



May 2009, Lecture #1
Statistical Mechanics:
Fundamentals

TSTC Lectures: Theoretical & Computational Chemistry

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This Lecture

- Part I: (“background”)
 - Post-Modern Classical Mechanics
 - Hamiltonian Mechanics
 - Numerical Considerations
 - Thermodynamics, Review
 - Cf. “Thermodynamics and an Introduction to Thermostatistics” by H. Callen, 2nd Ed. (Wiley, 1985)
- Part II:
 - Statistical Mechanics: Ideal
 - Cf. “Introduction to Modern Statistical Mechanics” by D. Chandler, (Oxford University Press, USA, 1987) —The green book ☺
 - Cf. “Statistical Mechanics” by B. Widom
 - Cf. “Basic concepts for simple and complex liquids” by J. L. Barrat & J- P. Hansen



Major Concepts, Part I —C.M.

- Newtonian Mechanics
- Hamiltonian Mechanics
 - Phase Space
 - Hamilton-Jacobi Equations
- Canonical Transformations
- Lagrangian (and Legendre Transformations)
- The Action
- Numerical Integration of Equations of Motion
 - Velocity-Verlet
 - Runge-Kutta
 - Predictor-Corrector, Gear, etc.
- Path Integrals (Quantum Mechanics)



Newtonian Mechanics, I

- Configuration space
 - Position: x, u
 - Velocity: v
- Equations of Motion:
$$\begin{cases} \dot{x} = v \\ \dot{v} = F/m \end{cases}$$
- Force:
$$F(x) = -\frac{dV(x)}{dx} = -\nabla V$$
 - Note: Potential is $U(x)$ or $V(x)$



Newtonian Mechanics, II

- Equations of Motion: $\begin{cases} \dot{x} = v \\ \dot{v} = F/m \end{cases}$
- Pedagogical Examples:
 - Free particle: $V(x) = \text{constant}$
(ballistic motion)
 - Harmonic Oscillator $V(x) = \frac{1}{2}kx^2$
 - Exactly Solvable
 - Leading nontrivial potential about a minimum
 - Approximates pendulum potential; the force is proportional to:
 $\sin kx \approx kx$



Hamiltonian Mechanics, I

- Phase space

- Position: x, u

- Momentum: p

- Equations of Motion: $\begin{cases} \dot{x} = p/m & (= mv/m = v) \\ \dot{p} = F & (= m\dot{v} = F) \end{cases}$

- Hamilton's e.o.m.:

$$\begin{aligned} \dot{x} &= \frac{d}{dp} \frac{p^2}{2m} \Rightarrow \dot{x} = \frac{d}{dp} \mathcal{H} \\ \dot{p} &= -\frac{d}{dx} V(x) \Rightarrow \dot{p} = -\frac{d}{dx} \mathcal{H} \end{aligned} \quad \left\{ \begin{array}{l} \dot{x} = \nabla_p \mathcal{H} \\ \dot{p} = -\nabla_x \mathcal{H} \end{array} \right\}$$

- Hamiltonian (is the Energy):

$$\begin{aligned} \mathcal{H} &= \text{Kinetic} + \text{Potential} = \text{Total Energy} \equiv E \\ &= \frac{p^2}{2m} + V(x) \end{aligned}$$



Hamiltonian Mechanics, II

- Key points:

$$\left\{ \begin{array}{l} \dot{x} = \nabla_p \mathcal{H} \\ \dot{p} = -\nabla_x \mathcal{H} \end{array} \right\}$$

- Hamiltonian is a constant of the motion

$$\begin{aligned} \frac{d\mathcal{H}}{dt} &= \frac{d}{dt} \left(\frac{p^2}{2m} + V(x) \right) \\ &= \frac{p}{m} \frac{dp}{dt} + \frac{dV}{dx} \frac{dx}{dt} \end{aligned} \quad \Rightarrow \quad \left\{ \begin{array}{l} \frac{d\mathcal{H}}{dt} = \frac{p}{m} \left(-\frac{dV}{dx} \right) + \left(\frac{dV}{dx} \right) \frac{p}{m} \\ \phantom{\frac{d\mathcal{H}}{dt}} = 0 \end{array} \right.$$

- Hamiltonian generates system dynamics
- x and p are on “equivalent” footing
- Hamiltonian (Operator) is also the generator of quantum evolution



Canonical Transformations, I

Algebraic/Passive <i>(Modify observables)</i>	vs.	Geometric/Active <i>(Modify states)</i>
Propagate the classical observables	vs.	Propagate the phase space variables (MD)

- “Quantum mechanics is a theory of transformations”
— Dirac
 - But so is classical mechanics
 - Unitary transformations are the quantum mechanical analogue to canonical transformations in classical mechanics
- Implications also on designing MD integrators:
 - Velocity-Verlet (so as to preserve the Energy)
 - Symplectic integrators (so as to preserve H-J equations)



Canonical Transformations, II

- Def: A C.T. of the phase space preserves the H-J equations w.r.t. the new Hamiltonian—“*The Kamiltonian*”
 - The analytic solution of a given \mathcal{H} reduces to the discovery of a C.T. for which \mathcal{K} is trivial.
 - But it's not so easy to do in general!
 - Perturbation theory can be constructed so that successive orders of the \mathcal{H} are trivialized by a successive C.T.'s :
 - Lie transform perturbation theory
 - van Vleck perturbation theory in Quantum Mechanics
 - A.k.a., CVPT
 - Not Raleigh-Ritz perturbation theory
 - Coupled cluster and MBPT in electronic structure theory
- Examples:
 - Point transformations
 - Action-Angle Variables for a harmonic oscillator
 - Propagation/evolution of phase space for some time step, t



Lagrangian

- The Lagrangian is: $\mathcal{L}(v, q) = \frac{1}{2}mv^2 - V(q)$

- This gives rise to the Euler-Lagrange E.o.M.:

$$\frac{\partial \mathcal{L}}{\partial q} = \frac{\partial}{\partial t} \frac{\partial \mathcal{L}}{\partial v}$$

