Introduction to Statistical Thermodynamics – 2

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Review of Previous Lecture

- Molecular Partition Function
  - Effective way of calculating average properties (macroscopic) of a system with given quantum state.
- Probability

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_j e^{-\beta\varepsilon_j}} = \frac{e^{-\beta\varepsilon_i}}{q}$$

- Molecular partition function

$$q = \sum_j e^{-\beta\varepsilon_j}$$

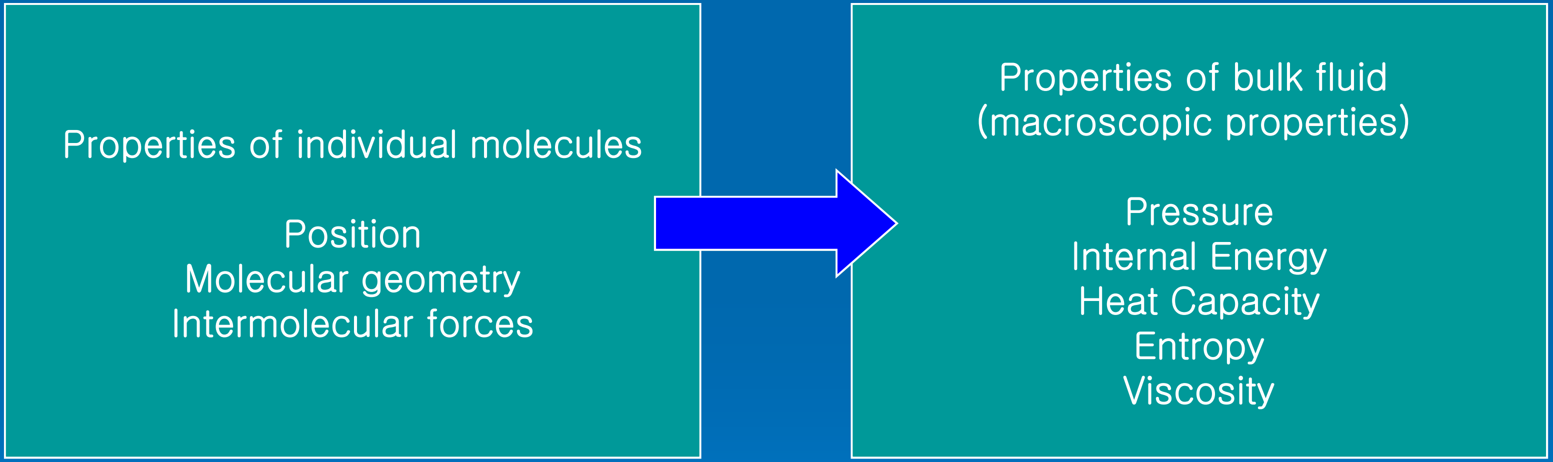
- Molecular partition function indicates number of possible state that are thermally available at T.

Objectives of 2nd Lecture

- Ensemble Average Method
- Thermodynamic properties and the Canonical Ensemble
- Link between classical and quantum mechanics : Phase Space
- Semi classical partition function
- Very Simple example of Monte-Carlo Simulation

Introduction

- Statistical Mechanics



Properties of individual molecules

Position
Molecular geometry
Intermolecular forces

Properties of bulk fluid
(macroscopic properties)

Pressure
Internal Energy
Heat Capacity
Entropy
Viscosity

What we have learned from previous lecture...

