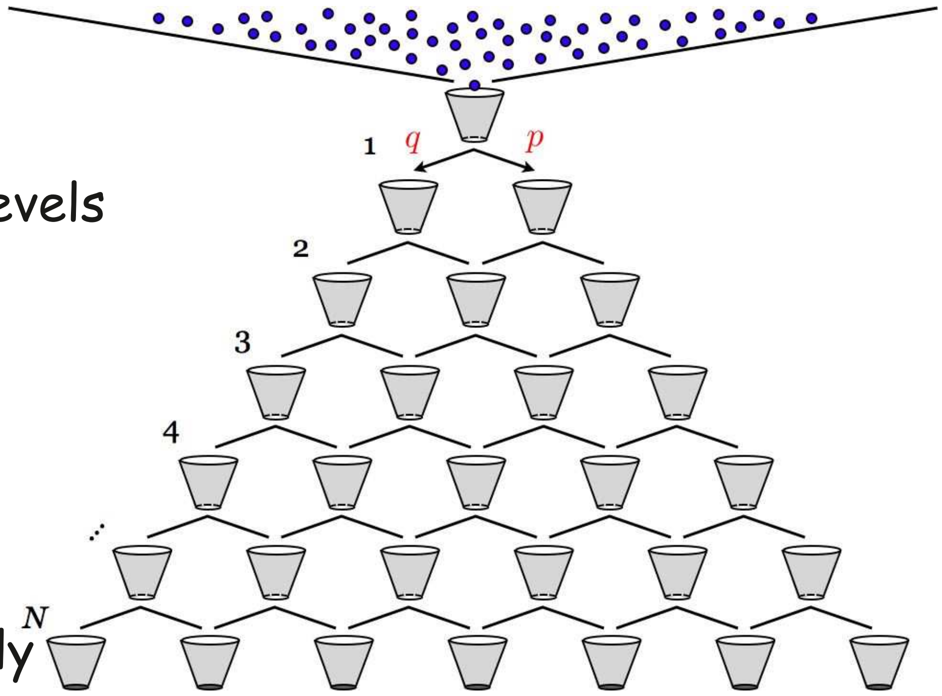
Luis Anchordoqui
Lehman College
City University of New York

Thermodynamics and Statistical Mechanics

Statistical Mechanics I
October 2014

- A statistical view
- Microstate and macrostate
- Thermodynamic probability
- Two-state particles
- Many-state particles
- Quantum states and energy levels
- Density of states

A STATISTICAL VIEW



Consider mechanical system ☛

A ball is released from top

which cascades consecutively through N levels

Details of each ball's motion

are governed by Newton's laws of motion

To predict where any given ball

will end up in bottom row is difficult

because ball's trajectory depends sensitively

on its initial conditions

and may even be influenced by random vibrations of entire apparatus

We therefore abandon all hope of integrating equations of motion

and treat the system statistically

We assume that ball moves to right with probability p

and to left with probability $q = 1 - p$

If there is no bias in system ☛ $p = q = \dfrac{1}{2}$

ONE-DIMENSIONAL RANDOM WALK

Position after N steps may be written

$$X = \sum_{j=1}^{N} \sigma_j \qquad \begin{aligned} \sigma_j &= +1 \quad \text{if ball moves to right at level } j \\ \sigma_j &= -1 \quad \text{if ball moves to left at level } j \end{aligned} \qquad (1)$$

A teach level ☛ probability for these two outcomes

$$P_\sigma = p\,\delta_{\sigma,+1} + q\,\delta_{\sigma,-1} = \begin{cases} p & \text{if } \sigma = +1 \\ q & \text{if } \sigma = -1 \end{cases} \qquad (2)$$

Multivariate distribution for all steps ☛ $\mathcal{P}(\sigma_1, \ldots, \sigma_N) = \prod_{j=1}^{N} P(\sigma_j)$

Our system is equivalent to a one-dimensional **random walk**

Inebriated pedestrian on sidewalk taking steps to right and left at random

After N steps ☛ pedestrian's location is X

VARIANCE AND ROOT MEAN SQUARE

$$\langle X\rangle = \langle\sum_{j=1}^{N}\sigma_j\rangle = N\langle\sigma\rangle = N\sum_{\sigma=\pm1}\sigma\,P(\sigma) = N\,(p-q) = N\,(2p-1)$$

$$\langle X^2\rangle = \langle\sum_{j=1}^{N}\sum_{j'=1}^{N}\sigma_j\sigma_{j'}\rangle = N\langle\sigma^2\rangle = N\sum_{\sigma=\pm1}\sigma^2P(\sigma) = N(p+q) = N$$

