Classical Statistical Mechanics: Part 1

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Classical Mechanics

- 1-Dimensional system with 1 particle of mass m
  - Newton's equations of motion for position $x(t)$ and momentum $p(t)$:

$$\begin{aligned} \dot{x}(t) &\equiv \frac{dx}{dt} \qquad & p = m\dot{x} \\ F(t) &= ma(t) \qquad & a(t) = \ddot{x}(t) \\ F(t) &= -\frac{dV}{dx} & \\ \dot{p}(t) &= m\ddot{x}(t) = F(t) = -\frac{dV}{dx} & \end{aligned}$$

  - Define an energy function called the *Hamiltonian* $H(x,p) = \frac{p^2}{2m} + V(x)$.
  - Introduce terminology

$$\frac{p^2}{2m} = \text{kinetic energy} \qquad V(x) = \text{potential energy}$$

  - Newton's laws can then be expressed as:

$$\dot{x} = \frac{p}{m} = \frac{\partial H}{\partial p} \qquad \dot{p} = -\frac{dV}{dx} = -\frac{\partial H}{\partial x}.$$

- These are coupled ordinary differential equations whose solution is uniquely specified by specifying two conditions, such as $x_0 = x(0)$ and $p_0 = p(0)$ at some reference time $t_0 = 0$.
- Example:Harmonic Oscillator $H = p^2/2m + m\omega^2/2x^2$

$$\begin{aligned} \dot{x} &= \frac{\partial H}{\partial p} = \frac{p}{m} \\ \dot{p} &= -\frac{\partial H}{\partial x} = -m\omega^2 x = m\ddot{x} \end{aligned}$$

  * Trajectories trace an ellipse whose size depends on total energy H, which is conserved (constant) along trajectory.

- 3-dimensional system of 1 particle
  - Notation: $\mathbf{r} = (x, y, z)$ and $\mathbf{p} = (p_x, p_y, p_z)$. Also, $\mathbf{p} \cdot \mathbf{p} = p_x^2 + p_y^2 + p_z^2$.
  - The Hamiltonian is: $\frac{\mathbf{p} \cdot \mathbf{p}}{2m} + V(\mathbf{r})$.
  - The equations of motion are:

$$\begin{aligned} \dot{\mathbf{r}} &= \frac{\partial H}{\partial \mathbf{p}} = \frac{\mathbf{p}}{m} \quad \xrightarrow{\text{shorthand for}} \quad \begin{pmatrix} \dot{r_x} \\ \dot{r_y} \\ \dot{r_z} \end{pmatrix} = \frac{1}{m} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} \\ \dot{\mathbf{p}} &= -\frac{\partial H}{\partial \mathbf{r}} = -\frac{\partial V}{\partial \mathbf{r}} \end{aligned}$$

- 2 particles in 3-dimensions
  - Hamiltonian: $H = \frac{\mathbf{p}_1 \cdot \mathbf{p}_1}{2m_1} + \frac{\mathbf{p}_2 \cdot \mathbf{p}_2}{2m_2} + V(\mathbf{r}_1, \mathbf{r}_2)$
  - Equations of motion are:

$$\begin{aligned} \dot{\mathbf{r}_1} &= \frac{\partial H}{\partial \mathbf{p}_1} = \frac{\mathbf{p}_1}{m_1} & \dot{\mathbf{r}_2} &= \frac{\partial H}{\partial \mathbf{p}_2} = \frac{\mathbf{p}_2}{m_2} \\ \dot{\mathbf{p}_1} &= -\frac{\partial H}{\partial \mathbf{r}_1} & \dot{\mathbf{p}_2} &= -\frac{\partial H}{\partial \mathbf{r}_2} \end{aligned}$$

  - Introduce generalized notation: $\mathbf{r}^{(2)} = (\mathbf{r}_1, \mathbf{r}_2)$ and $\mathbf{p}^{(2)} = (\mathbf{p}_1, \mathbf{p}_2)$.

$$\mathbf{p}^{(2)} \cdot \mathbf{p}^{(2)} = \mathbf{p}_1 \cdot \mathbf{p}_1 + \mathbf{p}_2 \cdot \mathbf{p}_2$$

- Equations of motion in this notation:

$$\dot{\mathbf{r}}^{(2)} = \frac{\partial H}{\partial \mathbf{p}^{(2)}} \qquad \dot{\mathbf{p}}^{(2)} = -\frac{\partial H}{\partial \mathbf{r}^{(2)}}.$$