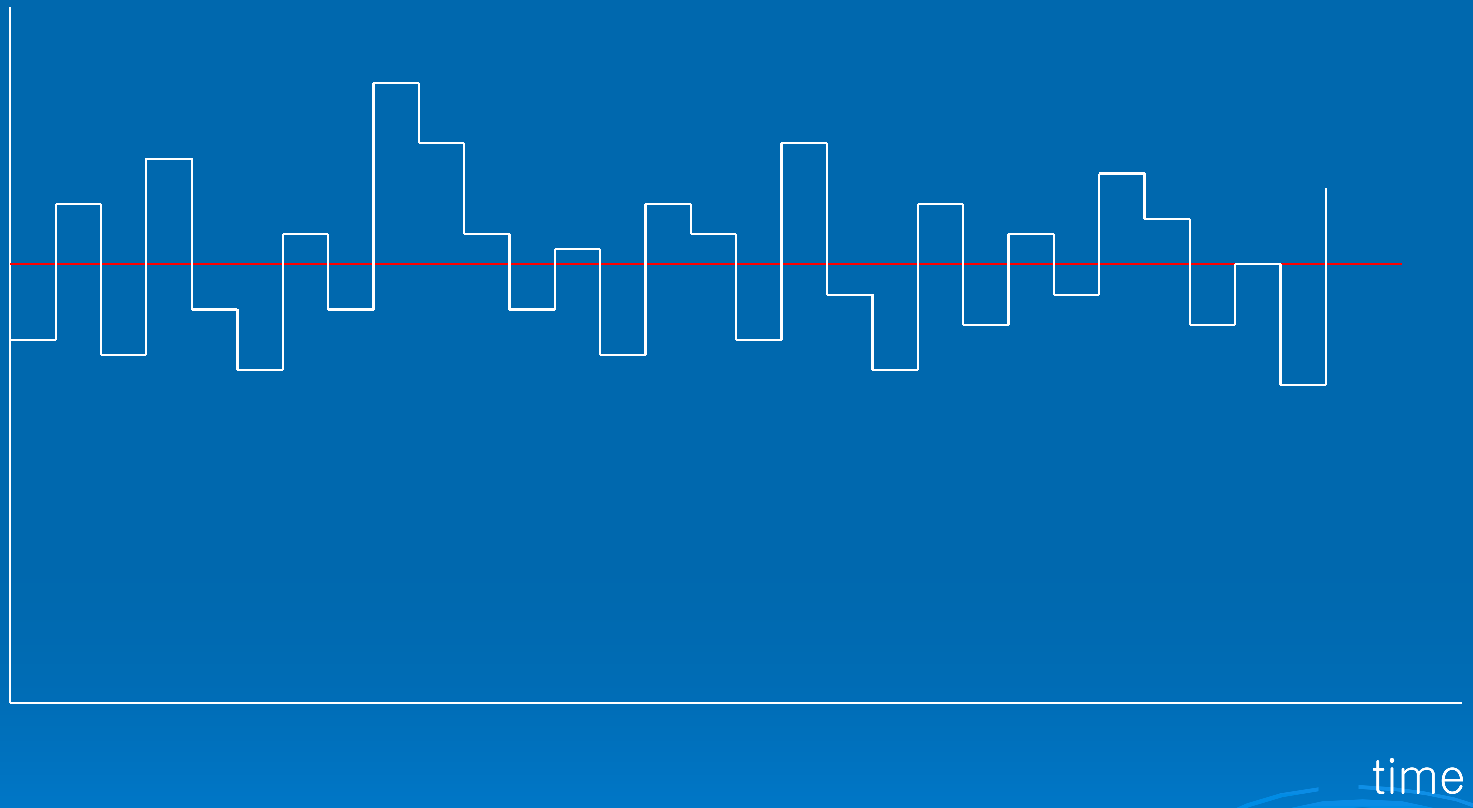
- Solution to Schrodinger equation (Eigen-value problem)
  - Wave function
  - Allowed energy levels : E_n

$$-\sum_i \frac{h^2}{8\pi^2 m_i}\nabla_i^2\Psi + U\Psi = E\Psi$$

- Using the molecular partition function, we can calculate average values of property at given QUANTUM STATE.

- Quantum states are changing so rapidly that the observed dynamic properties are actually time average over quantum states.

