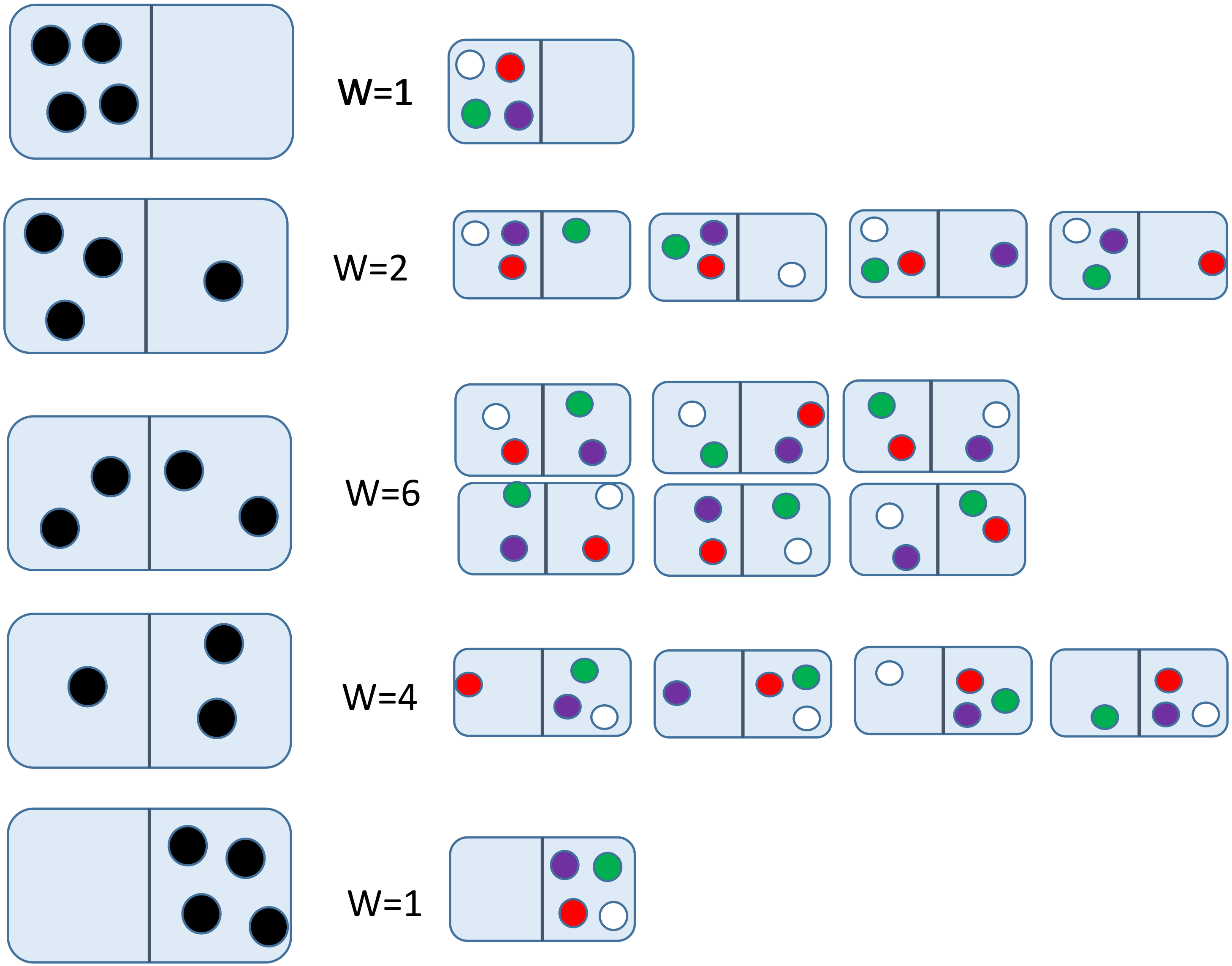
Second Law of Thermodynamics and Entropy