Variance ☛ $\mathrm{Var}\,(X) = \langle(\Delta\,X\,)^2\rangle \equiv \langle(X - \langle X\rangle)^2\rangle = \langle X^2\rangle - \langle X\rangle^2$

$$\mathrm{Var}(X) = N\left[1-(2p-1)^2\right] = N(4p-4p^2) = N4p(1-p) = 4Npq$$

Root mean square deviation ☛ $\Delta\,X_{\rm rms} = \sqrt{\mathrm{Var}(X)}$

$\langle X\rangle \propto N$ and $\Delta X_{\rm rms} \propto N^{1/2}$ ☛ $\lim_{N\to\infty}\Delta X_{\rm rms}/\langle X\rangle$ vanishes as $N^{-1/2}$

PROBABILITY DISTRIBUTION

$$P_N(X) = \begin{pmatrix} N \\ N_R \end{pmatrix} p^{N_R} q^{N_L} \qquad (3)$$

$N_{R/L}$ are numbers of steps taken to right/left

$N = N_R + N_L$ and $X = N_R - N_L$

There are many independent ways to take N_R steps to right

For each of these independent possibilities ☛ probability is $p^{N_R}\, q^{N_L}$

How many possibilities are there? ☛ $\begin{pmatrix} N \\ N_R \end{pmatrix} = \dfrac{N!}{N_R! N_L!}$

since $N \pm X = 2\, N_{R/L}$ ↴

$$P_N(X) = \frac{N!}{\left(\frac{N+X}{2}\right)!\,\left(\frac{N-X}{2}\right)!} p^{(N+X)/2} q^{(N-X)/2} \qquad (4)$$

STIRLING'S APPROXIMATION

Consider the limit $N \to \infty$ but with $x \equiv X/N$ finite

N is large ☛ x may be considered continuous variable

Using Stirling's asymptotic expansion ☛ $\ln N! \simeq N \ln N - N + \mathcal{O}(\ln N)$

$$P_N(X) \simeq N \ln N - N - \frac{1}{2}N(1+x)\ln\left[\frac{1}{2}N(1+x)\right] + \frac{1}{2}N(1+x) - \frac{1}{2}N(1-x)$$

$$\times \ln\left[\frac{1}{2}N(1-x)\right] + \frac{1}{2}N(1-x) + \frac{1}{2}N(1+x)\ln p + \frac{1}{2}N(1-x)\ln q$$

$$= -N\left[\left(\frac{1+x}{2}\right)\ln\left(\frac{1+x}{2}\right) + \left(\frac{1-x}{2}\right)\ln\left(\frac{1-x}{2}\right)\right] + N\left[\left(\frac{1+x}{2}\right)\right.$$

$$\left.\times \ln p + \left(\frac{1-x}{2}\right)\ln q\right]$$

Terms proportional to $N \ln N$ have all cancelled leaving quantity linear in N

$$\ln P_N(X) = -N f(x) + \mathcal{O}(\ln N) \qquad (5)$$

$$f(x) = \left[\left(\frac{1+x}{2}\right)\ln\left(\frac{1+x}{2}\right) + \left(\frac{1-x}{2}\right)\ln\left(\frac{1-x}{2}\right)\right] - \left[\left(\frac{1+x}{2}\right)\ln p + \left(\frac{1-x}{2}\right)\ln q\right]$$

PROBABILITY DISTRIBUTION IN LARGE N LIMIT

$$P_N(X) = \mathcal{C} e^{-N f(X/N)}$$

Since N is by assumption large ☛ probability is dominated by minima of $f(x)$

$$f'(x) = \frac{1}{2} \ln\left(\frac{q}{p} . \frac{1+x}{1-x}\right) \qquad f''(x) = \frac{1}{1-x^2}$$

$$f'(x) = 0 \quad ☛ \quad \frac{1+x}{1-x} = \frac{p}{q} \quad \Rightarrow \quad \bar{x} = p - q$$

Invoking Taylor's theorem ☛ $f(x) \underset{☟}{=} f(\bar{x}) + \frac{1}{2} f''(\bar{x}) (x - \bar{x})^2 + \ldots$

