

Mechanics 102

1/23/2025

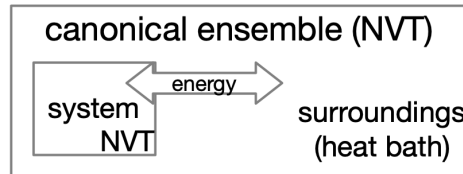
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Statistical Mechanics

microstates vs (macro)states

$$S = k_B \log \Omega$$

microcanonical ensemble (NVE)



$$p(x) \propto e^{-\frac{U(x)}{k_B T}} = e^{-\beta U(x)}$$

$$\beta = \frac{1}{k_B T} = \frac{1}{k_B} \left(\frac{\partial S}{\partial E} \right)_{V,N}$$

Partition Function

$$Z = \frac{m}{h} \int \int e^{-\frac{U(x) + \frac{mv^2}{2}}{k_B T}} dx dv$$

$$= \frac{1}{\lambda} \hat{Z} \quad \text{de Broglie wavelength} \quad \lambda = h / \sqrt{2\pi m k_B T}$$

Configurational Partition Function

$$\hat{Z} = \int e^{-\frac{U(x)}{k_B T}} dx$$

$$\langle U \rangle = \hat{Z}^{-1} \int_V U(x) e^{-\frac{U(x)}{k_B T}} dx$$

probability of A state

$$p_A = \hat{Z}^{-1} \int_{V_A} e^{-\frac{U(x)}{k_B T}} dx \propto e^{-\frac{F_A}{k_B T}}$$

$$F_A = -k_B T \log Z_A$$

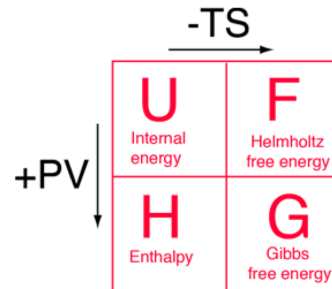
ΔG

Gibb's Free Energy

$$\Delta G = \Delta H - T \Delta S$$

Helmholtz's Free Energy

$$\Delta F = \Delta U - T \Delta S$$



$$\Delta G^\circ = -RT \log K_d$$

$$K_d = \frac{[A][B]}{[AB]} \quad R = N_A k_B$$

Entropy

$$S = \frac{\langle E \rangle - F}{T}$$

$$e^{\frac{F}{k_B T}} = e^{\frac{S}{k_B}} e^{-\frac{\langle E \rangle}{k_B T}}$$

$$S = -k_B \sum_i p_i \log p_i \quad \text{Gibbs}$$

$$H = - \sum_i p_i \log_2 p_i \quad \text{Shannon}$$

Classical Mechanics

velocity $v = \frac{dx}{dt}$

kinetic energy

$$\text{KE} = \frac{1}{2} m v^2 = \frac{p^2}{2m}$$

momentum $p = m v$

$$F = m a = \frac{dp}{dt}$$

potential energy

$$U_{\text{pot}}(x) = - \int_{\infty}^x F(r) dr$$

$$F = - \nabla_x U \quad - \frac{dU_{\text{pot}}(x)}{dx} = F(x)$$

physical space

configuration space

phase space

Newtonian

Lagrangian

Hamiltonian

$$\mathcal{H} = \text{KE} + U$$

Equations of Motion

$$\frac{dp}{dt} = - \frac{\partial \mathcal{H}}{\partial x}$$

$$\frac{dx}{dt} = \frac{\partial \mathcal{H}}{\partial p}$$

Verlet Integration

$$\mathbf{x}(t + \Delta t) = 2\mathbf{x}(t) - \mathbf{x}(t - \Delta t) + \frac{F}{m} \Delta t^2$$

Langevin Motion

$$\frac{dp}{dt} = - \frac{dU}{dx} - \gamma m \frac{dx}{dt} + \mathbf{R}$$

Langevin Integration

$$\mathbf{v}(t + \Delta t/2) = \mathbf{v}(t - \Delta t/2) \alpha + \mathbf{F}(x(t))(1 - \alpha)/(\gamma m) + \sqrt{k_B T(1 - \alpha^2)/m} \mathbf{R}$$

$$\mathbf{x}(t + \Delta t) = \mathbf{x}(t) + \mathbf{v}(t + \Delta t/2) \Delta t$$