Fluctuation with time…



Although we know most probable distribution of energies of individual molecules at given N and E (previous section – molecular partition function) it is almost impossible to get time average for interacting molecules

Thermodynamic Properties

- Entire set of possible quantum states

$$\Psi_1, \Psi_1, \Psi_1, \ldots \Psi_i, \ldots$$

$$E_1, E_2, E_3, \ldots, E_i, \ldots$$

- Thermodynamic internal energy

$$U = \lim_{\tau \to \infty} \frac{1}{\tau} \sum_i E_i \Delta t_i$$

Difficulties

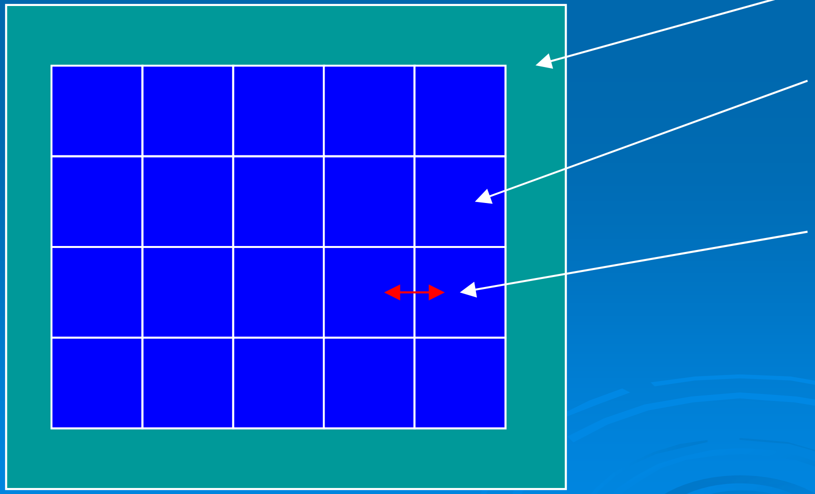
- Fluctuations are very small
- Fluctuations occur too rapidly

→ We have to use alternative, abstract approach.

→ Ensemble average method

Alternative Procedure

- Proposed by Gibbs
  - Ensemble Method
  - Ensemble ? : Infinite number of mental replica of the system of interest



Large Reservoir (const.T)

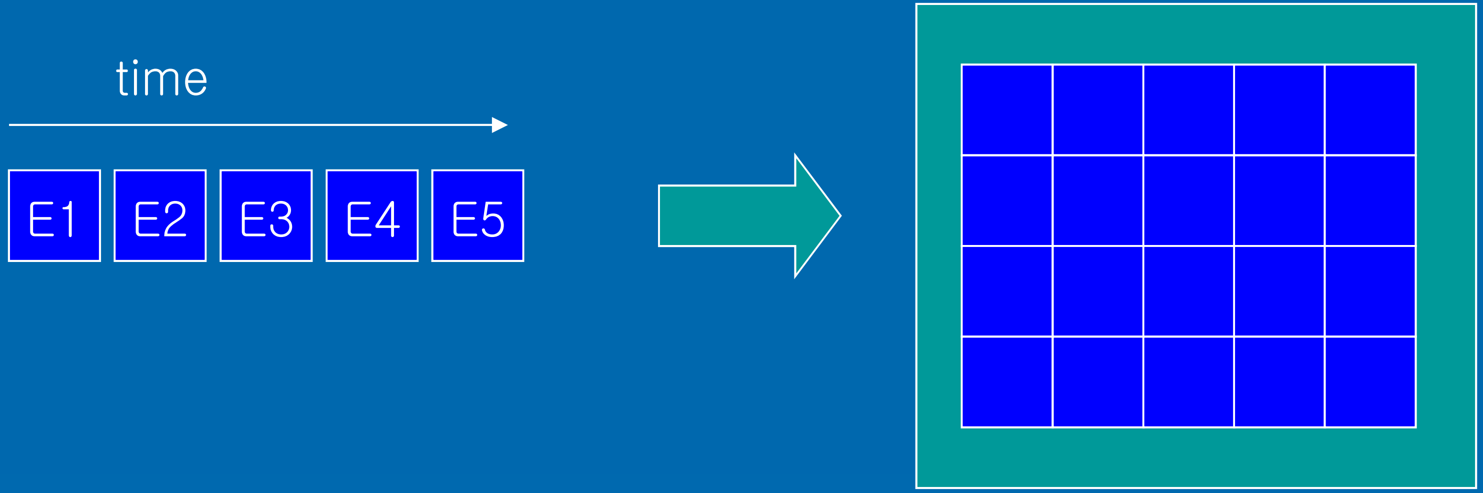
All the ensemble members have the Same N,V.T

