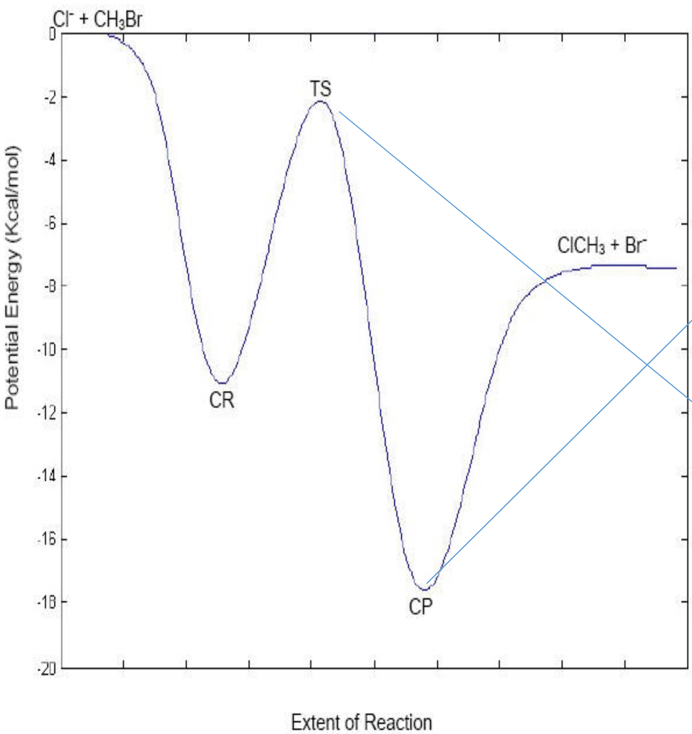
CHAPTER 2 EXTREMUM PRINCIPLES

Tendency of systems to minimize E, maximize S



From web page of W. Hase, Texas Tech

CR, CP, TS examples of extrema

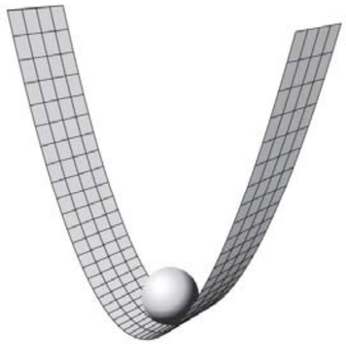
$$V = \frac{1}{2}kx^2$$

$$V' = kx = 0$$

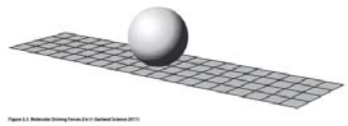
$$V'' = k > 0 \Rightarrow$$ a potential energy minimum

$$V' = 0$$

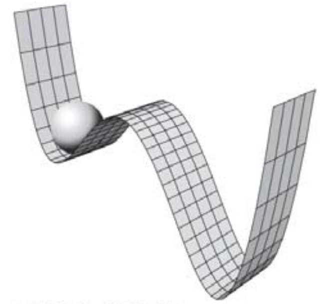
$$V'' < 0 \Rightarrow$$ maximum



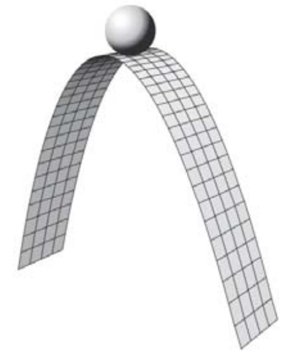
Stable extremum



Neutral system



locally, but not
globally stable



Unstable extremum

At equilibrium, force = 0

$$f = -\frac{\partial V}{\partial x}, \quad \text{V = potential}$$

so if $V = \gamma x^2$ $\quad f = -2\gamma x \longrightarrow$ 0, at an extremum

Most Probable Outcome ⟶ Maximizes Multiplicity

Consider the coin toss example

Which is more likely 4H's or 3H's and 1T?