Fokker-Planck Equation

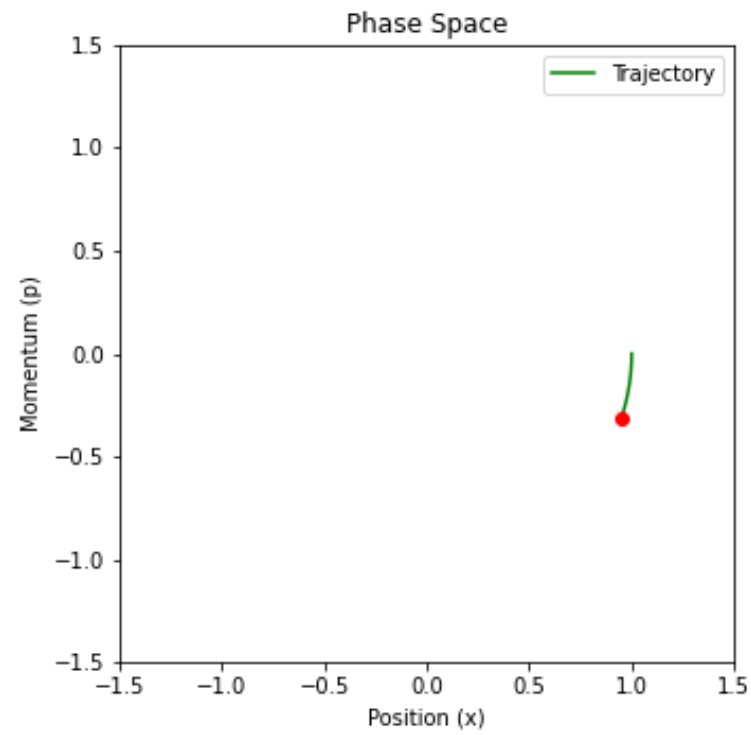
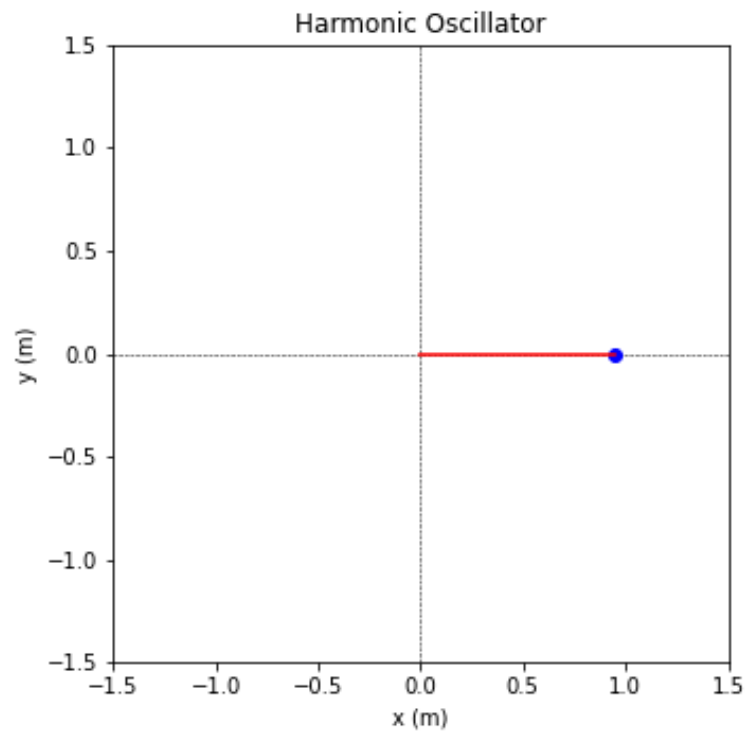
The Harmonic Oscillator



$$U(x) = U_0 + \frac{1}{2}\kappa(x - x_0)^2$$

where U_0 is the baseline potential energy, κ is the spring constant and x_0 is the center position.