Energies can be exchanged but molecules cannot.

Current <u>N</u> = 20
but <u>N</u> → infinity

Two postulates

- Long time average = Ensemble average at N → infinity


time

E1 E2 E3 E4 E5

- In an ensemble , the systems of enembles are distributed uniformly (equal probability or frequency)
  - → Ergodic Hypothesis
  - → Principle of equal a priori probability

Averaging Method

- Probability of observing particular quantum state i

$$P_i = \frac{n_i}{\sum_i n_i}$$

- Ensemble average of a dynamic property

$$< E >= \sum_i E_i P_i$$

- Time average and ensemble average

$$U = \lim_{\tau \to \infty} \sum E_i \Delta t_i = \lim_{n \to \infty} \sum_i E_i P_i$$

Calculation of Probability in Ensemble

- Several methods are available
  - Method of Undetermined multiplier
  - :
  - :

Maximization of Weight
– Most probable distribution

- Weight

$$W = \frac{N!}{n_1!n_2!n_3!\ldots} = \frac{N!}{\prod_i n_i!}$$

The Boltzmann Distribution

- Task : Find the dominating configuration for given N and total energy E.
- → Find Max. W which satisfies ;

$$\begin{aligned} N &= \sum_i n_i \\ E_t &= \sum_i E_i n_i \end{aligned} \quad \Longrightarrow \quad \begin{aligned} \sum_i dn_i &= 0 \\ \sum_i E_i dn_i &= 0 \end{aligned}$$

Method of Undetermined Multipliers

- Maximum weight , W
  - Recall the method to find min, max of a function…

$$d \ln W = 0$$

$$\left(\frac{\partial \ln W}{dn_i} \right) = 0$$

- Method of undetermined multiplier :
  - Constraints should be multiplied by a constant and added to the main variation equation.

Method of undetermined multipliers

$$d\ln W = \sum_i \left(\frac{\partial \ln W}{dn_i}\right) dn_i + \alpha \sum_i dn_i - \beta \sum_i E_i dn_i$$

$$= \sum_i \left\{ \left(\frac{\partial \ln W}{dn_i}\right) + \alpha - \beta E_i \right\} dn_i = 0$$

⇓

$$\left(\frac{\partial \ln W}{dn_i}\right) + \alpha - \beta E_i = 0$$

$$\ln W = N \ln N - \sum n_i \ln n_i$$

$$\left(\frac{\partial \ln W}{\partial n_i}\right) = \frac{\partial N \ln N}{\partial n_i} - \sum_j \frac{\partial (n_j \ln n_j)}{\partial n_i}$$

$$\frac{\partial N \ln N}{\partial n_i} = \left(\frac{\partial N}{\partial n_i}\right) \ln N + N \times \frac{1}{N}\left(\frac{\partial N}{\partial n_i}\right) = \ln N + 1$$

$$\sum_j \frac{\partial (n_j \ln n_j)}{\partial n_i} = \sum_j \left\{ \left(\frac{\partial n_j}{\partial n_i}\right) \ln n_j + n_j \times \frac{1}{n_j}\left(\frac{\partial n_j}{\partial n_i}\right) \right\} = \ln n_i + 1$$

$$\Downarrow$$

$$\frac{\partial \ln W}{\partial n_i} = -(\ln n_i + 1) + (\ln N + 1) = -\ln \frac{n_i}{N}$$

$$-\ln\frac{n_i}{N}+\alpha+\beta E_i=0$$

$$\frac{n_i}{N}=e^{\alpha-\beta E_i}$$

$$N=\sum_j n_j=Ne^{\alpha}\sum_j e^{-\beta E_j}$$

$$e^{\alpha}=\frac{1}{\sum_j e^{-\beta E_j}}$$

$$P_i=\frac{n_i}{N}=\frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}$$

Boltzmann Distribution

(Probability function for energy distribution)

