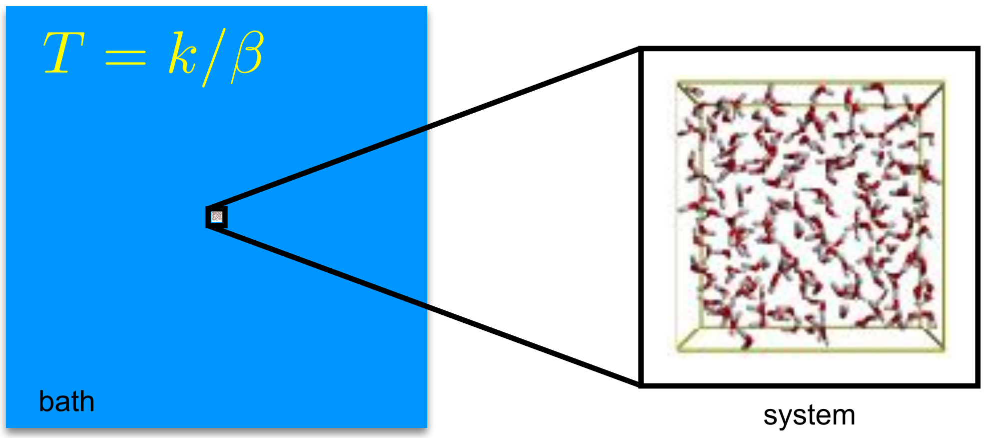
Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

entropy of system

probability of micro state i

$$p_i = \frac{1}{Z} e^{-\beta E_i} \qquad Z = \sum_i e^{-\beta E_i}$$

average energy of system

$$\langle E \rangle = \sum_i p_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\frac{\partial \ln Z}{\partial \beta}$$

what about entropy?

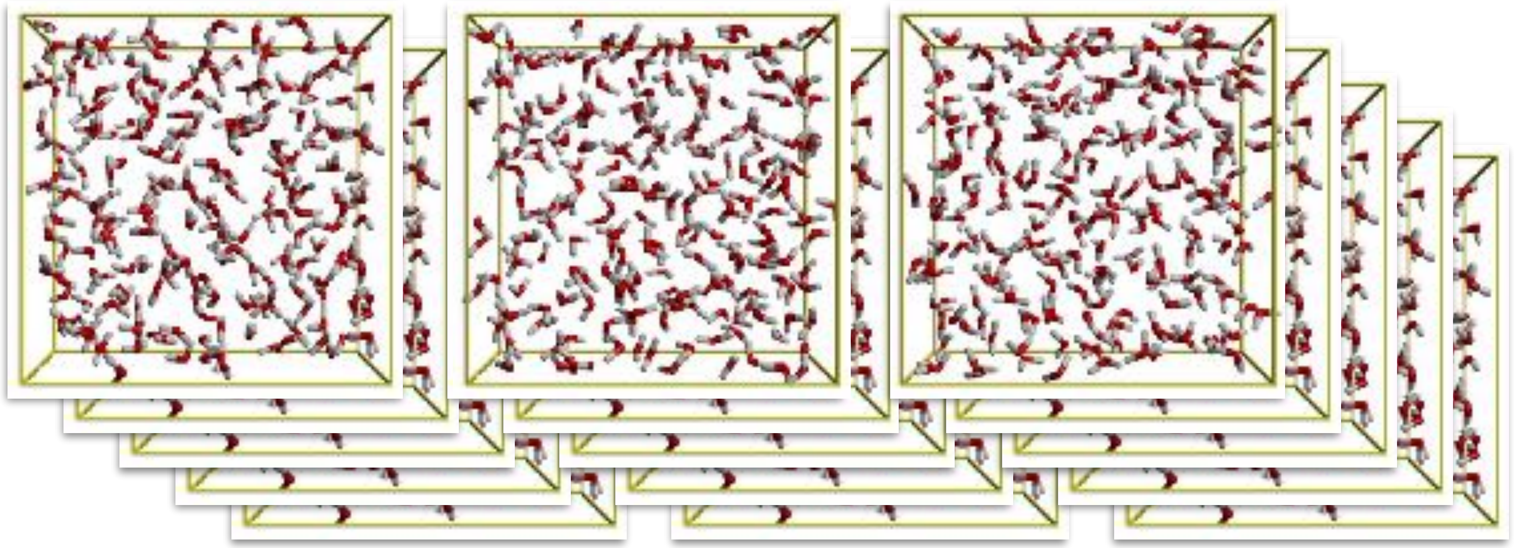
Statistical mechanics

entropy

general ensemble

replicate many time

ensemble of N replicas



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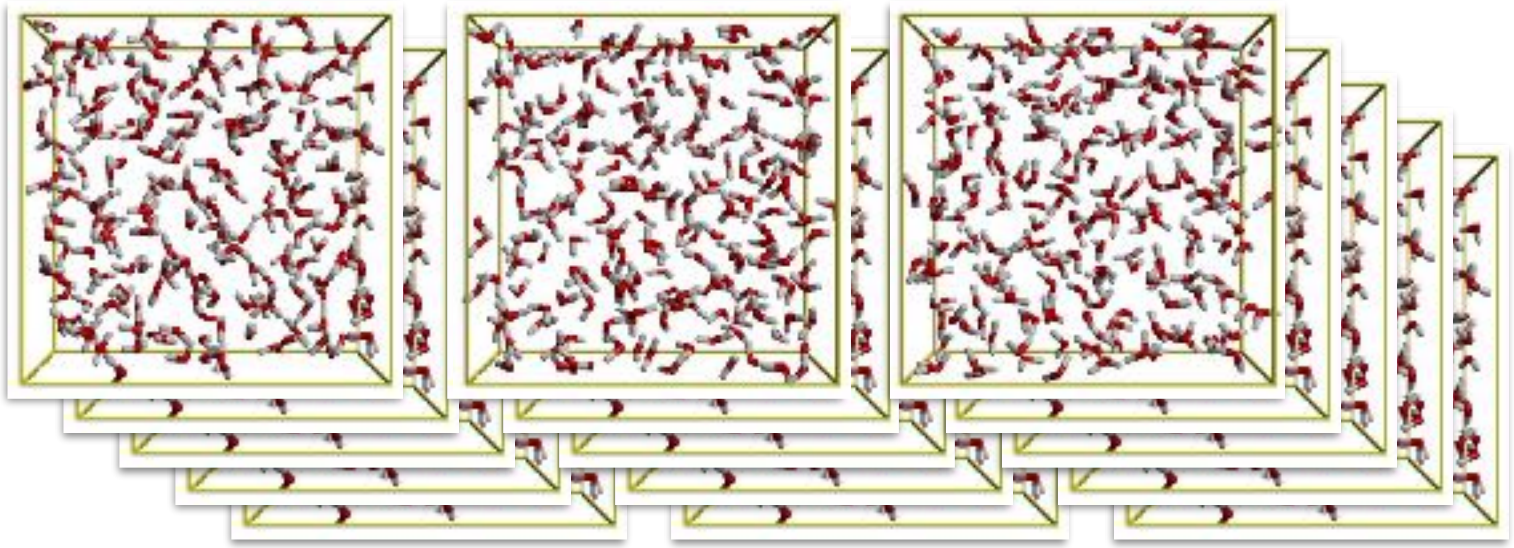

