CHAPTER 1

Atoms
Molecules → Thermodynamics

Statistical Thermodynamics (S.T.)

S.T. is the key to understanding driving forces.
e.g., determines if a process proceeds spontaneously.

Let's start with entropy
probabilities are important for understanding entropy

Suppose there are different outcomes (A, B, C, …) for some event

$$p_A = \frac{n_A}{N}$$

n_A ← # of outcomes giving A

N ← total # of outcomes

Prob of outcome A: $0 \leq p_A \leq 1$

prob of getting 4 when rolling a die = 1/6

Now consider 3 rolls
- prob of 3, 3, 4, in that order ?
- prob of rolling two 3's, 4 in any order?

- mutually exclusive: e.g., if A occurs, B does not
- collectively exhaustive: $A_1, A_2, \ldots A_t$ give all possible outcomes
- independent: A_1, A_2, A_3 ... independent if outcome of each is unrelated to outcome of others
- multiplicity: total # of ways different outcomes can be realized

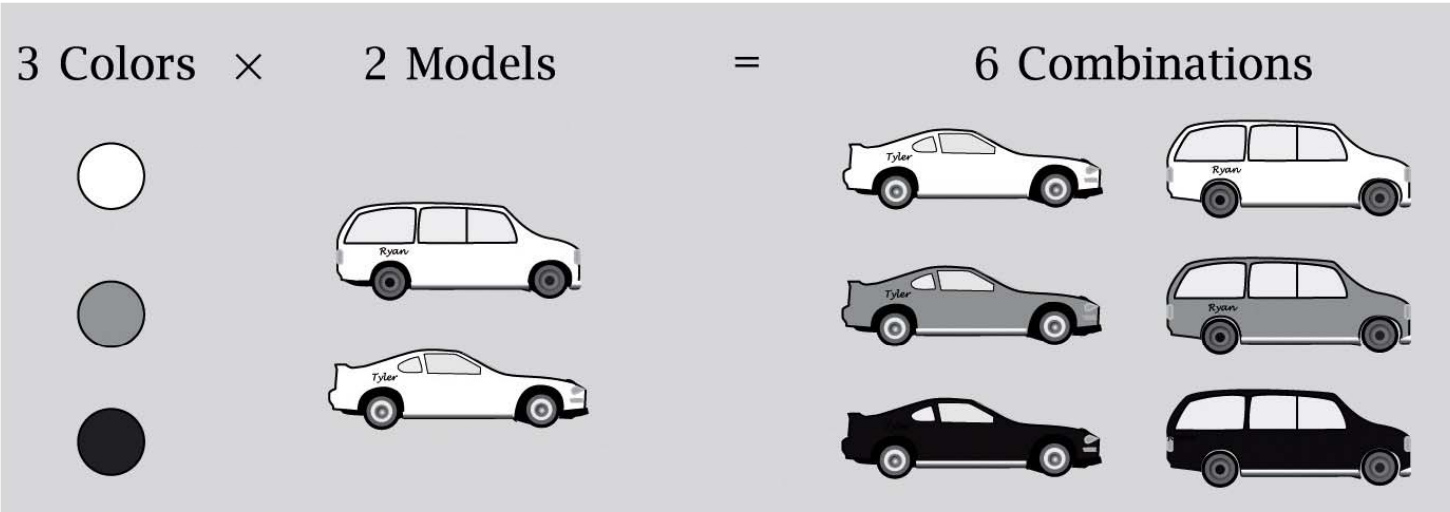

Figure 1.1 Molecular Driving Forces 2/e (© Garland Science 2011)

n_A = # of outcomes of A

n_B = # of outcomes of B

$W = n_A n_B$ = multiplicity

2 models
<u>3 colors</u>

6 different
outcomes

Addition Rule

if outcome A, B, … are mutually exclusive and occur with probabilities $p_A = \frac{n_A}{N}, p_B = \frac{n_B}{N}, \ldots$