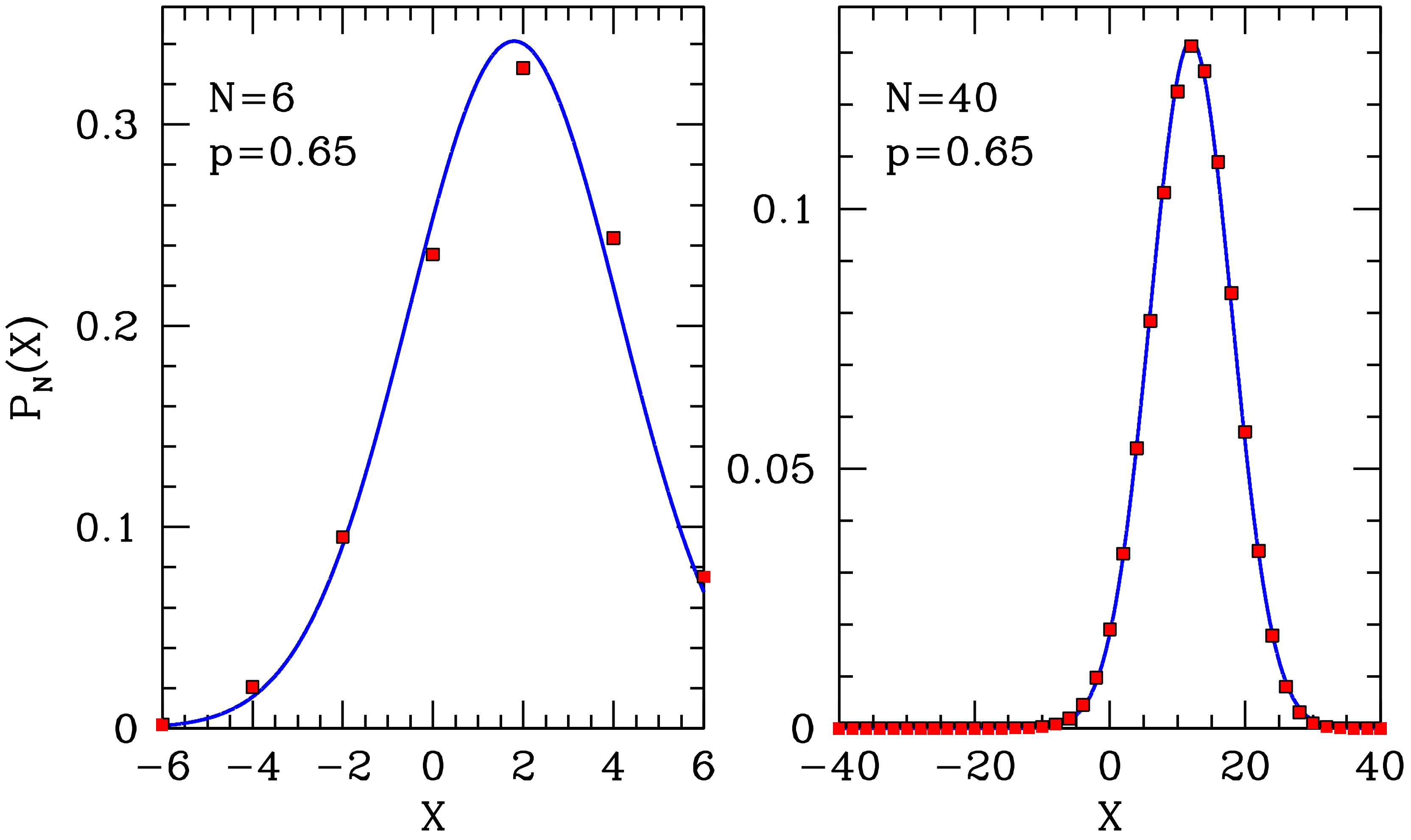
$$P_N(X) = \mathcal{C} \exp\left[-\frac{N(x-\bar{x})^2}{8pq}\right] = \mathcal{C} \exp\left[-\frac{(X-\bar{X})^2}{8Npq}\right] \qquad (6)$$

$$\bar{X} = \langle X \rangle = N(p-q) = N\,\bar{x}$$

$\mathcal{C} = (8\pi N pq)^{-1/2}$ determined by normalization condition ↴

$$\sum_{X=-\infty}^{\infty} P_N(X) \approx \int_{-\infty}^{+\infty} dX\, \mathcal{C} \exp\left[-\frac{(X-\bar{X})^2}{8Npq}\right] = \mathcal{C}\sqrt{8\pi N pq}$$

GAUSSIAN DISTRIBUTION



Comparison of exact distribution of (4) (red squares)

with the Gaussian distribution of (6) (blue line)

MICROSTATE

From quantum mechanics follows that ☛
states of system do not change continuously but are quantized

Huge number of discrete quantum states with corresponding energy values
being the main parameter characterizing these states

We formulate quantum statistics for systems of noninteracting particles
then results can be generalized

In absence of interactions ☛ each particle has its own set of quantum states
and for identical particles these sets of states are identical

Particles can be distributed over their own quantum states
in a great number of different ways called realizations

Each realization of this distribution is a **microstate** of the system

Main assumption of statistical mechanics ☛ all microstates occur with same probability

MACROSTATE

Information contained in microstates is excessive

only meaningful information is how many particles N_i are in energy level i

☟

which specify a **macrostate**

Each macrostate k can be realized by a very large number w_k of microstates

☟

thermodynamic probability

Probability of k-th macrostate is simply proportional to w_k

$$p_k = \frac{w_k}{\Omega} \qquad \Omega \equiv \sum_k w_k \tag{7}$$

True probability is normalized ☛
$$1 = \sum_k p_k \tag{8}$$

A microstate is specified by number of particles in each energy state

Degeneracy: In general ☛ more than 1 energy state (quantum state) for energy level