Configuration vs Phase Space

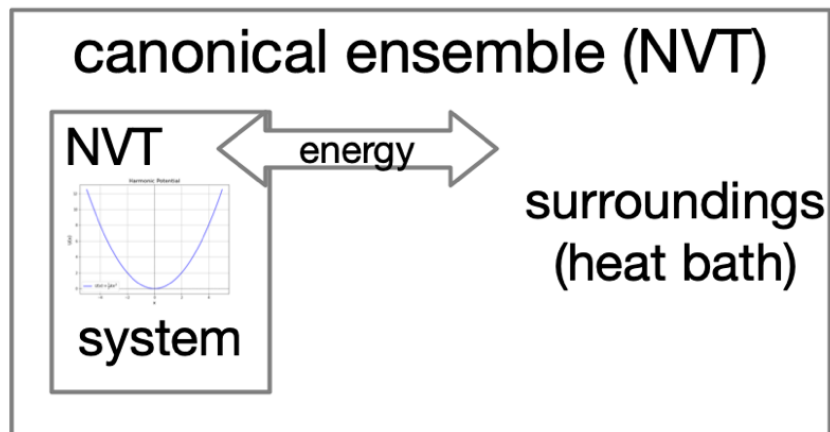


Boltzmann Distribution

The Boltzmann distribution converts the energy landscape of a system into a probability distribution

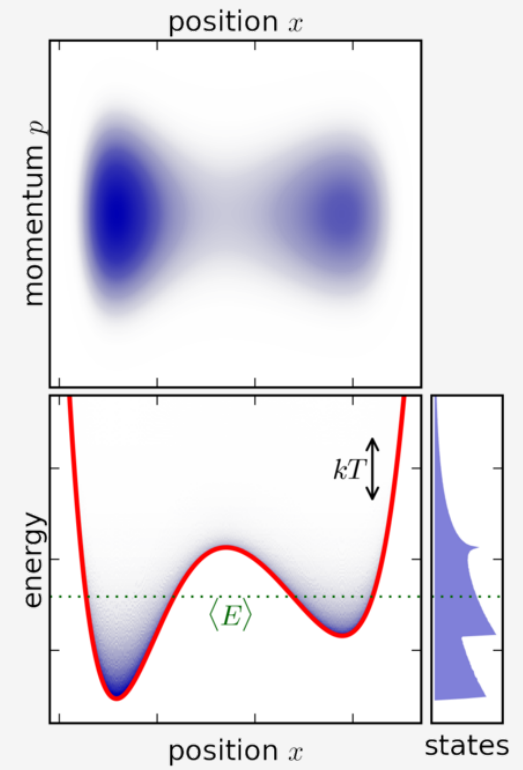
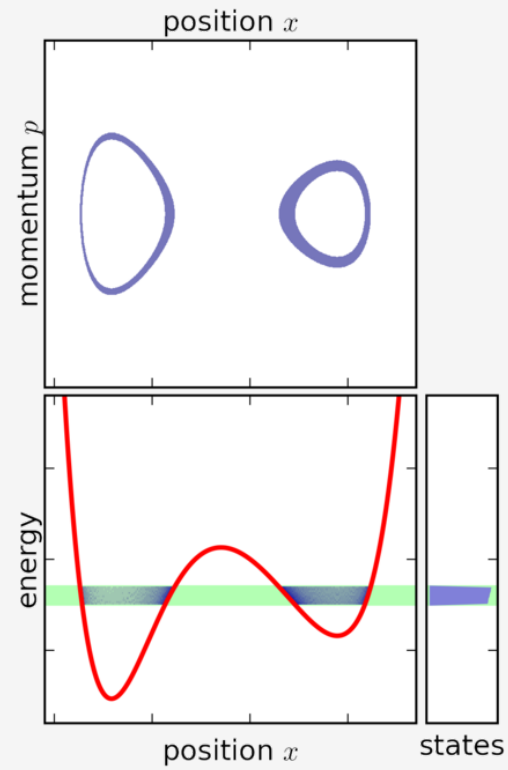
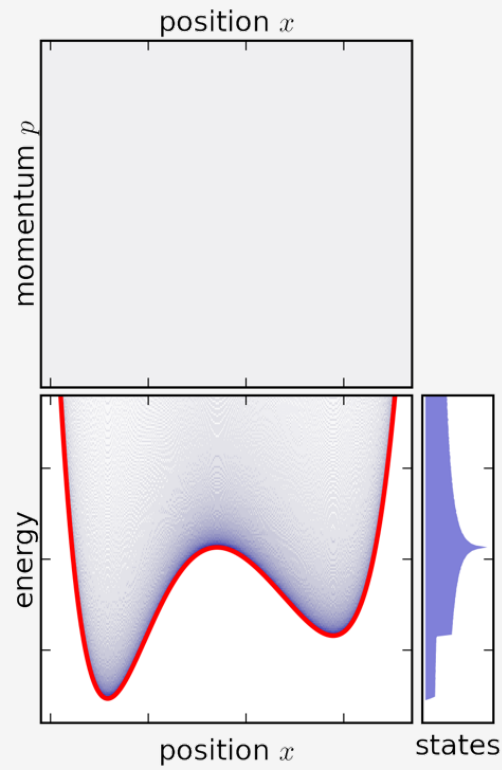
$$\rho(x) \propto e^{\frac{-U(x)}{k_B T}}$$

