Man was matter, that was Snowden's secret. Drop him out a window and he'll fall. Set fire to him and he'll burn. Bury him and he'll rot, like other kinds of garbage. The spirit gone, man is garbage. That was Snowden's secret. Ripeness was all.

-Joseph Heller, Catch-22

Chapter 2: Elements of Ensemble Theory

Section 1. Phase space of a classical system

- Microstate of a given classical system at some time t can be defined by instantaneous position and momentum
  - If you have N particles, 6N variables / dimensions (3N position, 3N momentum)
  - Phase space with (q_i, p_i) as a representative point
  - H, the Hamiltonian, is the energy expressed in terms of p_i + q_i
    - $\dot{q}_i = \frac{\partial H(q_i, p_i)}{\partial p_i}$
    - $\dot{p}_i = \frac{-\partial H(q_i, p_i)}{\partial q_i}$
- Example: Classical harmonic oscillator

$$H = p^2/2m + m\omega^2 q^2/2$$

$$\dot{q} = p/m, \quad p = m\dot{q} \Rightarrow \dot{p} = m\ddot{q}$$

$$\dot{p} = -m\omega^2 q$$

$$\ddot{q} = -\omega^2 q, \Rightarrow q = \exp(i\omega t)$$

$$q = \sqrt{\frac{2E}{m}} \cdot 1/\omega \cdot \sin\omega t$$

$$p = \sqrt{2mE} \cdot \cos\omega t$$

- If $H(q_i, p_i) = E$, corresponding trajectory is restricted to the hypersurface
- If $H(q_i, p_i)$ lies between $(E - \Delta/2, E + \Delta/2)$, trajectory is limited to the hypershell
- Ergotic hypothesis: A system passes arbitrarily close to every point in phase space allowed to it by Hamilton's equation over the course of time
- If ergodicity is true, then a time average is equivalent to a phase space average
- Ensemble is a collection of systems, all of which represent possible states
  - Each point in phase space defines a possible microstate
  - In the microcanonical ensemble, each microstate has the same E, N, V

The ensemble average of some physical quantity $f(q,p)$,

- $\langle f \rangle = \frac{\int f(p,q)\rho(p,q,t)\,d^{3N}q\,d^{3N}p}{\int \rho(p,q,t)\,d^{3N}q\,d^{3N}p}$
- The probability of finding system in box of volume $d^{3N}p\,d^{3N}q$ centered at $(q,p) = \rho(p,q,t)\,d^{3N}q\,d^{3N}p$

  ρ: probability density

- Ensemble is stationary if $\frac{\partial \rho}{\partial t} = 0$
  - $\langle f \rangle$ is independent of time
  - System is in equilibrium

Section 2. Liouville's theorem and its consequences

- Consider a volume ω in 6N dimensional space enclosed by surface σ
- Points pass in or out as they evolve according to Hamilton's equation
  - Rate at which number of representative points in this volume increases with time $= \frac{\partial}{\partial t}\int_\omega \rho\, d\omega$

    $d\omega = (d^{3N}q\,d^{3N}p)$
  - Rate at which points flow out $= \oint \rho\vec{v}\cdot\hat{n}\,d\sigma = \int_\omega \vec{\nabla}(\rho\vec{v})\,d\omega$

    $\vec{v} = (\dot{q}_1, \dot{q}_2, \dot{q}_3, \ldots \dot{q}_{3N}, \dot{p}_1, \dot{p}_2, \ldots, \dot{p}_{3N})$
- Since probability must be conserved,

  $\frac{\partial}{\partial t}\int \rho\, d\omega = -\int \vec{\nabla}\cdot(\rho\vec{v})\,d\omega$

  $\frac{\partial}{\partial t}\int \rho\, d\omega + \int \vec{\nabla}\cdot(\rho\vec{v})\,d\omega = 0$

  Since this is true for any volume element, this gives us the Continuity equation:

  $\frac{\partial \rho}{\partial t} + \vec{\nabla}(\rho\vec{v}) = 0$

$\frac{\partial \rho}{\partial t} + (\vec{\nabla}\rho)\cdot\vec{v} + \rho(\vec{\nabla}\cdot\vec{v}) = 0$

Using Hamilton's equations,

$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left\{\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right\} + \rho\sum_{i=1}^{3N}\left\{\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right\} = 0$

$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 \mathcal{H}}{\partial q_i \partial p_i}$

$\frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial^2 \mathcal{H}}{\partial p_i \partial q_i}$

$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left\{\frac{\partial \rho}{\partial q_i}\cdot\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\cdot\frac{\partial \mathcal{H}}{\partial q_i}\right\} + \rho\underbrace{\sum_{i=1}^{3N}\left\{\frac{\partial^2 \mathcal{H}}{\partial q_i \partial p_i} - \frac{\partial^2 \mathcal{H}}{\partial p_i \partial q_i}\right\}}_{0} = 0$

$\frac{\partial \rho}{\partial t} + (\vec{\nabla}\rho)\cdot\vec{v} = \frac{\partial \rho}{\partial t} + [\rho, \mathcal{H}] = \frac{d\rho}{dt} = 0$ Liouville's Theorem

The volume of a differential region $d\omega$ remains constant with time

- In equilibrium, $[\rho, \mathcal{H}] = 0 \Rightarrow \frac{\partial \rho}{\partial t} = 0$, which we can get if $\rho(q_i, p_i) = \rho_0$, a constant $\Rightarrow$ an ensemble of systems that at all times are uniformly distributed over all possible microstates.

Or rather, all states consistent with state variable are equally likely

$\langle f \rangle = \frac{1}{\omega}\int_\omega f(q,p)\,d\omega$

This is known as microcanonical ensemble

- Equal a priori probability: any member of the ensemble is equally likely to be in any of the various possible microstates

Section 3. The microcanonical ensemble

- The constraint $\mathcal{H}(q_i, p_i) = E$ is often difficult to meet, so often we allow small variations in E,

  $(E - \Delta/2) \le \mathcal{H}(q,p) \le (E + \Delta/2)$

This then allows us to define S if we can count the number of states in that shell

$S = k \ln(\omega/\omega_0)$

where $\omega_0 = h^{3N}$ by uncertainty principle considerations

Section 4. Examples

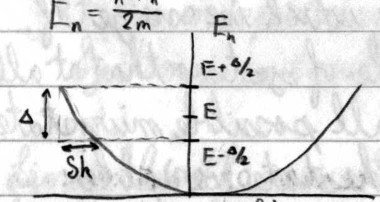
- Classical ideal gas composed of monatomic particles in a finite volume

$\psi = A\sin(k_n x)$; $k_n = \frac{n\pi}{L}$

$\psi_n(x) = \psi_n(x+L)$

$\Rightarrow \psi_n(x) = A\exp(ik_n x)$

$E_n = \frac{\hbar^2 k_n^2}{2m}$



How many k_n in the interval Δ?

If we ignore curvature, $\frac{dE}{dk} = \frac{\hbar^2 k}{m}$

$\frac{\Delta}{\delta k} = \frac{dE}{dk}$

$\#$ states in $\delta k = \frac{\delta k}{2\pi/L} = \frac{L\Delta}{2\pi \frac{dE}{dk}} = \Delta \frac{L}{2\pi}\cdot\frac{dk}{dE} = \Delta\frac{L}{2\pi\hbar}\cdot\frac{dp}{dE}$

$p = \hbar k =$ momentum

$\frac{\omega}{\omega_0} = 1/\omega_0 \int dp\,dq = 1/\omega_0\, L\int dp = L/\omega_0 \int_{E_-}^{E_+} \frac{dp}{dE}\cdot dE = L/\omega_0 \cdot \frac{dp}{dE}\Delta$

