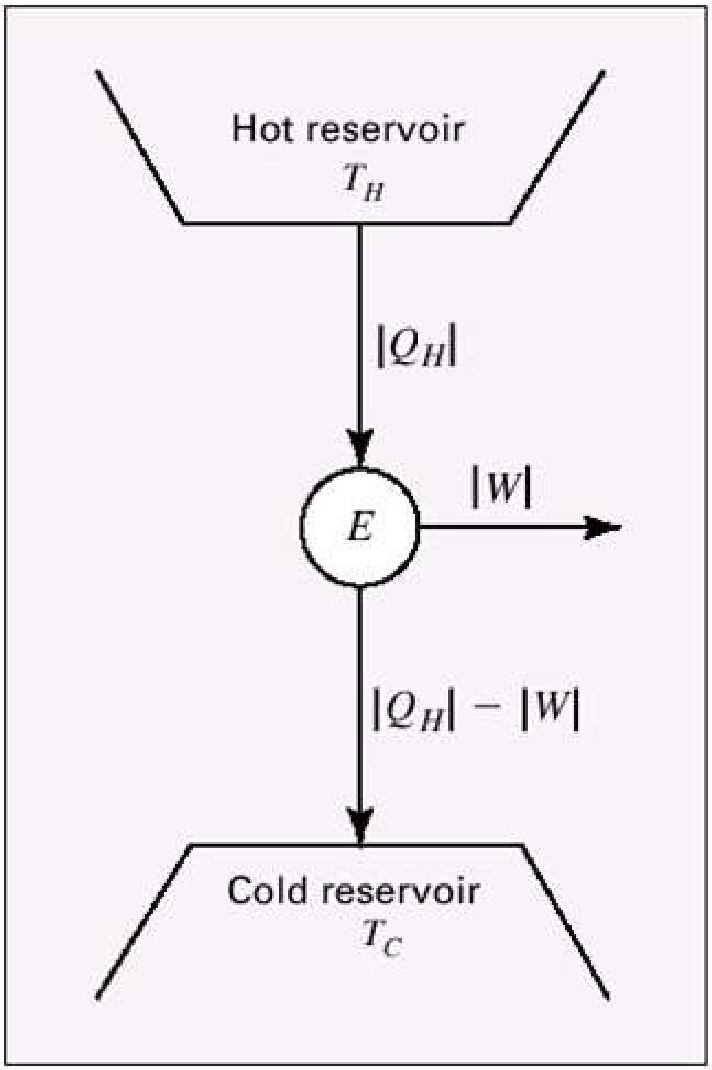
CH365 Chemical Engineering Thermodynamics

Lesson 25

3^{rd} Law and Entropy from the Microscopic Viewpoint

What is Entropy?

Implications



$$\eta = \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H}$$ (Eq. 5.8)

Third Law of Thermodynamics

The absolute entropy is zero for all perfect crystalline substances at absolute zero temperature.

$$S = S(T) = \int_0^{T_f} \frac{(C_P)_S}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{(C_P)_L}{T} dT + \frac{\Delta H_V}{T_V} + \int_{T_V}^{T} \frac{(C_P)_G}{T} dT$$

(Eq. 5.40)

This equation allows calculation of absolute entropy.