$k_B = 1.4 \times 10^{-23} \text{ J K}^{-1}$ is Boltzmann constant



microcanonical (NVE)

canonical (NVT)



$U(x) = 1/\beta$. What is the probability of x ?

- ☐ 1
- ☐ e
- ☐ β^2
- ☐ $1/e$
- ☐ None of the above

0 Answers

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Partition Function

The normalization factor for the Boltzmann distribution is called the Partition Function

$$\rho(x) = \frac{e^{-U(x)/k_B T}}{\int_V e^{-U(x)/k_B T} dx}$$

$$\int_V \rho(x) = 1$$

$$\hat{Z} \equiv \int_V e^{-U(x)/k_B T} dx = \lambda Z$$

Ensemble Properties

We can compute mean of any property of states (defined by function g) using the definition of expectation.

$$\langle g \rangle = \int_V g(x) \rho(x) dx$$
$$\langle g \rangle = \frac{\int_V g(x) e^{-U(x)/k_B T} dx}{\hat{Z}}$$

Average Energy of Harmonic System

$$U_{\text{harm}} = U_0 + \left(\frac{\kappa}{2} \right) (x - x_0)^2$$

$$\langle U_{\text{harm}} \rangle = \frac{\int_V U_{\text{harm}}(x) e^{-U_{\text{harm}}(x)/k_B T} dx}{\int_V e^{-U_{\text{harm}}(x)/k_B T} dx}$$

What is \hat{Z} ?



Partition Function of Harmonic Potential

$$\hat{Z}_{\text{harm}} = \int_V e^{-(U_0 + (\frac{\kappa}{2})(x-x_0)^2)/k_B T} dx$$
$$\hat{Z}_{\text{harm}} = e^{-U_0/k_B T} \int_{-\infty}^{\infty} e^{-\frac{\kappa(x-x_0)^2}{2k_B T}} dx = e^{-U_0/k_B T} \sqrt{\frac{2\pi k_B T}{\kappa}}$$

The **Gaussian integral**, also known as the **Euler–Poisson integral**, is the integral of the [Gaussian function](#) $f(x) = e^{-x^2}$ over the entire real line.

Named after the German mathematician [Carl Friedrich Gauss](#), the integral is

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}.$$

Average Energy

$$\langle U_{\text{harm}} \rangle = \frac{\int_V U_{\text{harm}}(x) e^{-U_{\text{harm}}(x)/k_B T} dx}{\int_V e^{-U_{\text{harm}}(x)/k_B T} dx}$$

This can be solved exactly (using additional [integration identities](#))

$$\langle U_{\text{harm}} \rangle = U_0 + \frac{1}{2} k_B T$$

This is the **equipartition theorem**. Any coordinate whose energy depends quadratically on its value (e.g., velocity = $1/2 mv^2$) will have an average energy of $\frac{1}{2} k_B T$.

