PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Plan for Lecture 6: Distribution of macrostates

Reading: Chapters 2.3-2.4

1. **Binomial distribution for small and large samples**
2. **Probability, mean value, variance**
3. **Central limit theorem**
4. **Stirling's approximation**

In this lecture we will continue our discussion of microstates and macrostates. The 2 state example can be described/generalized by use of the binomial distribution which will help us understand how to describe macroscopic systems.

PHY 341/641 Thermodynamics and Statistical Mechanics

MWF 12 and 2	Online and face-to-face	http://www.wfu.edu/~natalie/s21phy341/

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Course schedule for Spring 2021

(Preliminary schedule -- subject to frequent adjustment.) Reading assignments are for the **An Introduction to Thermal Physics** by Daniel V. Schroeder. The HW assignment numbers refer to problems in that text.

	Lecture date	Reading	Topic	HW	Due date
1	Wed: 01/27/2021	Chap. 1.1-1.3	Introduction and ideal gas equations	1.21	01/29/2021
2	Fri: 01/29/2021	Chap. 1.2-1.4	First law of thermodynamics	1.17	02/03/2021
3	Mon: 02/01/2021	Chap. 1.5-1.6	Work and heat for an ideal gas		
4	Wed: 02/03/2021	Chap. 1.1-1.6	Review of energy, heat, and work	1.45	02/05/2021
5	Fri: 02/05/2021	Chap. 2.1-2.2	Aspects of entropy		
6	Mon: 02/08/2021	Chap. 2.3-2.4	Multiplicity distributions	2.24	2/10/2021
7	Wed: 02/10/2021				
8	Fri: 02/12/2021				
9	Mon: 02/15/2021	Chap. 3.1			

In the last lecture, we introduced the notion of microstates and macrostates, introducing the multiplicity distribution $\Omega(N,n)$. Here we will first focus on the example of a spin ½ system where an example microstate may be

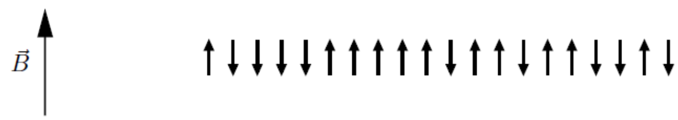


Figure 2.1. A symbolic representation of a two-state paramagnet, in which each elementary dipole can point either parallel or antiparallel to the externally applied magnetic field. Copyright ©2000, Addison-Wesley.

Here N denotes the total number of spins with $n = N_\uparrow$ up spins and $N - n = N_\downarrow$ down spins.

Example microstate

↑ ↓ ↓ ↓ ↓ ↑ ↑ ↑ ↑ ↑ ↓ ↑ ↑ ↓ ↑ ↑ ↓ ↓ ↑ ↓

The multiplicity of this state of N total spins with n up spins:

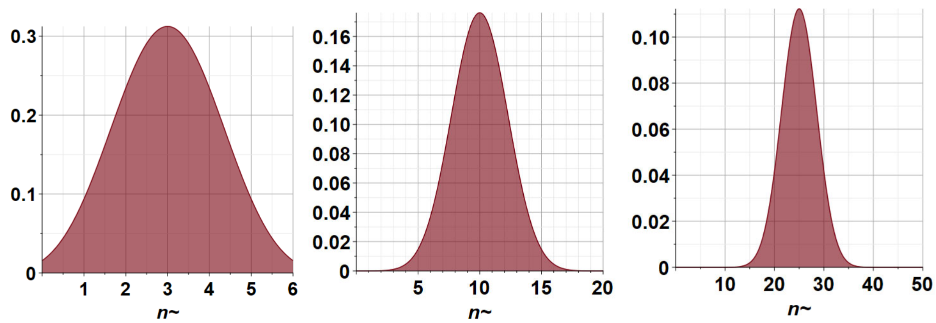
$$\Omega(N,n) = \frac{N!}{n!(N-n)!}$$

A related quantity is the probability of a finding among the macrostates, one that has n up spins when the probability of a single spin up state is p and q is the probability of a down spin.

$$P(N,n) = \Omega(N,n)\, p^n q^{N-n} = \frac{N!}{n!(N-n)!} p^n q^{N-n}$$

Note that $\displaystyle\sum_{n=1}^{N} P(N,n) = \sum_{n=1}^{N} \frac{N!}{n!(N-n)!} p^n q^{N-n} = \left(p+q\right)^N = 1$

$$P(N,n) = \frac{N!}{n!(N-n)!} p^n q^{N-n} \quad \text{for } p = q = \frac{1}{2}$$



N=6 *N=20* *N=50*

More results for the binomial probability distribution

$$P(N,n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$$

Average value of *n*:

$$\mu \equiv \langle n \rangle = \sum_{n=0}^{N} nP(N,n) = Np$$

Variance of *n*:

$$\sigma^2 \equiv \left\langle \left(n - \langle n \rangle\right)^2 \right\rangle = Npq$$