Untitled-1 * - Wolfram Mathematica 13.1

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Input

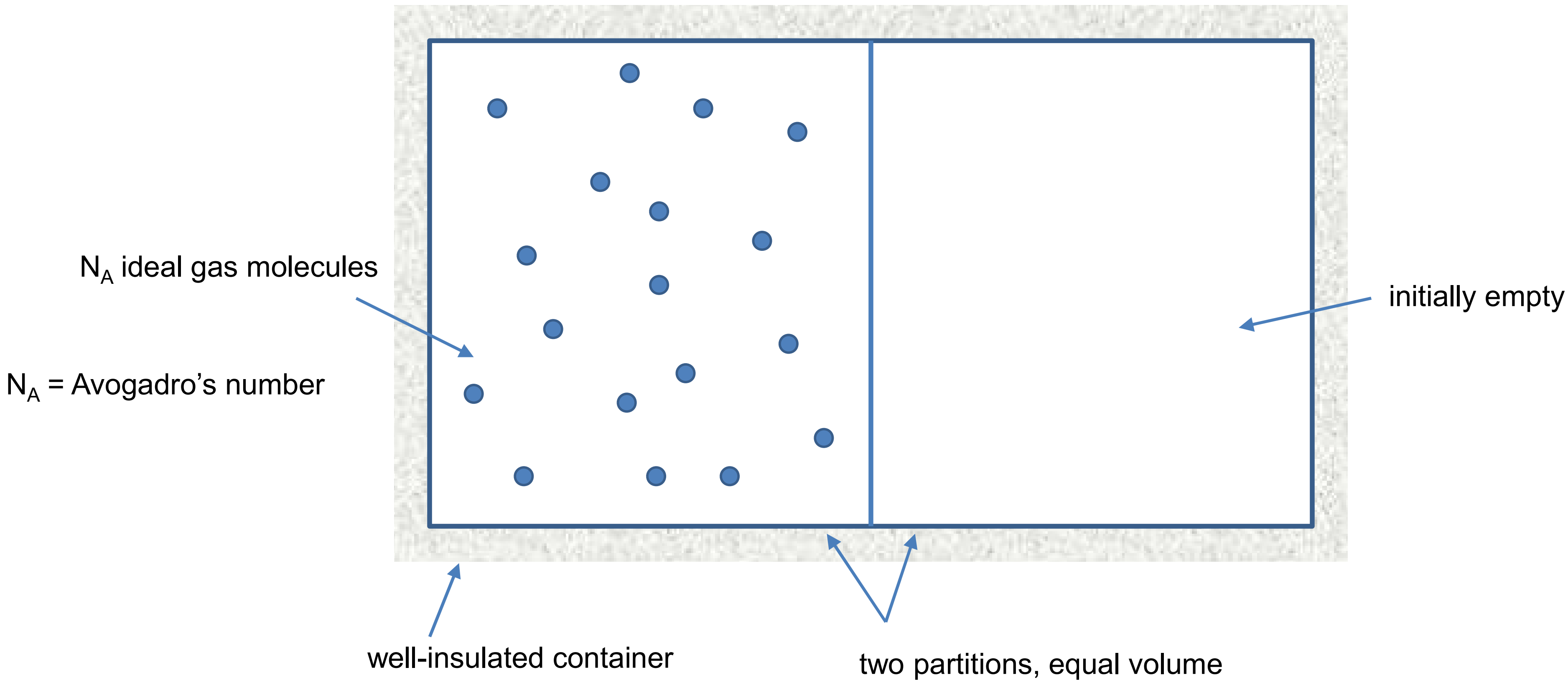
```
In[1]:= (*CaO(s) m.p. 2845 K*)
        (*Cp from Appendix C page 670*)
        Cp = 6.104 + .443 * 10^-3 * T - 1.047 * 10^5 * T^-2;
```

In[2]:= $\int_0^{273} \frac{Cp}{T} \, dT$

100%

Statistical Interpretation

- ideal gas
  - molecules do not interact
  - internal energy resides within the individual molecules



$$U = U(T, V)$$

ch. 4, p. 138, (un-numbered equation)

$$dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{\text{definition of } C_V} dT + \cancelto{0}{\left(\frac{\partial U}{\partial V}\right)_T} dV$$

