# Statistical Mechanics

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## 1 Introduction

These notes are taken from Leonard Susskind's first five lectures on Statistical Mechanics from Stanford University, and available on YouTube.

## 2 Entropy

Given a probability distribution over the discrete variable $x$ which make taken on values $i = 1..K$, the entropy is

$$S = -\sum_{i=1}^{K} p_i \log p_i \tag{1}$$

where $p_i \equiv p(x = i)$. If only M of the K states have non-zero probability and that probability is $1/M$ then $S = \log M$. In this special case the entropy is the log of the number of occupied states.

An analog of this special case in the continuous domain occurs in Liouville's Theorem. This states that if the volume of phase space (i.e. of the $x$ variable, but now multivariate and continuous) is some fixed value e.g. $\log M$ then after the system evolves the distribution over $x$ will change but the volume will be preserved. The density within the volume is assumed uniform.

Entropy can depend both on the state of a system itself and your knowledge of it (depending, presumably, on what distribution one is considering).

## 3 Temperature

The most general definition of temperature, $T$, is 'the amount of energy required to increase the entropy by 1 unit of information'. That is

$$T = \frac{dE}{dS} \tag{2}$$

where $E$ is energy. To show that this is a sensible definition, consider two volumes of material A and B that are connected to each other and so may exchange energy. Before this exchange occurs assume that each system is at steady state with temperatures $t_A$ and $t_B$ and that $t_B \geq t_A$.

From the first law of thermodynamics (L1) we know that the total energy is conserved. Hence

$$dE_A + dE_B = 0 \tag{3}$$

From the second law of thermodynamics we know entropy increases (L2)

$$dS_A + dS_B \geq 0 \tag{4}$$

Substituting our definintion of temperature into equation 3 gives

$$dS_B = \frac{-T_A}{T_B} dS_A \tag{5}$$

Pluggin this into equation 4, and assuming temperatures are positive, gives

$$(T_B - T_A) dS_A \geq 0 \tag{6}$$

Because we have defined B to be at higher temperature than A we have

$$dS_A \geq 0 \tag{7}$$

Multiplying by $T_A$ gives

$$dE_A \geq 0 \tag{8}$$

Thus the energy of system A increases. From L1, the energy of system B must therefore decrease. Hence energy flows from the higher temperature system to the lower until the temperatures are equal.

# 4 Equilibrium Distribution

Here we consider our system of interest as being in contact with a heat bath which is so large we can consider our system as being just one of N replicas of our system where N is a large number. We denote the number of replicas in state $k$ as $n_k$. We have

$$\sum_{k=1}^{K} n_k = N \tag{9}$$

For example if $n_1 = N$ all replicas are in state 1. Given that N is large we have $p_k = n_k / N$.

What is the distribution of states at thermal equilibrium ? i.e. what is $p_k$ ? Well, the $p_k$ are defined by the corresponding set of occupation numbers $n_k$. The more ways there are of supporting $\{n_1, ..., n_k, ..., n_K\}$ the more probable is that set. This number of combinations is given by

$$C = \frac{N!}{n_1! n_2! ... n_K!} \tag{10}$$

We now approximate

$$\log N! = \sum_{a=1}^{N} \log a \tag{11}$$

by the continuous integral

$$\begin{aligned} \log N! &\approx \int_1^N \log a da \\ &\approx N \log N - N \end{aligned} \tag{12}$$

Hence $N! = N^N e^{-N}$ which is Stirling's approximation. Plugging this into equation 10 gives

$$\begin{aligned} \log C &= N \log N - \sum_i n_i \log n_i \\ &= -\sum_{i=1}^{K} p_i \log p_i \\ &= S \end{aligned} \tag{13}$$

Thus the most probable distribution of states is the one with the highest entropy.

So, we can now finesse our question to be - what is the distribution of states with maximal entropy ? Given that the constraints on this distribution are

$$\begin{aligned} \sum_{k=1}^{K} p_k &= 1 \\ \sum_{k=1}^{K} p_k e_k &= E \end{aligned} \tag{14}$$

where $E$ is the energy, the solution can be found by minimising

$$V(p) = \sum_k p_k \log p_k + \alpha \left( \sum_k p_k - 1 \right) + \beta \left( \sum_k p_k e_k - E \right) \tag{15}$$

where $\alpha$ and $\beta$ are Lagrange multipliers. Differentiating with respect to $p_k$ and setting to zero gives

$$\log p_k = -(1+\alpha) - \beta e_k \tag{16}$$

Hence

$$p_k = \frac{1}{Z} \exp(-\beta e_k) \tag{17}$$

where $Z = e^{1+\alpha}$. This is the Boltzmann distribution.

# 5 The Partition Function

The quantity $\log Z$ is known as the partition function and the fundamental quantities entropy, energy and temperature can all be related to it.