- N particle system in 3-D
  - Equation of motion in generalized notation:

$$\dot{\mathbf{r}}^{(N)} = \frac{\partial H}{\partial \mathbf{p}^{(N)}} \qquad \dot{\mathbf{p}}^{(N)} = -\frac{\partial H}{\partial \mathbf{r}^{(N)}}.$$

  - A total of $6N$ equations!
  - At each point in time, the system is specified by $6N$ coordinates $(\mathbf{r}^{(N)}(t), \mathbf{p}^{(N)}(t)) \equiv \mathbf{x}^{(N)}(t)$ called the *phase point.*
  - The set of all phase points is called *phase space.*
  - Classical dynamics describes a path through the $6N$-Dimensional phase space.
  - Special properties of path through phase space:
    1. Certain quantities remain unchanged during the evolution of system.
       * Examples: energy, momentum and angular momentum may be *conserved* (constant) along the path or *trajectory* of the system.
       * Path remains on a hyper-surface of constant energy in phase space.
    2. Paths never cross in phase space. Each disjoint path, labelled by initial conditions, passes arbitrarily close to any point on the constant energy hypersurface.
       * Amount of time for the trajectory of the system from a given initial point in phase space to pass arbitrarily close to the initial point is called the *recurrence time*: Absolutely enormous for large, interacting systems.

- Consider an arbitrary function G of the phase space coordinate $\mathbf{x}^{(N)}$,

$$G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = G(\mathbf{x}^{(N)}, t).$$

Taking the time derivative,

$$\begin{aligned}\frac{dG(\mathbf{x}^{(N)},t)}{dt} &= \frac{\partial G(\mathbf{x}^{(N)},t)}{\partial t} + \frac{\partial G(\mathbf{x}^{(N)},t)}{\partial \mathbf{r}^{(N)}} \cdot \dot{\mathbf{r}}^{(N)} + \frac{\partial G(\mathbf{x}^{(N)},t)}{\partial \mathbf{p}^{(N)}} \cdot \dot{\mathbf{p}}^{(N)} \\ &= \frac{\partial G(\mathbf{x}^{(N)},t)}{\partial t} + \frac{\partial G(\mathbf{x}^{(N)},t)}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} - \frac{\partial G(\mathbf{x}^{(N)},t)}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}}.\end{aligned}$$

- We can define the *Liouville operator* $\mathcal{L}$ to be:

$$\mathcal{L} = \frac{\partial H}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial}{\partial \mathbf{r}^{(N)}} - \frac{\partial H}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial}{\partial \mathbf{p}^{(N)}}$$

  so that in terms of a general function B

$$\mathcal{L}B = \frac{\partial B}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{p}^{(N)}} - \frac{\partial B}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial H}{\partial \mathbf{r}^{(N)}}.$$

- In terms of the Liouville operator,

$$\frac{dG(\mathbf{x}^{(N)},t)}{dt} = \frac{\partial G(\mathbf{x}^{(N)},t)}{\partial t} + \mathcal{L}G(\mathbf{x}^{(N)},t).$$

- Functions of the phase space coordinate G that are not explicit functions of time t are conserved by the dynamics if $\mathcal{L}G = 0$.
- Formal solution of evolution is then

$$G(\mathbf{x}^{(N)},t) = e^{\mathcal{L}t}G(\mathbf{x}^{(N)},0).$$

- In particular,

$$\mathbf{x}^{(N)}(t) = e^{\mathcal{L}t}\mathbf{x}^{(N)}(0).$$

- Note that $\mathcal{L}H = 0$.
- Can also define the *Poisson bracket* operator via

$$\{A,B\} \equiv \frac{\partial A}{\partial \mathbf{r}^{(N)}} \cdot \frac{\partial B}{\partial \mathbf{p}^{(N)}} - \frac{\partial A}{\partial \mathbf{p}^{(N)}} \cdot \frac{\partial B}{\partial \mathbf{r}^{(N)}}.$$

- The relationship between the Poisson bracket and Liouville operators is

$$\mathcal{L}B = \{B,H\} \qquad so \qquad \frac{dG(\mathbf{x}^{(N)},t)}{dt} = \frac{\partial G(\mathbf{x}^{(N)},t)}{\partial t} + \{G(\mathbf{x}^{(N)},t), H(\mathbf{x}^{(N)})\}.$$