	W	$\ell n W$	
4H0T	1	0	
3H1T	4	1.39	
2H2T	6	1.79	⟵ most probable outcome
1H3T	4	1.39	
0H4T	1	0	

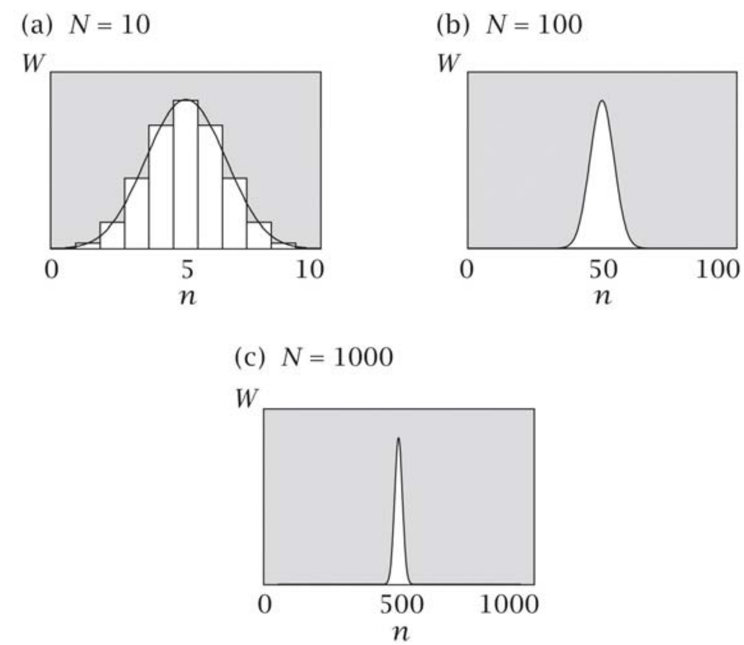


Figure 2.6 Molecular Driving Forces 2/e (© Garland Science 2011)

As the sample grows the distribution becomes more narrowly peaked

$$W(n,N) = \frac{N!}{n!(N-n)!}$$ becomes increasingly peaked with growing N

e.g., N = 100 # sequences

$$50H, 50T = \frac{100!}{50!50!} = 1.01x10^{29}$$

$$75H\,25T = \frac{100!}{25!75!} = 2.43x10^{23}$$

huge difference

to maximize W calculate $\frac{\partial W}{\partial n}$

what value of n* causes this to be zero?

$$\boxed{n^* = \frac{N}{2}}$$ For the coin flip problem

Systems tend to be found in states with maximum multiplicity.

Maximum multiplicity explains

expansion of gases

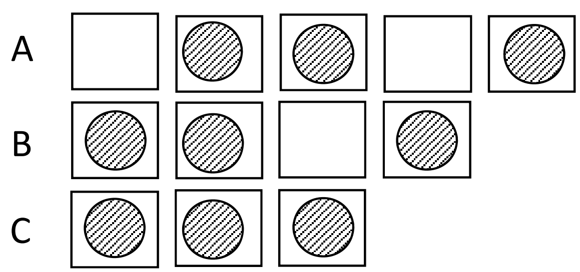
tendency of atoms/molecules to diffuse

Many of the key ideas can be illustrated by lattice models
in which sites are either occupied or empty

Simpler to work with than problems with continuous variables

Simple lattice model to understand why gases expand (exert pressure)

Suppose there are three volumes possible 3, 4, or 5



$\text{Vol} = M_5 \quad W = 10 \quad p_A = 10/15$

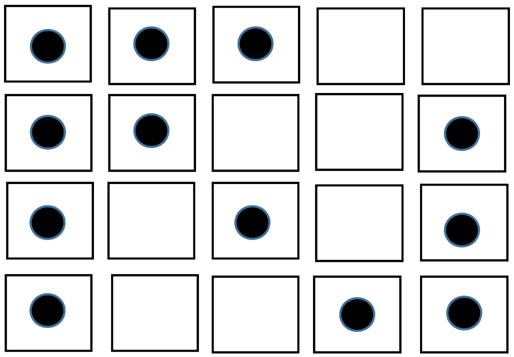
$\text{Vol} = M_4 \quad W = 4 \quad p_B = 4/15$