$= \Delta \frac{L}{2\pi\hbar}\cdot\frac{dp}{dE}$

$\omega_0 = 2\pi\hbar = h$

- Harmonic Oscillator in one-dimension

$\mathcal{H} = p^2/2m + 1/2\cdot m\Omega^2 q^2$

$\left.\begin{array}{l}\dot q = p/m \\ \dot p = -m\Omega^2 q\end{array}\right\}$ $\begin{array}{l} q = \sqrt{\frac{2E}{m}}\cdot 1/\Omega \sin\Omega t \\ p = \sqrt{2Em}\cos\Omega t\end{array}$

$\#$ states between $E - \Delta/2$ & $E + \Delta/2 = \frac{\text{Area}}{\omega_0}$

$\text{Area} = \int dp\,dq = m\Omega \int dp\, d\tilde q$; $\tilde q = \sqrt{2mE}\sin\Omega t = m\Omega q(t)$

$= (m\Omega)^{-1}\pi[2m(E+\Delta/2) - 2m(E-\Delta/2)]$

$= (m\Omega)^{-1}\pi\cdot 2m\Delta$

$\frac{\text{Area}}{\omega_0} = \frac{2\pi\Delta}{\omega_0\Omega}$

$E_n = (n+1/2)\hbar\Omega$

$E - 1/2\Omega \le E_n \le E + 1/2\Delta$

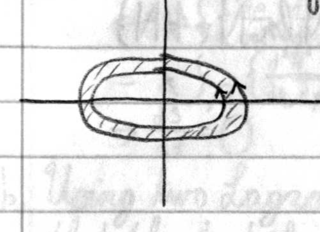
gives $\frac{\Delta}{\hbar\Omega}$ states

$\frac{\Delta}{\hbar\Omega} = \frac{2\pi\Delta}{\omega_0\Omega}$

$\omega_0 = 2\pi\hbar = h$

Section 5 Quantum states and the phase space

- Bohr-Sommerfeld quantization



$\oint p\,dq = n\hbar$, n integer

Volume between allowed orbits $= h$

$\Rightarrow$ Volume in phase space for each allowed state is h

Problems.

1. Ultrarelativistic Ideal Gas

Compute the entropy of an isolated system of N particles in a volume V at a very large fixed energy E, such that the total energy of a state is given by $E\{p_i\} = c\sum_i |\vec p_i|$. Use this to find the equation of state, temperature, and heat capacity of the system.

Compute $G(E)$, # states with energy $\le E$

$G(E) = 1/h^{3N}\int \Theta[E - c\sum_i |\vec p_i|]\, d^3x_1 \dots d^3x_N\, d^3p_1\dots d^3p_N$

$= V^N/h^{3N}\int\Theta[E - c\sum_i|\vec p_i|]\, d^3p_1\dots d^3p_N$

$W_R = R^{3N}\int\Theta[E - cR\sum_i |\vec q_i|]\, d^3q_1\dots d^3q_N$

define $\vec q = \vec p/R$ $\quad R = E/c \quad D = 3N$

$d\vec q = d\vec p/R$

$W_R = R^D\int\Theta[E(1 - \sum_i|q_i|)]\, d^3q_1\dots d^3q_N$

$= R^D\int\Theta[1 - \sum_i|q_i|]\, d^3q_1\dots d^3q_N = R^D W_1$

$\frac{dW_R}{dR} = DR^{D-1}W_1$

$\int_0^\infty \frac{dW_R}{dR}\exp(-R/R_0)\, dR = D\int_0^\infty R^{D-1}W_1\exp(-R/R_0)\, dR$

$= D\int_0^\infty x^{D-1}W_1\cdot R_0\exp(-x)\,dx$

$= DR_0^D W_1\int_0^\infty x^{D-1}\exp(-x)\,dx$

$= DR_0^D W_1\Gamma(D)$

$[\int_0^\infty \exp(-p_x/R_0)\, d^3p_x]^{3N} = [-R_0\exp(-p_x/R_0)|_0^\infty]^{3N} = R_0^{3N} = R_0^D$