ensemble of N replicas

number of replicas in micro-state i

$$n_i = N p_i \qquad \sum_i p_i = 1$$

Statistical mechanics

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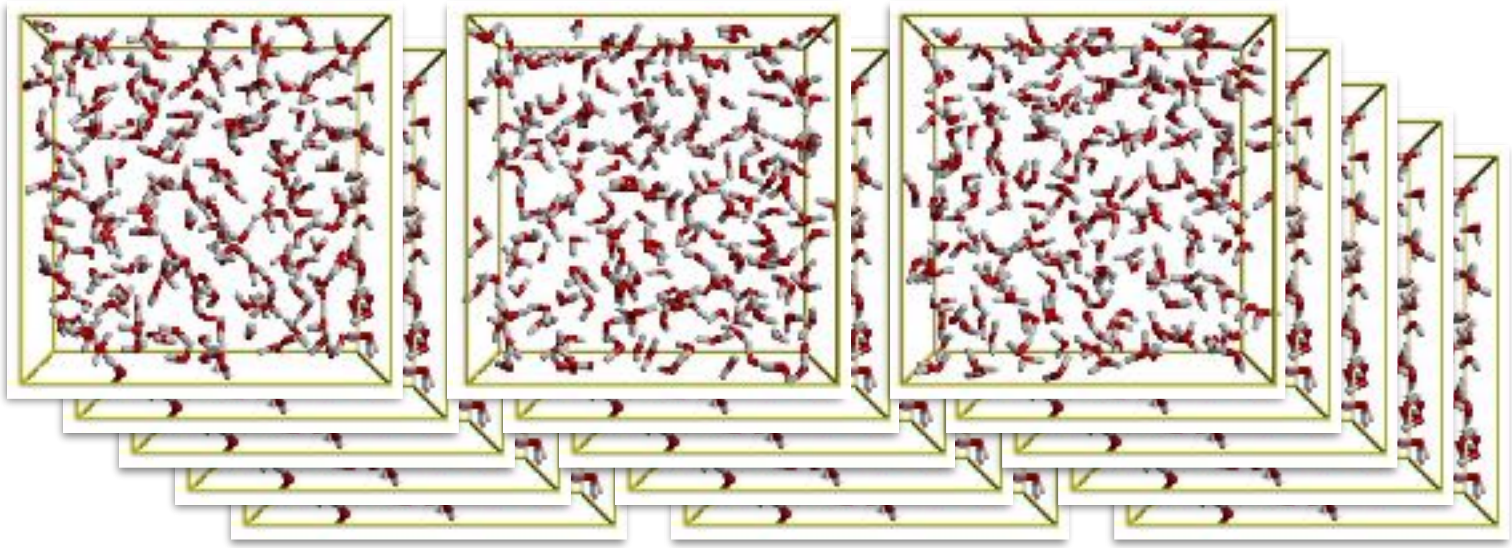

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total number of micro-states

$$\Omega_N = \frac{N!}{n_1!n_2!...n_i!...}$$

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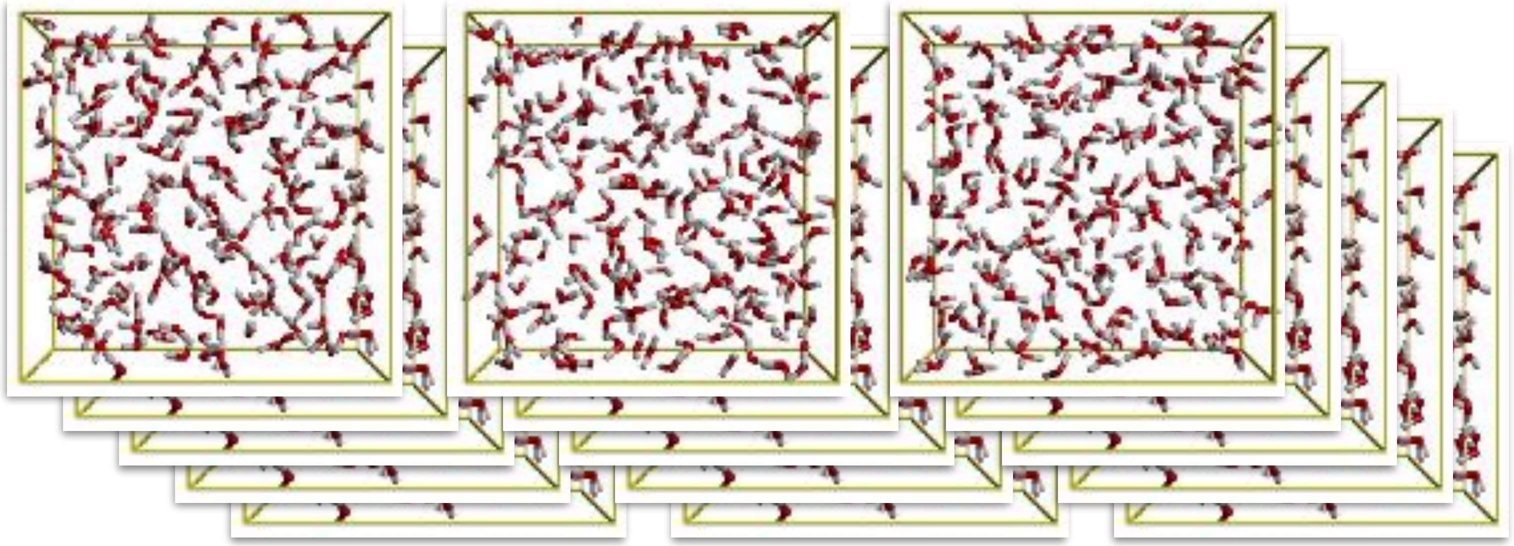

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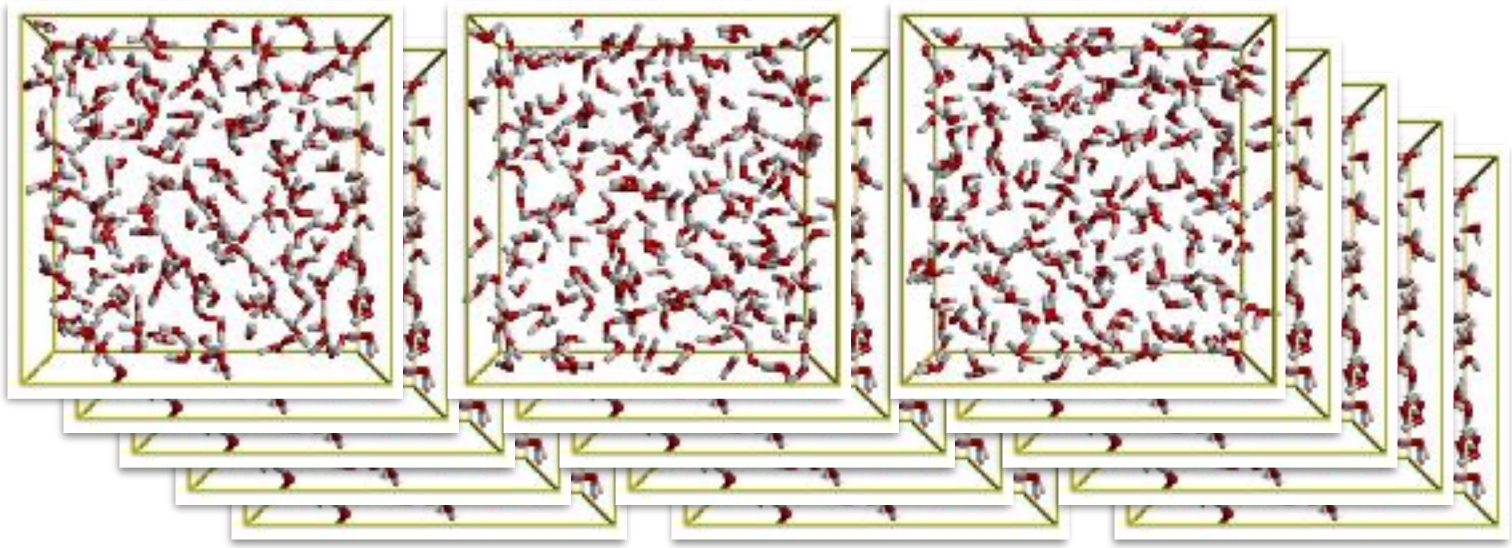
entropy of ensemble

