0$ for $T \to 0$ occurs regardless of what the other thermodynamic coordinates are. Looking at S_B, it is clear that S_B does not reach 0 for $T \to 0$ (it is singular) and it would only reach 0 for a carefully prescribed scaling with $n = \frac{N}{V}$. So S_B = Boltzmann entropy is not sufficient for a state fcn. of entropy.

Important aside:

Even though $S_B = -k_B H(t)$ is not exactly what we need for thermodynamic entropy, it is helpful in understanding basic information theory.

Cf. Blundell + Blundell, Chap. 15.

Consider how to communicate information

As an example, consider the following statements:

(1) Newton's birthday is on a particular day of the year.
(2) Newton's birthday is in the second half of the year.
(3) Newton's birthday is on the 25th of a month.

(FYI, Newton's birthday is December 25, 1642 [Julian]
= January 4, 1643 [Gregorian])

The first has no information content.
Second takes probability space + divides by 2.
Third has most information content.

We can quantify information content by, in the absence of prior information, how the possible probability space changes. Moreover, independent statements should multiply their probability restrictions, which we will take to be <u>additive</u> information quantities.

We thus define $Q = -k \log p$ as the information content of a statement, with $k > 0$. For $\log_2$, this counts information in bits.

For multiple statements, $Q_i = -k \log p_i$. There is an average information content $S = \langle Q \rangle = \sum_i Q_i p_i$
$= -k \sum_i p_i \log p_i$

This expression is called <u>Shannon entropy</u>, and it quantifies how much information is gained on average after a particular quantity is ~~constrained~~ measured (or constrained).

How is this intuitive? $S = -k_B \sum_{i=1}^{M} p(i) \ln(p(i))$

Consider extreme/limiting cases, such as $p(i) = \delta_{ij}$ as a delta-function (for discrete states). This has maximum information & ~~minimum~~ minimum entropy of zero, while a uniform distribution would have $p(i) = \frac{1}{M}$ and a maximum entropy of $\ln M$. S thus measures disorder in the distribution.

In statistical mechanics, we had $S = k_B \ln \Omega$, where Ω is the number of microstates associated with a given macrostate. We now introduce Gibbs's expression for entropy:

$$S = -k_B \sum_i P_i \ln P_i ,$$

where P_i = probability of a system to be in an i^{th} macrostate. This generalizes from $S = k_B \ln \Omega$ since we are allowing multiple macrostates. If we have N total microstates, then $\sum_i n_i = N$ where n_i is the number of microstates for each macrostate i. Then $P_i = \frac{n_i}{N}$. $S_{tot} = k_B \ln N$ and $S_i = k_B \ln n_i$ are the total entropy & the entropy of the microstates in the i^{th} macrostate.

We have to distinguish entropy of macrostate degeneracy (which is measurable) from microstate degeneracy.

$$S = S_{tot} - S_{micro}$$

$$S_{micro} = \langle S_i \rangle = \sum P_i S_i$$

$$S = k_B \ln N - k_B \sum P_i \ln n_i = k_B \sum_i P_i (\ln N - \ln n_i)$$

$$= k_B \sum_i P_i \ln\left(\frac{N}{n_i}\right) = k_B \sum_i P_i (-\ln P_i) = -k_B \sum_i P_i \ln P_i$$

Example:

System has 5 ~~microst~~ macrostates & each macrostate has 3 microstates.

$$S = k_B \ln 5$$

or $$S = k_B \ln 15 - k_B \ln 3$$

$$S = S_{tot} \qquad S_{micro}$$

Gibbs entropy holds for all systems, ~~allowing~~ not requiring system to be in single macrostate.

Stat. mech. entropy: Use $p_i = \frac{1}{N}$.

$$S = -k_B \cdot \sum_i \frac{1}{N} \ln \frac{1}{N}$$

$$= -k_B \cdot \frac{N}{N} \ln \frac{1}{N} = k_B \ln N \equiv k_B \ln \Omega$$

for single macrostate.

Next time: ~~Therom~~ Thermodynamic constraints, other expressions for entropy.
Maxwell relations