But C.T.'s don't preserve the E-L equations! ☹

- We need to define the Momentum: $p = \frac{\partial \mathcal{L}}{\partial v}$
- The Hamiltonian is the Legendre Transform of the Lagrangian, exchanging the dependence between v and p :

$$\mathcal{H}(p, q) = pv - \mathcal{L}(v, q)$$

$$-\mathcal{H}(p, q) = \mathcal{L}(v, q) - pv$$

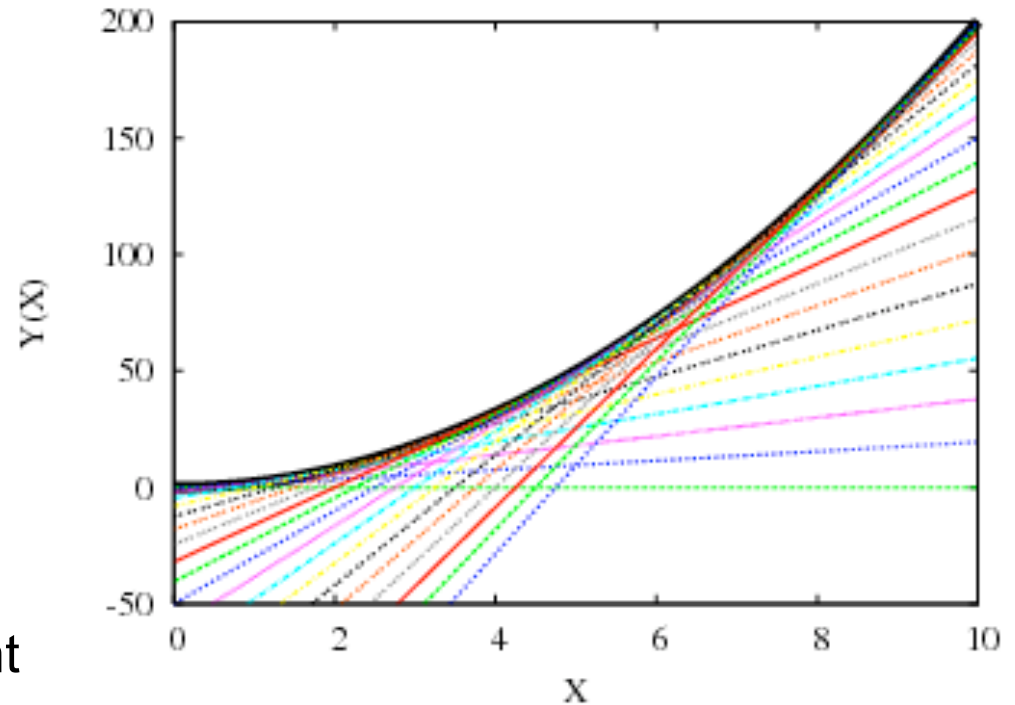


Legendre Transforms

- Goal:
 - Replace the independent variable with its derivative, e.g.:

$$\left(\frac{\partial Y(X)}{\partial X} \right) \equiv y$$

- Method:
 - Trade the function Y for the envelope of a family of tangent lines ψ .



$$\psi(y) = Y(X) - yX \quad \text{where } y \equiv \frac{\partial Y}{\partial X}$$



Action

$$S[p(\cdot), x(\cdot)] = \int_{t_0}^{t_1} \mathcal{L}[p(t), x(t)] dt$$

- The action is a functional of the path. (Note units!)
 - The usual action as stated above holds the initial and final points fixed
 - Hamilton's principal function (sometimes also called the action) looks the same but holds the initial point and time fixed (which is sometimes also called the initial-value representation.)
 - Hamilton's characteristic function, W , (sometimes also called the action) is obtained from a Legendre transform between E and t
- Least Action Principle or Extremal Action Principle
 - Classical paths extremize the action
 - Other paths give rise to interference:
 - The path integral includes all of them with the appropriate amplitude and phase (which depends on the action)
 - Many semi-classical corrections are formulated on the approximate use of these other paths
 - E.g., Centroid MD
- Stationary Phase Approximation



Numerical Integration of E.o.M.

- Molecular Dynamics (MD)

- In 1D:

$$x(t + \tau) \approx x(t) + \tau v$$

$$v(t + \tau) \approx v(t) + \tau F/m$$

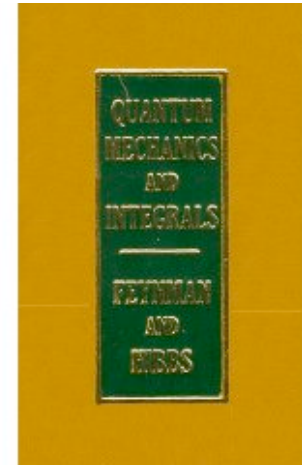
- The difficulty in treating molecular systems lies in
 - Knowing the potential
 - Dealing with many particles in 3D

- Integrators:

- Runge-Kutta integrators
 - Verlet or velocity-Verlet
 - Symplectic integrators



Path Integrals, I



- C.f., Feynman & Hibbs, “Quantum Mechanics and Path Integrals”
- The kernel or amplitude for going from a to b in time t :
(FH Eq. 2-25)

$$\begin{aligned}
 K(b, a) &\equiv \langle b | e^{-i\hat{H}t/\hbar} | a \rangle \\
 &= \int_a^b \mathcal{D}x(t) e^{iS[b,a]/\hbar} = \int_a^b \mathcal{D}x(\cdot) e^{iS\{x(\cdot), p(\cdot)\}/\hbar}
 \end{aligned}$$