AVERAGE OCCUPATION NUMBER

Both w_k and p_k depend on whole set of N_j

$$p_k = p_k \left(N_1, N_2, ...\right) \tag{9}$$

For isolated system number of particles N and energy U are conserved

$$\sum_j N_j = N \tag{10}$$

ε_j ☛ energy of particle in level j

$$\sum_j N_j \varepsilon_j = U \tag{11}$$

Number of particles $\bar{N}_j$ averaged over all macrostates k

$$\bar{N}_j = \frac{\sum_k N_j^{(k)} \omega_k}{\sum_k \omega_k} = \frac{\sum_k N_j^{(k)} \omega_k}{\Omega} = \sum_k N_j^{(k)} p_k \tag{12}$$

$N_j^{(k)}$ ☛ number of particles in microstate j corresponding to macrostate k

MAXIMUM PROBABILITY

For each macrostate thermodynamic probabilities differ by a large amount

Macrostates having small p_k practically never occur

and state of system is dominated by macrostates with largest p_k

Consideration of particular models shows that:

maximum of p_k is very sharp for large number of particles
whereas $N_j^{(k)}$ is a smooth function of k

In this case (6) becomes ☛ $$\bar{N}_j \simeq N_j^{(k_{\rm max})} \sum_k p_k = N_j^{(k_{\rm max})} \qquad (13)$$

$k_{\rm max}$ corresponds to maximum of p_k

For large N ☛ dominating true probability p_k

is found by maximization with respect to all N_j obeying two constraints above

TWO-STATE PARTICLES

A tossed coin can land in two positions ☛ head up or tail up

Considering coin as a particle ☛ has two **quantum** states

N_1 ➢ head

$N_2 = N - N_1$ ➢ tail

If N coins are tossed

this can be considered as a system of N particles with 2 quantum states each

Microstates of system are specified by states occupied by each coin

As each coin has 2 states there are total

$$\Omega = 2^N \quad \text{microstates} \qquad (14)$$

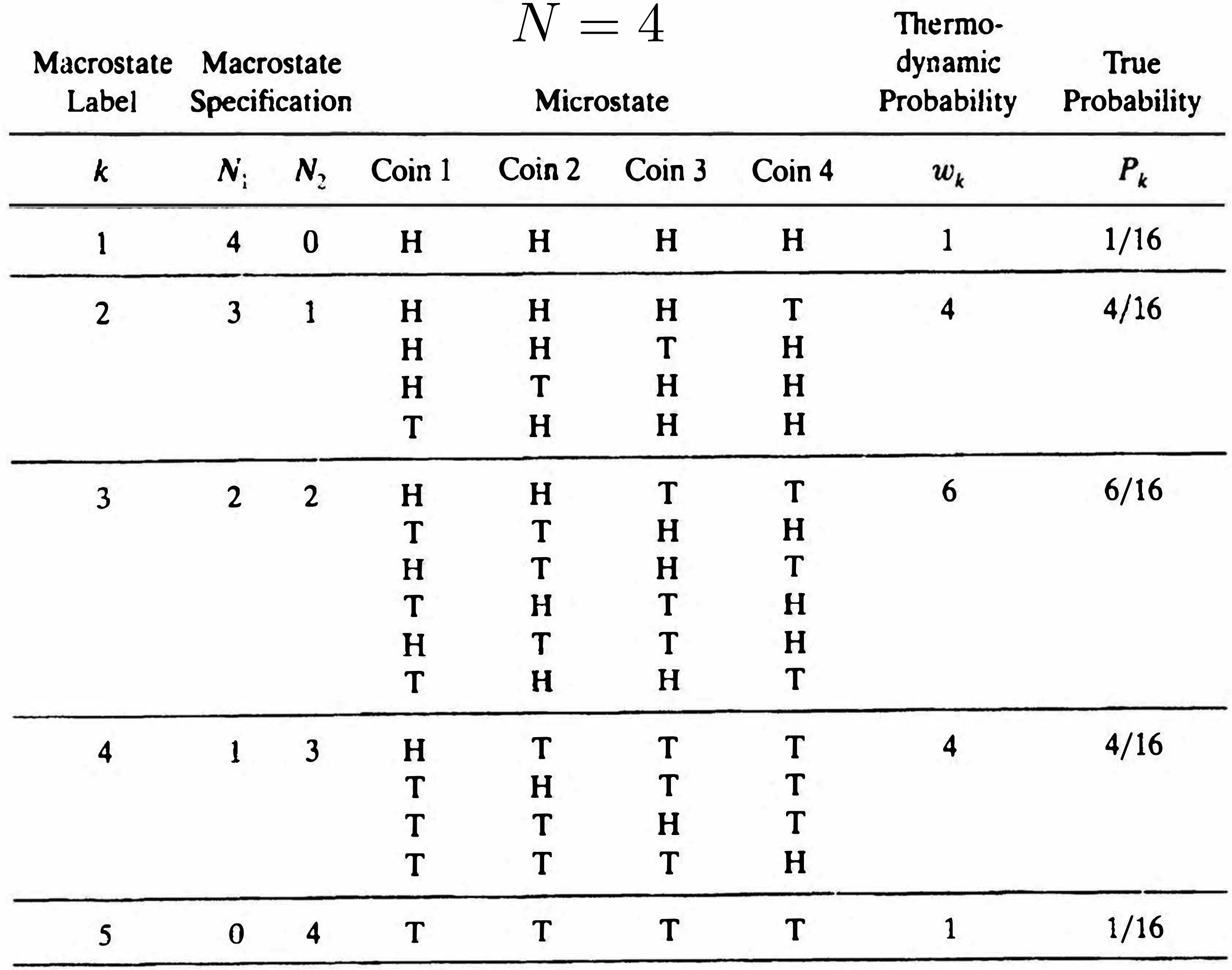
Macrostates of this system are defined by numbers of particles in each state:

N_1 and N_2

Luis Anchordoqui

POSSIBLE OUTCOMES OF COIN-TOSSING EXPERIMENT

$$N = 4$$



Macrostate Label	Macrostate Specification		Microstate				Thermodynamic Probability	True Probability
k	N_1	N_2	Coin 1	Coin 2	Coin 3	Coin 4	w_k	P_k
1	4	0	H	H	H	H	1	1/16
2	3	1	H	H	H	T	4	4/16
			H	H	T	H		
			H	T	H	H		
			T	H	H	H		
3	2	2	H	H	T	T	6	6/16
			T	T	H	H		
			H	T	H	T		
			T	H	T	H		
			H	T	T	H		
			T	H	H	T		
4	1	3	H	T	T	T	4	4/16
			T	H	T	T		
			T	T	H	T		
			T	T	T	H		
5	0	4	T	T	T	T	1	1/16

$$\Omega = \sum_{k=1}^{5} \omega_k = 16$$

$$\bar{N}_1 = \frac{1}{16}[(4 \times 1) + (3 \times 4) + (2 \times 6) + (1 \times 4) + (0 \times 1)] = 2$$

$$\bar{N}_2 = 2$$

$$\bar{N}_1 + \bar{N}_2 = 4 = N$$

THERMODYNAMIC PROBABILITY

We need a way of computing thermodynamic probability without tabulating actual state of each coin

Binomial coefficient ☛ $$\omega = \frac{N!}{N_1!(N-N_1)!} = \binom{N}{N_1} \qquad (15)$$

This formula can be derived ↴

Pick N_1 particles to be in state 1 and all others will be in state 2

How many ways are there to do this?

N ways to pick first coin ☛ leaving $N-1$ ways for the second

$N-2$ ways for the third ...

Total number of ways of picking N_1 heads is

$$N \times (N-1) \times (N-2) \times \ldots \times (N-N_1+1) = \frac{N!}{(N-N_1)!} \qquad (16)$$

factorial ☛ $$N! \equiv N \times (N-1) \times \ldots \times 2 \times 1 \qquad 0! = 1 \qquad (17)$$

(16) isn't yet thermodynamical probability because contains multiple counting of same microstates

order of coins is not important ☛ divide by $N_1!$ permutations

MOST PROBABLE MACROSTATE

(14) is satisfied $$\Omega = \sum_k \omega_k = \sum_{N_1=0}^{N} \frac{N!}{N_1!(N-N_1)!} = 2^N \qquad (17)$$

Thermodynamic probability w has a maximum at $N_1 = N/2$

half of coins head and half of coins tail

To prove that $N_1 = N/2$ is maximum of ω

rewrite (15) in terms of new variable $p = N_1 - N/2$

$$\omega = \frac{N!}{(N/2+p)!(N/2-p)!}$$

ω is symmetric around $N_1 = N/2$ ☛ $p = 0$

Working out ratio ↴

$$\frac{\omega_{N/2\pm1}}{\omega_{N/2}} = \frac{(N/2)!(N/2)!}{(N/2\,+\,1)!(N/2-1)!} = \frac{N/2}{N/2\,+\,1} < 1$$