Notice there is no κ in this result!

Each degree of freedom that appears quadratically in the expression for the total energy contributes an average energy of $\frac{1}{2} k_B T$ to the system

What is the average kinetic energy of a single atom (NVT)?

- ☐ $\frac{1}{2}k_{\beta}T$
- ☐ $k_{\beta}T$
- ☐ $\frac{3}{2}k_{\beta}T$
- ☐ $-k_{\beta}T$

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The Full (1D) Partition Function

$$\frac{m}{h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{\frac{mv^2}{2} + U(x)}{k_B T}} dx dv$$

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$$\int_{-\infty}^{\infty} e^{-a(x+b)^2} dx = \sqrt{\frac{\pi}{a}}.$$

The Full (1D) Partition Function

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$$= \frac{m}{h} \sqrt{\frac{2\pi k_B T}{m}} \int_{-\infty}^{\infty} e^{-\frac{U(x)}{k_B T}} dx$$

The Full (1D) Partition Function

$$\frac{m}{h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{\frac{mv^2}{2} + U(x)}{k_B T}} dx dv$$

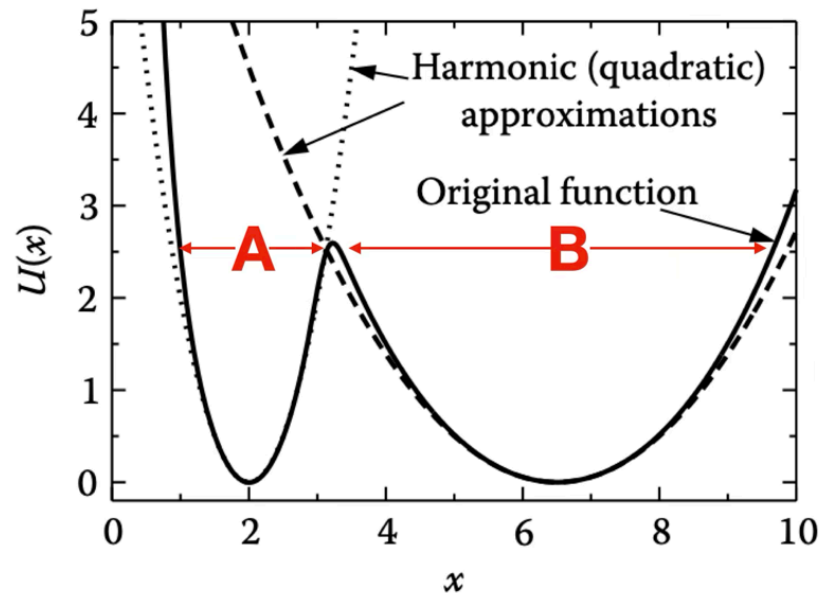
$$= \frac{m}{h} \int_{-\infty}^{\infty} e^{-\frac{\frac{mv^2}{2}}{k_B T}} dv \int_{-\infty}^{\infty} e^{-\frac{U(x)}{k_B T}} dx$$

$$\int_{-\infty}^{\infty} e^{-a(x+b)^2} dx = \sqrt{\frac{\pi}{a}}.$$

$$= \frac{m}{h} \sqrt{\frac{2\pi k_B T}{m}} \int_{-\infty}^{\infty} e^{-\frac{U(x)}{k_B T}} dx$$

States

Biomolecules have an essentially infinite set of configurations. We are interested in the sets of configurations that behave in a “similar way.” States represent a way to cluster configurations of biomolecules by function.



- What are the relative probabilities to observe molecule in state A vs. state B?
- What properties affect these probabilities?