## 5.1 Energy

Using the definition of energy we have

$$\begin{aligned} E &= \sum_k e_k p_k \\ &= \frac{1}{Z} \sum_k e_k \exp(-\beta e_k) \end{aligned} \tag{18}$$

and given that Z is the normalisation constant, we have

$$\begin{aligned} Z &= \sum_k \exp(-\beta e_k) \qquad (19) \\ \frac{dZ}{d\beta} &= -\sum_k e_k \exp(-\beta e_k) \end{aligned}$$

Hence

$$\begin{aligned} E &= -\frac{1}{Z}\frac{dZ}{d\beta} \qquad (20) \\ &= -\frac{d\log Z}{d\beta} \end{aligned}$$

### 5.2 Entropy

Using the definition of entropy we have

$$S = -\sum_k p_k \log p_k \qquad (21)$$

and from the Boltzmann distribution we know

$$\begin{aligned} p_k &= \frac{1}{Z}\exp(-\beta e_k) \qquad (22) \\ \log p_k &= -\beta e_k - \log Z \end{aligned}$$

Hence

$$\begin{aligned} S &= \beta \sum_k p_k e_k + \log Z \sum_k p_k \qquad (23) \\ &= \beta E + \log Z \end{aligned}$$

### 5.3 Temperature

From the above relation between $S$ and $\log Z$ we can write

$$\begin{aligned} dS &= \beta dE + E d\beta + \frac{d\log Z}{d\beta} d\beta \qquad (24) \\ &= \beta dE + E d\beta - E d\beta \end{aligned}$$

Hence

$$\beta = \frac{dS}{dE} \qquad (25)$$

Therefore $\beta = 1/T$ is the inverse temperature.

## 6 Helmholtz Free Energy

We can rewrite equation 23, by multiplying through by temperature, $T = 1/\beta$, and re-arranging as

$$E - TS = -T \log Z \qquad (26)$$

The Helmholtz Free Energy, $A$, is then defined as the above quantity

$$\begin{aligned} A &= E - TS \\ &= -T \log Z \end{aligned} \tag{27}$$

So, $A$ is a function of temperature.

# 7 Adiabatic Change

In dependent variables that one may vary experimentally are referred to as control parameters. For example, one may alter volume, $V$, and measure what is the effect on the dependent variable energy.

We can define pressure on eg. a piston connected to a volume of material as

$$P = -\frac{\partial E}{\partial V} \tag{28}$$

Increasing the volume results in less pressure on the piston. An adiabatic change is defined as one which does not change the entropy. Thus if the volume changes adiabatically we have

$$P = -\left.\frac{\partial E}{\partial V}\right|_S \tag{29}$$

From basic calculus (see section 1.6.1) we can write

$$\begin{aligned} -P &= \left.\frac{\partial E}{\partial V}\right|_T - \left.\frac{\partial E}{\partial S}\right|_V \left.\frac{\partial S}{\partial V}\right|_T \\ &= \left.\frac{\partial E}{\partial V}\right|_T - T\left.\frac{\partial S}{\partial V}\right|_T \\ &= \left.\frac{\partial}{\partial V}(E - TS)\right|_T \\ &= \left.\frac{\partial A}{\partial V}\right|_T \end{aligned} \tag{30}$$

where the second line follows from the definition of temperature, and the last line follows from the definition of the Helmholtz Free Energy. We therefore also have

$$P = T\left.\frac{\partial \log Z}{\partial V}\right|_T$$

Pressure is sometimes referred to as the 'thermodynamic conjugate' of volume (cf. dependent and independent variables).

### 7.0.1 Example: Ideal gas

For an ideal gas

$$\begin{aligned} Z &= \frac{V^N}{N!} f(\beta) \\ \log Z &= N \log V + \log f(\beta) + ... \\ \frac{\partial \log Z}{\partial V} &= \frac{N}{V} \end{aligned} \tag{31}$$

Hence $PV = NT$, the ideal Gas law, or if you measure temperature in kelvin $PV = NkT$.

# Appendix

## Calculus for Adiabatic Change

The change in entropy given by a change in volume and temperature is

$$dS = \left.\frac{\partial S}{\partial V}\right|_T \Delta V + \left.\frac{\partial S}{\partial T}\right|_V \Delta T \tag{32}$$

Therefore, if there is no change in entropy $dS = 0$ we must have

$$\frac{\Delta T}{\Delta V} = \frac{-\left.\frac{\partial S}{\partial V}\right|_T}{\left.\frac{\partial S}{\partial T}\right|_V} \tag{33}$$

This is our adiabatic constraint. Similarly, the change in energy given by a change in volume and temperature is

$$\Delta E = \left.\frac{\partial E}{\partial V}\right|_T \Delta V + \left.\frac{\partial E}{\partial T}\right|_V \Delta T \tag{34}$$

Therefore, the change in energy per change in volume is

$$\begin{aligned} \frac{\Delta E}{\Delta V} &= \left.\frac{\partial E}{\partial V}\right|_T + \left.\frac{\partial E}{\partial T}\right|_V \frac{\Delta T}{\Delta V} \\ &= \left.\frac{\partial E}{\partial V}\right|_T + \left.\frac{\partial E}{\partial S}\right|_V \left.\frac{\partial S}{\partial T}\right|_V \frac{\Delta T}{\Delta V} \end{aligned} \tag{35}$$

Finally, plugging in equation 33 (our adiabatic constraint) into this last equation gives

$$\left.\frac{\partial E}{\partial V}\right|_S = \left.\frac{\partial E}{\partial V}\right|_T - \left.\frac{\partial E}{\partial S}\right|_V \left.\frac{\partial S}{\partial V}\right|_T \tag{36}$$