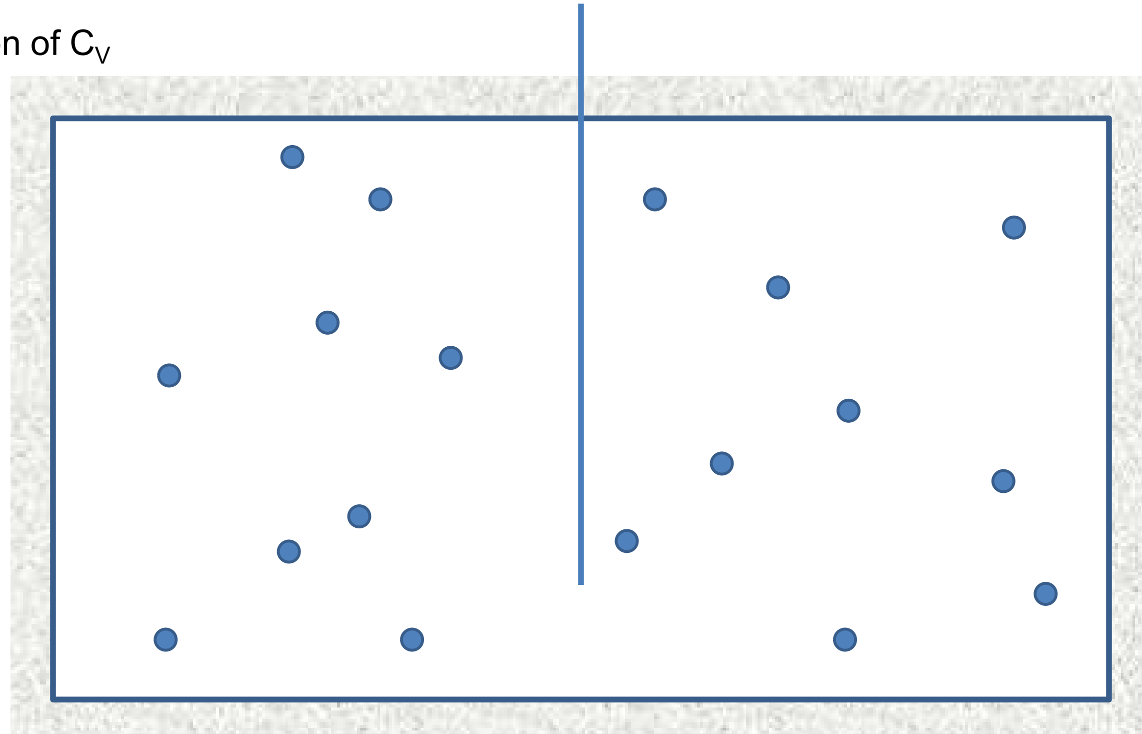
0 → Because molecules don't interact

$$\frac{\Delta S}{R} = \underbrace{\cancelto{0}{\int_{T_{before}}^{T_{after}} \frac{C_P^{ig}}{R}\frac{dT}{T}}}_{\text{0, no change in T}} - \ln\underbrace{\left(\frac{P_{final}}{P_{initial}}\right)}_{\text{P drops by half}}$$

(Eq. 5.10)

ch. 3, p. 79, (Eq. 3.13a)

$$dU = C_V dT$$



Recall:

ch. 3, p. 79, (Eq. 3.14a)

$$dH = C_P dT$$

definition of C_P:

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$$

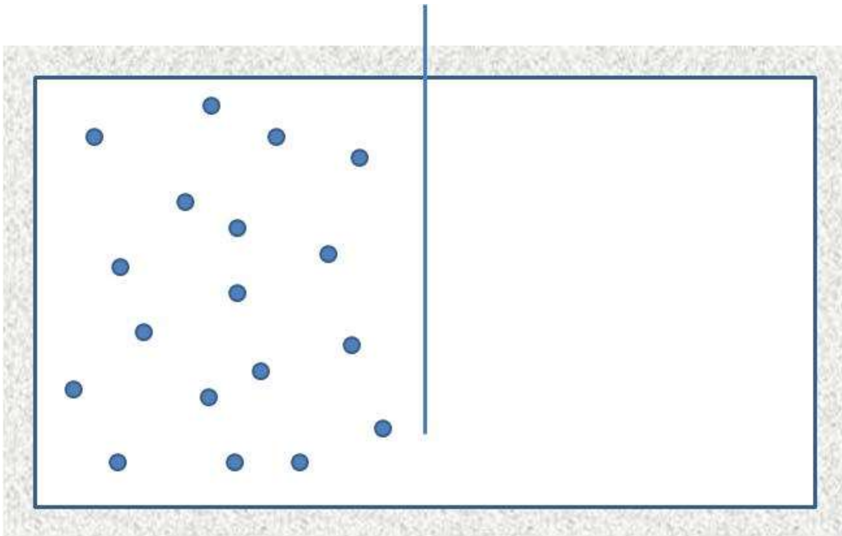
$$\Delta U = C_V \Delta T = 0$$

But if ΔU=0, then T does not change.

