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**

Record!!!

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			
10	Wed: 02/17/2021				

Your questions –

From Parker -- Why is it that at the microscopic level processes are reversible, I thought reversible processes were always an approximation? The principle of detailed balance lets this happen at microscopic, but I think not macroscopic levels.

From Kristen -- 1. For the example in 2.3, why is the multiplicity of the total system the product of the two solids, not the sum? (Figure 2.4) 2. I would love to go through some of the math to get to equation 2.22 because I am a bit confused.

From Annelise -- What is the significance of knowing which macrostate is most plausible? Why does that matter?

From Rich -- When would it be useful to use Sterling's approximation of a factorial?

From Leon -- So for large samples binomial distribution converges to the Gaussian distribution, but if it comes to a small sample can we still use this approximation or we should do something else?

From Zezhong -- I would how to get the final approximation of equation 2.26 and how to get equation 2.27? Also, I wonder what is the meaning of variance for Physics since I forget it.

Your questions – continued –

From Michael -- For a Gaussian function, how do we classify the probability of an energy outside that of the width of (qN^-.5) from the omega maximum occurring? How far outside this width is it a realistic estimation that this solution could occur?

Some discussion –

Question -- Why is it that at the microscopic level processes are reversible, I thought reversible processes were always an approximation? The principle of detailed balance lets this happen at microscopic, but I think not macroscopic levels.

Comment – At the atomic level, we expect that basic reversible physics applies, such as Newton’s laws, quantum mechanics, etc. At the macroscopic level, we cannot know all of the details of each particle motion and we are dealing with averages of properties.   How exactly irreversisiblity comes into this story is an active intellectual challenge even today.

Some discussion –

Your question -- What is the significance of knowing which macrostate is most plausible? Why does that matter?

Comment – In this treatment, we are preparing for how to reconcile the atomic and macroscopic viewpoints. At the atomic level, we can solve Newton's equations if we know initial of boundary values. At the macroscopic, we cannot know the initial or boundary values of 10^{23} particles; the best we can do is estimate averages based on some macroscopic measurements such as T, P, V, S…… But because there are so many particles, even the averaging is difficult and in these sections we are finding that there are some simplifying patterns that can help us. In particular, for some macrostate property, there is a small range of values that have a very large multiplicity and the others are much smaller multiplicities.

Discussion –

Question -- When would it be useful to use Sterling's approximation of a factorial?

Comment – $10! \sim 10^6$

Question -- For the example in 2.3, why is the multiplicity of the total system the product of the two solids, not the sum? (Figure 2.4)

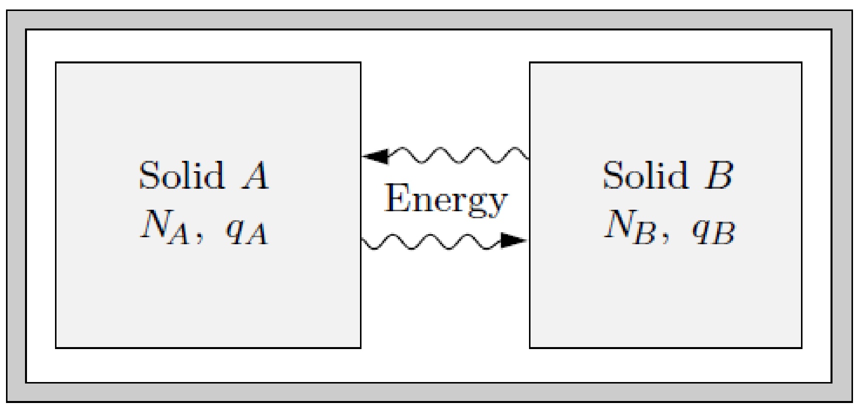


Figure 2.3. Two Einstein solids that can exchange energy with each other, isolated from the rest of the universe. Copyright ©2000, Addison-Wesley.

q_A	Ω_A	q_B	Ω_B	$\Omega_{\text{total}} = \Omega_A \Omega_B$
0	1	6	28	28
1	3	5	21	63
2	6	4	15	90
3	10	3	10	100
4	15	2	6	90
5	21	1	3	63
6	28	0	1	28
				$462 = \binom{6+6-1}{6}$