- Important property:

$$e^{\mathcal{L}t}\left(A(\mathbf{x}^{(N)})B(\mathbf{x}^{(N)})\right) = \left(e^{\mathcal{L}t}A(\mathbf{x}^{(N)})\right)\left(e^{\mathcal{L}t}B(\mathbf{x}^{(N)})\right) = A(\mathbf{x}^{(N)}(t))B(\mathbf{x}^{(N)}(t)).$$

Statistical Mechanics

- Will discuss Gibb's formulation of statistical mechanics corrected for quantum behavior.
- Quantum formulation discussed later.
- The system consists of N identical point particles - behave classically and have no internal degrees of freedom.
- Recall properties of dynamics: a path or trajectory through phase space.
  - Path never crosses itself.
  - Path is closed: can define the Poincaré recurrence time.
  - For conservative systems, paths explore an equal energy hypersurface of phase space (lower dimensionality). Same is true for other conserved quantities of the dynamics.
- Consider some arbitrary dynamical variable $G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = G(\mathbf{x}^{(N)})$ (function of phase space coordinates and hence possibly evolving in time).
- An experimental measurement of quantity corresponds to a *time* average of some (possibly short) sampling interval τ.

$$G_{\text{obs}}(t) = \frac{1}{\tau}\int_0^\tau d\sigma\, G\left(\mathbf{r}^{(N)}(t+\sigma), \mathbf{p}^{(N)}(t+\sigma)\right).$$

  - $\tau \gg \tau_m$. where τ_m is a *microscopic time scale*. Hence fluctuations on microscopic time scale a smoothed out.
  - For most systems, evolution of $G(t)$ cannot be solved analytically and so must resort to
    1. Numerically solving evolution (computer simulation)
    2. Developing a new theoretical framework relating time averages to something that can be calculated.
- Josiah Willard Gibb's idea: Time average of dynamical variable corresponds to an average over a properly weighted set of points of phase space (called an *ensemble*). The statistical average is called an *ensemble average*.

  - Each point in phase space corresponds to a different configuration of the system.
  - Ensemble average therefore corresponds to a weighted average over different configurations of the system.

- Define a probability density for phase space (often loosely called the "distribution function')':

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) \quad = \quad \text{distribution function}$$

and hence

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \quad = \quad \begin{array}{l} \text{prob. of finding a system in ensemble with coordinates between} \\ (\mathbf{r}^{(N)}, \mathbf{r}^{(N)} + d\mathbf{r}^{(N)}) \text{ and } (\mathbf{p}^{(N)}, \mathbf{p}^{(N)} + \\ d\mathbf{p}^{(N)}) \text{ at time } t. \end{array}$$

- The *ensemble average* is defined as:

$$\overline{G(t)} = \langle G(t) \rangle \equiv \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \; G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t).$$

- *microcanonical ensemble*: All systems in ensemble have the same total energy.
  - All dynamical trajectories with same energy compose a set of states in microcanonical ensemble.
  - Technically, all conserved quantities should also be the same.

What is the connection between the ensemble average and the experimental observation (time average)?

- **Quasi-ergodic theorem:** As $\mathbf{t} \to \infty$, a dynamical trajectory will pass arbitrarily close to each point in the constant-energy (if only conserved quantity) hypersurface of phase space.
  - Another statement: For all initial states except for a set of zero measure, the phase space is connected.
  - Hypersurfaces of phase space covered by trajectory.

- Consequence: The length of time that a systme spends in a volume Ω of phase space is proportional to that volume.

$$\frac{t_1}{t_2} = \frac{\Omega_1}{\Omega_2}.$$

  - Follows from properties of the dynamics.

- As $t \to \infty$:

$$G_{\text{obs}}(t) = \frac{1}{\tau}\int_0^\tau d\sigma\; G\left(\mathbf{r}^{(N)}(t+\sigma), \mathbf{p}^{(N)}(t+\sigma)\right) = \frac{1}{\Omega}\int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\; G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)})$$

  hence

$$G_{\text{obs}}(t) = \overline{G}(t) = \int G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) \qquad \text{if } f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = 1/\Omega..$$

  - All points on hypersurface have the same weight (equally probable).
  - Ensemble analogy: each point in restricted phase space corresponds to a configuration of the system with the same macroscopic properties.

- Procedure: We will construct an axiomatic approach to find equilibrium distributions.

- Alternate method: Asymptotic solution of the Boltzmann equation for distribution functions - describes collisions of pairs from Newton's equations an adds an assumption of statistical behavior.