$DR_0^D W_1\Gamma(D) = R_0^D$

$W_1 = \frac{1}{D\Gamma(D)}$

$$G(E) = \frac{V^N}{h^{3N}} \left(\frac{E}{c}\right)^{3N} (8\pi)^N \cdot 1/D!$$

$$S = k \ln\left[\frac{G}{N!}\right] = k \ln\left[\frac{V^N}{h^{3N}} (E/c)^{3N} (8\pi)^N \cdot 1/3N!\,N!\right]$$

$$= k\left\{N \ln\left[\frac{8\pi V}{h^3}(E/c)^3\right] - 3N \ln 3N - N \ln N + 4N\right\}$$

$$= kN\left\{\ln\left[\frac{8\pi V}{Nh^3}\left(\frac{E}{3cN}\right)^3\right] + 4\right\}$$

$$P/T = \frac{\partial S}{\partial V} = \frac{kN}{\frac{8\pi V}{Nh^3}\left(\frac{E}{3cN}\right)^3} \cdot \frac{8\pi}{Nh^3}\left(\frac{E}{3cN}\right)^3 = \frac{kN}{V}$$

$$PV = NkT$$

$$1/T = \frac{\partial S}{\partial E} = \frac{3Nk}{E}$$

$$T = \frac{E}{3Nk}$$

$$C_v = \frac{\partial E}{\partial T} = 3Nk$$

2. Liouville's Theorem and the Evolution of Entropy

Suppose we have some normalized probability density in phase space $\rho(\omega, t)$ where ω is a point in phase space. In general, the average of any quantity $\mathcal{O}(\omega, t)$ with respect to the distribution is $\langle \mathcal{O} \rangle = \int d\omega\, \rho(\omega, t)\, \mathcal{O}(\omega, t)$. The time derivative of this average satisfies $\frac{d\langle \mathcal{O}\rangle}{dt} = \int d\omega\, \frac{\partial[\rho(\omega,t)\mathcal{O}(\omega,t)]}{\partial t}$. Note the distinction between the full and partial derivatives in this equation.

The "von Neumann entropy" for a normalized probability density $\rho(\omega, t)$ takes the form $S(t) = -k_B \int d\omega\, \rho(\omega, t) \ln \rho(\omega, t)$, where ω is a point in phase space. Suppose the distribution is such that $\rho(\omega) \to 0$ if any particle coordinate or momentum becomes very large, i.e., if x_i or p_i approaches $\pm\infty$ for any i.

a. Show that if the particles follow Hamiltonian dynamics for some classical Hamiltonian $\mathcal{H}$, then $\frac{dS}{dt} = 0$.

$$\frac{dS}{dt} = -k \int \frac{\partial}{\partial t}(\rho \ln \rho)\, d\omega$$

$$= -k \int \left[\frac{\partial \rho}{\partial t} \ln \rho + \frac{\partial \rho}{\partial t}\right] d\omega$$

$$\frac{\partial \rho}{\partial t} = -(\vec{\nabla} \cdot \boldsymbol{\rho}) \cdot \vec{v}$$

$$\vec{\nabla}\rho \cdot \vec{v} = \sum_{i=1}^{3N} \left\{\frac{\partial \rho}{\partial q_i} \cdot \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \cdot \frac{\partial \mathcal{H}}{\partial q_i}\right\}$$

$$\frac{dS}{dt} = k \int [\ln \rho + 1] \sum_i \left\{\frac{\partial \rho}{\partial q_i} \cdot \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \cdot \frac{\partial \mathcal{H}}{\partial q_i}\right\} d\omega$$