Canonical Partition Function

- Boltzmann Distribution

$$P_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Q}$$

- Canonical Partition Function

$$Q = \sum_j e^{-\beta E_j}$$

Thermodynamic Properties and Canonical Ensemble

Internal Energy

$$U =< E >= \sum_i E_i P_i == \frac{1}{Q} \sum_{i(qs)} E_i e^{-\beta E_i}$$

$$\left(\frac{\partial Q}{\partial \beta} \right)_{N,V} = -\sum_{i(qs)} E_i e^{-\beta E_i}$$

$$U = -\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{N,V} = -\left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V}$$

Thermodynamic Properties and Canonical Ensemble

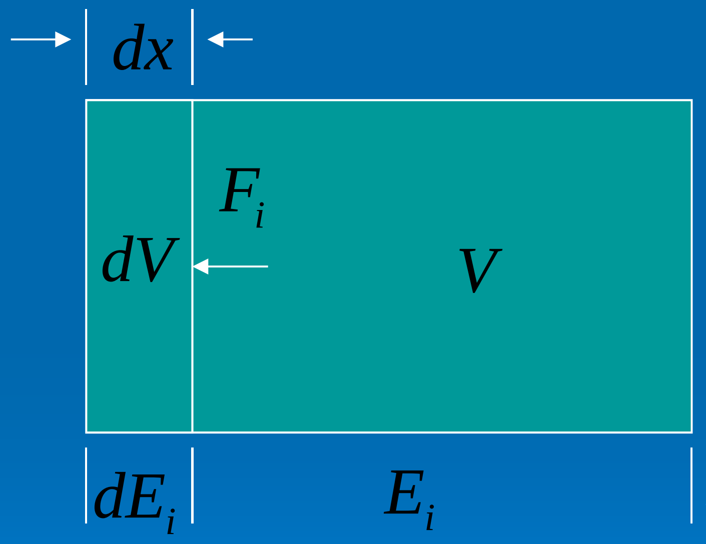
Pressure at i state

$$(\delta w_i)_N = P_i dV = F_i dx$$

$$(dE_i)_N = -F_i dx = -P_i dV = -\delta w_i$$

$$P_i = -\left(\frac{\partial E_i}{\partial V}\right)_N$$

Small Adiabatic expansion of system



Thermodynamic Properties and Canonical Ensemble

Pressure

Pressure at
quantum state i

Probability

$$P = \langle P \rangle = \sum_i P_i \mathrm{P}_i$$

$$P = \frac{1}{Q}\sum_i P_i e^{-\beta E_i} = \frac{1}{Q}\sum_i \left(\frac{\partial E_i}{\partial V}\right)_N e^{-\beta E_i}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{\beta,N} = \frac{\beta}{Q}\sum_i \left(\frac{\partial E_i}{\partial V}\right)_N e^{-\beta E_i}$$

$$P = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\ln V}\right)$$

→ *Equation of State in Statistical Mechanics*

Thermodynamic Properties and Canonical Ensemble

Entropy

$$dU = \delta q_{rev} - \delta w_{rev}$$

$$dU = d\left(\sum_i E_i P_i\right) = \sum_i E_i dP_i + \sum_i P_i dE_i$$

$$\sum_i P_i dE_i = \sum_i P_i \left(\frac{\partial E_i}{\partial V}\right)_N dV = -PdV = -\delta w_{rev}$$