- Can be obtained from the infinitesimal kernel:

$$\begin{aligned}
 \rho(x, y; \tau) &= \langle x | e^{-\hat{H}\tau} | y \rangle && \text{where } \tau \text{ is complex} \\
 &\approx \langle x | e^{-\hat{V}\frac{\tau}{2}} e^{-\hat{T}\tau} e^{-\hat{V}\frac{\tau}{2}} | y \rangle && \text{(Trotter)} \\
 \rho(x, y; \tau) &= \left(\frac{1}{2\pi\Omega\tau} \right)^{\frac{1}{2}} e^{-\frac{(x-y)^2}{2\Omega\tau} - \frac{\tau}{2}[V(x)+V(y)]}, && \text{where } \Omega \equiv \frac{\hbar^2}{m} \\
 &\approx \left(\frac{1}{2\pi\Omega\tau} \right)^{\frac{1}{2}} e^{-\frac{\tau\hbar^2}{2m^2\Omega}\bar{p}^2 - \frac{\tau}{2}[V(x)+V(y)]}, && \text{where } \bar{p} \in (p(x), p(y)) \\
 &\approx \left(\frac{1}{2\pi\Omega\tau} \right)^{\frac{1}{2}} e^{-\tau\mathcal{L}(p_x, x)/2} e^{-\tau\mathcal{L}(p_y, y)/2}
 \end{aligned}$$



Path Integrals, II

- EXAMPLE: The free particle kernel:

$$\begin{aligned}
 K(b, a) &= \langle b | e^{-i\hat{\mathcal{H}}t/\hbar} | a \rangle && \text{let } x_0 = a, x_N = b \\
 &= \lim_{\epsilon \rightarrow 0} \int dx_1 \cdots \int dx_{N-1} \prod_{i=1}^N \rho(x_i, x_{i-1}; i\epsilon/\hbar), && \text{where } N \equiv \frac{t}{\epsilon} \\
 &= \lim_{\epsilon \rightarrow 0} \int dx_1 \cdots \int dx_{N-1} \prod_{i=1}^N \left(\frac{m}{2\pi\hbar\epsilon i} \right)^{\frac{N}{2}} e^{\frac{im}{2\hbar\epsilon}(x_i - x_{i-1})^2}
 \end{aligned}$$

- But:

$$\begin{aligned}
 \int dx_j \left(\frac{m}{2\pi\hbar\epsilon i} \right) e^{\frac{im}{2\hbar\epsilon}(x_{j+1} - x_j)^2} e^{\frac{im}{2\hbar\epsilon}(x_j - x_{j-1})^2} &= \left(\frac{m}{2\pi\hbar 2\epsilon i} \right)^{\frac{1}{2}} e^{\frac{im}{2\hbar(2\epsilon)}(x_{j+1} - x_{j-1})^2} \\
 \implies K(b, a) &= \left(\frac{m}{2\pi\hbar N \epsilon i} \right)^{\frac{1}{2}} e^{\frac{im}{2\hbar(N\epsilon)}(x_N - x_0)^2} \quad \text{by recursion} \\
 &= \left(\frac{m}{2\pi\hbar t i} \right)^{\frac{1}{2}} e^{\frac{im}{2\hbar t}(b - a)^2}
 \end{aligned}$$

- For the free particle ($V = \text{constant} = 0$)



Polymer Isomorphism

- Recognizing the fact that the partition function for a quantum system looks just like the partition function for a classical polymer system
- Chandler & Wolynes, JCP **74**, 4078 (1981)
- This is not PRISM! (The latter is an approach for solving an integral equation theory—more later!)



Path Integrals

- Isomorphism between Quantum Mechanics and Classical Statistical Mechanics of ring polymers:

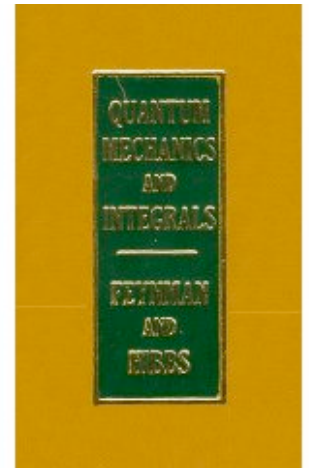
$$\begin{aligned}
 Q &= \text{Tr} \left[e^{-\beta \hat{\mathcal{H}}} \right] \\
 &= \lim_{p \rightarrow \infty} \text{tr} \left[\left(e^{-\beta \hat{\mathcal{H}}} \right)^p \right] \\
 &= \lim_{p \rightarrow \infty} \int dx_1 \cdots dx_p \prod_i^p \rho(x_i, x_{i+1}; \tau)
 \end{aligned}$$

where $\tau = \beta/p$ is the imaginary time (Wick's Theorem)

Primitive (Trotter): $\rho(x, y; \tau) \approx \left\langle x \left| e^{-\frac{\tau}{2} \hat{T}} e^{-\tau \hat{V}} e^{-\frac{\tau}{2} \hat{T}} \right| y \right\rangle$

$$\rho(x, y; \tau) \approx (2\pi\Omega\tau)^{-1/2} \exp \left\{ -\frac{(x-y)^2}{2\Omega\tau} - \frac{\tau}{2} [V(x) + V(y)] \right\}$$

where $\Omega \equiv \hbar^2/m$



Major Concepts, Part II — Ideal

- Thermodynamics (macroscopic theory)
 - S-conjugate variables
 - Legendre Transforms
- Statistical Mechanics—Fundamentals
 - Ensemble
 - Ensemble Averages & Observables
 - Partition Functions
 - Ergodicity
- Entropy and Probability
- Ensembles
 - Extensive vs. Intensive variables
- Harmonic Oscillator
- Ideal Gas

Sampling by:

- Monte Carlo
- Molecular Dynamics

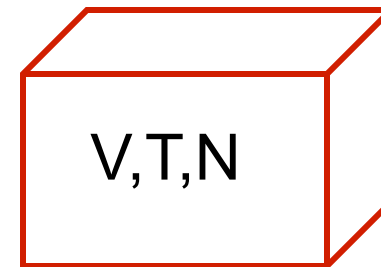
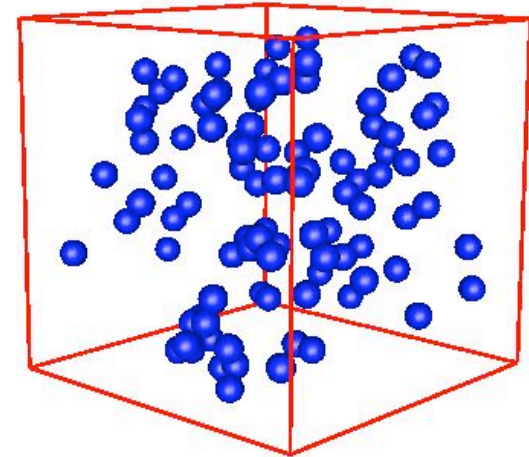
Ensembles:

- (S, V, N) μ canonical
- (T, V, N) Canonical (or Gibbs)
- (T, V, μ) Grand-Canonical
- (T, P, N) Isothermal-Isobaric



Thermodynamics (Review?)