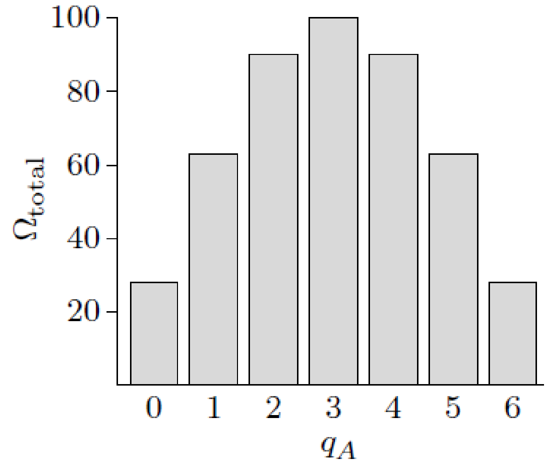
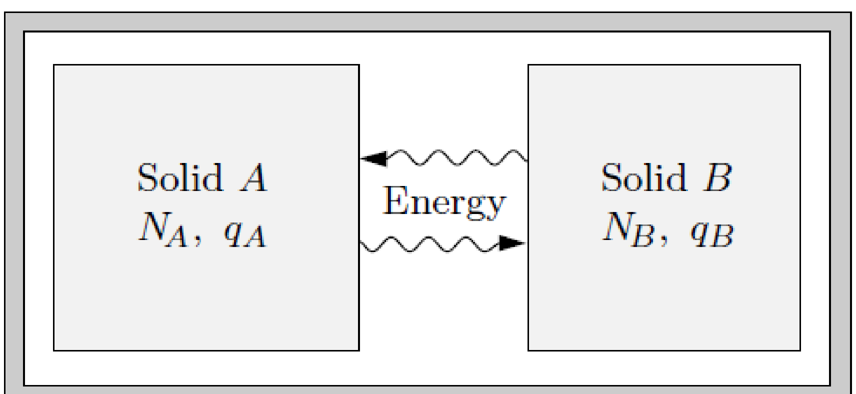


Figure 2.4. Macrostates and multiplicities of a system of two Einstein solids, each containing three oscillators, sharing a total of six units of energy. Copyright ©2000, Addison-Wesley.

$\Omega_{total} = \Omega_A \Omega_B$ because each configuration in *A* matches with all possible configurations in *B*.



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

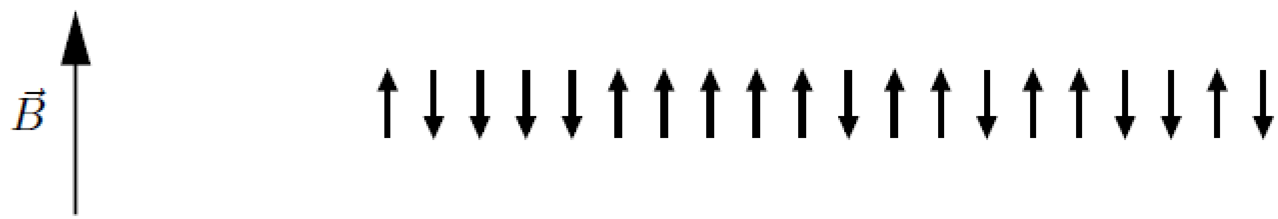
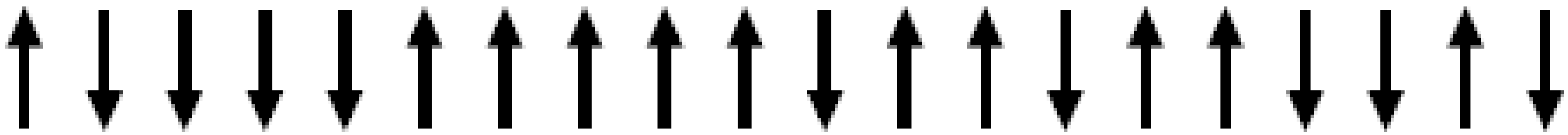


Figure 2.1. A symbolic representation of a two-state paramagnet, in which each elementary dipole can point either parallel or antiparallel to the externally applied magnetic field. Copyright ©2000, Addison-Wesley.

