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[TP] How many distinguishable ways can 5 ink molecules be arranged among 13 water molecules?

17% 1. 1450
17% 2. 3260
17% 3. 8568
17% 4. 12650
17% 5. 14950
17% 6. 65780

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Wednesday, April 10, 2019

Begin ch 17: Spontaneous change: How far?

- The essence of change
- Counting particle dispersal
- Maximum particle dispersal = uniform pressure
- Arrangements ⟶ Entropy

Next lecture: Continue ch17

Notes: Spontaneity: Second law of thermodynamics
http://quantum.bu.edu/courses/ch102-spring-2018/handouts.html

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Spontaneous change: How Far?

Mahaffy et al., ch 17 and

Notes: Spontaneity: Second law of thermodynamics, PDF, 14 pages

http://quantum.bu.edu/courses/ch102-spring-2019/handouts.html

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The essence of change

Why does a drop of ink in water disperse?

Why do salt water and fresh water mix?

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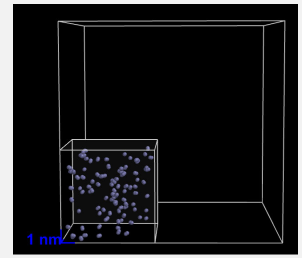
The essence of change

all complexity is an illusion ...

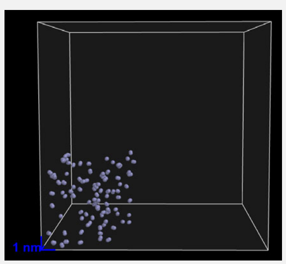
things happen simply because they can happen
and because they are statistically
most likely to happen."

Michael Munowitz, "Principles of Chemistry," W. W. Norton, 2000

A gas fills its container



A gas fills its container



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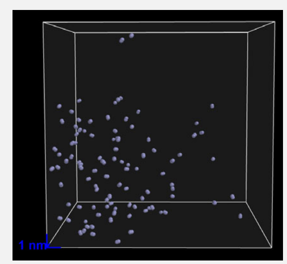
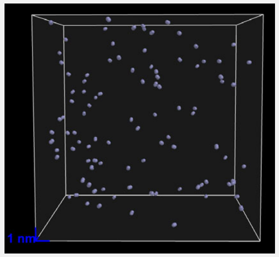


A gas fills its container



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A gas fills its container

Gas all on left of container

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A gas fills its container

Gas evenly distributed throughout container

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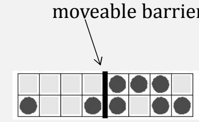
Pressure in a gas is uniform

moveable barrier



P proportional to n/V (“lattice gas”)
P higher on the right

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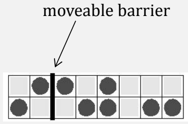
Pressure in a gas is uniform

moveable barrier



P proportional to n/V ("lattice gas")
P the same on the left and right

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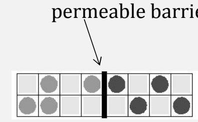
Gases mix evenly

permeable barrier



One gas on left, another on right

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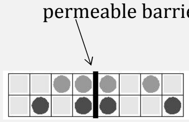
Gases mix evenly

permeable barrier



Equal amounts throughout

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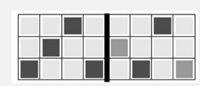
Osmotic pressure across semipermeable membrane



Pressure equal (n/V) on both sides of membrane,
but solute (light grey) cannot pass across
membrane to left

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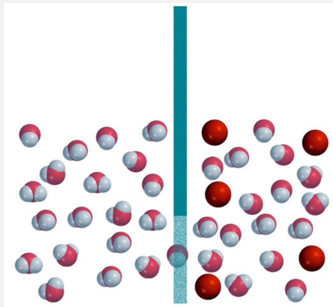
Osmotic pressure across semipermeable membrane



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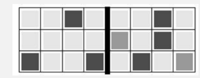
Osmotic pressure across semipermeable membrane



Solvent passes across membrane to right making pressure higher (n/V) on right

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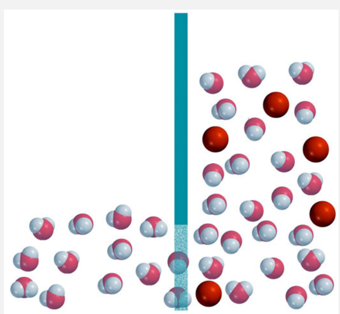
Osmotic pressure across semipermeable membrane



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Blind chance & dumb luck

Everything—absolutely everything—that happens, happens solely because of blind chance and dumb luck.