$$S_N = k\ln\Omega_N = k\ln\left[\frac{N!}{n_1!n_2!...n_i!...}\right]$$

Statistical mechanics



entropy

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Stirling approximation:

$$\lim_{x\to\infty} \ln x! = x\ln x - x$$

Statistical mechanics

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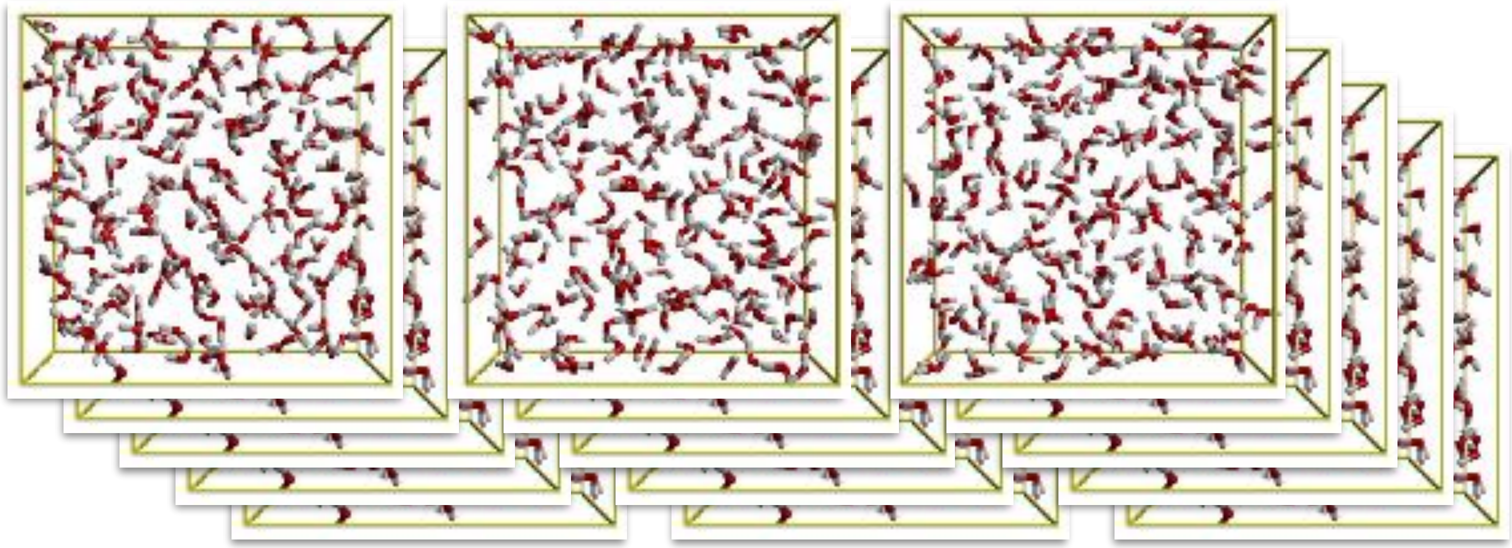

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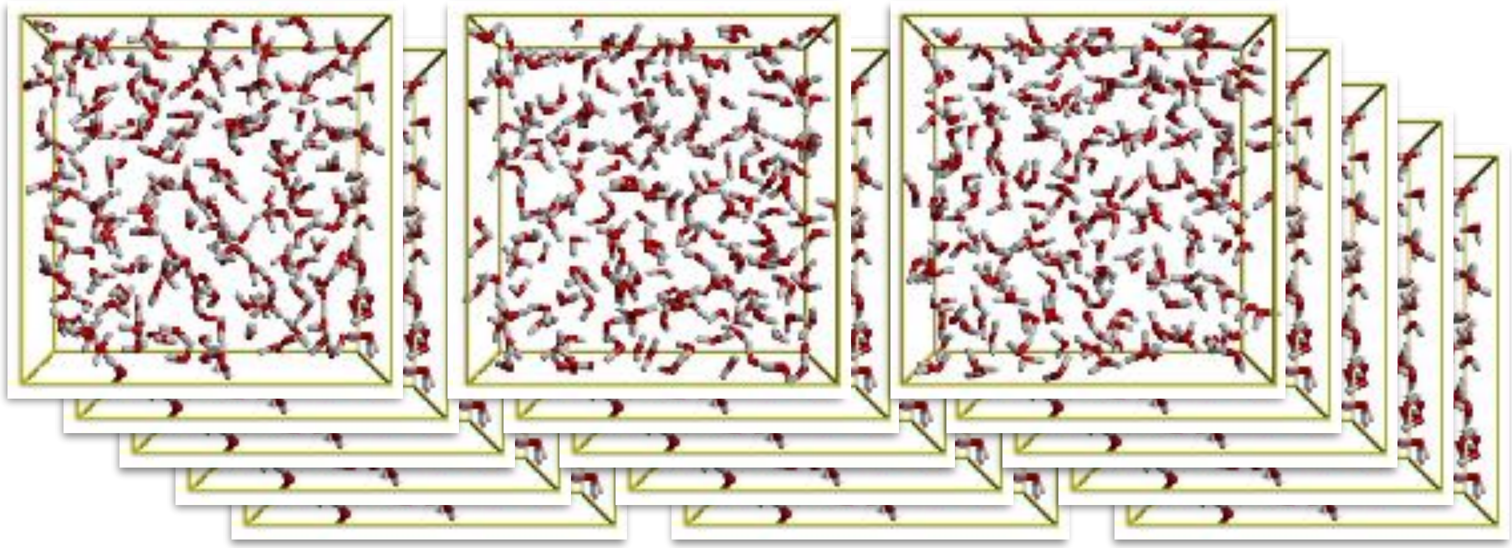

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$$S_N = k \left[N \ln N - N - \sum_i (n_i \ln n_i - n_i) \right]$$