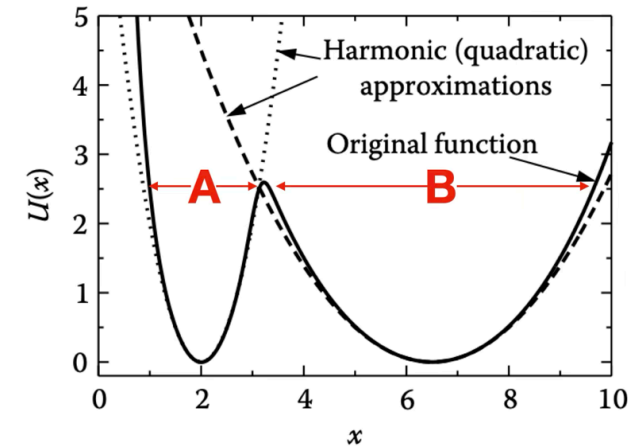
State Probabilities

$$p_A = \hat{Z}^{-1} \int_{V_A} e^{-U(x)/k_B T} dx \approx \hat{Z}^{-1} \int_{-\infty}^{\infty} e^{-U_A(x)/k_B T} dx$$

$$p_B = \hat{Z}^{-1} \int_{V_B} e^{-U(x)/k_B T} dx \approx \hat{Z}^{-1} \int_{-\infty}^{\infty} e^{-U_B(x)/k_B T} dx$$

The ratio of probabilities is given by:

$$\frac{p_A}{p_B} = \frac{\int_{V_A} e^{-U(x)/k_B T} dx}{\int_{V_B} e^{-U(x)/k_B T} dx} \approx \sqrt{\frac{\kappa_b}{\kappa_a}}$$



In this diagram, which state is more probable?

- ☐ A
- ☐ B
- ☐ Neither

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Free Energy of a State

$$\begin{aligned}\frac{p_A}{p_B} &= \frac{\int_{V_A} dx e^{-U(x)/k_B T}}{\int_{V_B} dx e^{-U(x)/k_B T}} \\ &\equiv \frac{e^{-F_A/k_B T}}{e^{-F_B/k_B T}}\end{aligned}$$

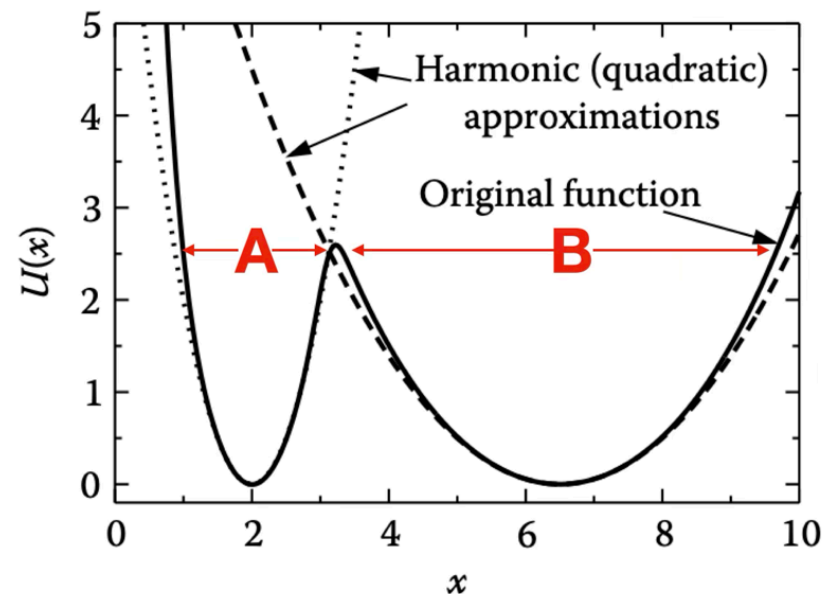
In general for a state i we have

$$F_i = -k_B T \ln(Z_i)$$

This is we call the free energy of state i .