prob of seeing A or B: $p(A \text{ or } B) = p_A + p_B$

n_A, n_B, … are statistical weights

if outcomes n_A, n_B, … n_E are collectively exhaustive and mutually exclusive

$n_A + n_B + \ldots + n_E = N$

$p_A + p_B + \ldots + p_E = 1$

Multiplication Rule

If outcomes A, B, …, E are independent

prob of seeing A and B and … E

$$p(A \text{ and } B \text{ and } \ldots E) = p_A p_B \ldots p_E$$

Examples

Rolling a die

prob of 1 <u>or</u> 4 = 1/6 + 1/6 = 1/3

Roll die twice

prob of 1 <u>and</u> then 4 = 1/6•1/6 = 1/36

prob of five heads in a row in coin flips

$(1/2)^5 = 1/32$

prob of two heads, one tails, two heads on successive coin flips

$P_H^2 P_t P_H^2 = 1/32$ one of 32 possible sequences

Independent events p_A, p_B

prob that both happen = $p_A p_B$
prob A happens, B does not = $p_A(1-p_B)$
prob neither happens = $(1-p_A)(1-p_B)$

prob that something happens (A or B or Both)
= 1 –prob(not A and not B) = $1 - (1-p_A)(1 - p_B) = p_A+p_B - p_A p_B$

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prob of 1 on first roll of die and 4 on 2nd roll = 1/36

prob of 1 on first roll or 4 on 2nd roll = ?

(1, 1)*	(1, 2)*	(1, 3)*	(1, 4)*	(1, 5)*	(1, 6)*
(2, 1)	(2, 2)	(2, 3)	(2, 4)*	(2, 5)	(2, 6)
(3, 1)	(3, 2)	(3, 3)	(3, 4)*	(3, 5)	(3, 6)
(4, 1)	(4, 2)	(4, 3)	(4, 4)*	(4, 5)	(4, 6)
(5, 1)	(5, 2)	(5, 3)	(5, 4)*	(5, 5)	(5, 6)
(6, 1)	(6, 2)	(6, 3)	(6, 4)*	(6, 5)	(6, 6)

prob = 11/36 – By counting all possibilities

Not a viable approach in general

class A	1 and anything but 4:	5/36
class B	anything but 1 and 4:	5/36
class C	1 and 4:	1/36
	p(1 or 4) =	11/36

Another approach is the following:

prob(1) = 6/36
probl(4) = 6/36
prob(1 and 4) = 1/36
prob(1 or 4) = 6/36 + 6/36 – 1/36 = 11/36

Essentially all questions can be reexpressed in terms of a combination of <u>and</u> and <u>or</u> operations.

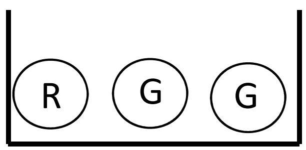
Here is a third approach to the above problem

p(fail) = p(not 1 first) and p(not 4 second)
= 5/6·5/6 = 25/36
p(success) = 1 – p(fail) = 11/36

Correlated Events

outcome of an event depends on the outcomes of other events

Example: Balls from barrel with replacement



one red and two green balls in a barrel

prob of G = 2/3 on 1st try; prob of R = 1/3 on 1st try

probabilities on second try depends on whether ball put back after first try

if put back → uncorrelated

if not put back → correlated

If one does not return balls to the barrel, the three possible sequences are:

Move # → 3	2	1	
G	G	R	$1 \cdot 1 \cdot 1/3 = 1/3$
G	R	G	$1 \cdot 1/2 \cdot 2/3 = 2/6$
R	G	G	$1 \cdot 1/2 \cdot 2/3 = 2/6$

Σ all possibilities = 1

Note: We have to renormalize on moves after the 1st

“Gambling Eq.”