STIRLING FORMULA

Analysis of expressions with large factorials is simplified by Stirling formula

$$N! \simeq \sqrt{2\pi N} \left(\frac{N}{e} \right)^N \qquad (18)$$

(13) becomes

$$\omega \simeq \frac{\sqrt{2\pi N}(N/e)^N}{\sqrt{2\pi(N/2+p)}[(N/2+p)/e]^{N/2+p}\sqrt{2\pi(N/2-p)}[(N/2-p)/e]^{N/2-p}}$$

$$= \sqrt{\frac{2}{\pi N}} \frac{1}{\sqrt{1-(\frac{2p}{N})^2}} \frac{N^N}{(N/2+p)^{N/2+p}(N/2-p)^{N/2-p}}$$

$$= \frac{\omega_{N/2}}{\sqrt{1-(\frac{2p}{N})^2}\ (1+\frac{2p}{N})^{N/2+p}(1-\frac{2p}{N})^{N/2-p}} \qquad (19)$$

where

$$\omega_{N/2} \simeq \sqrt{\frac{2}{\pi N}}\ 2^N \qquad (20)$$

is maximal value of the thermodynamic probability

MAXIMUM VALUE OF THERMODYNAMIC PROBABILITY

(16) can be expanded for $p \ll N$

Since p enters both bases and exponents ☛ careful must be taken ☟

expand $\ln \omega$ rather than ω itself

Square root term in (16) discarded ☛ gives negligible contribution $\mathcal{O}(p^2/N^2)$

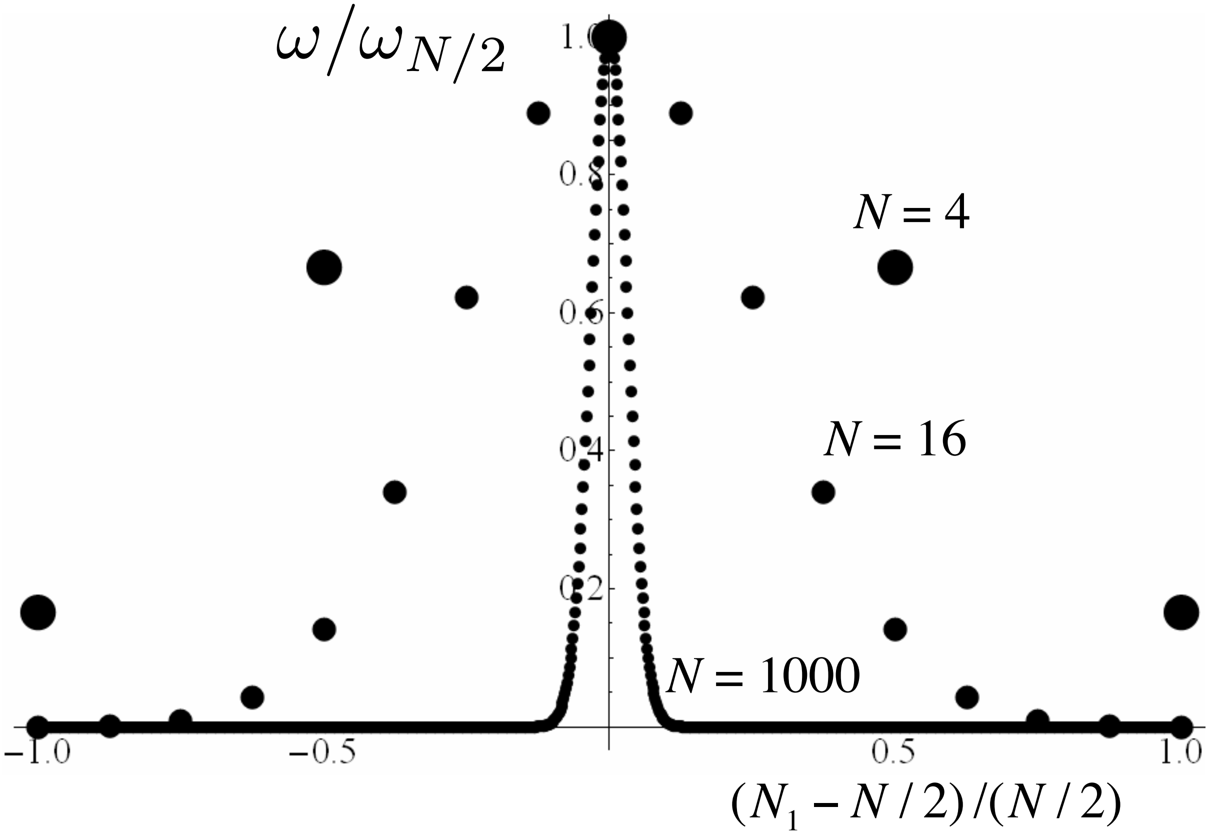
$$\begin{aligned}
\ln \omega &\simeq \ln \omega_{N/2} - \left(\frac{N}{2} + p\right) \ln\left(1 + \frac{2p}{N}\right) - \left(\frac{N}{2} - p\right) \ln\left(1 - \frac{2p}{N}\right) \\
&\simeq \ln \omega_{N/2} - \left(\frac{N}{2} + p\right) \left[\frac{2p}{N} - \frac{1}{2}\left(\frac{2p}{N}\right)^2\right] - \left(\frac{N}{2} - p\right) \left[-\frac{2p}{N} - \frac{1}{2}\left(\frac{2p}{N}\right)^2\right] \\
&\simeq \ln \omega_{N/2} - p - \frac{2p^2}{N} + \frac{p^2}{N} + p - \frac{2p^2}{N} + \frac{p^2}{N} \\
&= \ln \omega_{N?2} - \frac{2p^2}{N} \qquad (21)
\end{aligned}$$