$$\sum_i E_i dP_i = -\frac{1}{\beta}\left(\sum_i \ln P_i dP_i + \ln Q \sum_i dP_i\right)$$

$$= -\frac{1}{\beta}\sum_i \ln P_i dP_i$$

Thermodynamic Properties and Canonical Ensemble

Entropy

$$\sum_i P_i dE_i = -\frac{1}{\beta}\sum_i \ln P_i dP_i = \delta q_{rev}$$

$$\beta\delta q_{rev} = -d(\sum_i P_i \ln P_i) = \beta T dS$$

$$\beta\delta q_{rev} = d(U + \ln Q) = \beta T dS$$

$$S = k\ln Q + U/T + \cancel{S_0}$$

$$S = k\ln Q + U/T$$

$$S = -k\sum_i P_i \ln P = -k < \ln P >$$

The only function that links heat (path integral) and state property is TEMPERATURE.

$$\beta = 1/kT$$

Summary of Thermodynamic Properties in Canonical Ensemble

$$U = kT\left(\frac{\partial \ln Q}{\partial \ln T}\right)_{V,N}$$

$$S = k\left(\ln Q + \left(\frac{\partial \ln Q}{\partial \ln T}\right)_{V,N}\right)$$

$$H = kT\left(\left(\frac{\partial \ln Q}{\partial \ln T}\right)_{V,N} + \left(\frac{\partial \ln Q}{\partial \ln V}\right)_{T,N}\right)$$

$$A = -kT \ln Q$$

$$G = -kT\left(\ln Q - \left(\frac{\partial \ln Q}{\partial \ln V}\right)_{T,N}\right)$$

$$\mu_i = -kT\left(\frac{\partial \ln Q}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

All thermodynamic properties
Can be obtained from
“PARTITION FUNCTION”

Classical Statistical Mechanics

- It is not easy to derive all the partition functions using quantum mechanics

- Classical mechanics can be used with negligible error when energy difference between energy levels (Ei) are smaller thank kT.

- However, vibration and electronic states cannot be treated with classical mechanics. (The energy spacings are order of kT)

Phase Space

- Recall Hamiltonian of Newtonian Mechanics

$$H(\mathbf{r}^N, \mathbf{p}^N) = \mathrm{KE}(\text{kinetic energy}) + \mathrm{PE}(\text{potential energy})$$