5 horses A, B, C, D, E
prob of winning $p_{A,}$ $p_{B,}$ $p_{C,}$ $p_{D,}$ p_E (e.g., odds from Las Vegas)

Suppose C wins, what are probabilities for A, B, D, E to come in second?

$$p_A\left(2^{nd},\ \text{C first}\right) = \frac{p_A}{p_A + p_B + p_D + p_E} = \frac{p_A}{1 - p_C},\ \text{etc.}$$

prob p_C is first, p_A is second, p_B is third

$$p_C\left(\frac{p_A}{1 - p_C}\right)\left(\frac{p_B}{1 - p_C - p_A}\right) = \frac{p_A p_B p_C}{(1 - p_C)(1 - p_C - p_A)}$$

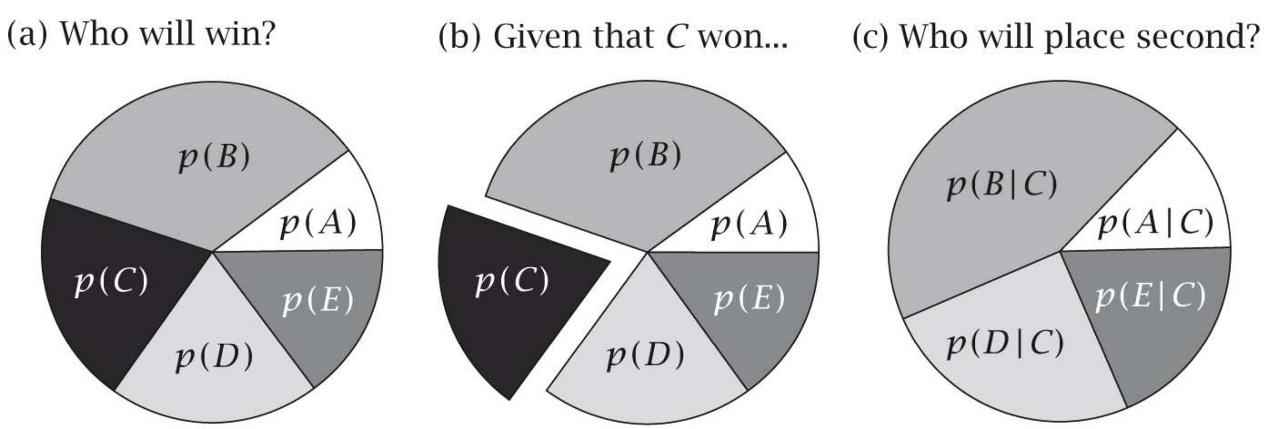


Figure 1.2 Molecular Driving Forces 2/e (© Garland Science 2011)

Combinatorics: Composition rather than sequence of events is important

Consider coin tosses

prob of seeing HTHH? → a sequence question

prob of seeing 3H1T regardless of order → a composition question

prob of 3H, 1T

16 total arrangements from 4H, 3H1T, 2H2T, 1H3T, 4T

The number of ways of getting 3H, 1T is 4
(so prob = 4/16 = 1/4)

We will show that the answer is given by $\frac{4!}{3!1!} = 4$

Consider letters x, y, z, w

4 possibilities at first draw
3 possibilities at 2nd draw
2 possibilities at 3rd draw
1 possibility at 4th draw

4! = 24 sequences

letters of alphabet: 26! sequences

Distinguishable and indistinguishable

$$\frac{\text{letters} \qquad \text{AHA}}{\text{3 distinguishable arrangements}} \quad \text{vs.} \quad \frac{A_1 H A_2}{3! = 6 \text{ arrangements}}$$

$$\frac{3!}{2!} = 3$$

accounts for the fact we cannot distinguish the two As.