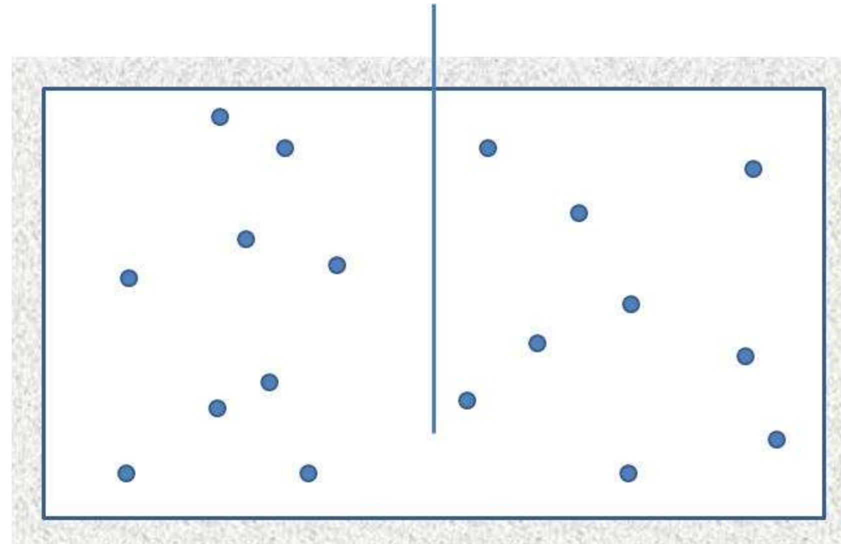
$$\Delta S = -R \cdot \ln\left(\frac{P_{after}}{P_{before}}\right) = \underbrace{R \cdot \ln(2)}_{\text{>0 (irreversible)}}$$

Result of *classical* thermodynamics

more ordered → less random → less disordered



less ordered → more random → more disordered



- immediately after opening
- molecules are not randomly distributed over the total volume
- crowded into half the space

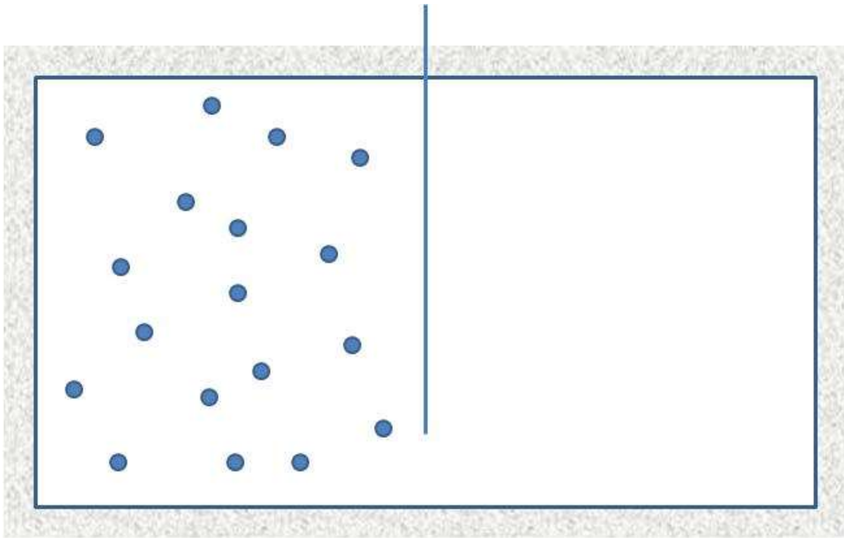
Increasing disorder (or decreasing structure) on the molecular level corresponds to increasing entropy.