The probability distribution of states follows the Boltzmann distribution in free energy

$$p_i \propto e^{-F_i/k_B T}$$

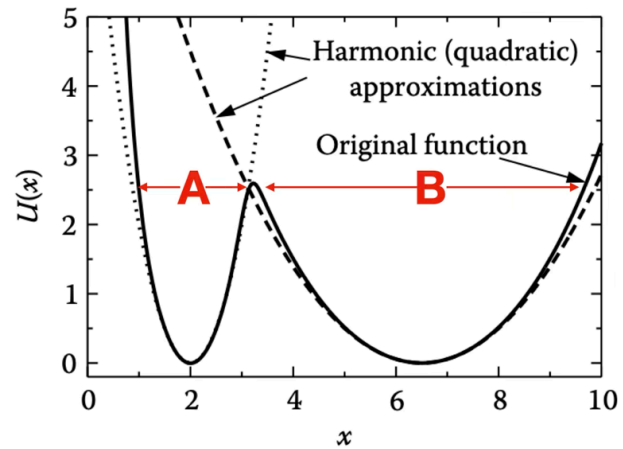


Free Energy of Harmonic Well

$$U_i(x) = U_i + \left(\frac{\kappa_i}{2} \right) (x - x_i)^2$$

$$\hat{Z}_i = \int_{V_i} e^{-U_i/k_B T - \frac{1}{2} \kappa_i (x - x_i)^2 / k_B T} dx = e^{-U_i/k_B T} \sqrt{\frac{2\pi k_B T}{\kappa_i}}$$

$$F_i = U_i - k_B T \ln \left(\lambda^{-1} \sqrt{\frac{2\pi k_B T}{\kappa_i}} \right)$$



In this diagram, which state has higher entropy?

- ☐ A
- ☐ B
- ☐ Neither

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Entropy

Alternatively:

$$F = \langle E \rangle - TS$$

The probability of a state i can then be written

$$p_i \propto e^{-F_i/k_B T} = e^{+S_i/k_B} e^{-\langle E \rangle_i/k_B T}$$

The Boltzmann factor for a state is just the Boltzmann factor for its average energy times a factor, which will turn out to be related to volume in configuration space (or number of states in a discrete space).

Entropy



Dictionary

Definitions from [Oxford Languages](#) · [Learn more](#)



en·tro·py

/ˈentɹəpē/

noun

1. PHYSICS

a thermodynamic quantity representing the unavailability of a system's thermal energy for conversion into mechanical work, often interpreted as the degree of disorder or randomness in the system.

"the second law of thermodynamics says that entropy always increases with time"

$$S = k_B \ln \Omega$$

(Only applies to microcanonical ensemble.)

Gibb's Entropy

$$S_{\text{Gibbs}} = -k_B \sum_i p_i \ln p_i$$

What happens when $p_i = \frac{1}{N}$?

What about $p_i = Z^{-1} e^{-\frac{U(i)}{k_B T}}$?

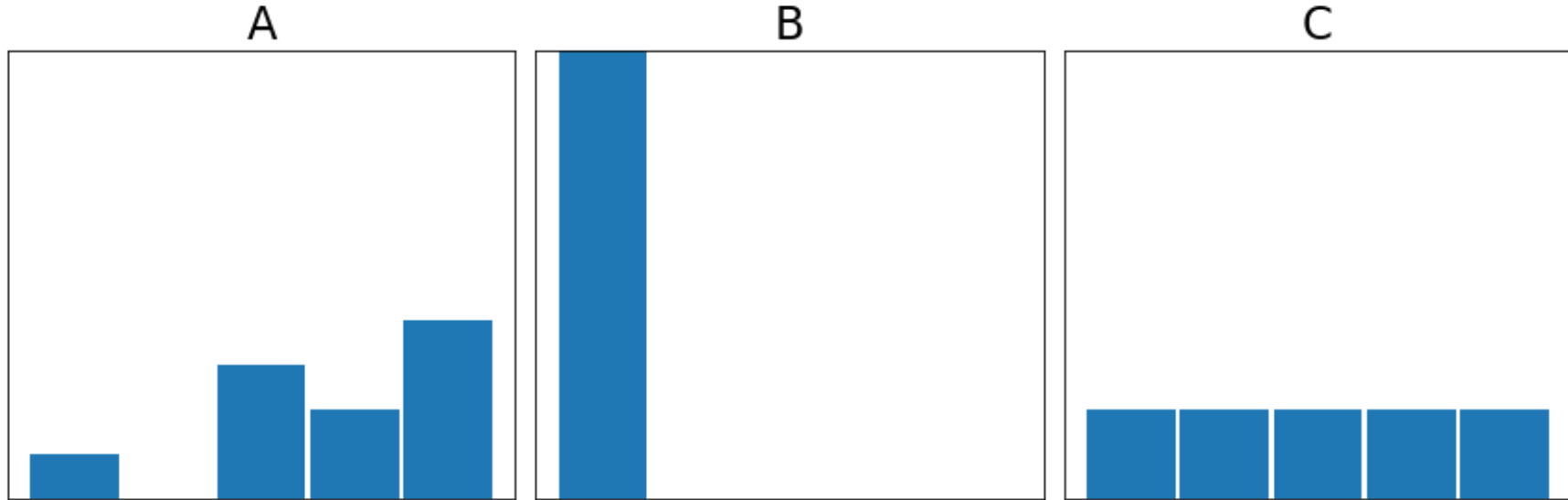
Shannon Entropy (Information Theory)

