

Random walk, Binom, Gaussian

- 1D random walk, $P(R) = p, P(L) = 1 - p$, gait = L , # step = N . Find: prob of position $x = ml$.

$$P_N(m) = \frac{N!}{\left[\frac{N+m}{2}\right]! \left[\frac{N-m}{2}\right]!} p^{\frac{N+m}{2}} (1-p)^{\frac{N-m}{2}}. \quad [1]$$

- Mean: $\bar{x} := \sum_{i=1}^N P(x_i) x_i$
- Var: $\text{var}(x) := \overline{(x - \bar{x})^2} = \overline{x^2} - \bar{x}^2$
- RMS: $\Delta x_{\text{rms}} = \sqrt{\overline{x^2} - \bar{x}^2}$
- For Binomial Distribution: $\bar{x} = Np$,
dispersion: $\text{var}(x) = Npq$, $\Delta x_{\text{rms}} = \sqrt{Npq}$
Relative Width: $\frac{\Delta n_{1,\text{rms}}}{\bar{n}_1} = \frac{q}{p} \frac{1}{\sqrt{N}} \rightarrow 0 \quad (n \gg 1)$
- Sterling's formula

$$N! \approx \sqrt{2\pi N} N^N e^{-N} \Rightarrow \ln(N!) = N \ln N - N + \frac{1}{2} \ln(2\pi N). \quad [2]$$

Use sterling's to approximate binom, we have $P_N = \sqrt{\frac{N}{2\pi n(N-n)}} \exp(-N f(\frac{n}{N}))$; and expanding around $\tilde{n} = Np$ yields a Gaussian approximation:

$$P_N(n) \approx \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(n - \mu)^2}{2\sigma^2}\right]; \quad \mu = Np, \quad \sigma^2 = Npq. \quad [3]$$

Multivariables Prob.

- Unconditioned prob. dist'n:

$$P_u(u_i) = \sum_{j=1}^N P(u_i, v_j), \quad P_v(v_j) = \sum_{i=1}^N P(u_i, v_j) \quad [4]$$

- Uncorrelated variable: $P(u_i, v_j) = P_u(u_i) P_v(v_j)$
- Change of variables: For r.v. x and $y = f(x)$; given $p(x)$:

$$\tilde{p}(y) = \sum_i p(x_i) \left| \frac{dx}{df} \right|_{x=x_i} \quad [5]$$

Example: 2D vector \vec{B} with fixed length, equally likely to point in any direction. What is $\tilde{p}(B_x)$?

Prob. = prob. density \times infinitesimal angle

$$p(\theta) d\theta = \frac{d\theta}{2\pi}; B_x(\theta) = B \cos \theta. \quad [6]$$

$$\tilde{p}(B_x) = p(\theta_1) \left. \frac{d\theta}{dB_x} \right|_{\theta=\theta_1} + p(\theta_2) \left. \frac{d\theta}{dB_x} \right|_{\theta=\theta_2} \quad [7]$$

Notice $\frac{dB_x}{d\theta} = -B \sin \theta$, and $B_x = B \cos \theta_1 = B \cos \theta_2$:

$$\left. \frac{dB}{d\theta} \right|_{\theta=\theta_1} = B \sqrt{1 - \cos^2 \theta_1} = \sqrt{B^2 - B_x^2} = \left. \frac{dB}{d\theta} \right|_{\theta=\theta_2} \quad [8]$$

Thus

$$\begin{aligned} \tilde{p}(B_x) &= 2 * \frac{1}{2\pi} * \frac{1}{\sqrt{B^2 - B_x^2}} \\ &= \begin{cases} 1/(\pi \sqrt{B^2 - B_x^2}) , & \text{if } |B_x| < B \\ 0 & \text{otherwise} \end{cases} \end{aligned} \quad [9]$$

Stat. Mech setup

- $\Omega(E, V)$: # of accessible states in range $(E, E + dE)$
 - More genrally: number of all possible states.
- Fundamental Postulate: All accessible states are equally likely.

$$p(\mu_i) = \frac{1}{\Omega(E, V)} , \text{ if } \mu_i = \text{acc.} \quad [10]$$

- Probability and average of states: prob of system havin gsome value of macro. param. $y = y_k$ is given by

$$p(y_k) = \frac{\Omega(E; y_k)}{\Omega(E)} \quad [11]$$

- Average value of the parameter y :

$$\bar{y} = \sum_k p(y_k) y_k = \sum_k \frac{\Omega(E; y_k)}{\Omega(E)} y_k \quad [12]$$

Example: 1D harmonic Oscillator. $H(q, p) = \frac{p^2}{2m} + \frac{1}{2}kq^2$, $H = E_n = (n + \frac{1}{2})\hbar\omega$ const. $n = 0, 1, 2, \dots$; $\omega = \sqrt{k/m}$ Defines an ellipse in phase space. Consider energy variation δE , phase space cell resides on a ring.