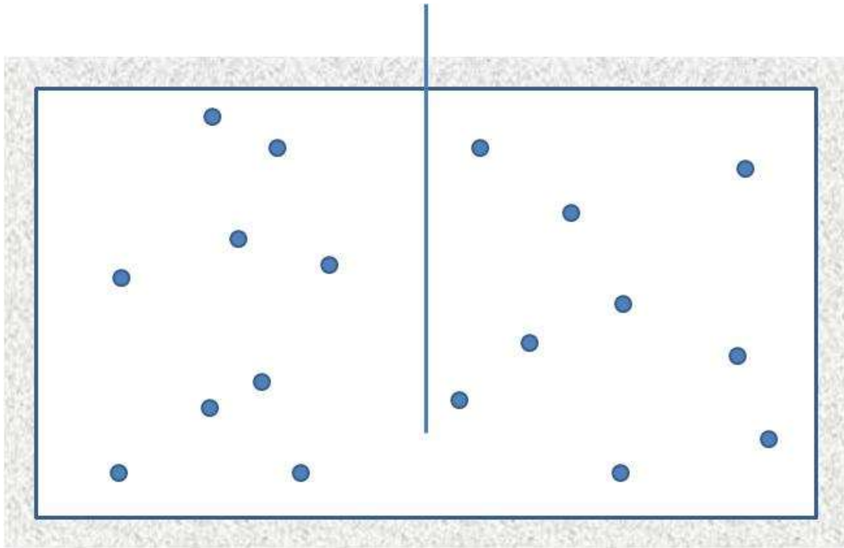
Expression for disorder postulated by J.W. Gibbs and L. Boltzmann, 1878.

Quantitative Expression of Disorder

more ordered = less random = less disordered

less ordered = more random = more disordered

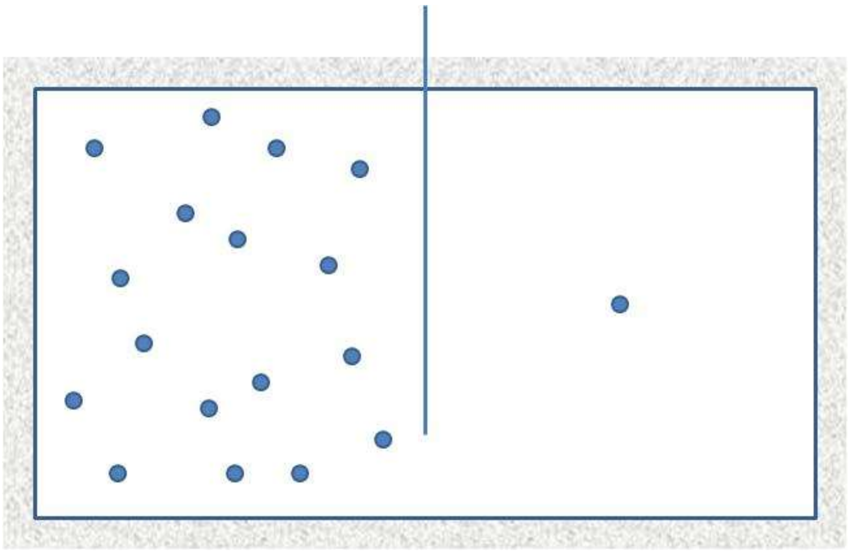


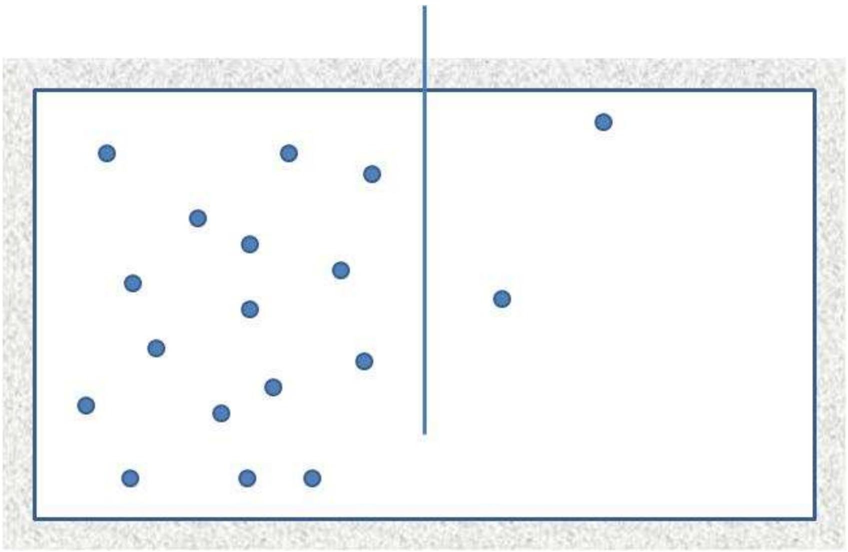


All molecules are in one of the two states.