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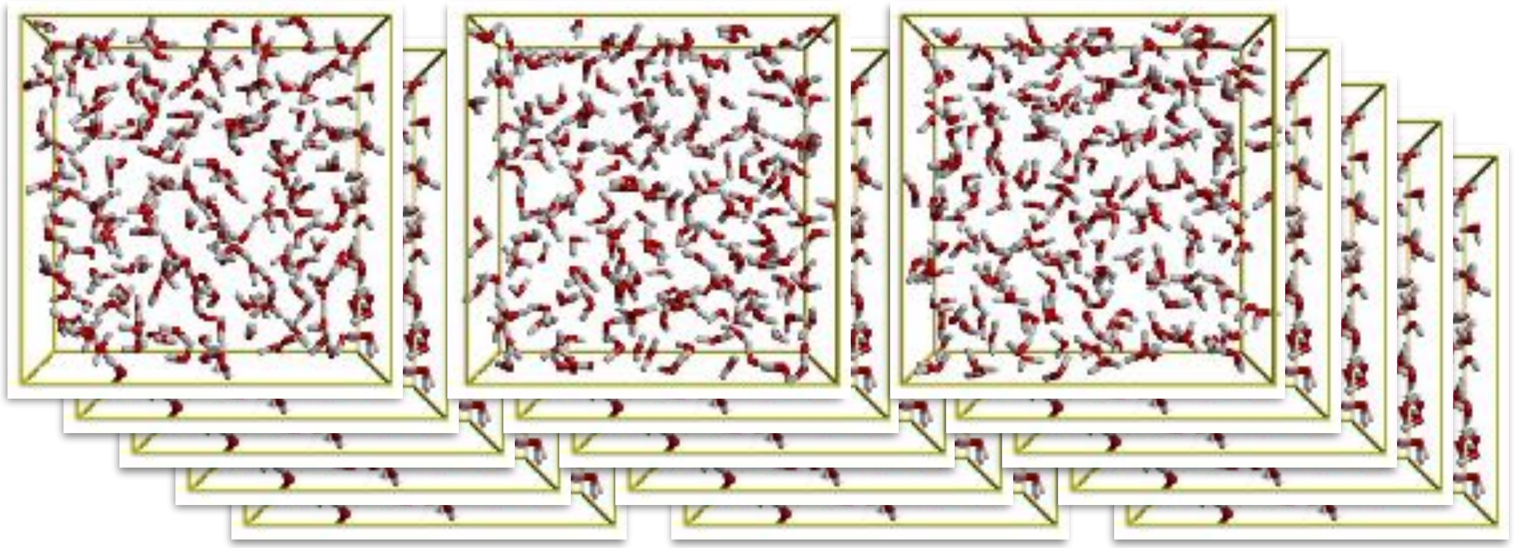

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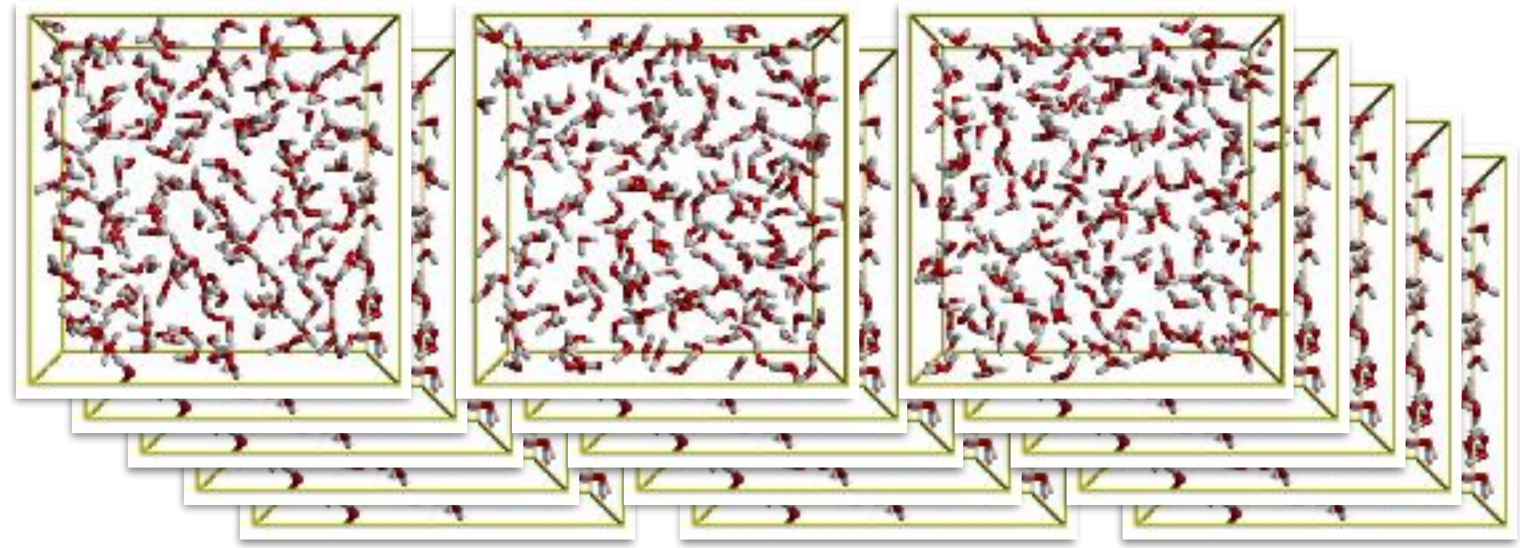
Statistical mechanics



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general ensemble

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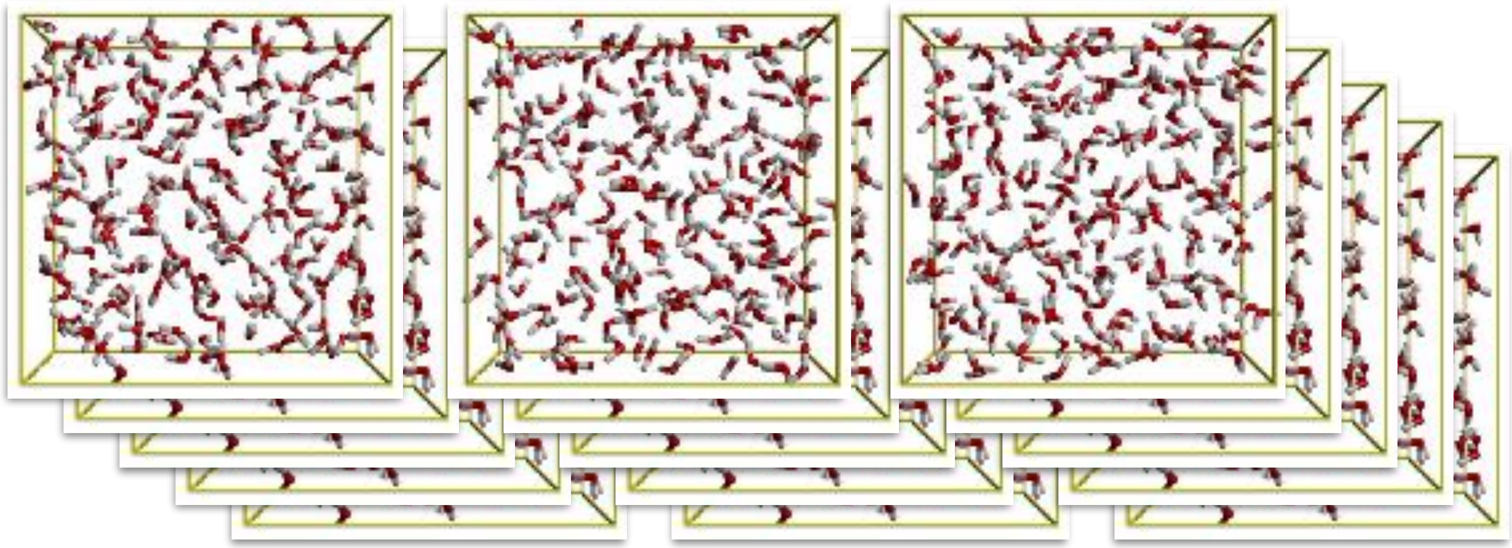

