Statistical Mechanics

Problem Set 1

Probability, Statistics and Fluctuations

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Probability, statistics and fluctuations

1.4

We have the probabilities $P(\text{boy}) = P(\text{girl}) = 1/2$. Consider the conditional probability:

$$P(\text{at least one girl}|\text{at least one boy}) = \frac{P(\text{at least one girl} \cap \text{at least one boy})}{P(\text{at least one boy})} \tag{1}$$

This is a combinatorial problem. The number of ways to have at least one boy and one girl is $2^2 - 2 = 2$. The number of ways to have at least one boy out of the two children is $2^2 - 1 = 3$. Therefore, the conditional probability is $2/3$.

On the other hand, if we are informed that **a particular child** (in this case the taller one) is a boy, then the conditional probability is:

$$P(\text{at least one girl}|\text{the taller one is a boy}) = \frac{P(\text{at least one girl} \cap \text{the taller one is boy})}{P(\text{the taller one is a boy})} \tag{2}$$

There is only one way to have one girl and one taller boy, and there are two ways to have the taller one to be a boy. Therefore, the conditional probability is $1/2$.

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1.5

The number of ways to achieve $N/2$ heads and $N/2$ tails out of N coin tosses is given by the binomial coefficient:

$$\binom{N}{N/2} = \frac{N!}{(N/2)!(N/2)!} \tag{3}$$

The number of ways to have $N/2 - m$ heads and $N/2 + m$ tails is given by:

$$\binom{N}{N/2 - m} = \frac{N!}{(N/2 - m)!(N/2 + m)!} \tag{4}$$

For this to be half of the previous number, we must have:

$$\left(\frac{N}{2} - m\right)! \left(\frac{N}{2} + m\right)! = 2\left(\frac{N}{2}!\right)^2 \tag{5}$$

Consider the expansion of the left hand side:

$$\left(\frac{N}{2}-m\right)!\left(\frac{N}{2}+m\right)! = \left(\frac{N}{2}!\right)^2 \frac{(N/2+1)(N/2+2)\cdots(N/2+m)}{(N/2-m+1)(N/2-m+2)\cdots(N/2)} \tag{6}$$

We can thus cancel the $(N/2)!$ term and obtain:

$$\left(\frac{N}{2}+1\right)\left(\frac{N}{2}+2\right)\cdots\left(\frac{N}{2}+m\right) = 2\left(\frac{N}{2}-m+1\right)\left(\frac{N}{2}-m+2\right)\cdots\left(\frac{N}{2}\right) \tag{7}$$

Retaining only terms of order m and $m-1$ in N, we have:

$$\left(\frac{N}{2}\right)^m + \left(\sum_{r=1}^{m} r\right)\left(\frac{N}{2}\right)^{m-1} \approx 2\left[\left(\frac{N}{2}\right)^m + \left(\sum_{r=1}^{m} r - m\right)\left(\frac{N}{2}\right)^{m-1}\right] \tag{8}$$

But the second sum is just $-m$ through to -1, so the equation becomes:

$$\left(\frac{N}{2}\right)^m + \left(\sum_{r=1}^{m} r\right)\left(\frac{N}{2}\right)^{m-1} \approx 2\left(\frac{N}{2}\right)^m - 2\left(\sum_{r=1}^{m} r\right)\left(\frac{N}{2}\right)^{m-1} \tag{9}$$

For large m, the sums can be approximated as:

$$\sum_{r=1}^{m} r = \frac{m(m+1)}{2} \approx \frac{m^2}{2} \tag{10}$$

leading to:

$$\begin{gathered}\left(\frac{N}{2}\right)^m + \frac{m^2}{2}\left(\frac{N}{2}\right)^{m-1} \approx 2\left(\frac{N}{2}\right)^m - m^2\left(\frac{N}{2}\right)^{m-1} \\ \frac{3}{2}m^2 \approx \left(\frac{N}{2}\right) \\ m \approx \sqrt{\frac{3N}{2}}\end{gathered} \tag{11}$$

For N of the order 10^{23}, we have $m \approx 10^{11.5}$, which is very small compared to N. This means that the peak around $N/2$ is very sharp.

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1.6

We divide each molar heat capacity by R and obtain:

Al	2.93	Pb	3.18
Ar	2.50	Ne	2.50
Au	3.06	N2	3.50
Cu	2.94	O2	3.53
He	2.50	Ag	3.07
H2	3.47	Xe	2.50
Fe	3.02	Zn	3.01

There is a trend that gaseous substances have a higher molar heat capacity than solid substances. This is because the heat capacity of a solid is dominated by the lattice vibrations whereas the heat capacity of a gas is dominated by the translational and rotational degrees of freedom.

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1.7

From direct calculation, we have $\ln 15! = 27.8993$. Stirling's approximation gives:

$$\ln 15! \approx 15 \ln 15 - 15 = 25.6208 \tag{12}$$

which is not a very good approximation.

The leading error made by using Stirling's approximation is:

$$\frac{\ln N}{N} \tag{13}$$

For this to be less than 0.02, we need $N > 282.1$.

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1.8

There exists only one microstate where all particles have the same energy ϵ. The given macrostate of three zero energy particle, one ϵ energy particle and one 2ϵ energy particle has the degeneracy:

$$\binom{5}{1} \times \binom{4}{1} \times \binom{3}{3} = 20 \tag{14}$$

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1.9

The number of microstates for the given macrostate is:

0	ϵ	2ϵ	3ϵ	4ϵ	5ϵ	Number
4					1	5
3	1			1		20
3		1	1			20
2	2		1			30
2	1	2				30
1	3	1				20
	5					1

$$\binom{16}{1} \times \binom{15}{2} \times \binom{13}{2} \times \binom{11}{4} \times \binom{7}{7} = 43243200 \tag{15}$$

The entropy is:

$$S = \ln \Omega = 17.58 \tag{16}$$

The temperature can be approximated by:

$$T = \frac{E}{k_B \ln \Omega} \tag{17}$$

so that in terms of ϵ/k_B, the temperature is:

$$\frac{18}{\ln 43243200} = 1.02 \tag{18}$$

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Extra

Consider a system of N particles in an isolated system, such that the total energy U is fixed. The entropy of the system is given by (up to a constant):

$$S = -\sum_i P_i \ln P_i \tag{19}$$

where P_i is the probability of the system being in the i-th microstate.

On the other hand, to fulfil the constraint of fixed energy, we require:

$$\sum_i P_i E_i = U \tag{20}$$

where E_i is the energy of the i-th microstate.

To maximise the entropy, we use the method of Lagrange multipliers. Consider the modified entropy:

$$S' = -\sum_i P_i \ln P_i + \beta \left(\sum_i P_i E_i - U \right) \tag{21}$$

The extremum of S' is given by the conditions:

$$\begin{aligned} \frac{\partial S'}{\partial P_i} &= -\ln P_i - 1 - \beta E_i = 0 \\ \frac{\partial S'}{\partial \lambda} &= U - \sum_i P_i E_i = 0 \end{aligned} \tag{22}$$

The first equation gives the Boltzmann distribution:

$$P_i = \frac{1}{Z} e^{-\beta E_i} \tag{23}$$

where Z is a normalisation constant given by:

$$Z = \sum_i e^{-\beta E_i} \tag{24}$$

The β factor is determined by the equation:

$$-\frac{\partial \ln Z}{\partial \beta} = U \tag{25}$$

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