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Slides on particle dispersal, pressure equilibration, and entropy
CH102 Spring 2016, A1 and A2 lecture 27

- Enumerating particle dispersal
- Practice with particle dispersal
- Maximum particle dispersal = uniform pressure
- Arrangements → entropy

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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

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Counting *distinguishable* (unique) arrange

Say we have three girls and four boys.

What is the probability of calling them into line in the order *gggbbb*?

$$\frac{3}{7} \times \frac{2}{6} \times \frac{1}{5} = \frac{1}{35}$$

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Counting *distinguishable* (unique) arrange

Say we have three girls and four boys.

What is the probability of calling them into line in the order *bgbgbg*?

$$\frac{4}{7} \times \frac{3}{6} \times \frac{3}{5} \times \frac{2}{4} \times \frac{2}{3} \times \frac{1}{2} = \frac{1}{35}$$

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Counting *distinguishable* (unique) arrange

Say we have three girls and four boys.

If we ignore whether a child is boy or girl, what is the total number of arrangements?

$$7 \times 6 \times 5 \dots \times 1 = 7! = 5040$$

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Counting *distinguishable* (unique) arrange

Say we have three girls and four boys.

For each particular arrangement, say *bgbgbg*, how many ways can it come about?

$$3!4! = 144$$

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Counting *distinguishable* (unique) arrange

Say we have three girls and four boys.

This means the total number of arrangements can be expressed as

$$7! = W \times 3!4!$$
$$5040 = 144W$$
$$W = 5040/144 = 35$$

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Counting *distinguishable* (unique) arrange

More generally, say we have j girls and k boys.

The number of unique arrangements of n_1 objects of one kind and n_2 object of another kind is


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

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Practice with particle dispersal



See page 3 of
<http://quantum.bu.edu/courses/ch102-spring-2016/notes/SecondLaw.pdf>

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[TP] How many *distinguishable* ways can 3 water molecules and 2 ink molecules be arranged?



- 0% 1. 8
- 0% 2. 10
- 0% 3. 12
- 0% 4. 120
- 0% 5. None of these

 Response Counter  20

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[TP] How many *distinguishable* ways can 5 water molecules and 2 ink molecules be arranged?

- 0% 1. 14
- 0% 2. 21
- 0% 3. 240
- 0% 4. 5040
- 0% 5. None of these

 Response Counter  22

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[TP] How many **distinguishable** ways can 2 ink molecules be arranged among 12 water molecules?

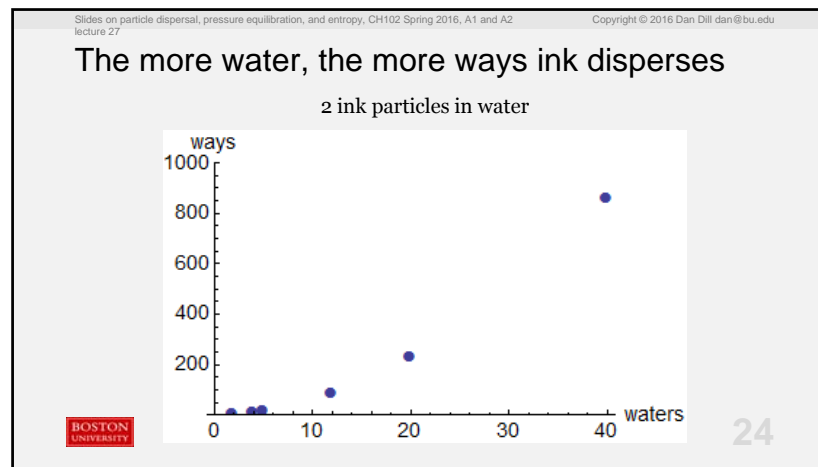
- 0% 1. 36
- 0% 2. 240
- 0% 3. 455
- 0% 4. 720
- 0% 5. None of these

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Response Counter

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Maximum particle dispersal = uniform pressure

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Pressure in a gas is **unequal**

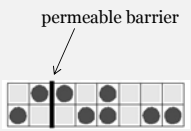
permeable barrier

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Pressure in a gas is **uniform**



permeable barrier

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Pressure in a gas **becomes uniform**

Why?

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Lattice gas model of pressure


$1/(RT) P = n/V = \text{gas density}$
 $n = \text{particles}$
 $V = \text{lattice positions}$

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




Left side: $n/V = 2/4$, $W_{\text{left}} = \dots$
 6

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

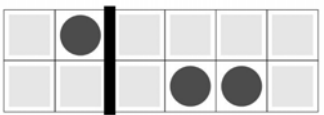
$W_{\text{total}} = W_{\text{left}} \times W_{\text{right}} = 6 \times 8 = 48$

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



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

Right side: $n/V = 2/8$, $W_{\text{right}} = \dots$
28

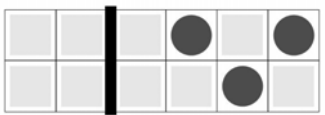
$W_{\text{total}} = W_{\text{left}} \times W_{\text{right}} = 4 \times 28 = 112$

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



Left side: $n/V = 0/4$, $W_{\text{left}} \dots$
1

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

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$S = k_B \ln(W)$



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$S = k_B \ln(W)$

Why natural log?

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

Doubling size of system: $S \rightarrow 2S$, so ...

Boltzmann's definition makes S *scale with size of system* (extensive).

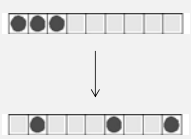
$k_B = R/N_A = 1.4 \times 10^{-23} \text{ J/K}$

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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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