

## 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:  $\text{var}(x) := \overline{(x - \bar{x})^2} = \bar{x^2} - \bar{x}^2$
- RMS:  $\Delta x_{\text{rms}} = \sqrt{\bar{x^2} - \bar{x}^2}$
- 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

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

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

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

## 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 generally: 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.  $H(q, p) = \frac{p^2}{2m} + \frac{1}{2} k q^2$ ,  $H = E_n = (n + \frac{1}{2}) \hbar \omega$  const.  $n = 0, 1, 2, \dots$ ;  $\omega = \sqrt{k/m}$  Defines an ellipse in phase space. Consider energy variation  $\delta E$ , 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

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

## Density of states

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

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

$$\begin{aligned} H &= \sum_i^N \frac{\vec{p}_i^2}{2m}, \text{ energy range } (E, E + \delta E). \\ \Omega(E) &\propto V^N \int_E^{E+\delta E} \prod_i d^3 \vec{p}_i \\ &\propto V^N E^{3N/2} \delta E \\ \omega(E) &\propto V^N E^{3N/2} \end{aligned} \quad [17]$$

## Interaction between Macro bodies

- Thermal Interaction: External param. fixed.
  - $Q \equiv \Delta E$ . heat absorbed (+) or released (-) by system.
- Mech. Interaction: External param. can change.
  - $W \equiv -\Delta_x \overline{E}$ . 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:

$$\delta Q \equiv d\overline{E} + \delta W \quad [18]$$

## Quasistatic process

- Slow int. s.t. system remains in equil. at all times, so that intensive params. are uniform throughout the system.

- Generalzed force: consider sys. with ext. param  $x$  and  $H(q, p; x)$ :

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

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

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

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,  $\{E_1, \Omega_1(E_1)\}, \{E_2, \Omega(E_2)\}$ .  $E_1 + E_2 = E$  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

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

- 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 =  $\frac{\Delta_x E}{\tilde{E}_1} \approx \frac{1}{\sqrt{N}}$
  - $\frac{\partial T}{\partial E} \geq 0$

## The 2nd law

For two systesm in themal 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  $\frac{dS}{dt} > 0$

## Fundamental relation

- For general interaction btwn macro bodies, equilibrium relation:

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

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  $dS = \frac{\delta Q}{T} = \frac{C_x}{T} dT$  :

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

- Compressibility

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

- Expansivity:

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

### Ideal Gas

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

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

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

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

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

$$pV = \nu RT, \quad R \equiv N_A k_B \tag{42}$$

- 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:  $\delta Q \mid_V = C_V \mathrm{d}T = \nu c_v \mathrm{d}T$ . A general relation is

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

for ideal gas:  $\mathrm{d}E = \nu c_v \mathrm{d}T$

- Similarly,Const. p:  $\delta Q \mid_p = C_p \mathrm{d}T = \nu c_p \mathrm{d}T$ . A general relation is

$$c_p = c_v + R \tag{44}$$

#### - adiabatic Index

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

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

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:

$$\delta Q = \mathrm{d}E + \delta W = 0 \Longrightarrow 0 = \nu c_v \mathrm{d}T + p \mathrm{d}V. \tag{46}$$

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

$$\gamma \frac{\mathrm{d}V}{V} + \frac{\mathrm{d}p}{p} = 0 \tag{47}$$

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

$$\gamma \ln V + \ln p = C \Rightarrow pV^\gamma = C. \tag{48}$$