$$= -k \int \left\{\rho\left[\frac{\partial \ln \rho}{\partial q_i} \cdot \frac{\partial \mathcal{H}}{\partial p_i} + (1 + \ln \rho) \cdot \frac{\partial^2 \mathcal{H}}{\partial q_i \partial p_i}\right] - \rho\left[\frac{\partial \ln \rho}{\partial p_i} \cdot \frac{\partial \mathcal{H}}{\partial q_i} + (1 + \ln \rho)\frac{\partial^2 \mathcal{H}}{\partial q_i \partial p_i}\right]\right\} d\omega$$

$$= -k \int \left\{\frac{\partial \rho}{\partial q_i} \cdot \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \cdot \frac{\partial \mathcal{H}}{\partial q_i}\right\} d\omega$$

$$= k \int \rho \left\{\frac{\partial^2 \mathcal{H}}{\partial q_i \partial p_i} - \frac{\partial^2 \mathcal{H}}{\partial p_i \partial q_i}\right\} d\omega = 0$$

$$\Rightarrow \frac{dS}{dt} = 0$$

b. Using two Lagrange multipliers, α to enforce the constraint that the distribution should be normalized, and β to constrain the average energy $\langle \mathcal{H} \rangle = \int \rho \mathcal{H}\, d\omega = E$, find the function $\rho_{max}(\omega)$ that maximizes the functional $S[\rho]$. What is the physical interpretation of β?

$$\mathcal{L} = S + \alpha\left(\int \rho\, d\omega - 1\right) + \beta\left(\int \rho \mathcal{H}\, d\omega - E\right) = 0$$

$$= -k \int \rho \ln \rho\, d\omega + \alpha\left(\int \rho\, d\omega - 1\right) + \beta\left(\int \rho \mathcal{H}\, d\omega - E\right) = 0$$

$$\frac{\partial \mathcal{L}}{\partial \rho} = -k(\ln \rho + \rho \cdot 1/\rho) + \alpha + \beta \mathcal{H} = 0$$

$$\alpha + \beta \mathcal{H} = k(\ln \rho + 1)$$

$$\rho_{max} = \exp\left(\frac{\alpha + \beta \mathcal{H}}{k} - 1\right)$$

$$E = \frac{\int \rho_{max} \mathcal{H}\, d\omega}{\int \rho_{max}\, d\omega} = \frac{\int \mathcal{H} \exp(\beta \mathcal{H}/k)\, d\omega}{\int \exp(\beta \mathcal{H}/k)\, d\omega} = \int {}^{k\rho}/_{\beta}\left[\ln \rho_{max} + \ln \int \exp(\beta \mathcal{H}/k)\, d\omega\right] d\omega$$

$$= -S/\beta + k/\beta \ln \int \exp(\beta \mathcal{H}/k)\, d\omega$$

$$\frac{\partial S}{\partial E} = -\beta = 1/T$$

$$\Rightarrow \rho_{max} = \text{constant} \cdot \exp(-\mathcal{H}/k_B T)$$

c. Show that the solution to part (b) is stationary, i.e. $\frac{\partial \rho_{max}}{\partial t} = 0$

$$\rho_{max} = c \exp\left(-\mathcal{H}/kT\right)$$

$$\frac{d\langle \mathcal{H}\rangle}{dt} = 0 = \int \frac{\partial \rho \mathcal{H}}{\partial t}\, d\omega$$

$$= \int \frac{\partial \rho}{\partial t} \cdot \mathcal{H}\, d\omega + \int \rho \cdot \frac{\partial \mathcal{H}}{\partial t}\, d\omega = 0$$

$$\frac{\partial \mathcal{H}}{\partial t} = 0 \Rightarrow \int \frac{\partial \rho}{\partial t} \cdot \mathcal{H}\, d\omega = 0$$

$$\text{since } \mathcal{H} \neq 0 \Rightarrow \frac{\partial \rho}{\partial t} = 0$$