- Microscopic variables:
 - Mostly irrelevant ☺
- Macroscopic observables:
 - Pressure, temperature, volume,...
- 3 Laws of Thermodynamics:
 - ➔ Free Energies
 - ➔ Entropy
 - ➔ Kelvin Temperature
- Thermodynamics provides consistency between representations



Free Energies

Internal Energy (E :Microscopic :: U :Macroscopic)

$$E(S, X) = TS - fX$$

where f :: intensive e.g., $p, -\mu$
 x :: extensive e.g., V, N

$$dE = TdS - fdX$$

e.g., $dE = TdS - PdV + \sum_j^n \mu_j dN_j$ for an n -component system

Other free energies: (connected by Legendre Transforms)

- Helmholtz: $A(T, V, N) = E - TS$
- Enthalpy: $H(S, P, N) = E + PV$
- Gibbs: $G(T, P, N) = E - TS + PV$

Take-home Message: f & X are “ E ”-conjugate



Entropies

Recall: $E(S, X) = TS - fX$

Entropy:

$$k_B^{-1} dS(E, X) = \beta dE + \beta f dX$$

where $\begin{cases} k_B [= R/N_a] & \text{is Boltzmann's Constant} \\ \beta = \frac{1}{k_B T} & \text{is the inverse temperature} \end{cases}$

Other entropies: (connected by Legendre Transforms)

Take-home Message: β & E , and βf & X are “S”-conjugate

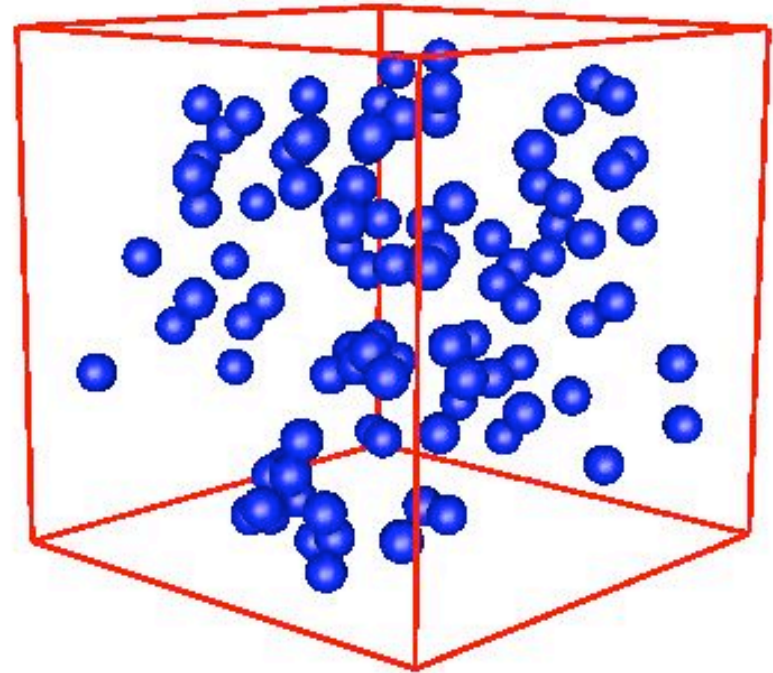
$$k_B^{-1} S(\beta, X) = k_B^{-1} S(E, X) - \beta E$$

but $S(T, X) = S(\beta, X)$



The Fundamental Problem

- Problem:
 - How to arrive at thermodynamics from microscopic considerations?
- Answer:
 - Obviously we need averaging, but what and how do we average?



Observables in Stat. Mech.

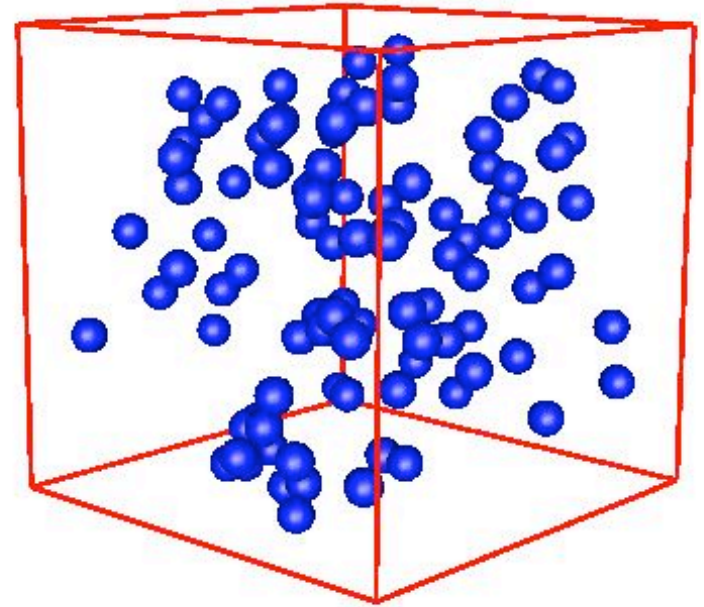
- Definitions:
 - Ensemble
 - The set of all possible configurations of a system (ξ)
 - Ensemble Average:
 - Average over the ensemble

$$\langle A \rangle_{\xi} = \frac{1}{V_{\xi}} \sum_{\xi \in \xi} A(\xi) P(\xi) \quad \text{If Countable}$$

$$\langle A \rangle_{\xi} = \frac{1}{V_{\xi}} \int_{\xi} A(\xi) P(\xi) d\xi \quad \text{If Continuous}$$