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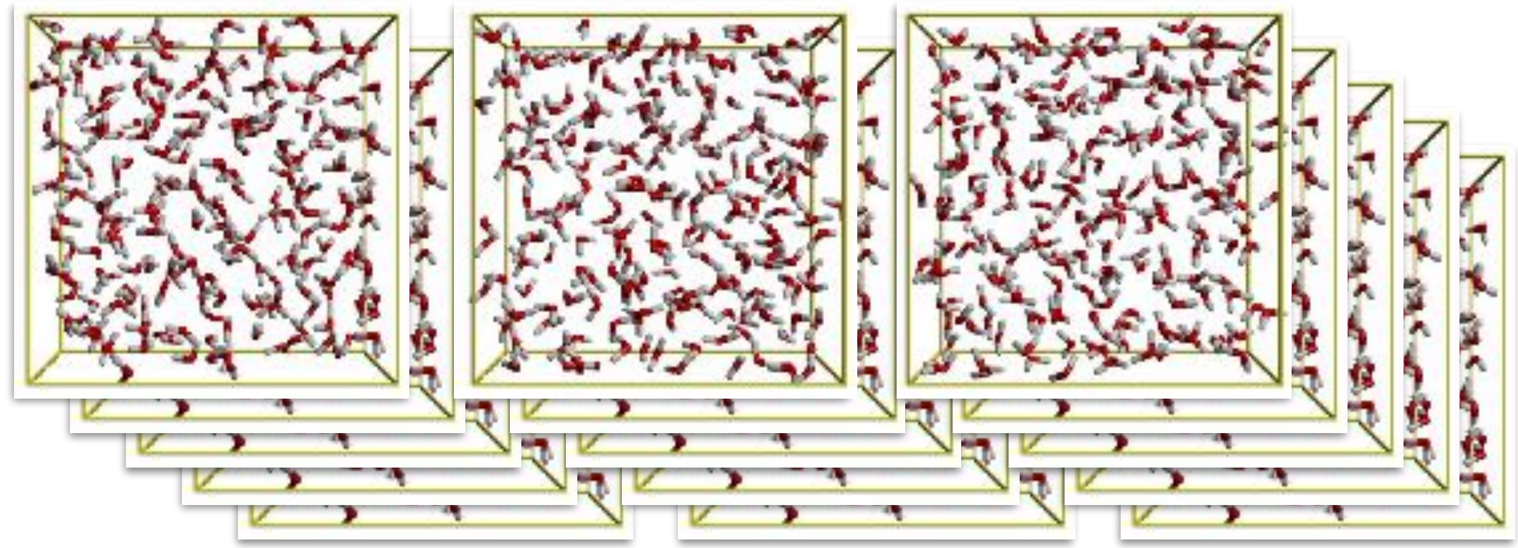
Statistical mechanics



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$$S_N = k\left[\cancel{N\ln N} - \cancel{N} - \cancel{N\ln N} - N\sum_i p_i \ln p_i - \cancel{N}\right]$$

$$S_N = -Nk\sum_i p_i \ln p_i$$

Statistical mechanics

entropy

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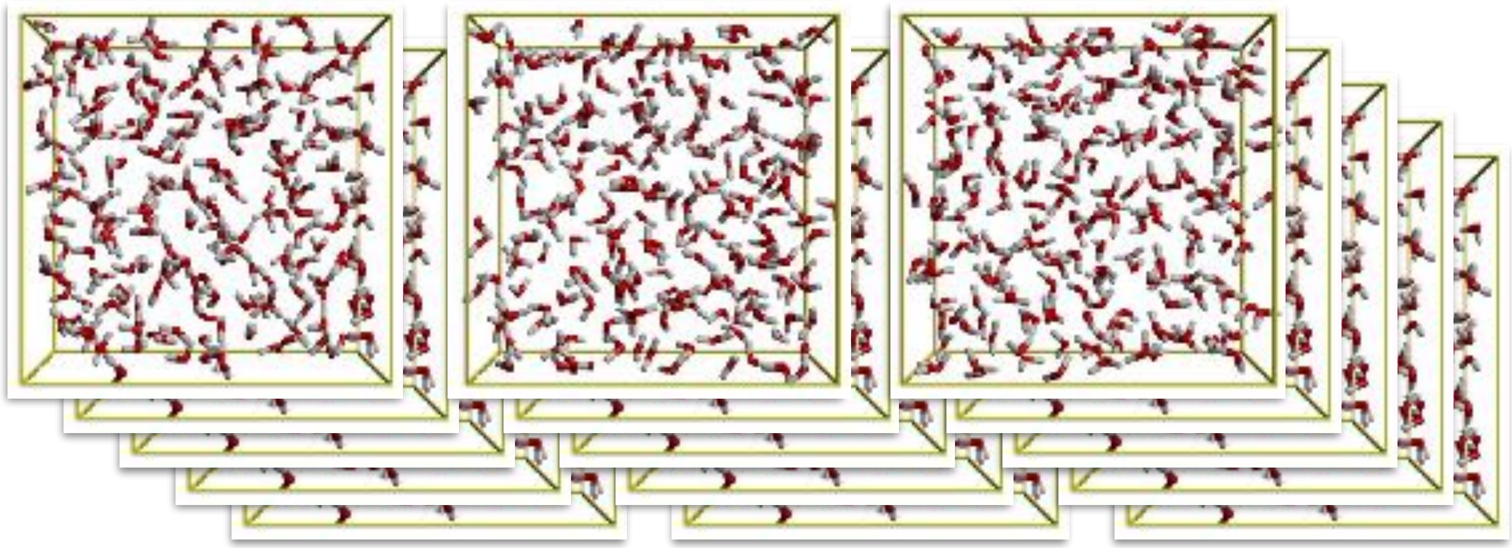

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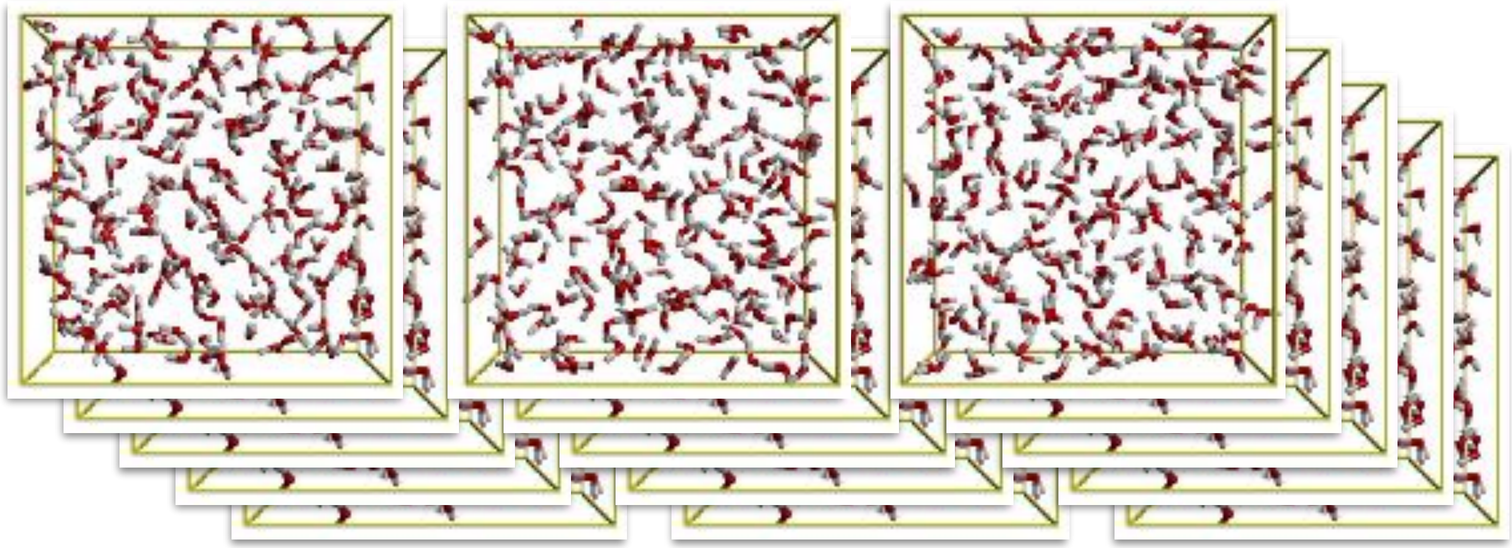