☟

$$\omega \simeq \omega_{N/2} \exp\left(-\frac{2p^2}{N}\right) \qquad (22)$$

BINONIAL DISTRIBUTION FOR N TWO-STATE PARTICLES

- ω becomes very small if $|p| \equiv |N_1 - N/2| \geq N$ that is much smaller than N for large N
- ω is small in most of the interval $0 \leq N_1 \leq N$ and is sharply peaked near $N_1 = N/2$



THERMODYNAMIC LIMIT

For $N \to \infty$

most nearly random configuration (macrostate) is the one almost always occurs

$$N_1 = N_2$$

"ordered regions" almost never occur

ω is extremely small compared to $\omega_{\max}$

We are led to a very important conclusion:

total number of microstates is very nearly equal to maximum number

$$\Omega = \sum_k \omega_k \approx \omega_{\max} \qquad (23)$$

THERMODYNAMIC PROBABILITY AND ENTROPY

Main postulate of statistical mechanics

observed macrostate is realized by greatest number of microstates

We have seen in thermodynamics that

isolated system initially in a non-equilibrium state

evolves to equilibrium state characterized by maximal entropy

Entropy S and thermodynamic probability ω should be related

one being a monotonic function of the other

Form of this function can be found ☟

noticing that entropy is additive while thermodynamic probability is multiplicative

If system consists of two subsystems that weakly interact with each other

$$S = S_1 + S_2 \qquad \text{whereas} \qquad \omega = \omega_1 \omega_2$$

Boltzmann entropy ☛ $S = k_B \ln \omega$ (24)

$$k_B = 1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}}$$

MANY-STATE PARTICLES

Number of ways to distribute N particles over n boxes
so that there are particles in N_i box $i\mathrm{th}$

Number of microstates in macrostate described by numbers N_i

Thermodynamic temperature $$\omega = \frac{N!}{N_1!N_2!\ldots N_n!} = \frac{N!}{\prod_{i=1}^{n} N_i!} \qquad (25)$$

This formula can be obtained by using (15) successively

Number of ways to put N_1 particles in box 1
and other $N - N_1$ in other boxes is given by (15)

Number of ways to put N_2 particles in box 2 is given by (15) with replacement

$$N \to N - N_1 \quad \text{and} \quad N_1 \to N_2$$

$$\begin{pmatrix} N - N_1 \\ N_2 \end{pmatrix} = \frac{(N-N_1)!}{N_2!(N-N_1-N_2)!} = \frac{(N-N_1)!}{N_2!N_3!}$$

Iteration continues for box 3 until last box

MANY-SATE PARTICLES (cont'd)

Resulting number of microstates is

☟

$$\omega = \frac{N!}{N_1!(N-N_1)!} \times \frac{(N-1)!}{N_2!(N-N_1-N_2)!} \times \frac{(N-N_1-N_2!}{N_3!(N-N_1-N_2-N_3)!} \times \frac{(N_{n-2}+N_{n-1}+N_n)!}{N_{n-2}!(N_{n-1}+N_n)!} \times \frac{(N_{n-1}+N_n)!}{N_{n-1}!N_n!} \times \frac{N_n!}{N_n!0!} \qquad (26)$$

All numerators in (26) except for first one and all second terms in denominators

☟

cancel each other

☟

so that (25) follows

STATIONARY SCHRÖDINGER EQUATION

In formalism of quantum mechanics

quantized states and their energies are solutions of **eigenvalue** problem

$$\hat{H}\Psi = \varepsilon\Psi \qquad (27)$$

$\Psi = \Psi(\mathbf{r})$ ☛ complex function called **wavefunction**

$|\Psi(\mathbf{r})|^2$ ☛ probability for a particle to be found near space point $\mathbf{r}$

$$1 = \int d^3 r \, |\Psi(\mathbf{r})|^2 \qquad (28)$$

$\hat{H} = \dfrac{\hat{\mathbf{p}}^2}{2m} + U(\mathbf{r})$ ☛ Hamilton operator or Hamiltonian

classical momentum $\mathbf{p}$ is replaced by operator ☛ $\hat{\mathbf{p}} = -i\hbar\dfrac{\partial}{\partial\mathbf{r}}$