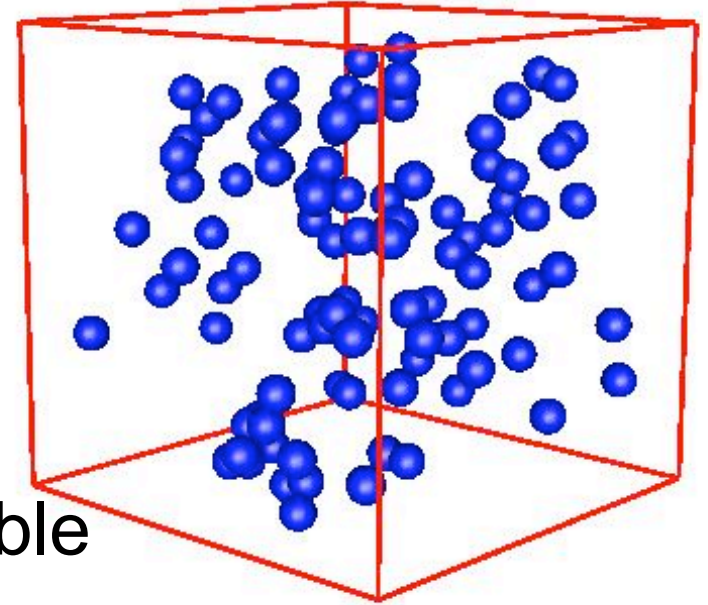
- Partition Function:

- V_{ξ} :: “Volume of the ensemble” but more than just normalization



Stat. Mech. & Ergodicity

$$\langle A \rangle_t = \frac{1}{t} \int_0^t A(\xi(t')) dt'$$



- Fundamental hypothesis:
 - Ensemble average = Observable
 - Ergodicity:
 - all accessible states of a given energy are equally probable over a long period of time

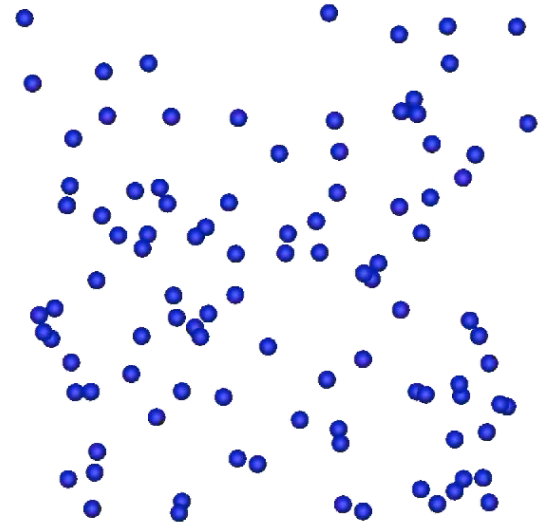
$$\langle A \rangle_{\xi} = \langle A \rangle_t$$

- Poincare Theorem suggests, but does not prove it!



Time- vs. Ensemble- Averages & MD Simulations

- Exploring the ensemble computationally
 - Molecular dynamics:
 - Integrate Newton's equations of motion
 - Configurations are “snapshots” of the system at different instances in time



$$\langle A \rangle = \frac{1}{T} \int_0^T dt A(t)$$

$$\langle KE \rangle = \frac{1}{\chi} \sum_i \left(\sum_j^N \frac{p_i^2}{2m_i} \right)_j$$



Time- vs. Ensemble- Averages & MC Simulations

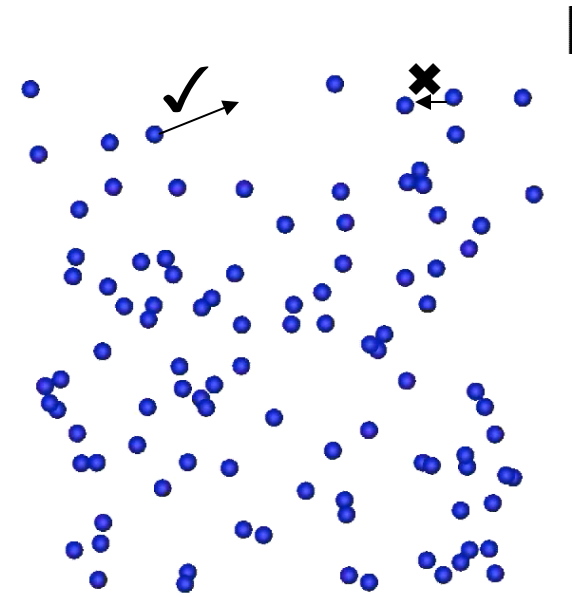
- Exploring the ensemble computationally

- Monte Carlo:

- Choose different configurations randomly

$$\langle A \rangle = \frac{1}{N} \sum_{\xi} A(\xi) P(\xi)$$

- Accept or reject a new configurations based on energy criterion (biased sampling, e.g., Metropolis)



Entropy and Probability

- Boltzmann Equation:

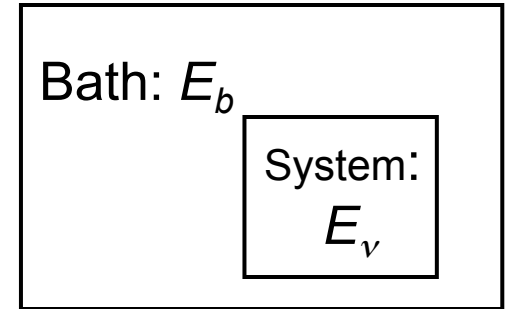
$$S = k_B \ln(\Omega(N, V, E))$$

- Statistical mechanics thereby connects macroscopic and microscopic mechanics (viz., thermo & CM)!
- Ω is the microcanonical partition function
 - number of states available at a given N, V, E
- Information theory entropy
 - Why the log?
 - Ω is a product of the number of states, but S is an extensive variable
- Units! (Energy/Temperature)