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:

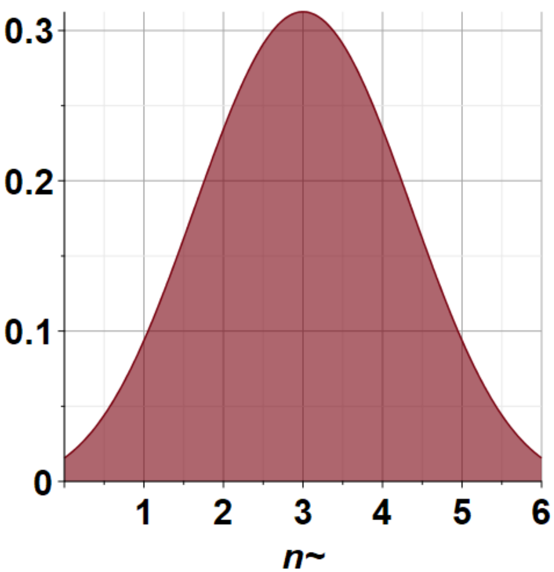
$$\Omega(N,n) = \frac{N!}{n!(N-n)!}$$

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.

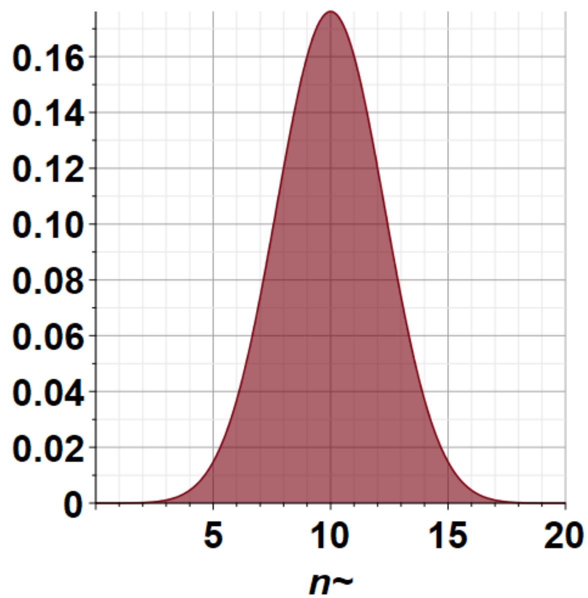
$$P(N,n) = \Omega(N,n)\, p^n q^{N-n} = \frac{N!}{n!(N-n)!} p^n q^{N-n}$$

Note that $$\sum_{n=0}^{N} P(N,n) = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} p^n q^{N-n} = \left(p+q\right)^N = 1$$

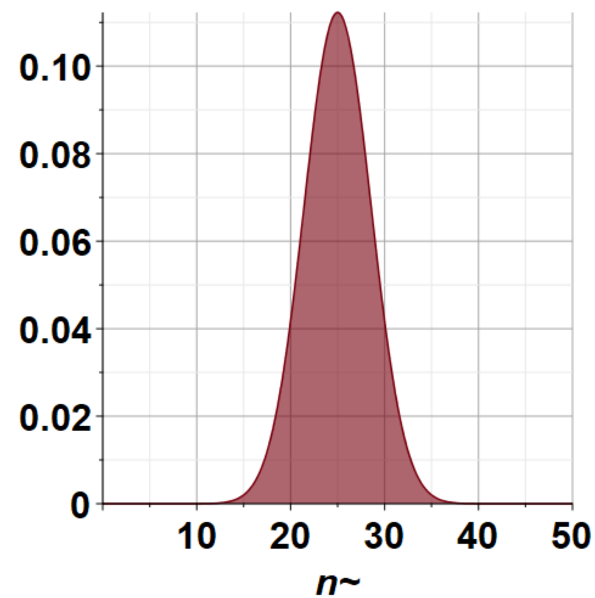
$$P(N,n) = \frac{N!}{n!(N-n)!} p^n q^{N-n} \quad \text{for } p = q = \frac{1}{2}$$