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entropy of replica

$$S = -k \sum_i p_i \ln p_i$$

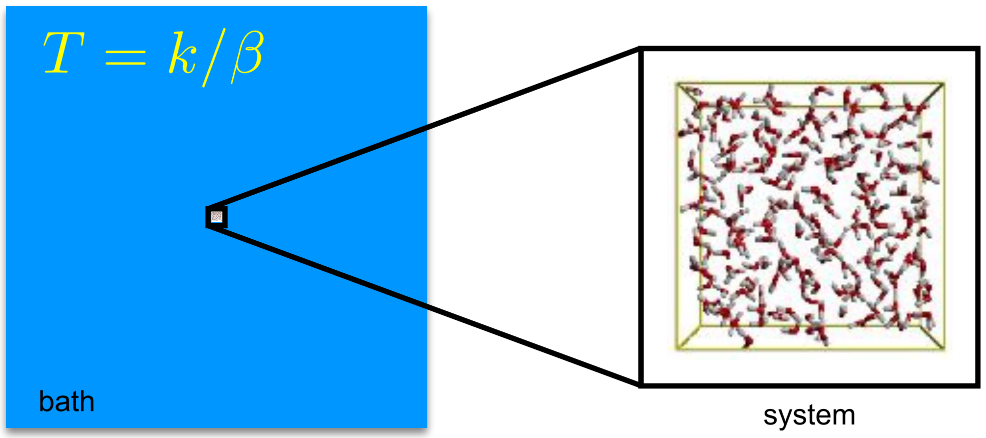
Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath

entropy of system

$$S = -k \sum_i p_i \ln p_i$$



Statistical mechanics

canonical ensemble

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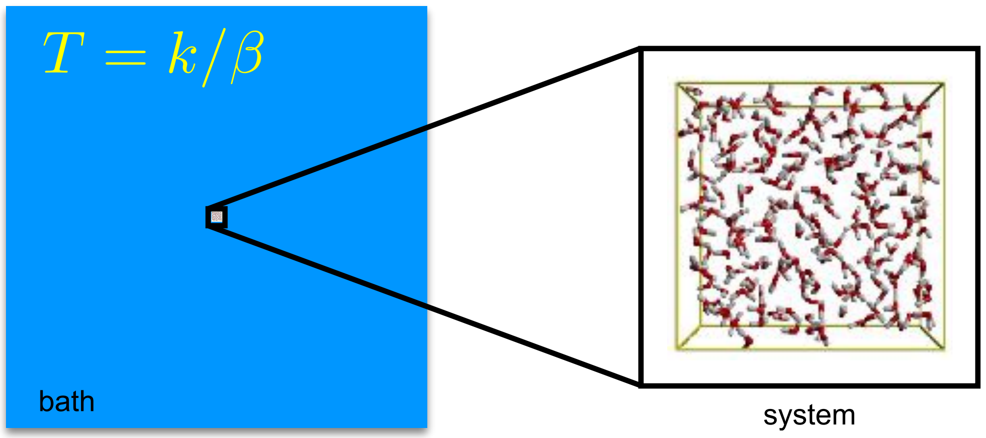

entropy of system

$$S = -k \sum_i p_i \ln p_i$$

Boltzmann distribution

$$p_i = \frac{1}{Z} e^{-\beta E_i} \qquad Z = \sum_i e^{-\beta E_i} \qquad \beta \equiv \frac{1}{kT}$$

Statistical mechanics

canonical ensemble

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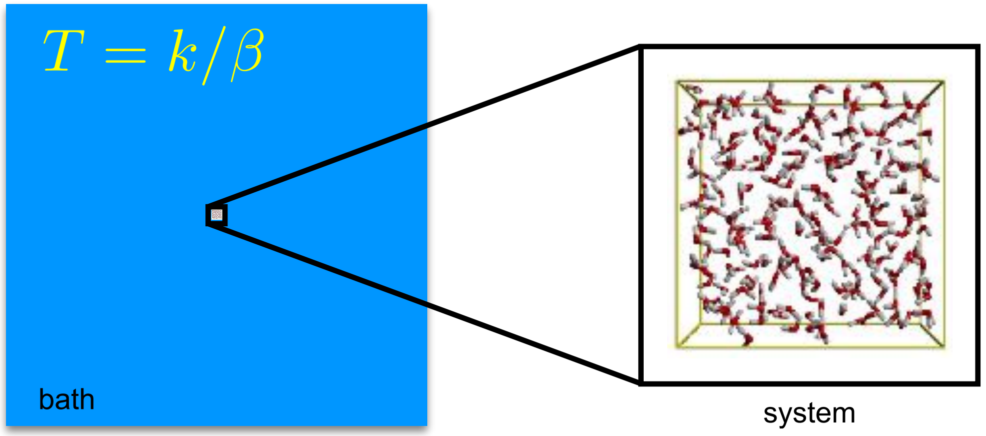

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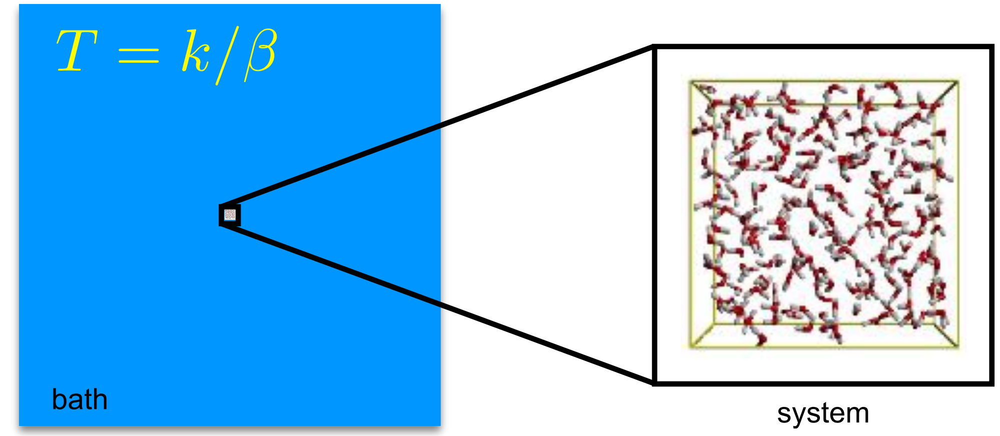
substituting and rearranging

$$S = \frac{k}{Z} \sum_i e^{-\beta E_i} \beta E_i + \frac{k}{Z} \sum_i e^{-\beta E_i} \ln Z$$