In general, the # of permutations is

$$W = \frac{N!}{n_1!n_2!...n_t!}$$

n_1 indistinguishable members of 1
n_2 indistinguishable members of 2

n_t indistinguishable members of t

When there are only two categories, n_1 and n_2

$$W = \frac{N!}{n_1!n_2!} = \frac{N!}{n_1!(N-n_1)!} = \binom{N}{n_1}$$

So for the 3HT coin flip example

\# of distinguishable arrangements $\frac{4!}{3!1!} = 4$

flip a coin 117 times

How many arrangements have 36 heads? $W = \frac{117!}{36!81!} = 1.84x10^{30}$

6 coin tosses

6H	6!/6!0! = 1
5H1T	6!/5!1! = 6
4H2T	6!/4!2! = 15
3H3T	6!/3!3! = 20
2H4T	= 15
1H5T	= 6
0H6T	= 1

← most probable situation is equal # heads and tails

Roll die 15 times: How many ways can we achieve three 1, one 2, one 3, five 4, two 5, three 6

$$\frac{15!}{3!1!1!5!2!3!} = 151,351,200$$ sequences

prob of royal flush in poker

Ace, King, Queen, Jack, 10 of same suit 52 cards

$$4\left[\frac{5}{52}\bullet\frac{4}{51}\bullet\frac{3}{50}\bullet\frac{2}{49}\bullet\frac{1}{48}\right] = 1.53x10^{-6} \text{ probability}$$

the factor of 4 accounts for the four suits

Bose-Einstein statistics

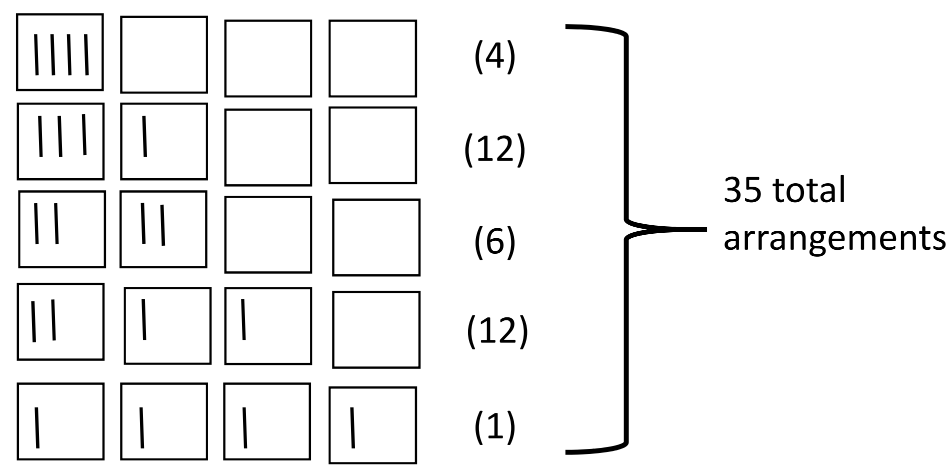
ways n indistinguishable particles can be put in M boxes with no constraint on # in a box

$$W(n,M) = \frac{(M+n-1)!}{(M-1)!n!}$$

rather than m boxes consider M – 1 walls

to check: 4 particles in 4 boxes

$$W(4,4) = \frac{7!}{3!4!} = 35$$



Distribution functions

- discrete
- continuous

In general, probability distributions should be normalized

given g(x) on interval [a, b]

If discrete $$\sum_{i=1}^{t} p(i) = 1$$

$$g_o = \int_a^b g(x)dx$$

$$p(x) = \frac{g(x)}{g_o}$$

Note: $\int_a^b p(x)dx = 1$

Normalized, as advertised

Binomial and multinomial distributions

Binomial: two outcomes (e.g., heads, tails)

p_1 $\quad p_2 = 1 - p_1$

coin toss $p_H = p_T = \frac{1}{2}$

all combinations of two events

$$p_1^2 + p_1 p_2 + p_2 p_1 + p_2^2 = p_1^2 + (1 - p_1) + (1 - p_1)\, p_1 + (1 - p_1)^2$$