3. *Rigid Rotator, Pathria 2.4*

A classical rigid rotator is a simple for a diatomic molecule, consisting of two point masses separated by a fixed distance. The state of the rotator is determined by the orientation of its axis, with spherical coordinates (θ, ϕ), and corresponding momenta (p_θ, p_ϕ). Classical mechanics gives us the angular momentum M of the rotator obeying the equation $M^2 = p_\theta^2 + p_\phi^2/\sin^2\theta$

a. Evaluate the volume of phase space available to a rigid rotator with $M \le M_0$, and show that the corresponding number of microstates available is $(M_0/\hbar)^2$

$$V = \int dp_\theta \, dp_\phi \, d\theta \, d\phi$$

$$M_0^2 = p_\theta^2 + p_\phi^2/\sin^2\theta$$

$$M_0^2 \sin^2\theta - p_\theta^2 \sin^2\theta = p_\phi^2$$

$$|p_\phi| \le \sqrt{M_0^2 \sin^2\theta - p_\theta^2 \sin^2\theta}$$

$$V = 2\pi \int_0^\pi \int_{-M_0}^{M_0} \sqrt{M_0^2 \sin^2\theta - p_\theta^2 \sin^2\theta} \; dp_\theta \, d\theta$$

$$= 4\pi \int_{-M_0}^{M_0} \sqrt{M_0^2 - p_\theta^2} \, dp_\theta$$

$$= 4\pi \left[\frac{p_\theta \sqrt{M_0^2 - p_\theta^2}}{2} + \frac{M_0^2}{2} \sin^{-1}\left(\frac{p_\theta}{M_0}\right) \right] \Big|_{-M_0}^{M_0}$$

$$= 4\pi^2 M_0^2$$

$$\Delta p \Delta x = h \Rightarrow \Omega = (M_0/\hbar)^2$$

b. Quantum mechanics tells us that angular momentum is quantized as $M_j = \hbar\sqrt{j(j+1)}$ with either $j = 0, 1, 2, \ldots$ or $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$, in either case with a degeneracy $2j+1$. Use this to evaluate the number of states available to a quantum rotator with $j \le j_0$, and compare to the result of (a). Under what circumstances do the results agree?

For $M_0 = \hbar\sqrt{j_0(j_0+1)}$, $G = \sum_{j \le j_0} (2j+1)$ with j either integer or half-integer

For integers: $G = \sum_{j=0}^{j_0} (2j+1) = \frac{2 j_0 (j_0+1)}{2} + (j_0+1) = (j_0+1)^2$

$$j_0^2 + j_0 = M_0^2/\hbar^2$$

$$j_0 = \tfrac{1}{2}\left[-1 + \left[1 + 4M_0^2/\hbar^2\right]^{1/2}\right]$$

$$(j_0+1)^2 = \tfrac{1}{4}\left\{1 + \left[1 + 4M_0^2/\hbar^2\right]^{1/2}\right\}^2 = \tfrac{1}{4}\left[2 + 4M_0^2/\hbar^2 + 2\left(1 + 4M_0^2/\hbar^2\right)^{1/2}\right]$$

$$= M_0^2/\hbar^2 \left\{1 + \tfrac{1}{2}\left(\hbar/M_0\right)^2 \left(1 + 4M_0^2/\hbar^2\right)^{1/2} + \tfrac{1}{2}\right\}$$

$$= M_0^2/\hbar^2 \left(1 + \mathcal{O}(\hbar/M_0)\right) \approx M_0^2/\hbar^2$$

For half-integer, $G = 2 \cdot \tfrac{1}{2} \left(\frac{2j_0+1}{2}\right)\left(\frac{2j_0+3}{2}\right) = j_0^2 + 2j_0 + \tfrac{3}{4}$

$$= j_0(j_0+1) + j_0 + \tfrac{3}{4}$$

$$= M_0^2/\hbar^2 + \mathcal{O}(\hbar/M_0) \approx M_0^2/\hbar^2$$