4 Coins

CONFIG	MICROSTATES
0H	1
1H	4
2H	6
3H	4
5H	1

$$C_4^n = \frac{4!}{n!\,(4-n)!}$$

$$C_4^0 = 1 \qquad C_4^1 = 4 \qquad C_4^2 = \frac{4!}{2!\,2!} = 6$$

$$C_4^4 = 1 \qquad C_4^3 = 4$$

$$\text{Prob}(2H) = \frac{6}{1+4+6+4+1} = \frac{C_4^2}{\sum_{m=0}^{4} C_4^m}$$

N COINS

$$\text{Prob}(nH) = \frac{C_N^n}{\sum_{s=0}^{N} C_N^s}$$

MATHEMATICA EXAMPLES

Prob(100 H)

Boltzmann Distribution

In[394]:=
```
Date[]
```

Out[394]=
```
{2006, 4, 20, 23, 30, 37.908065}
```

In[479]:=

$$\text{perm}[n\_, m\_] = \frac{m!}{n!\,(m-n)!}$$

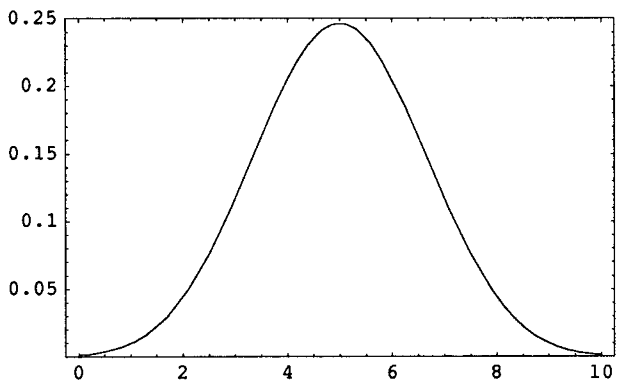
Out[479]=

$$\frac{m!}{(m-n)!\,n!}$$

In[418]:=

$$\text{probn}[n\_, m\_] := \frac{\text{perm}[n, m]}{\sum_{s=0}^{m} \text{perm}[s, m]} \; // \; N$$

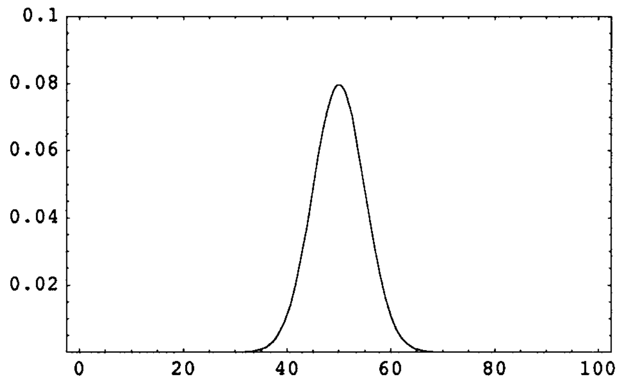
In[439]:=
```
Plot[{probn[x, 10]}, {x, 0, 10}, PlotRange → {0, .25}, Frame → True]
```



Out[439]=
```
- Graphics -
```

In[436]:=

```
Plot[{probn[x, 100]}, {x, 0, 100}, PlotRange → {0, .1}, Frame → True]
```

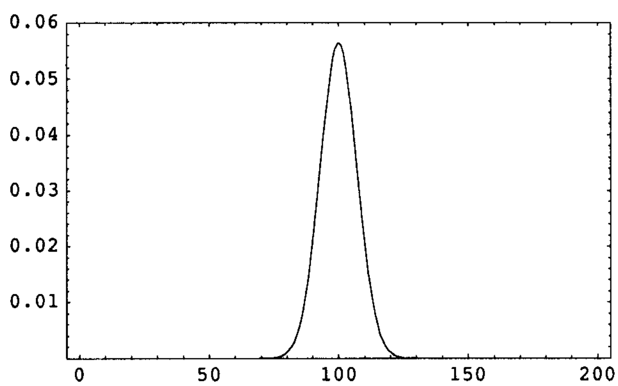


Out[436]=

- Graphics -

In[442]:=

```
Plot[{probn[x, 200]}, {x, 0, 200}, PlotRange → {0, .06}, Frame → True]
```



Out[442]=

- Graphics -

In[476]:=

```
perm[70, 200] // N
perm[100, 200] // N
perm[130, 200] // N
```

Out[476]=

1.0181×10^{55}

Out[477]=

9.05485×10^{58}

Out[478]=

1.0181×10^{55}

In[473]:=

```
probn[70, 200]
probn[100, 200]
probn[130, 200]
```

Out[473]=

6.33565×10^{-6}

Out[474]=

0.0563485

Out[475]=

6.33565×10^{-6}

In[445]:=

$$\sum_{n=0}^{200} \mathbf{probn[n, 200]}$$

Out[445]=

1.