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:

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

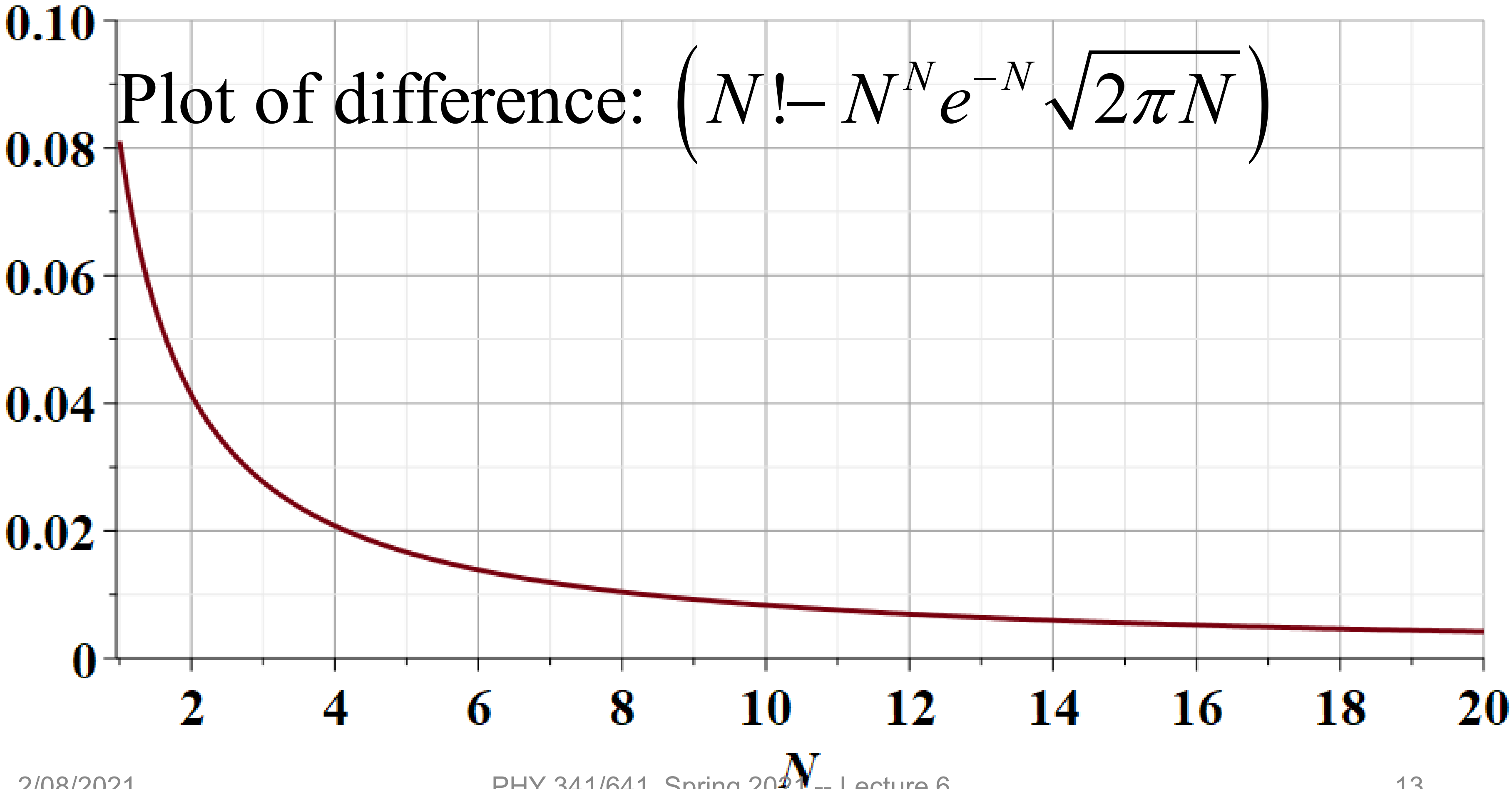
Useful formula -- Stirling's approximation of factorial