$$= p_1^2 + p_1 - p_1^2 + p_1 - p_1^2 + 1 - 2p_1 + p_1^2 = 1$$

$$p(n,N) = p^n (1-p)^{N-n} \bullet \frac{N!}{n!(N-n)!} = \begin{pmatrix}\text{prob of one event}\\ \text{regardless of order}\end{pmatrix}\begin{pmatrix}\#\\ \text{sequences}\end{pmatrix}$$

$$\frac{N!}{n!(N-n)!}$$

$N = 0$: $p(0,0) = 1$

$N = 1$:

$$= \frac{1!}{0!1!} = 1$$

$$= \frac{1!}{1!0!} = 1$$

$N = 2$:

$$= \frac{2!}{0!2!} = 1$$

$$= \frac{2!}{1!1!} = 2$$

$$= \frac{2!}{2!0!} = 1$$

Pascal's triangle:

N = 0					1				
N = 1				1		1			
N = 2			1		2		1		
N= 3		1		3		3		1	
N = 4	1		4		6		4		1

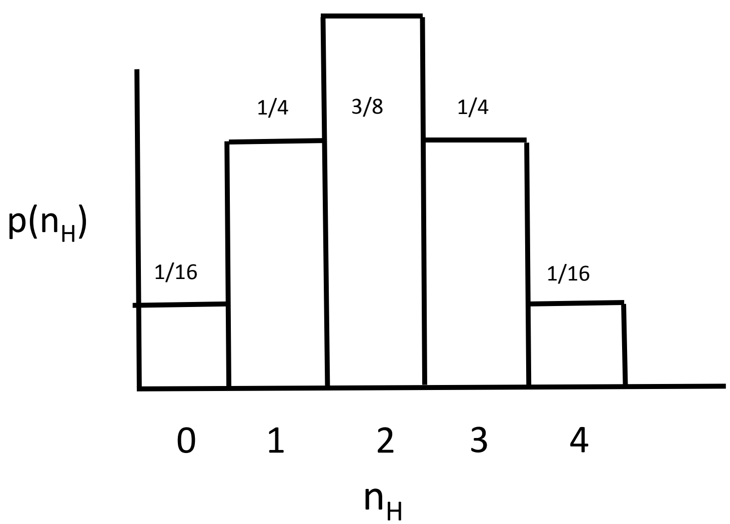
2 coins HH $pp(1-p)^0 = 1/4$

HT $p(1-p) = 1/2(1/2) = 1/4$

TT $p^o(1-p)^2 = 1/4$

3 coins HHH $p^3(1-p)^0 = 1/8$

HHT $= (1/2)^2 (1/2) = 1/8$ Etc.



Multinomial prob distrib : $p_1^{n1} p_2^{n2} \dots p_t^{nt} \dfrac{N!}{n_1!n_2!\dots n_t!}$ $\left(\sum_i n_i = N \right)$

Averages

If continuous:

$$\left\langle x^n \right\rangle = \int_a^b x^n p(x)dx = n^{th} moment$$

$$\left\langle f(x) \right\rangle = \int_a^b f(x)p(x)dx$$

If discrete: $\langle i \rangle = \sum_{i=1}^{t} ip(i)$

$$\left\langle f(i) \right\rangle = \sum_{i=1}^{t} f(i)\,p(i)$$

assuming the distribution is normalized

<x> = mean, or average

$$g = \int_a^b p(x)dx$$

$$p' = p(x)/g$$

This converts p(x) to a normalized distribution p'(x) average of 3, 3, 2, 2, 2, 1, 1

$$\langle i \rangle = \frac{sum\ of\ \ numbers}{\#\ of\ \ samples} = \frac{14}{7} = 2$$

$$p_1 = \frac{2}{7},\ p_2 = \frac{3}{7},\ p_3 = \frac{3}{7}$$

$$\langle i \rangle = 1\left(\frac{2}{7}\right) + 2\left(\frac{3}{7}\right) + 3\left(\frac{2}{7}\right)$$
$$= \frac{2+6+6}{7} = 2$$