Microcanonical to Canonical

- Construct canonical ensemble using a (β, V, N) subsystem inside a large microcanonical (E, V, N) bath
- If the system is in state, ν , the # of states accessible to S+B: $\Omega(E_b) = \Omega(E - E_\nu)$
- The probability to observe the system in state ν :



$$E_T = E_b + E_\nu = \text{const}$$

$$E_b \gg E_\nu$$

$$P_\nu = \frac{\Omega(E_b)}{\Omega(E)} \propto \Omega(E - E_\nu)$$

$$\propto \exp[\ln(\Omega(E - E_\nu))]$$

$$\propto \exp\left[\ln(\Omega(E)) - E_\nu \frac{d \ln \Omega}{dE}\right]$$

$$\Rightarrow P_\nu \propto e^{-\beta E_\nu}$$

- From the probabilities, we obtain the partition function:

$$Q(\beta, N, V) = \sum_\nu e^{-\beta E_\nu}$$



Q: Observables & Ω

- The average energy:

$$\langle E \rangle = \frac{1}{Q} \sum_v E_v e^{-\beta E_v} = -\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right) = -\frac{\partial \ln(Q)}{\partial \beta}$$

- Also, the Helmholtz free energy:

$$-\frac{\partial \ln(Q)}{\partial \beta} = \langle E \rangle = \frac{\partial(\beta A)}{\partial \beta} \Rightarrow \beta A = -\ln(Q)$$

- Q and Ω are Laplace Transforms of each other w.r.t. S-conjugate variables, β and E !

$$Q(\beta, N, V) = \sum_v e^{-\beta E_v} = \int \Omega(E) e^{-\beta E} dE$$



Generalized Ensembles, I

$$\frac{1}{k_B} dS(E, X) = \beta dE + (\beta f) dX$$

In general:

$$P_v \left(\beta, \{X_i\}, \{-\beta f_j\} \right) = e^{-\beta E_v + \beta f_j X_{v,j}}$$

Legendre transform the exponent to identify the S-conjugate variables with to Laplace transform between ensembles

The Gibb's entropy formula:

$$S \left(\beta, \{X_i\}, \{-\beta f_j\} \right) = k_B \sum_v P_v \ln(P_v)$$



Generalized Ensembles, II

- Microcanonical: $\Omega(N, V, E)$ or $\Omega(E, V, N)$
- Canonical: $Q(N, V, \beta)$ or $Q(T, V, N)$
- Grand Canonical: $\Xi(\beta\mu, V, \beta)$ or $\Xi(T, V, \mu)$
- Isothermal-Isobaric: $\Delta(N, -\beta P, \beta)$ or $\Delta(T, P, N)$

e.g., for constant pressure and N (Isothermal-Isobaric) simulations, the probabilities are:

$$P_v(\beta, -\beta P, N) = e^{-\beta E_v + \beta P V_v}$$



Noninteracting Systems

- Separable Approximation

$$\text{if } H(q_a, q_b, p_a, p_b) = H(q_a, p_a) + H(q_b, p_b)$$

$$\Rightarrow Q = Q_a Q_b$$

- Note: $\ln Q$ is extensive!
- Thus noninteracting (ideal) systems are reduced to the calculation of one-particle systems!
- Strategy: Given any system, use CT's to construct a non-interacting representation!
 - Warning: Integrable Hamiltonians may not be separable



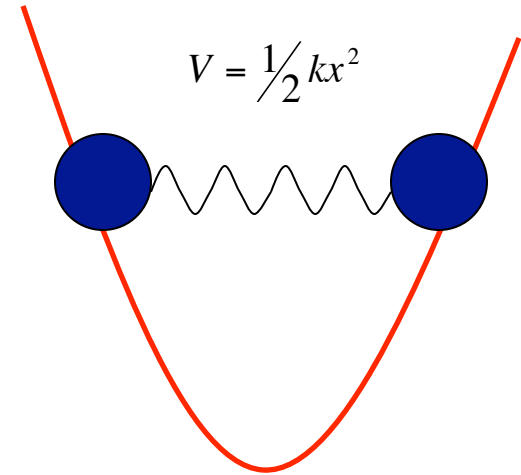
Harmonic Oscillator, I

In 1-dimension, the H-O potential:

$$V = \frac{1}{2} kx^2$$

The Hamiltonian:

$$H = T + V = \frac{p^2}{2m} + \frac{1}{2} kx^2 = E$$



The Canonical partition function:

$$Q = \left(\frac{1}{2\pi\hbar} \right) \int dx \int dp e^{-\beta H(x,p)} = \left(\frac{1}{2\pi\hbar} \right) \int e^{-\frac{\beta}{2} kx^2} dx \int e^{-\frac{\beta p^2}{2m}} dp$$





Gaussian Integrals

$$x = r \cos \theta$$

$$y = r \sin \theta$$

$$r^2 = x^2 + y^2$$

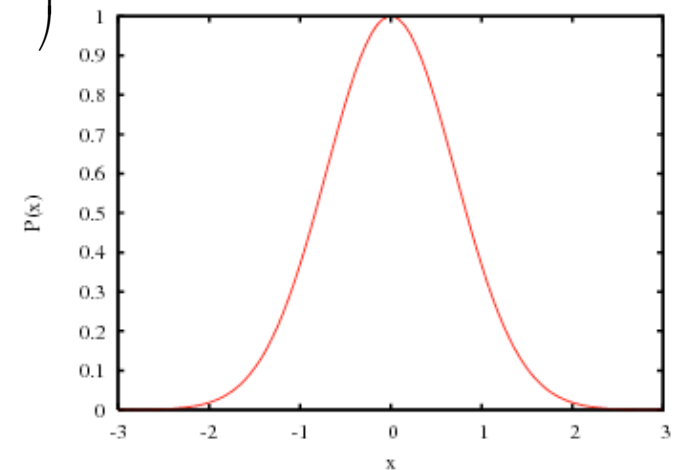
$$dxdy = r dr d\theta$$

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \left(\int_{-\infty}^{\infty} e^{-ay^2} dy \int_{-\infty}^{\infty} e^{-ax^2} dx \right)^{1/2} = \left(\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{-a(x^2+y^2)} \right)^{1/2}$$

$$= \left(\int_0^{2\pi} d\theta \int_0^{\infty} r e^{-ar^2} dr \right)^{1/2}$$

$$= \left(2\pi \times \frac{1}{2} \int_0^{\infty} e^{-au} du \right)^{1/2} \quad \text{where } u = r^2 \text{ and } du = 2r dr$$

$$= \left(\pi \left(0 - \frac{1}{a} \right) \right)^{1/2} = \left(\frac{\pi}{a} \right)^{1/2}$$