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

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

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

Example: Gaussian probability function

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

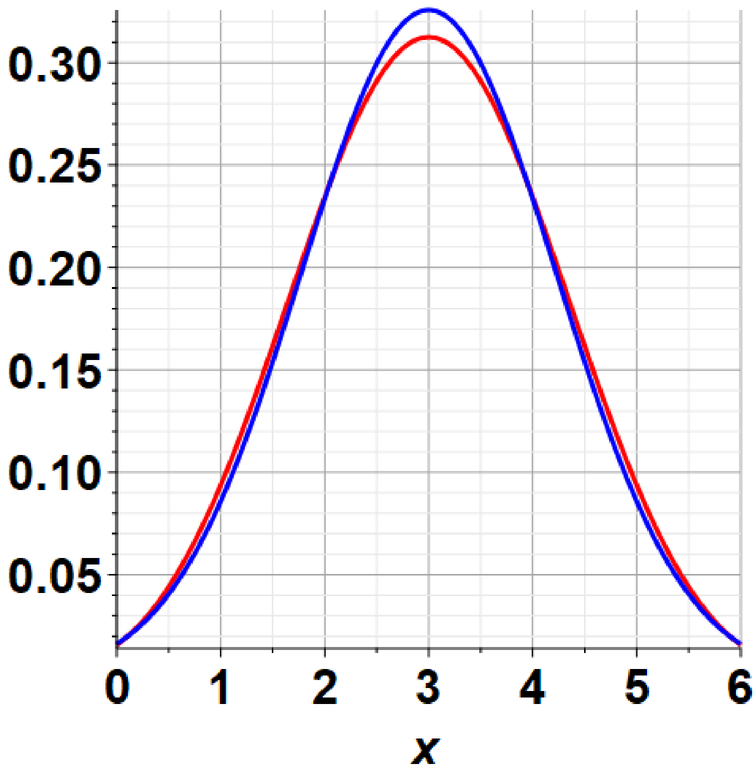
It can be shown that:

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

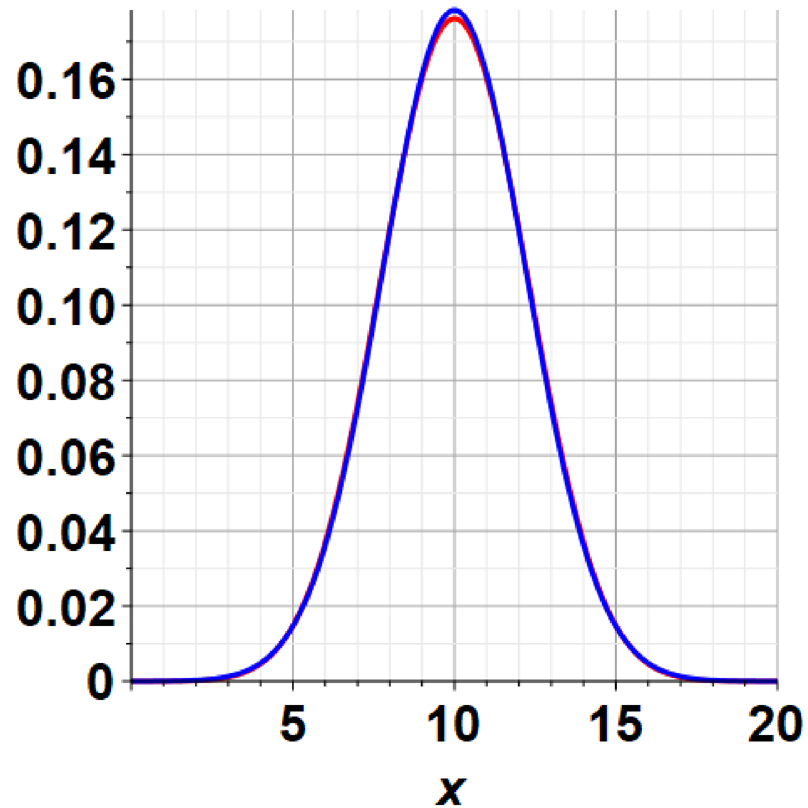
$$\left\langle \left(x - \langle x \rangle\right)^2 \right\rangle = \int_{-\infty}^{\infty} \left(x - \langle x \rangle\right)^2 P_G(x;\mu,\sigma^2) = \sigma^2$$

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 $\sigma_s{}^2$. 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 $N \rightarrow \infty$

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

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 $N \to \infty$

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

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

➔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.