Alexei Tkachenko

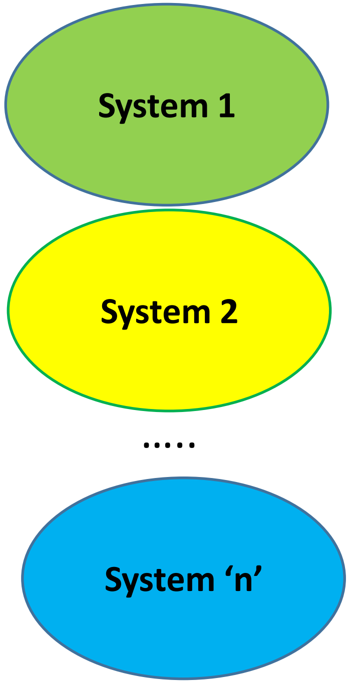
Let’s count “microstates”



Can *W* be the entropy?
No. Entropy must be *additive*

- Volume: $V_{total} = V_1 + V_2 + \ldots + V_n$
- Energy: $E_{total} = E_1 + E_2 + \cdots + E_n$
- Number of molecules: $N_{total} = N_1 + N_2 + \cdots + N_n$
- Entropy: $S_{total} = S_1 + S_2 + \cdots + S_n$

- Number of “microstates”: $W_{total} = W_1 \times W_2 \times \cdots \times W_n$



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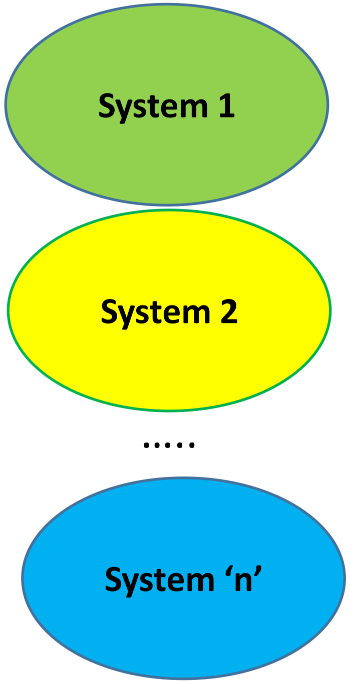

Let us use magic of **logarithm**: $y = a^x \rightarrow \quad x = \log_a y$

$$y_1 \times y_2 \rightarrow x_1 + x_2$$

$$S = k \log W$$

$k = 1.38 \cdot 10^{-23} \frac{J}{K}$ - Boltzmann constant

Boltzmann Distribution

"Thermal Bath" at Temperature T

Let a system of interest has energy E
(say, an atom or molecule)

E

$$\Delta S = -\frac{E}{T}$$

Entropy "cost" of
taking away energy E

$$S = k \log W$$

Therefore , the probability of a state with Energy E is proportional to

$$Prob \sim e^{\Delta S} = e^{-\frac{E}{kT}}$$

Homework

Problem 1 An electron can be removed from the Helium atom, but that requires energy of **E=24.6** electron volts (eV), known as ionization energy. Use this information, and *Boltzmann probability formula*, $\boldsymbol{Prob} \sim \boldsymbol{e}^{-\frac{\boldsymbol{E}}{\boldsymbol{kT}}}$, to estimate the fraction of helium atoms that are ionized (i.e., missing one electron) at room temperature $T = 300\ K$.

Note that Boltzmann constant $k = 1.38 \cdot 10^{-23} \frac{J}{K}$, and $1eV = 1.6 \cdot 10^{-19}\ J$

Problem 2 Assume that morning fog consists of water droplets, each with radius $r = 1\ \mu m$. The gravitational potential energy of a droplet at height h above the ground is

$$E = mgh$$

where $m = 4\pi\rho r^3/3$ is the mass of the droplet, $g = 10m/s^2$ is the acceleration due to gravity, and h is the height. Using the *Boltzmann probability formula*, estimate the characteristic height h over which the fog can extend above the ground at temperature $T = 300\ K$.