$n_0 \quad n_1 \quad n_2 \quad n_3 \qquad N \quad (n_0, n_1, n_2, n_3)$

$$N = n_0 + n_1 + n_2 + n_3$$

$$C_N^{n_0, n_1, n_2, n_3} = \frac{N!}{n_0!\, n_1!\, n_2!\, n_3!}$$

<u>CONDITION</u> $(\varepsilon_n = n\epsilon)$

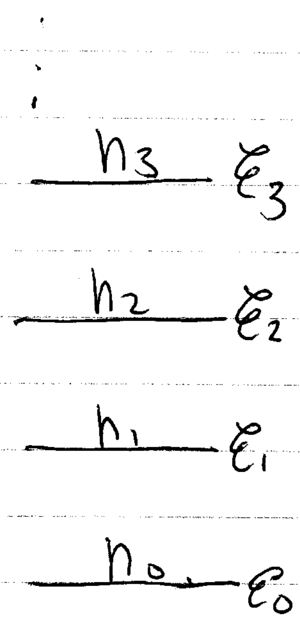
$$E = n_0\varepsilon_0 + n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3$$

$$E = 3\epsilon \Rightarrow \begin{array}{c}(0,3,0,0)\\(1,1,1,0)\\(2,0,0,1)\end{array}$$

$$C_3^{0,3,0,0} = \frac{3!}{3!} = 1$$

$$C_3^{1,1,1,0} = 3! = 6$$

$$C_3^{2,0,0,1} = \frac{3!}{2!} = 3$$



CONFIGURATION $(n_0, n_1, n_2, n_3, \dots)$

$$N = \sum_{i=0} n_i$$

$$E = \sum_{i=0} n_i \varepsilon_i$$

$$\boxed{C_N^{n_0, n_1, n_2, n_3, \dots} = \frac{N!}{\prod_{i=0} n_i!}}$$

$$W_i = \frac{N!}{\prod_i n_i!}$$

$$P(n_i) = \frac{W_i}{\sum_{j=0} W_j}$$

PROOF: BOLTZMAN DISTRIBUTION

CONSIDER A SET OF ENERGY LEVELS

$$\{E_0, E_1, E_2, \ldots, E_n\}$$

ALSO CONSIDER A SET OF MOLECULES

$$\{n_0, n_1, n_2, \ldots, n_n\}$$

WHERE WE HAVE n_0 PARTICLES IN THE GROUND STATE, n_i IN THE i^{th} ENERGY LEVEL. IF

$$N = \sum_{i=0}^{n} n_i ,$$

THE CONFIGURATION CAN BE ACHIVED IN W DIFFERENT WAYS

$$W = \frac{N!}{n_0!\, n_1! \cdots n_n!}$$

$$\ln W = \ln(N!) - \sum_i \ln(n_i!)$$

STIRLING'S FORMULA

$$\ln(x!) \simeq x \ln x - x$$

$$\ln W \simeq N \ln N - \cancel{N} - \sum_i (n_i \ln n_i - \cancel{n_i})$$

$$\boxed{\ln W \simeq N \ln N - \sum_i n_i \ln n_i}$$

WHICH IS THE DOMINANT CONFIGURATION?

IF W IS A FUNCTION OF THE n_iS, WHICH

COMBINATION OF n_iS GIVE US THE

max OF W?

$$d(\ln W) = +\sum_i \left(\frac{\partial}{\partial n_i}(\ln W)\right) dn_i$$

HOWEVER WE HAVE TWO OTHER CONDITIONS (CONSTRAINTS)

$$\sum_i n_i E_i = E_T = \text{CONST}$$

$$\sum_i n_i = N = \text{CONST}$$

OR

$$0 = \sum_i E_i \, dn_i$$

$$0 = \sum_i dn_i \, .$$

IF WE INCLUDE THESE CONSTRAINTS

$$d(\ln W) = \sum_i \left\{ \frac{\partial}{\partial n_i}(\ln W) + \alpha - \beta E_i \right\} dn_i$$

AND

$$\frac{\partial}{\partial n_i}(\ln W) = -\alpha + \beta E_i$$

$$\frac{\partial}{\partial n_i} \ln W = \ln N + 1 - \ln n_i - 1$$
$$= -\ln\left(\frac{n_i}{N}\right)$$

THEREFORE

$$-\ln\left(\frac{n_i}{N}\right) = -\alpha + \beta E_i$$
$$\frac{n_i}{N} = e^{\alpha} e^{-\beta E_i}$$

$$\sum n_i = N = N e^{\alpha} \sum_i e^{-\beta E_i}$$

$$\boxed{e^{\alpha} = \frac{1}{\sum e^{-\beta E_i}} \equiv \frac{1}{q}}$$

$$\frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

$$\boxed{\frac{n_i}{n_j} = e^{-\beta(E_i - E_j)} = e^{-\beta \Delta E_{ij}}}$$

RELATIVE POPULATION OF ENERGY LEVELS.

DEGENERATE ENERGY LEVELS g_i

$$\boxed{P_i =} \boxed{\frac{n_i}{N} = \frac{g_i e^{-\beta E_i}}{q}}$$

$$\boxed{q = \sum_{i=0} g_i e^{-\beta E_i}}$$

THE BOLTZMANN DISTRIBUTION APPLIES ONLY TO SYSTEMS IN THERMAL EQUILIBRIUM

EXAMPLES

H(g) AT 25°C

$$\frac{N(1^{st}\text{ EXCITED elec})}{N(\text{GROUND elec})} \simeq 10^{-175}$$

CO(g)

$$\frac{N(1^{st}\text{ EXCITED vib})}{N(\text{GROUND vib})} \simeq 10^{-5}$$

$$\frac{N(1^{st}\text{ EXCITED rot})}{N(\text{GROUND rot})} \simeq 2.9$$

IF WE CONSIDER ONLY FREE PARTICLES WITH TRANSLATIONAL MOTION, WHERE $\tau_{COLL} << \tau_{BETWEEN\ COLL}$, THE BOLTZMANN DISTRIBUTION YIELDS A SPEED DISTRIBUTION KNOWN AS THE MAXWELL-BOLTZMANN DISTRIBUTION AND WE RECOVER THE KINETIC THEORY OF GASES