Another example of microstate ←→ microstate analysis – the Einstein oscillators model

Another example of microstate and microstate modeling

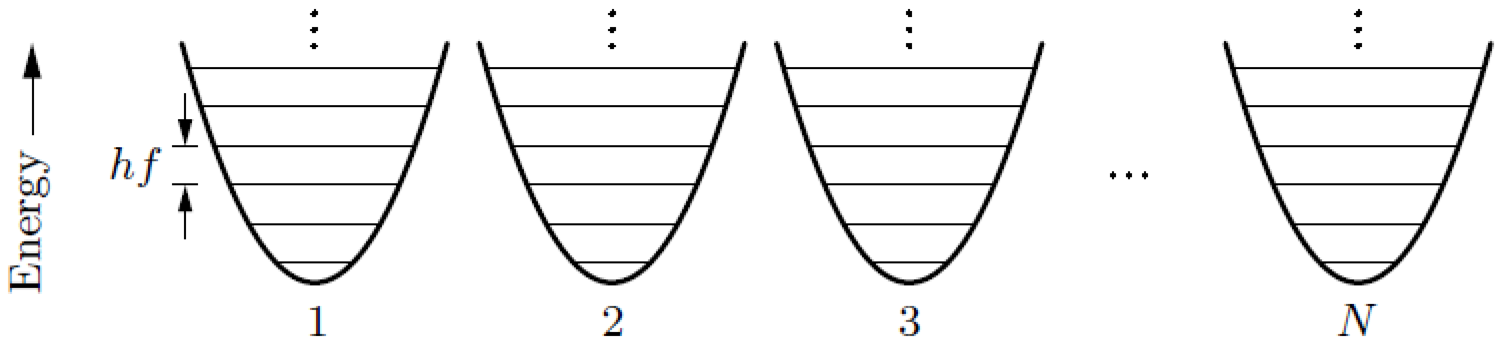


Figure 2.2. In quantum mechanics, any system with a quadratic potential energy function has evenly spaced energy levels separated in energy by hf, where f is the classical oscillation frequency. An Einstein solid is a collection of N such oscillators, all with the same frequency. Copyright ©2000, Addison-Wesley.

A system of independent harmonic oscillators

each with energies $E_n = hf\,(n+\tfrac{1}{2}) \equiv \hbar\omega(n+\tfrac{1}{2})$

In the following we will use "*q*" instead of "*n*" --

Multiplicity for N harmonic oscillators

with q energy units ($E_{total} = \hbar\omega(q + \frac{N}{2})$)

$$\Omega = \frac{(N+q-1)!}{q!(N-1)!}$$

For N and q very large --

$$\ln\Omega \approx \ln\left(\frac{(N+q)!}{q!(N)!}\right) \approx (q+N)\ln(q+N) - q\ln q - N\ln N$$

Thanks to Stirling approximation

Further simplification

$$\ln(q+N) = \ln\left(q\left(1+\frac{N}{q}\right)\right) = \ln q + \ln\left(1+\frac{N}{q}\right)$$

$$\approx \ln q + \frac{N}{q}$$

When the dust clears --

$$\ln \Omega \approx N \ln \frac{q}{N} + N + \frac{N^2}{q}$$

If $q \gg N$ the last term is much smaller (neglibile)

$$\Omega \approx \exp\left(N \ln \frac{q}{N} + N \right) \approx \exp\left(N \left(\ln \frac{q}{N} + \ln e \right) \right) = \exp\left(\ln\left(\left(\frac{qe}{N} \right)^N \right) \right)$$

$$= \left(\frac{qe}{N} \right)^N$$