$\text{Vol} = M_3 \quad W = 1 \quad p_C = 1/15$

A, B, C macrostates made up of 1 or more microstates

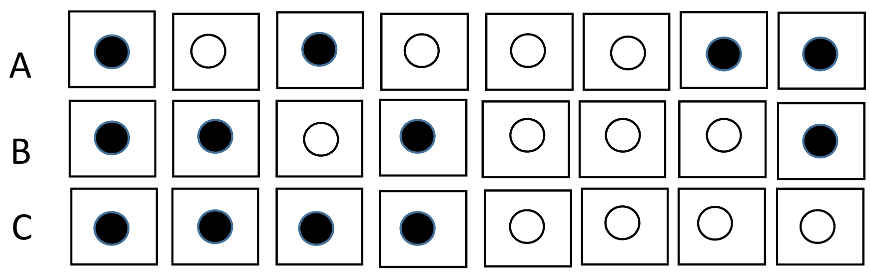
all microstates equally probable

A slightly different way of seeing that it is favorable for the gas to spread out



More likely to be spread out than to be bunched at one side

Next consider a model that explains why gasses diffuse



$$6 \bullet 6 = 36$$

$$4 \bullet 4 = 16$$

$$1$$

multiplicities

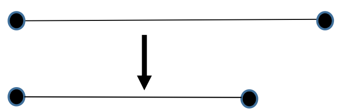
White and black spheres denote different atoms

If we start with C, the system will evolve towards A

More arrangements when the two species are randomized

Stretched rubber band

More favorable to be unstretched. Why?



Systems tend toward maximum entropy

In Chapter 5 we will show that

entropy $S = \ell n W$

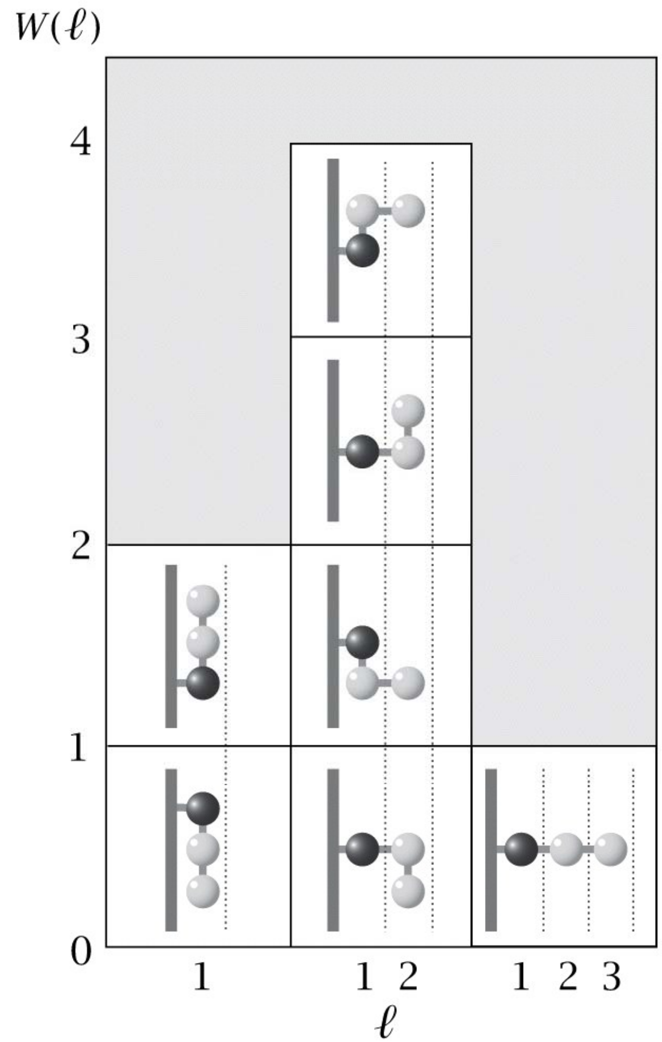


Figure 2.9 Molecular Driving Forces 2/e (© Garland Science 2011)