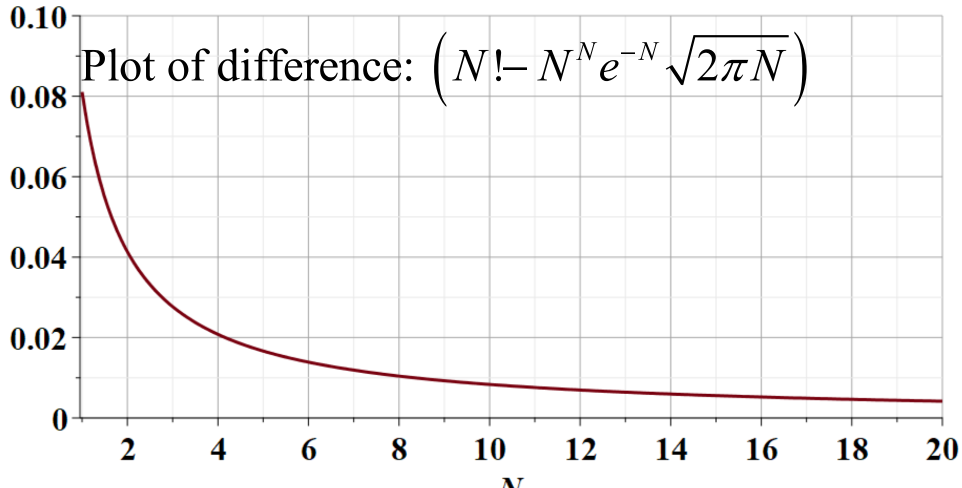
Useful formula -- Stirling's approximation of factorial

$$M! \approx M^M e^{-M} \sqrt{2\pi M}$$

Small digression --

Useful formula -- Stirling's approximation of factorial

$M! \approx M^M e^{-M} \sqrt{2\pi M}$



Now consider a continuous probability function $P(x)$

for $-\infty \leq x \leq \infty$ $\int_{-\infty}^{\infty} P(x)dx = 1$

Mean value: $\mu = \int_{-\infty}^{\infty} xP(x)dx$ Variance: $\sigma^2 = \int_{-\infty}^{\infty} (x-\mu)^2 P(x)dx$

Example: Gaussian probability function

$$P_G(x;\mu,\sigma^2) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2}$$

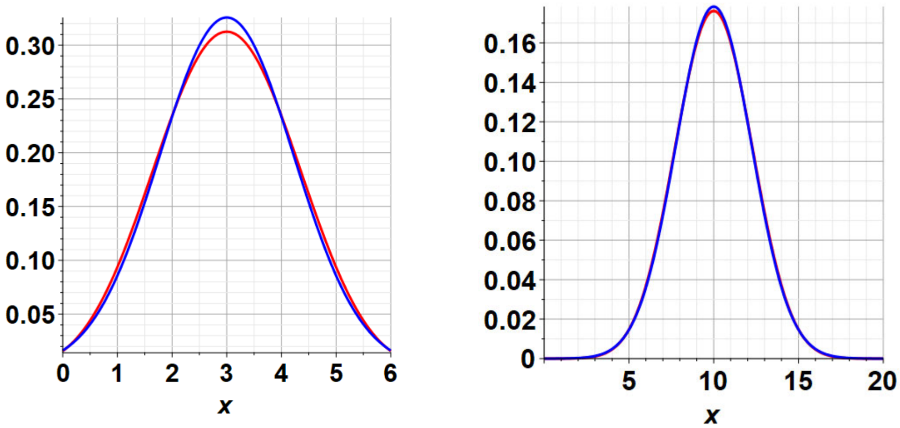
It can be shown that:

$$\langle x \rangle = \int_{-\infty}^{\infty} xP_G(x;\mu,\sigma^2) = \mu$$

$$\left\langle (x - \langle x \rangle)^2 \right\rangle = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 P_G(x;\mu,\sigma^2) = \sigma^2$$

Comparison of binomial probability and Gaussian probability

Binomial
Gaussian



N=6 *N=20*

Is it an accident that for large samples the binomial distribution converges to the Gaussian distribution?

➔It is possible to prove that the probability density of a collection of N independent random variables with finite variance, summed together, is a Gaussian distribution in the limit that $N \rightarrow$ infinity. This is called the "Central Limit Theorem".

Some details of the central limit theorem as explained by Essential Statistical Physics by Malcolm P. Kennett, Cambridge U. Press, 2021

Suppose that we have *N* random variables s_i that can take on multiple different values. These variables have a mean <*s*> and a variance σ_s^2 . We then determine their sum *S* and examine the probability distribution for the value of *S.*

$$S \equiv \sum_{i=1}^{N} s_i$$

The central limit theorem says that for $N \to \infty$

$$P(S) = \frac{1}{\sqrt{2\pi \langle S \rangle}} e^{-(S-\langle S \rangle)^2/2\sigma_S^2} \quad \text{where } \langle S \rangle = N \langle s \rangle \text{ and } \sigma_S^2 = N\sigma_s^2$$

Recap --

Recall that the variances are defined to be

$$\sigma_s^2 \equiv \left\langle \left(s - \langle s \rangle\right)^2 \right\rangle \quad \text{and} \quad \sigma_S^2 \equiv \left\langle \left(S - \langle S \rangle\right)^2 \right\rangle$$

The central limit theorem says that for $N \rightarrow \infty$

$$P(S) = \frac{1}{\sqrt{2\pi \langle S \rangle}} e^{-(S-\langle S \rangle)^2/2\sigma_S^2} \quad \text{where} \quad \langle S \rangle = N \langle s \rangle \text{ and } \sigma_S^2 = N\sigma_s^2$$

$$\Rightarrow \frac{\sigma_S}{\langle S \rangle} = \frac{1}{\sqrt{N}} \frac{\sigma_s}{\langle s \rangle}$$

➔As the sample becomes very large, independent of the details of the system, the probability distribution of the variables becomes increasing peaked about the mean value.

Are these ideas generalizable to continuous variables such as found in the description of an ideal gas for example? This is the subject of Section 2.5 of your textbook which we will examine next time.