Variance (σ^2) = width of distribution

$$\sigma^2 = \left\langle \left(x-a\right)^2 \right\rangle = \left\langle x^2 - 2ax + a^2 \right\rangle; \quad \langle x \rangle = a = mean$$
$$= \langle x^2 \rangle - 2a\langle x \rangle + a^2$$
$$= \langle x^2 \rangle - a^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$\sigma = \sqrt{\sigma^2}$ standard deviation

If do four coin flips many times
what will you find for the average # of heads (obviously 2)

How to compute this mathematically

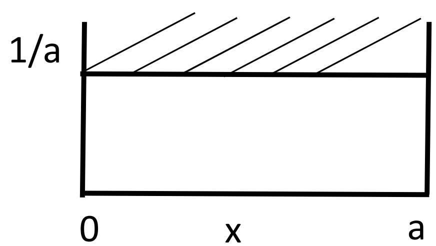
$$\langle n_H \rangle = \sum_{n_H=0}^{4} n_H \, p(n_H, N)$$

$$= 0\left(\frac{1}{16}\right) + 1\left(\frac{4}{16}\right) + 2\left(\frac{6}{16}\right) + 3\left(\frac{4}{16}\right) + 4\left(\frac{1}{16}\right)$$

$$= \frac{4+12+12+4}{6} = 2$$

$$\langle n_H^2 \rangle = 5 \qquad \langle n_H^2 \rangle - \langle n_H \rangle^2 = 5 - 2^2 = 1 \qquad \sigma^2 = 1$$

Uniform distribution



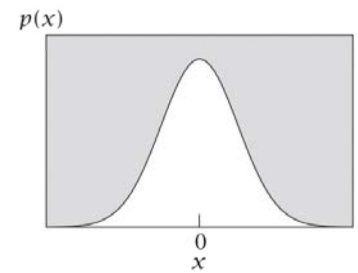
$$\langle x \rangle = \frac{a}{2} \qquad \langle x^2 \rangle = \frac{a^2}{3}$$

$$\langle x^2 \rangle - \langle x \rangle^2 = \frac{a^2}{12}$$

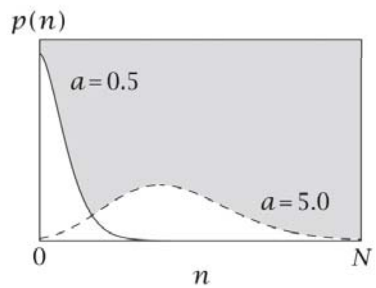
Exponential distribution $$g_o = \int_0^\infty e^{-ax} dx = \frac{1}{a}$$

$$p(x) = ae^{-x}, \quad 0 \le x \le \infty$$ $$\langle x \rangle = a\int_\partial^\infty xe^{-ax} dx = \frac{1}{a}$$

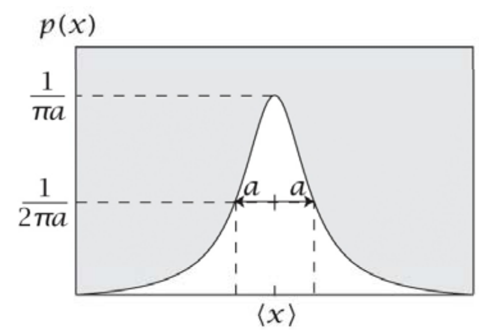
Gaussian $$p(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-x^2/2\sigma^2} \qquad -\infty \le x \le \infty$$



Poisson $$p(n) = \frac{a_n e^{-a}}{n!}$$



Lorentizian $$p(x) = \frac{1}{\pi} \frac{a}{\left(x - \langle x \rangle\right)^2 + a^2} \qquad -\infty \le x \le \infty$$



Power law $p(x) = \frac{1}{x^q}$, q is a constant, $-\infty \le x \le \infty$