To quantify this …

1. Learn to count the ways
2. Search for greatest number of ways

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Counting distinguishable (unique) arrangements

The number of distinguishable arrangements of
j identical objects of one kind (water molecules, say) and
k identical objects of another kind (ink molecules, say) is …

$$W(j,k) = \frac{(j+k)!}{j! \times k!}$$

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Counting distinguishable (unique) arrangements

The number of distinguishable arrangements of
j identical objects of one kind, say $j = 4$ water molecules, and
k identical objects of another kind, say $k = 3$ ink molecules …

$$W(4,3) = \frac{(4+3)!}{4!\,3!} = \cdots$$

$$\frac{7 \times 6 \times 5 \times 4!}{4!\,3!} = \frac{7 \times 6 \times 5}{3 \times 2} = 7 \times 5 = 35$$

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[TP] How many distinguishable ways can 5 ink molecules be arranged among 13 water molecules?

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Maximum particle dispersal = uniform pressure

The goal: To see that what "happens" corresponds to the maximum number of arrangements

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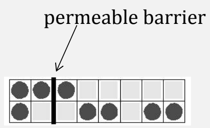
Pressure in a gas is unequal



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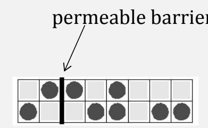
Pressure in a gas is uniform



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Pressure in a gas becomes uniform

Why?

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Lattice gas model of pressure

$\frac{P}{RT} = n/V =$ gas density

$n =$ particles

$V =$ lattice positions

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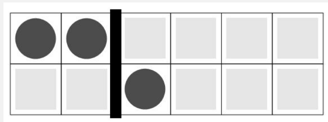
$P_{\text{left}} > P_{\text{right}}$



Left side: $n/V = 2/4$, $W_{\text{left}} = \ldots$

6

Right side: $n/V = 1/8$, $W_{\text{right}} = \ldots$

8

$W_{\text{total}} = W_{\text{left}} \times W_{\text{right}} = 6 \times 8 = 48$

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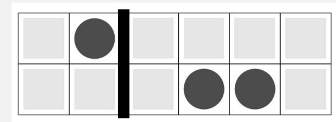
$P_{\text{left}} = P_{\text{right}}$



Left side: $n/V = 1/4$, $W_{\text{left}} = \ldots$

4

Right side: $n/V = 2/8$, $W_{\text{right}} = \ldots$

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$W_{\text{total}} = W_{\text{left}} \times W_{\text{right}} = 4 \times 28 = 112$

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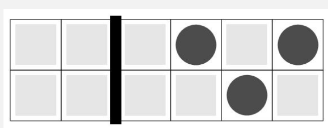
$P_{\text{left}} < P_{\text{right}}$



Left side: $n/V = 0/4$, $W_{\text{left}} \ldots$

1

Right side: $n/V = 3/8$, $W_{\text{right}} = \ldots$

56

$W_{\text{total}} = W_{\text{left}} \times W_{\text{right}} = 1 \times 56 = 56$

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Pressure in a gas becomes uniform

Why?

$P_{\text{left}} > P_{\text{right}}$ has $W_{\text{total}} = 48$

$P_{\text{left}} = P_{\text{right}}$ has $W_{\text{total}} = 112$

$P_{\text{left}} < P_{\text{right}}$ has $W_{\text{total}} = 56$

Uniform pressure maximizes W!

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Arrangements → Entropy

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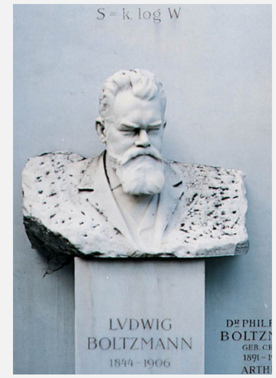
$S = k_B \ln(W)$



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$S = k_B \ln(W)$

$k_B = R/N_A = 1.4 \times 10^{-23}$ J/K

Why natural log?

Doubling size of system: $W \longrightarrow W \times W = W^2$

Doubling size of system: $S \rightarrow k_B \ln(W^2) = 2k_B \ln(W) = 2S$, so …

Boltzmann's definition in terms of natural log makes S …

scale with size of system (extensive).

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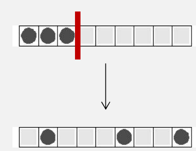
Spontaneous?



Calculate the entropy change.

$W_i = 1 \rightarrow W_f = (6+3)!/(6!\,3!) = 84$

$\Delta S = S_f - S_i = k_B \ln(W_f/W_i) = k_B \ln(84/1) > 0$

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