  - System naturally evolves from an initial state to states with static macroscopic properties corresponding to "equilibrium" properties - Can model this with simple spin systems like the Kac ring model.
  - Measure of disorder, the statistical entropy, increases as the system evolves: maximized in equilibrium.

1 Ensembles and Observables

- Consider some arbitrary dynamical variable $G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = G(\mathbf{x}^{(N)})$ (function of phase space coordinates and hence possibly evolving in time).

- An experimental measurement of quantity corresponds to a *time* average of some (possibly short) sampling interval τ.

$$G_{\rm obs}(t) = \overline{G(t)} \equiv \frac{1}{\tau}\int_0^\tau d\sigma\; G\left(\mathbf{r}^{(N)}(t+\sigma), \mathbf{p}^{(N)}(t+\sigma)\right).$$

  - $\tau \gg \tau_m$. where τ_m is a *microscopic time scale*. Hence fluctuations on microscopic time scale a smoothed out.
  - For most systems, evolution of $G(t)$ cannot be solved analytically and so must resort to
    1. Numerically solving evolution (computer simulation)
    2. Developing a new theoretical framework relating time averages to something that can be calculated.

- Ensemble Average: Infinite/long time average of dynamical variable corresponds to an average over a properly weighted set of points of phase space (called an *ensemble*). The statistical average is called an *ensemble average*.
  - Each point in phase space corresponds to a different configuration of the system.
  - Ensemble average therefore corresponds to a weighted average over different configurations of the system.

- Define a probability density for phase space (often loosely called the "distribution function')':

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) \;=\; \text{distribution function}$$

  and hence

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \;=\; \begin{array}{l}\text{prob. of finding a system in ensemble with coordinates between } (\mathbf{r}^{(N)}, \mathbf{r}^{(N)}+d\mathbf{r}^{(N)}) \text{ and } (\mathbf{p}^{(N)}, \mathbf{p}^{(N)}+ \\ d\mathbf{p}^{(N)}) \text{ at time } t.\end{array}$$

  - Note that the distribution function is normalized:

$$\int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}\, f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = 1$$

- The *ensemble average* is defined as:

$$\langle G(t) \rangle \equiv \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \; G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) \, f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t).$$

- *microcanonical ensemble*: All systems in ensemble have the same total energy.
  - All dynamical trajectories with same energy compose a set of states in microcanonical ensemble.
  - Technically, all conserved quantities should also be the same.

What is the connection between the ensemble average and the experimental observation (time average)?

- **Quasi-ergodic hypothesis:** As $\mathbf{t} \to \infty$, a dynamical trajectory will pass arbitrarily close to each point in the constant-energy (if only conserved quantity) hypersurface of phase space (metrically transitive).
  - Another statement: For all initial states except for a set of zero measure, the phase space is connected through the dynamics.
  - Hypersurfaces of phase space covered by trajectory.
- So in some sense, as $\tau \to \infty$:, we expect

$$G_{\text{obs}}(t) = \frac{1}{\tau} \int_0^\tau d\sigma \; G\left(\mathbf{r}^{(N)}(t+\sigma), \mathbf{p}^{(N)}(t+\sigma)\right) = \frac{1}{\Omega} \int' d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \; G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)})$$

where

$$\Omega = \int' d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} = \int_{E < H(\mathbf{x}^{(N)}) < E + \delta E} d\mathbf{r}^{(N)} d\mathbf{p}^{(N)}$$

hence

$$G_{\text{obs}}(t) = \overline{G}(t) = \int G(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) \; d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \quad \text{if } f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}, t) = 1/\Omega.$$

  - All points on hypersurface have the same weight (equally probable).

  - Ensemble analogy: each point in restricted phase space corresponds to a configuration of the system with the same macroscopic properties.

- Can utilize an axiomatic approach to find equilibrium distributions: Maximize statistical entropy subject to constraints.

- Alternate method: Asymptotic solution of the Boltzmann equation for distribution functions - describes collisions of pairs from Newton's equations and adds an assumption of statistical behavior (molecular chaos).

  - System naturally evolves from an initial state to states with static macroscopic properties corresponding to "equilibrium" properties - Can model this with simple spin systems like the Kac ring model.
  - Measure of disorder, the statistical entropy, increases as the system evolves: maximized in equilibrium (H theorem).

- Idea: Construct an axiomatic approach based on the idea that the disorder, or "entropy", is maximized in equilbrium.

  - According to the quasi-ergodic theorem, the distribution function should be constant on the constant energy hypersurface.