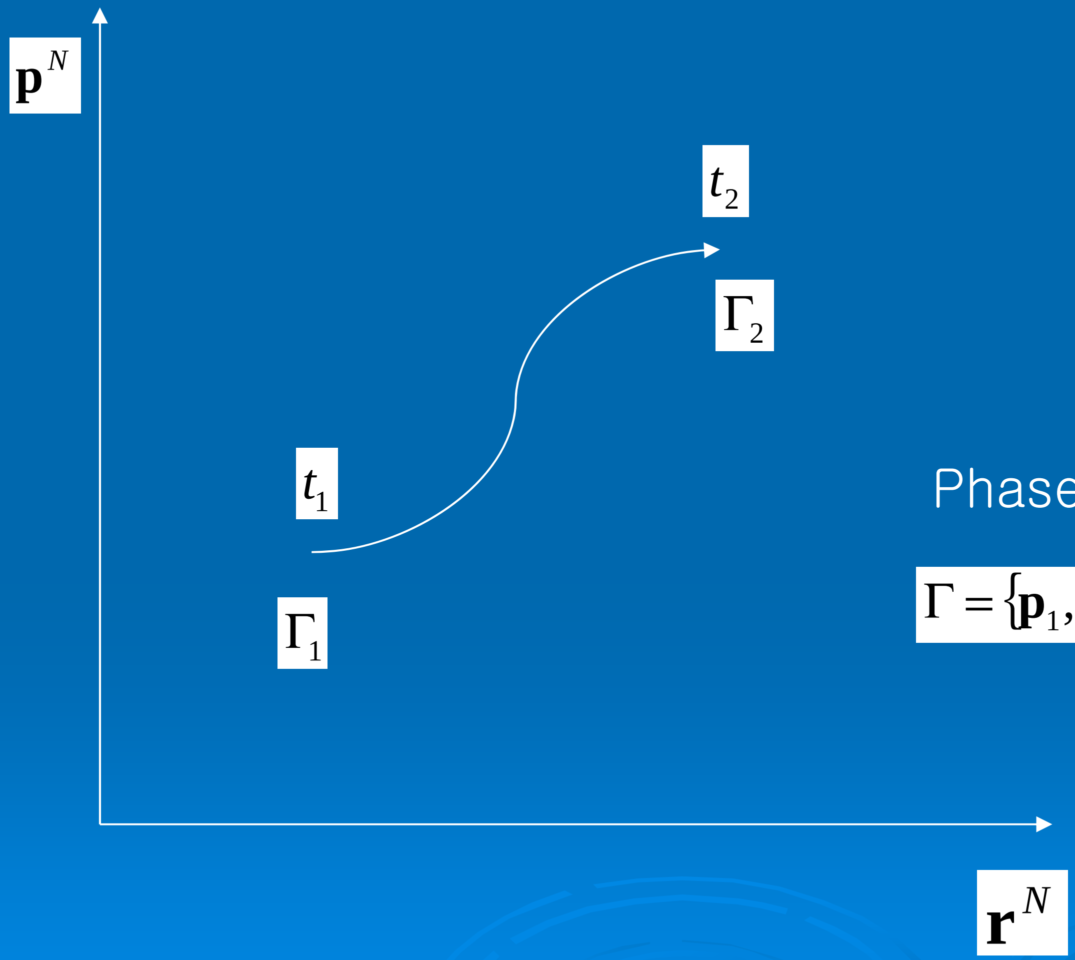
$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_i \frac{\mathbf{p}_i}{2m_i} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

$$\left[\frac{\partial H}{\partial \mathbf{r}_i}\right] = -\dot{\mathbf{p}}_i$$

$$\left[\frac{\partial H}{\partial \mathbf{p}_i}\right] = \dot{\mathbf{r}}_i$$

- Instead of taking replica of systems (ensemble members), use abstract ‘phase space’ compose of momentum space and position space (6N)
- → Average of infinite phase space

Phase Space



Phase space

$$\Gamma = \{\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, \ldots, \mathbf{p}_N, \mathbf{r}_1, \mathbf{r}_1, \mathbf{r}_3, \ldots, \mathbf{r}_N\}$$

Ensemble Average

$$U = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} E(\Gamma)d\tau = \lim_{n\to\infty}\int \mathcal{P}_N(\Gamma)E(\Gamma)d\Gamma$$

$$\mathcal{P}_N(\Gamma)d\Gamma$$ → Fraction of Ensemble members in this range (Γ τo Γ+dΓ)

↓ Using similar technique used for Boltzmann distribution

$$\mathcal{P}_N(\Gamma)d\Gamma = \frac{\exp(-H/kT)d\Gamma}{\int\ldots\int \exp(-H/kT)d\Gamma}$$

Canonical Partition Function

Phase Integral

$$\mathcal{T} = \int \ldots \int \exp(-H/kT)\,d\Gamma$$

Canonical Partition Function

$$Q = c \int \ldots \int \exp(-H/kT)\,d\Gamma$$

Match between Quantum and Classical Mechanics

$$c = \lim_{T \to \infty} \frac{\sum_i \exp(-E_i/kT)}{\int \ldots \int \exp(-H/kT)\,d\Gamma} \quad \longrightarrow \quad c = \frac{1}{N!\,h^{NF}}$$