$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$



Harmonic Oscillator, II

The Canonical partition function:

$$Q = \left(\frac{1}{2\pi\hbar} \right) \int e^{-\frac{\beta}{2} kx^2} dx \int e^{-\frac{\beta p^2}{2m}} dp$$

After the Gaussian integrals:

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

$$Q = \left(\frac{1}{2\pi\hbar} \right) \left(\sqrt{\frac{2\pi}{\beta k}} \right) \left(\sqrt{\frac{2\pi m}{\beta}} \right) = \sqrt{\frac{m}{\hbar^2 \beta^2 k}}$$

Where:

$$\omega \equiv \sqrt{\frac{k}{m}} \quad \Rightarrow \quad Q = \frac{1}{\hbar\beta\omega}$$



Harmonic Oscillator, III

The Canonical partition function:

$$Q = \left(\frac{1}{2\pi\hbar} \right) \int e^{-\frac{\beta}{2} kx^2} dx \int e^{-\frac{\beta p^2}{2m}} dp$$

But transforming to action-angle variables...

$$Q = \left(\frac{1}{2\pi\hbar} \right) \int_0^{2\pi} d\theta \int_0^{\infty} e^{-\beta\omega I} dI$$

$$= \left(\frac{1}{2\pi\hbar} \right) \times 2\pi \times \left(\frac{1}{\beta\omega} \right)$$

$$\Rightarrow Q = \frac{1}{\hbar\beta\omega}$$



Classical Partition Function

- Note that we have a factor of Planck's Constant, h , in our classical partition functions:

$$Q = \left(\frac{1}{2\pi\hbar} \right)^N \int dx^N \int dp^N e^{-\beta H(x^N, p^N)}$$

- This comes out for two reasons:
 - To ensure that Q is dimensionless
 - To connect to the classical limit of the quantum HO partition function...

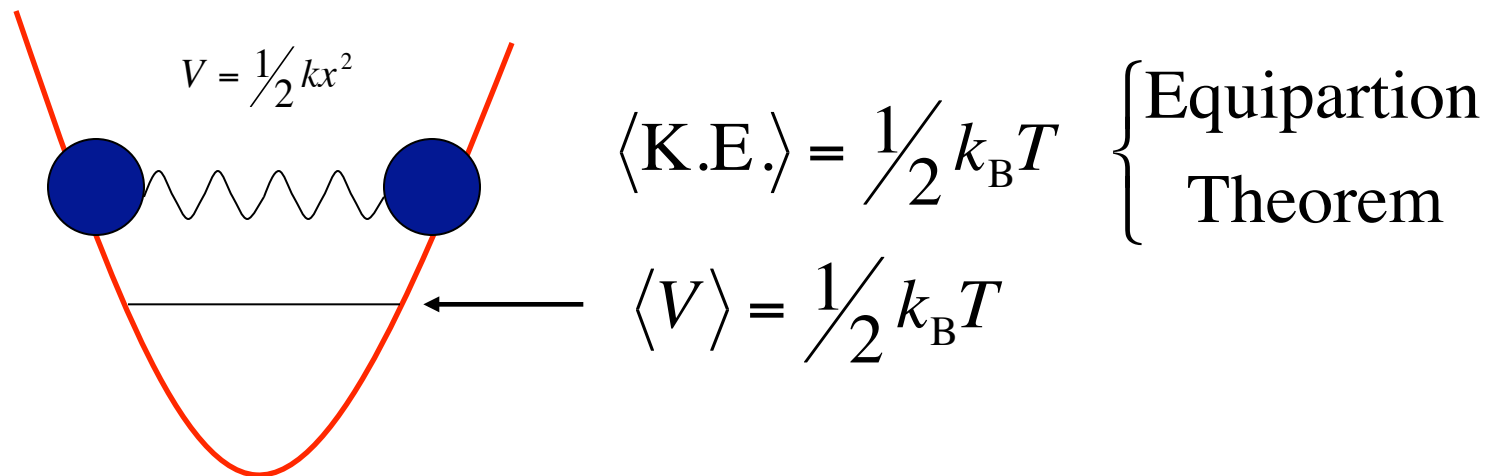


Harmonic Oscillator $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$

The Canonical partition function:

$$Q = \frac{1}{\hbar\beta\omega}$$

Recall $\langle E \rangle = -\frac{\partial \ln(Q)}{\partial \beta} = \frac{\partial}{\partial \beta} (\ln(\hbar\beta\omega)) = \frac{1}{\beta} = k_B T$



Gas

Consider N particles in volume, V
with a generic two-body potential:

$$V(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i < j} V_{ij}(|\vec{r}_i - \vec{r}_j|)$$