- Following Boltzmann, we define the statistical entropy

$$S = k \ln W$$

where

$$W = \begin{array}{l}\text{number of possible states for system of energy } E' \text{ in} \\ \text{the range } [E, E+\delta E] \text{ for a system of } N \text{ particles in} \\ \text{a volume } V.\end{array}$$

  - Energy $H(\mathbf{x}^{(N)})$ is fixed within allowance δE due to uncertainty principle, $\delta E \delta t \sim h$, where δt is the observation time.

- We wish to obtain the distribution in which all states on energy hypersurface are equally probable. From the normalization condition this implies

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = \begin{cases} \frac{1}{\Omega(E,\delta E,N,V)} & \text{for } E < H(\mathbf{x}^{(N)}) < E + \delta E \\ 0 & \text{otherwise} \end{cases}$$

– Ω is the effective "volume" of the phase space region:

$$\begin{aligned}\Omega(E,\delta E,N,V) &= \int_{E<H(\mathbf{x}^{(N)})<E+\delta E} d\mathbf{r}^{(N)}d\mathbf{p}^{(N)} \\ &= \int_{E}^{E+\delta E} dE' \overbrace{\int d\mathbf{r}^{(N)}d\mathbf{p}^{(N)}\ \delta(H(\mathbf{r}^{(N)},\mathbf{p}^{(N)})-E')}^{\tilde{N}(E')} \\ &= \int_{E}^{E+\delta E} dE'\ \tilde{N}(E') = \text{number of states in energy shell.}\end{aligned}$$

– $\tilde{N}(E')$ is called the *density of states*.

– In the limit of small δE, $\tilde{N}(E)\delta E \approx \Omega(E,\delta E,N,V)$.

- Let $W(E,\delta E,N,V)$ be the number of possible quantum states for the set $\{E,\delta E,N,V\}$ for N indistinguishable particles.

  – For quantum systems, the statistical entropy is $S = k\ln(W(E,\delta E,N,V))$.

$$W(E,\delta E,N,V) = \sum_{E<E_l<E+\delta E} = \Omega(E,\delta E,N,V).$$

- What about classical systems? What is the relation between number of unique states and the volume Ω of phase space?

Considerations:

1. Uncertainty principle: Since $\delta p_x \delta r_x \sim h$, one cannot differentiate between phase points with (r_x, p_x) and (r'_x, p'_x) if $|r_x - r'_x| < \delta r_x$ and $|p'_x - p_x| < \delta p_x$.
   – Limited resolution of phase space: must coarse grain
   – Classically, systems *are* different: must correct for this over-counting factor.

$$\begin{aligned}dp_x dr_x &\Rightarrow \frac{1}{h}dp_x dr_x \\ d\mathbf{r}^{(N)}d\mathbf{p}^{(N)} &\Rightarrow \frac{1}{h^{3N}}d\mathbf{r}^{(N)}d\mathbf{p}^{(N)}\end{aligned}$$

2. Quantum statistics
   - In QM, state of N-particle system given by $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_n)$.
   - Consider a 2-particle classical system with phase space coordinates:

Particle 1: $(\mathbf{r}, \mathbf{p})$	Particle 1: $(\mathbf{r}', \mathbf{p}')$
Particle 2: $(\mathbf{r}', \mathbf{p}')$	Particle 2: $(\mathbf{r}, \mathbf{p})$

   - These states are *different* classically and identical in QM (wavefunction obeys Bose, Fermi-Dirac, ... statistics).
   - Permuting labels of N particle system gives different classical and identical QM system. For correspondance, must divide number of classical states by $N!$.

- So classically,

$$W(E, \delta E, N, V) = \frac{1}{h^{3N} N!} \int_{E < H(\mathbf{x}^{(N)}) < E + \delta E} d\mathbf{x}^{(N)} = \frac{1}{h^{3N} N!} \Omega(E, \delta E, N, V).$$

- Since $f(\mathbf{x}^{(N)}) = 1/\Omega$

$$\begin{aligned} S &= k \ln(W) = k \ln \left(\frac{\Omega(E, \delta E, N, V)}{h^{3N} N!} \right) \\ &= -k \ln \left(h^{3N} N! f(\mathbf{x}^{(N)}) \right) \\ &= -k \int d\mathbf{x}^{(N)} \; f(\mathbf{x}^{(N)}) \ln \left(h^{3N} N! f(\mathbf{x}^{(N)}) \right). \end{aligned}$$

   - Provides general definition of statistical entropy as an average over the distribution.