$$S_{\text{Shannon}} = - \sum_i p_i \log_2 p_i$$

With \log_2 the units of Shannon entropy are "bits" or "Shannons."

In information theory, the entropy of a random variable quantifies the average level of uncertainty or information associated with the variable's potential states or possible outcomes. This measures the expected amount of information needed to describe the state of the variable, considering the distribution of probabilities across all potential states.

--[Wikipedia](#)



Which distribution is most disordered (highest entropy)?

- ☐ A
- ☐ B
- ☐ C

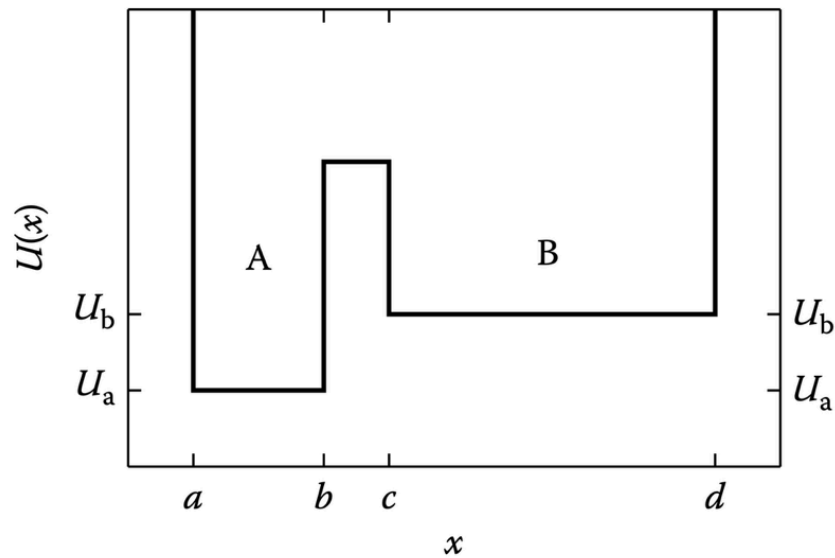
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Summary

	Microstate = single configuration	Macrostate = set of configurations
Partition function	-	$\hat{Z} = \int_V e^{-U(x)/k_B T} dx$
Configuration energy	$U(x)$	$\langle U \rangle = \hat{Z}^{-1} \int_V U(x) e^{-U(x)/k_B T} dx$
Relative probability	$e^{-U(x)/k_B T}$	$e^{-F/k_B T} \propto e^{S/k_B} e^{-\langle U \rangle/k_B T}$
Free energy	-	$F = -k_B T \ln Z$
Entropy	-	$S = \frac{k_B}{2} + \frac{\langle U \rangle - F}{T}$

Double square well potential



For each state, A and B , what is Z , F , and S ? Between the states, what is ΔF and ΔS ?