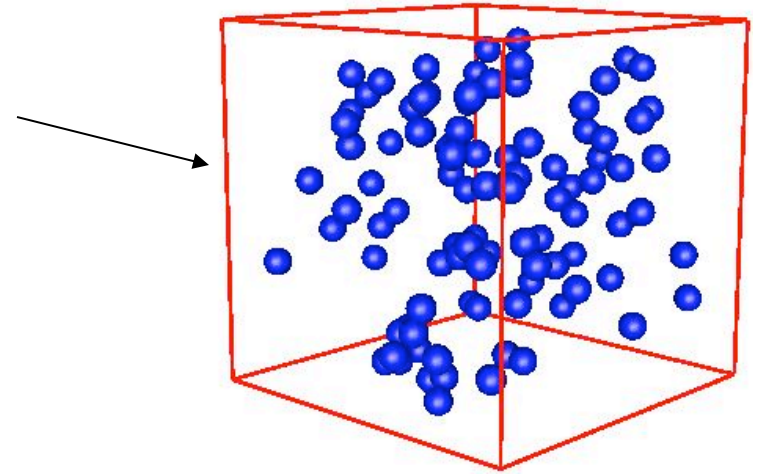
and kinetic energy:

$$T(\vec{p}_1, \dots, \vec{p}_N) = \sum_i \frac{\vec{p}_i^2}{2m_i}$$

The Canonical partition function:

$$Q = \left(\frac{1}{2\pi\hbar} \right)^{3N} \int d\vec{r} \int d\vec{p} e^{-\beta H(\vec{r}, \vec{p})}$$

$$d\vec{r} = dr_1 dr_2 \dots dr_N$$

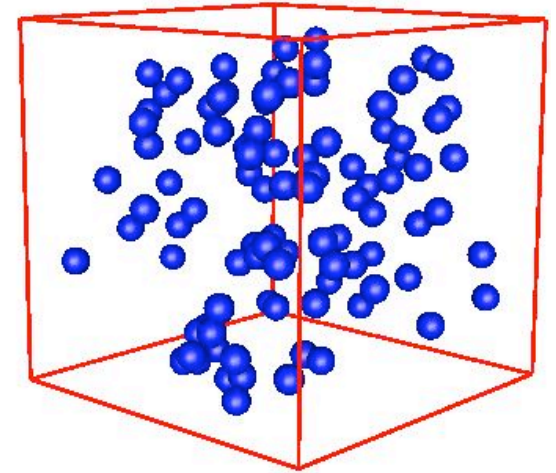


Integrating the K.E. Q in a Gas

$$Q = \left(\frac{1}{2\pi\hbar} \right)^{3N} \int d\vec{r} \int d\vec{p} e^{-\beta H(\vec{r}, \vec{p})}$$

May generally be written as: (**Warning:**
this is not separability!)

$$Q = \left(\frac{1}{2\pi\hbar} \right)^{3N} \int d\vec{p} e^{-\beta \sum_i^N \frac{p_i^2}{2m_i}} \int d\vec{r} e^{-\beta V(\vec{r})}$$



$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

With the generic solution for *any* system

$$Q = \left(\frac{1}{2\pi\hbar} \right)^{3N} \prod_i^N \left(\frac{2m_i\pi}{\beta} \right)^{3/2} \int d\vec{r} e^{-\beta V(\vec{r})}$$



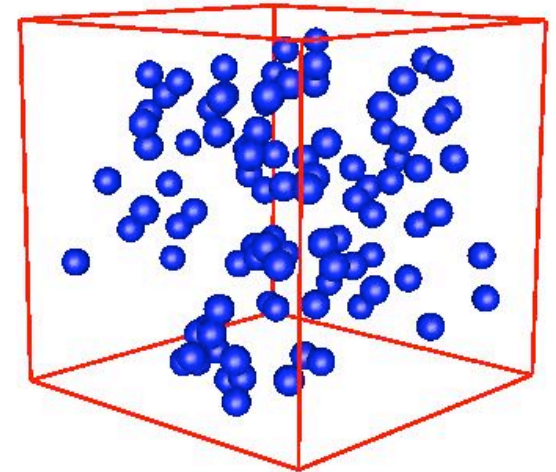
Interacting→Ideal Gas

Assume:

1. Ideal Gas $\rightarrow V(r)=0$
2. Only one molecule type: $m_i=m$

$$\int d\vec{r} e^{-\beta V(\vec{r})} = \int d\vec{r} = V^N$$

$$\prod_i^N \left(\frac{2m_i\pi}{\beta} \right)^{3/2} = \left(\frac{2m\pi}{\beta} \right)^{3N/2}$$



The ideal gas partition function:

$$Q = \left(\frac{1}{2\pi\hbar} \right)^{3N} \left(\frac{2m\pi}{\beta} \right)^{3N/2} V^N$$



The Ideal Gas Law

$$Q = \left(\frac{1}{2\pi\hbar} \right)^{3N} \left(\frac{2m\pi}{\beta} \right)^{3N/2} V^N$$

Recall:

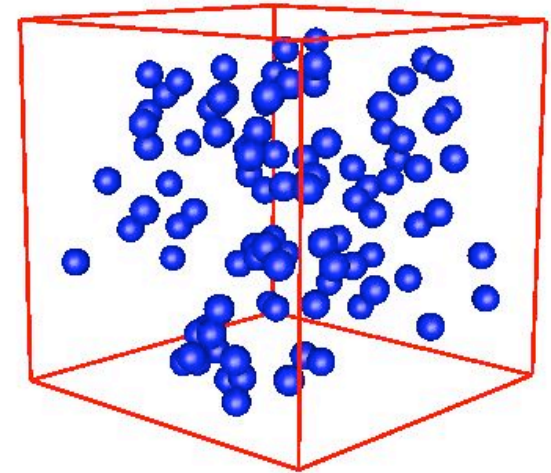
$$dA = -SdT - PdV + \mu dN$$

$$A = -k_B T \ln(Q)$$

The Pressure

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T,N}$$

$$P = k_B T \frac{\partial \ln(Q)}{\partial V}$$



$$P = k_B T \frac{N}{V}$$

Ideal Gas Law!



Ideal Gas: Other Observables

$$E(T, V, N) = -\frac{\partial \ln Q}{\partial \beta}$$

$$Q = \left(\frac{1}{2\pi\hbar} \right)^{3N} \left(\frac{2m\pi}{\beta} \right)^{3N/2} V^N$$

$$A(T, V, N) = -kT \ln Q$$

$$S(T, V, N) = \frac{E - A}{T} \quad \text{Recall: } A = E - TS$$

$$\Delta(T, P, N) = \int_0^{\infty} e^{-\beta PV} Q(T, V, N) dV$$

$$G(T, p, N) = -kT \ln \Delta$$

$$S(T, p, N) = k \ln \Delta + kT \left(\frac{\partial \ln \Delta}{\partial T} \right)_{N, P}$$