$$\Omega_{\text{initial}} = \frac{N_A!}{(N_A!)(0!)} = \frac{18!}{(18!)(0!)} = 1$$

$$\Omega_{\text{final}} = \frac{N_A!}{\left(\frac{N_A}{2}!\right)\left(\frac{N_A}{2}!\right)} = \frac{18!}{9!\cdot 9!} = 48{,}620$$





$$\Omega_1 = \frac{18!}{(17!)(1!)} = 18$$

$$\Omega_2 = \frac{18!}{(16!)(2!)} = 153$$

unbounded as N_A increases

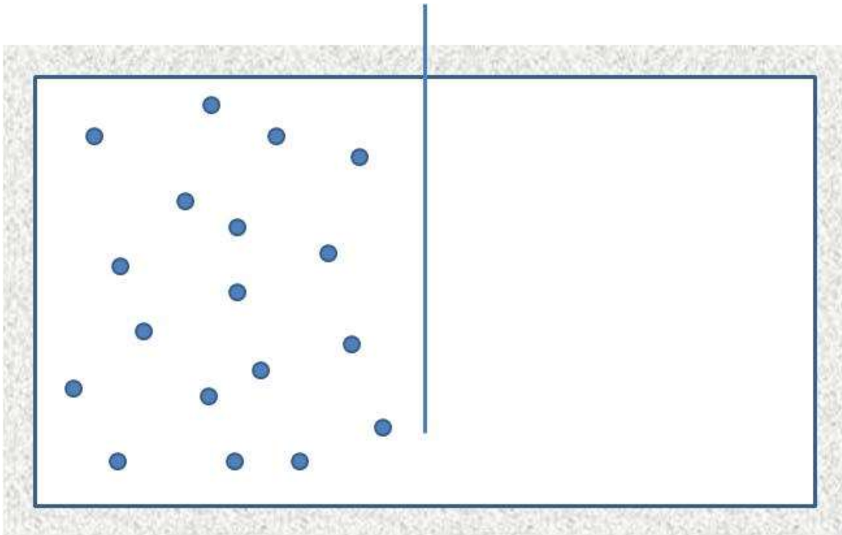
for the 18 particles, $\Omega_{final} = 48,620$

How about $N_A = 10^{23}$?

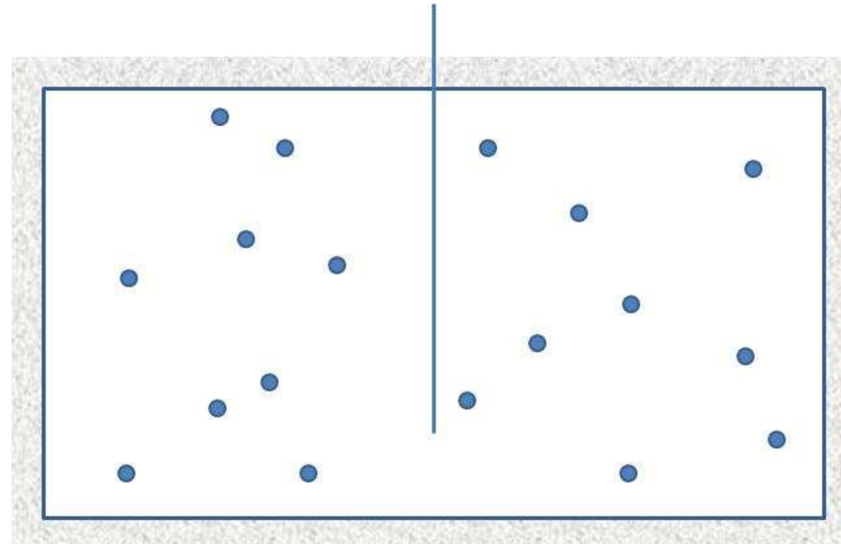
Boltzmann's thought process:

Boltzmann's thought process, continued:

more ordered less random less disordered



less ordered more random more disordered



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https://en.wikipedia.org/wiki/File:Zentralfriedhof_Vienna_-_Boltzmann.JPG

Questions?

Homework