Number of measurements dN of total N measurements

in which particle is found in elementary volume $d^3 r = dxdydz$ around $\mathbf{r}$

$$dN = N \, |\Psi(\mathbf{r})|^2 \, d^3 r \qquad (29)$$

ONE-DIMENSIONAL RIGID BOX

Consider particle in a one-dimensional rigid box $0 \leq x \leq L$

momentum becomes ☛ $$\hat{\mathbf{p}} = -i\hbar \frac{d}{dx} \qquad (30)$$

(27) takes form ☛ $$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi(x) = \varepsilon \, \Psi(x) \qquad (31)$$

rewritten as ☛ $$\frac{d^2}{dx^2} \Psi\,(x) + k^2 \, \Psi\,(x) = 0 \qquad (32)$$

Solution of this equation satisfying boundary conditions $\Psi\,(0) = \Psi\,(L) = 0$

$$\Psi_n(x) = A \sin(k_n x) \quad k_n = \frac{n\pi}{L} \qquad n = 1, 2, 3, \cdots \qquad (33)$$

Eigenstates are labeled by index n and normalization (28) yields $A = \sqrt{2/L}$

ENERGY LEVELS OF A PARTICLE IN A BOX

Energy eigenvalues are ☛ $$\varepsilon_n = \frac{\hbar k_n^2}{2m} = \frac{\pi^2 \hbar^2 n^2}{2mL^2} \qquad (34)$$

Energy ε is quadratic in momentum $p = \hbar k$ (as it should be)

de Broglie relation

Energy levels are discrete because of quantization

For very large box ☛ $L \to \infty$ and energy levels become quasicontinuous

Lowest-energy level with $n = 1$ **ground state**

For a three-dimensional box with sides L_x, L_y, L_z ☛ similar calculation yields energy levels parametrized by three quantum numbers ☛ n_x, n_y, n_z

$$\varepsilon_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_Z^2} \right) \qquad (35)$$

ground state ☛ $n_x = n_y = n_z = 1$

We order states in increasing ε and number them by index j

ground state being $j = 1$

DEGENERACY

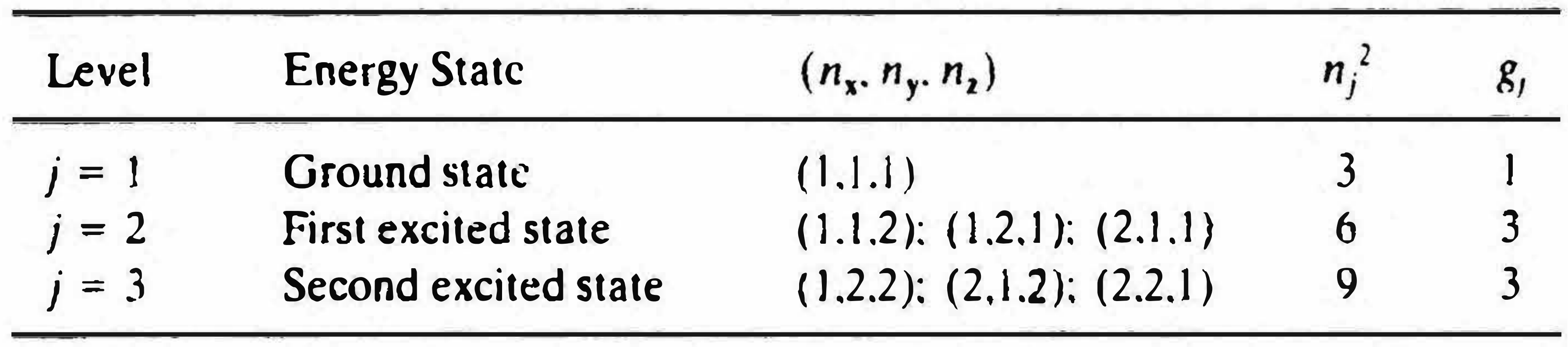
If $L_x = L_y = L_z = L$

$$\varepsilon_j = \varepsilon_{n_x, n_y, n_z} = \frac{\pi \hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) = \frac{\pi^2 \hbar^2}{2mL^2} n_j^2 \qquad (36)$$

Same value of ε_j can be realized for different sets of (n_x, n_y, n_z)

number of different sets having same ε_j is called degeneracy g_j

First three states of a three-dimensional infinite potential well



Level	Energy State	(n_x, n_y, n_z)	n_j^2	g_j
$j = 1$	Ground state	(1,1,1)	3	1
$j = 2$	First excited state	(1,1,2); (1,2,1); (2,1,1)	6	3
$j = 3$	Second excited state	(1,2,2); (2,1,2); (2,2,1)	9	3

DENSITY OF QUANTUM STATES

For systems of a large size and very finely quantized states

we define density of states $\rho(\varepsilon)$ as number of energy levels dn_ε in interval $d\varepsilon$

$$dn_\varepsilon \; = \; \rho(\varepsilon)\, d\varepsilon \tag{37}$$

It is easily seen that

$$dn_\varepsilon \; = \; \frac{\pi}{4} V \left(\frac{2m}{\pi^2 \hbar^2} \right)^{3/2} \sqrt{\varepsilon} d\varepsilon \tag{38}$$

$$\rho(\varepsilon) \; = \; \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} \tag{39}$$