For rigorous derivation see Hill, Chap.6

Canonical Partition Function in Classical Mechanics

$$Q = \frac{1}{N!h^{NF}} \int \ldots \int \exp(-\mathbf{H}/kT)\,d\Gamma$$

Example : Translational Partition Function for an Ideal Gas

$$H(\mathbf{r}^N,\mathbf{p}^N) = \text{KE(kinetic energy)} + \text{PE(potential energy)}$$

$$H(\mathbf{r}^N,\mathbf{p}^N) = \sum_i \frac{\mathbf{p}_i}{2m_i} + U(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$$

$$H = \sum_i^{3N} \frac{p_i^{\,2}}{2m_i}$$

No potential energy, 3 dimensional space.

$$Q = \frac{1}{N!h^{3N}} \int\ldots\int \exp(-\sum_i \frac{p_i^2}{2m_i}) dp_1\ldots dp_N dr_1\ldots dr_N$$

$$= \frac{1}{N!h^{3N}} \left[\int_{-\infty}^{\infty} \exp(-\frac{p}{2m_i}) dp \right]^{3N} \left[\int_0^V dr_1 dr_2 dr_3 \right]^N$$

$$= \frac{1}{N!} \left[\frac{2\pi mkT}{h^2} \right]^{3N/2} V^N$$

Semi-Classical Partition Function

The energy of a molecule is distributed in different modes

- Vibration, Rotation (Internal : depends only on T)
- Translation (External : depends on T and V)

Assumption 1

Hamiltonian operator can be separated into two parts
(internal + center of mass motion)

$$H_{op} = H_{op}^{CM} + H_{op}^{\text{int}}$$

$$Q = \sum \exp(-\frac{E_i^{CM} + E_i^{\text{int}}}{kT}) = \sum \exp(-\frac{E_i^{CM}}{kT}) \sum \exp(-\frac{E_i^{\text{int}}}{kT})$$

$$Q = Q_{CM}(N,V,T) Q_{\text{int}}(N,T)$$

Semi-Classical Partition Function

- Internal parts are density independent and most of the components have the same value with ideal gases.

$$Q_{\text{int}}(N,\rho,T)=Q_{\text{int}}(N,0,T)$$

- For solids and polymeric molecules, this assumption is not valid any more.

Semi-Classical Partition Function

Assumption 2

For T > 50K, classical approximation can be used for translational part.

$$H_{CM} = \sum_i \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2m} + U(r_1, r_2, \ldots, r_{3N})$$

$$Q = \frac{1}{N!h^{3N}} \int \ldots \int \exp(-\sum_i \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2mkT}) dp^{3N} \int \ldots \int (-U / kT) dr^{3N}$$

$$= \frac{\Lambda^{-3N}}{N!} Z$$

$$\Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{1/2}$$

$$Z = \int \ldots \int (-U / kT) dr_1 dr_2 \ldots dr_{3N}$$

Configuration Integral

$$Q = \frac{1}{N!} Q_{\text{int}} \Lambda^{-3N} Z$$

For non-central forces (orientation effect)

$$Z = \left(\frac{1}{\Omega} \right)^N \int \ldots \int (-U / kT) dr_1 dr_2 \ldots dr_{3N} d\omega_1 \ldots d\omega_N$$

$$\Omega = \int d\omega$$

Configuration Integral and Molecular Simulation

$$< A >= \frac{\int A(\mathbf{r})(-U(\mathbf{r})/kT)d\mathbf{r}}{\int (-U(\mathbf{r})/kT)d\mathbf{r}}$$

Introduction to Monte-Carlo Simulation

- Monte Carlo Method : Wide range of problem solving tool using RANDOM NUMBERS
- Monte Carlo ? – coined after casino
  - In principle any method that uses random number to solve a problem is a Monte Carlo Method

A Classical Example

- Calculation of pi

- Trial shots are generated between 0 and 1 (x and y)
- Compare x^2 + y ^2 < 1 or not
- If true, add to the number of successful shot
- Pi = 4H/N
  - N : Area of Rectangle (1*1)
  - 4H : Area of ¼ circle (pi*1*1/4)