$$\Omega(E) = \frac{\text{area of ring}}{\text{area of phase space cell}} \quad [13]$$

Example: 1D particle in a box :

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}, n = 1, 2, 3, \dots \quad [14]$$

Example: Three spin $-1/2$ particles in equil, in ext. H field. The energy of each spin is $-\mu H$ (if $m = \frac{1}{2}$); $+\mu H$ (if $m = -\frac{1}{2}$) There are $2^3 = 8$ possible combinations of states. Microstate is specified by m_1, m_2, m_3 . Suppose the total energy is known to be $-\mu H$, then the accessible states are

$$\left\{ +\frac{1}{2}, +\frac{1}{2}, -\frac{1}{2} \right\}, \left\{ +\frac{1}{2}, -\frac{1}{2}, +\frac{1}{2} \right\}, \left\{ -\frac{1}{2}, +\frac{1}{2}, +\frac{1}{2} \right\} \quad [15]$$

The prob. that first spin has $m_1 = +\frac{1}{2}$ is given by

$$\begin{aligned}\Omega\left(E; m_1 = +\frac{1}{2}\right) &= 2; \Omega(E) = 3 \\ \Rightarrow p\left(m_1 = +\frac{1}{2}\right) &= \frac{2}{3}.\end{aligned}\tag{16}$$

Density of states

Define $\omega(E)$ to be density of states, s.t. $\Omega(E) = \omega(E) dE$

- TO find relation Ω with (E, N) s.t. $\Omega = \Omega(N, E)$, consider **Classical Monatomic ideal gas**, enclosed in vol. V :

$H = \sum_i^N \frac{\vec{p}_i^2}{2m}$, energy range $(E, E + \delta E)$.

$$\begin{aligned}\Omega(E) &\propto V^N \int_E^{E+\delta E} \prod_i d^3\vec{p}_i \\ &\propto V^N E^{3N/2} \delta E \\ \omega(E) &\propto V^N E^{3N/2}\end{aligned}\tag{17}$$

Interaction between Macro bodies

- Thermal Interaction: External param. fixed.
 - $Q \equiv \overline{\Delta E}$. heat absorbed (+) or released (-) by system.
- Mech. Interaction: External param. can change.
 - $W \equiv -\overline{\Delta_x E}$. macro work done by system with variation in ext. param. x
- **General int.:** $Q \equiv \Delta \overline{E} - \Delta_x \overline{E} = \Delta \overline{E} + W$, ttl change in energy in exclusion of that due to mech. interaction (change in ext. param. x).

From genreal interaction we arrive at the first law:

$$\delta Q \equiv d\overline{E} + \delta W\tag{18}$$

Quasistatic process

- Slow int. s.t. system remains in equil. at all times, so that intensive params. are uniform throughout the system.
- Generalized force: consider sys. with ext. param x and $H(q, p; x)$:

$$\frac{dH}{dt} = \frac{\partial H}{\partial x} \frac{dx}{dt} \Rightarrow dE = \frac{\partial H}{\partial x} \frac{dx}{dt} dt.\tag{19}$$

Quasistatic so we can avg this over equil. ensemble with value of x at time t . Noticing $dE = -\delta W$:

$$\delta W = -\frac{\partial \overline{H}}{\partial x} \frac{dx}{dt} dt \equiv X dx,\tag{20}$$

where $X \equiv -\frac{\partial \overline{H}}{\partial x}$:generalized force

Example: Piston (ext. param. $x = V$)

$$\delta W = \bar{p} dV. \quad [21]$$

For vol. change $V_i \rightarrow V_f$:

$$W = \int_{V_i}^{V_f} \delta W = \int_{V_i}^{V_f} \bar{p}(V) dV. \quad [22]$$

Thermal int. btwn sys: Entropy

- Consider adiabatic system with two partitions, $\{E_1, \Omega_1(E_1)\}, \{E_2, \Omega_2(E_2)\}$. $E_1 + E_2 = E$ const.

- $\Omega(E) = \sum_{E_1} \Omega_1(E_1) \Omega_2(E - E_1)$, and prob. of sys 1 has energy $= E_1$ is

$$P_1(E_1) = \frac{\Omega_1(E_1) \times \Omega_2(E - E_1)}{\Omega(E)}, \quad [23]$$

with $\Omega(E) \approx E^{aN}$.