Statistical mechanics

canonical ensemble



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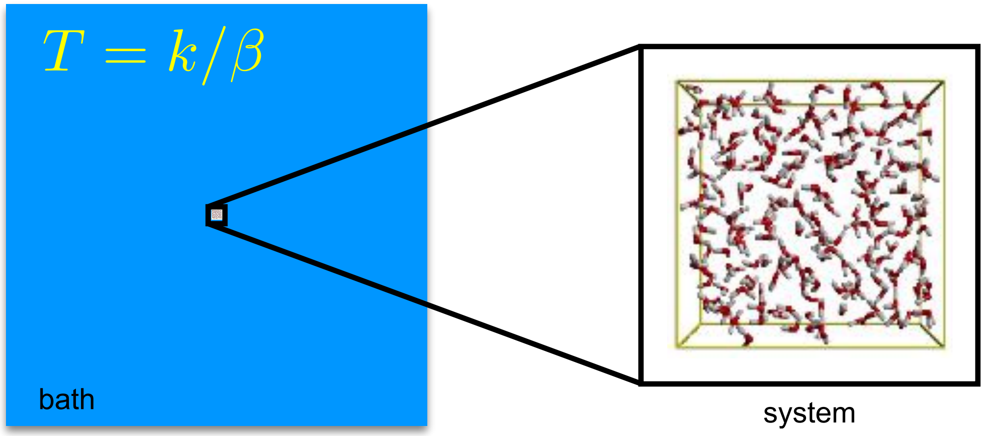
an almost familiar expression

$$S = \frac{1}{T} \langle E \rangle + k \ln Z$$

Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath



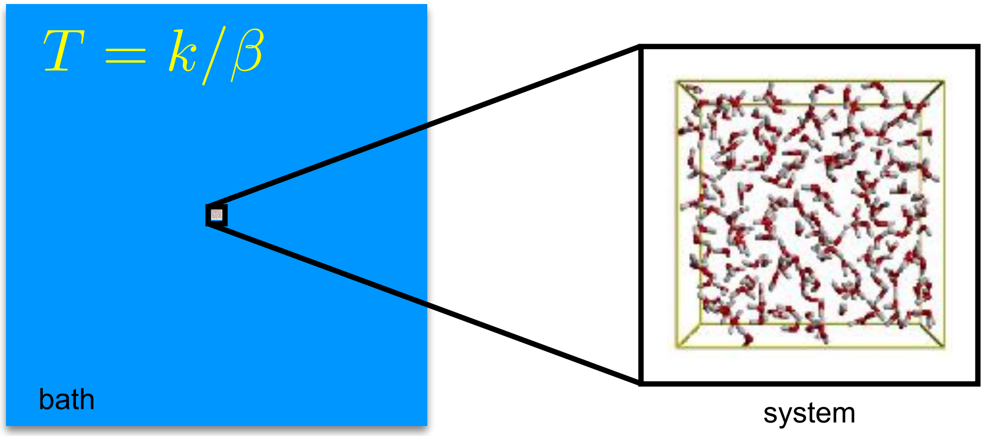
free energy of system

microscopic entropy

$$S = \frac{1}{T}\langle E\rangle + k \ln Z$$

Statistical mechanics

canonical ensemble



system in thermal equilibrium with bath

free energy of system

microscopic entropy

$$S = \frac{1}{T}\langle E\rangle + k\ln Z$$

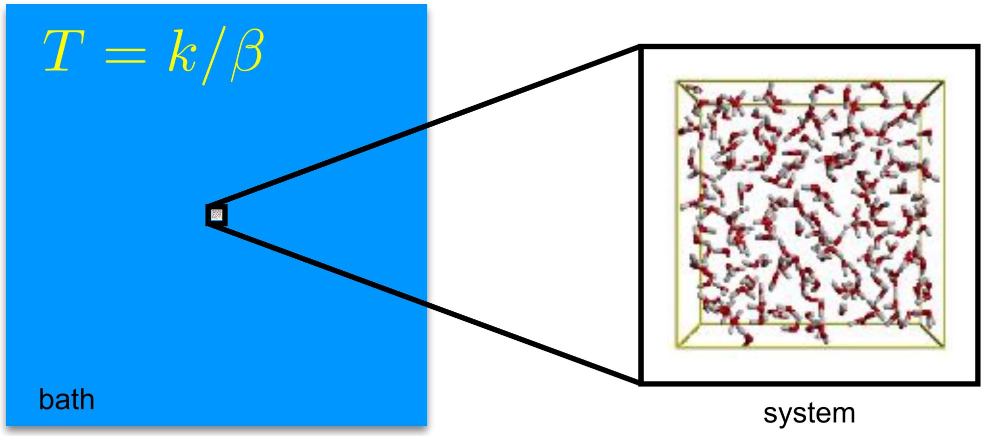
microscopic free energy

$$-kT\ln Z = \langle E\rangle - TS$$

Statistical mechanics

canonical ensemble

system in thermal equilibrium with bath



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$$-kT \ln Z = \langle E \rangle - TS$$

$$A = -kT \ln Z$$

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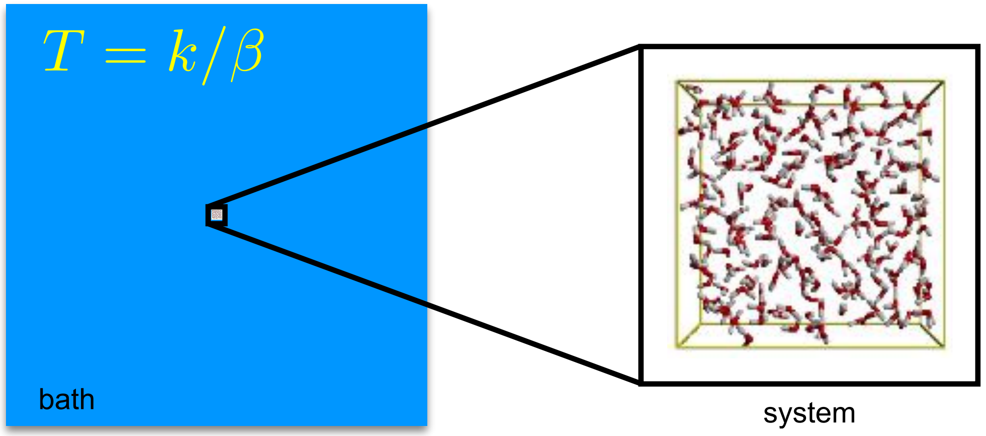

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macroscopic free energy

$$A = U - TS$$

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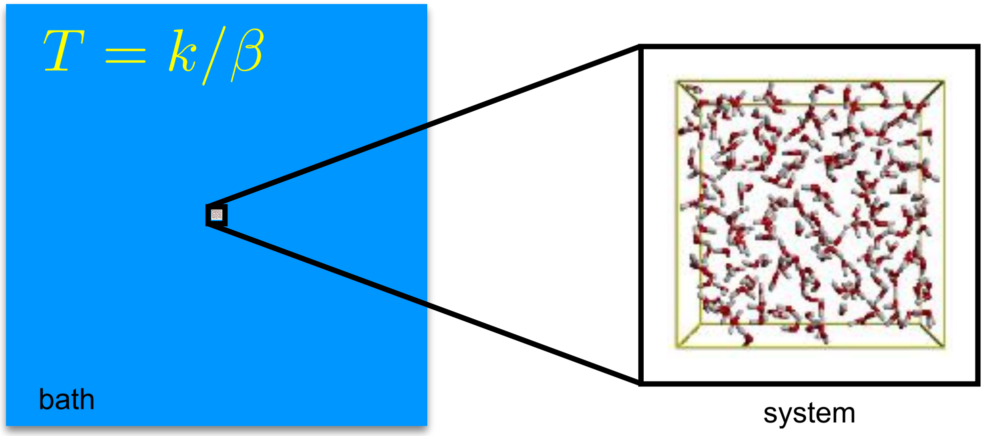

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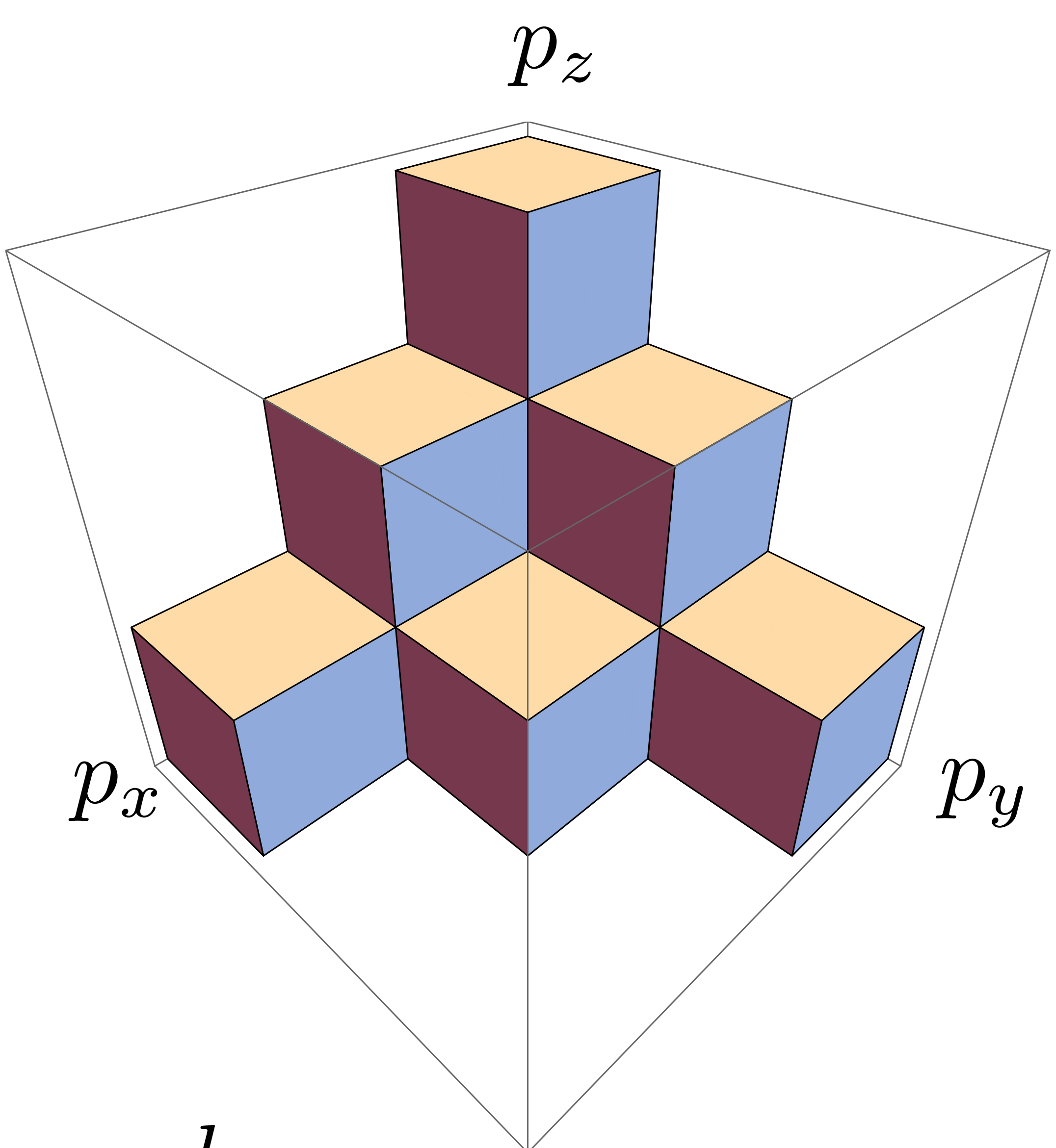
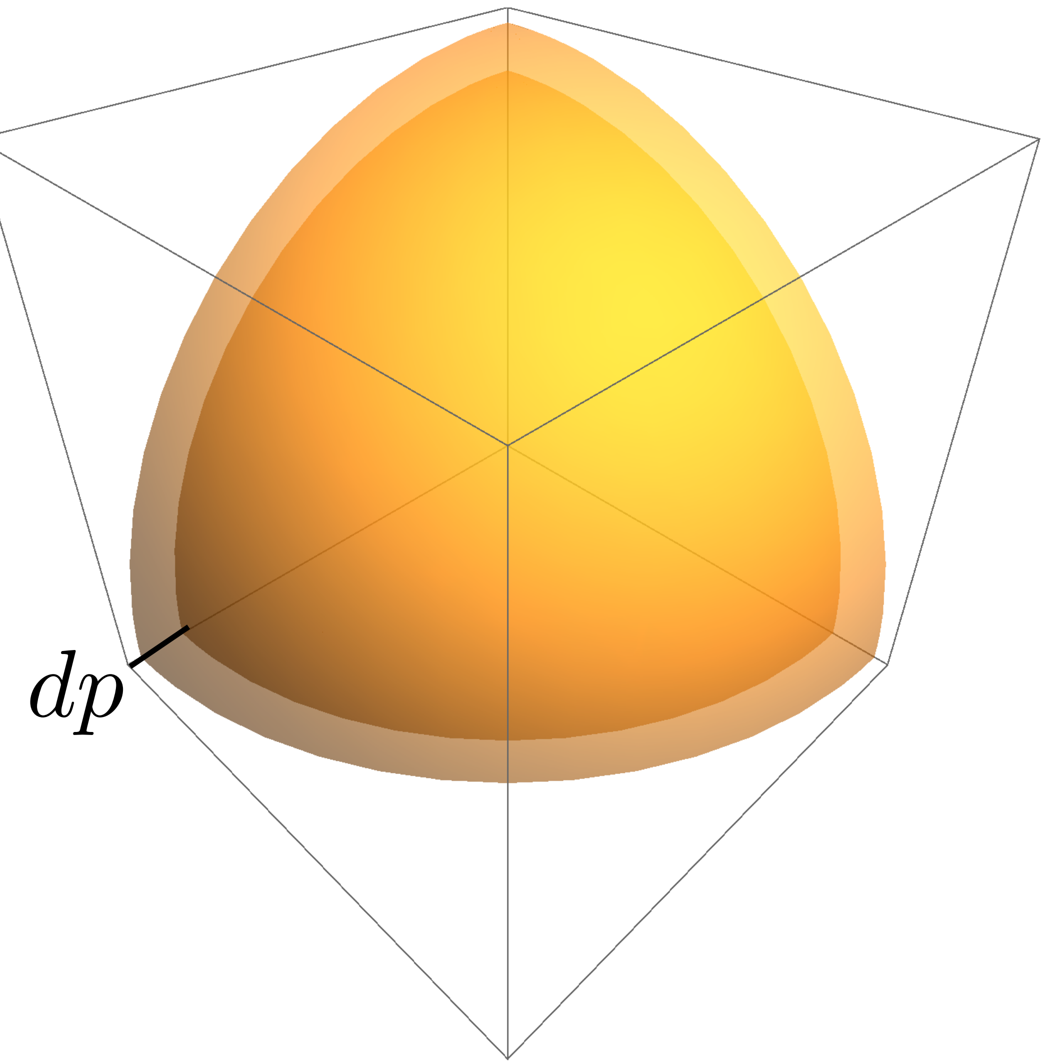
from micro to macro: generate partition function

Monte Carlo

molecular dynamics simulations



$$A = 4\pi p^2$$



$$p_x = \frac{hn_x}{2L}$$

$$p_y = \frac{hn_y}{2L}$$

$$V(p + \delta p) = 4\pi p^2 dp$$

$$p_z = \frac{hn_z}{2L} \qquad n_x, n_y, n_z = 1, 2, 3, \ldots$$