- Finding \tilde{E}_1 s.t. $P_1(E_1) = \max : \frac{\partial P_1(E_1)}{\partial E_1} = 0$

$$\Rightarrow \left. \frac{\partial \ln \Omega_1}{\partial E_1} \right|_{E_1=\tilde{E}_1} = \left. \frac{\partial \ln \Omega_2}{\partial E_2} \right|_{E_2=E-\tilde{E}_1} \quad [24]$$

- We are motivated to define entropy:

$$S(E, x) \equiv \ln \Omega(E, x) \quad [25]$$

so that P_1 peaks when

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \Leftrightarrow S = S_1 + S_2 = \max \quad [26]$$

- Further define temperature:

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E} \quad [27]$$

So that P_1 peaks when $T_1 = T_2$

- Sharpness of $P_1(E_1)$:
 - Rel. width $= \frac{\Delta^* E}{\tilde{E}_1} \approx \frac{1}{\sqrt{N}}$
 - $\frac{\partial T}{\partial E} \geq 0$

The 2nd law

For two systems in thermal contact

$$\begin{aligned} \frac{dS(E)}{dt} &= \frac{dS_1}{dt} + \frac{dS_2}{dt} = \left[\left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) \frac{dE_1}{dt} \right] \\ &= \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \frac{dE_1}{dt} \geq 0 \end{aligned} \quad [28]$$

Reversible and Irreversible process

- Reversible: ttl entropy of isolated sys. constant $\frac{dS}{dt} = 0$
 - Irreversible: ttl entropy of isolated sys increases $\frac{dS}{dt} > 0$
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Fundamental relation

- For general interaction btwn macro bodies, equilibrium relation:

$$\begin{cases} T_1 = T_2 \\ \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} = \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2} \end{cases} \quad [29]$$

where

$$\left(\frac{\partial S}{\partial V}\right)_{E_1} = \frac{p}{T} \quad [30]$$

Applied to the total differential of entropy, we have

$$\boxed{dE = T dS - p dV.} \quad [31]$$

- Further, for quasistatic process, we have $dE = \delta Q - p dV$. Comparing terms gives

$$dS = \frac{\delta Q}{T} \quad [32]$$

- Particullary, for adiabatic process, $\delta Q = 0$ so $dS = 0$, so adiabatic \Rightarrow reversible.
- Revisiting equil. condition:

$$\left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} = \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2} \Rightarrow p_1 = p_2 \quad [33]$$

Laws of Thermodynamics

- 0th law: thermal transitivity. If A, C in equil; B,C in equil; then A,B in equil.
- 1st Law:

$$dE = \delta Q - \delta W \quad [34]$$

- 2nd Law:

$$dS \geq \frac{\delta Q}{T} \quad [35]$$

- 3rd Law:

$$\lim_{T \rightarrow 0} S = 0 \quad [36]$$

Response function

- Heat Capacities: $\delta Q|_x = C_x dT$
 - for $\delta Q|_V = (dE + \delta W)|_V \Rightarrow C_V = \left(\frac{\partial E}{\partial T}\right)_V$.
 - for $\delta Q|_p = (dE + \delta W)|_p \Rightarrow C_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$.

Useful so that combined with $dS = \frac{\delta Q}{T} = \frac{C_V}{T} dT$:

$$S(x, T_2) = S(x, T_1) + \int_{T_1}^{T_2} \frac{C_x}{T} dT \quad [37]$$

- Compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad [38]$$

- Expansivity:

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad [39]$$

Ideal Gas

- For ideal Monatomic gas, recall $\Omega(E) = BV^N E^{3N/2}$

$$S = \ln \Omega = N \ln V + \frac{3N}{2} \ln E + C. \quad [40]$$

Combined with $p = T \left(\frac{\partial S}{\partial V} \right)_E$, $\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_V$ we have

$$pV = NT; \quad E = \frac{3}{2} NT = \frac{3}{2} \nu RT \quad [41]$$

- Ideal Gas Law Writing $N = \nu N_A$, we have

$$pV = \nu RT, \quad R \equiv N_A k_B \quad [42]$$

- It is proved that $E = E(T)$, independent of V .

- Specific Heat:

- Define $c_x \equiv \frac{C_x}{\nu}$, “heat capacity per mole”.
- Const. V: $\delta Q|_V = C_V dT = \nu c_v dT$. A general relation is

$$c_v = \frac{1}{\nu} \left(\frac{\partial E}{\partial T} \right)_V > 0. \quad [43]$$

for ideal gas: $dE = \nu c_v dT$

- Similarly, Const. p: $\delta Q|_p = C_p dT = \nu c_p dT$. A general relation is

$$c_p = c_v + R \quad [44]$$

- adiabatic Index

Using $E = \frac{3}{2}\nu RT$; $c_v = \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_V$, we have

$$c_v = \frac{3}{2}R; c_p = c_v + R = \frac{5}{2}R. \quad [45]$$

So that adiabatic index $\gamma \equiv c_p/c_v = 5/3$

Ideal Gas in Various Process

- Isothermal: cons. T. $\Rightarrow pV = C$.
- Adiabatic: no heat transfer.

By first law:

$$\delta Q = dE + \delta W = 0 \Rightarrow 0 = \nu c_v dT + p dV. \quad [46]$$

using eqn of state : $pV = \nu RT$:

$$\gamma \frac{dV}{V} + \frac{dp}{p} = 0 \quad [47]$$

Since $c_v = \frac{3}{2}$ is constant, integrate the above gives

$$\gamma \ln V + \ln p = C \Rightarrow pV^\gamma = C. \quad [48]$$