

## Statistical Mechanics

### Description

- 1) *Mechanics*: **Classical**: position, momentum, force, equations of motion, time evolution  
**Quantum**: uncertainty principle, wave function, “wave” equations
- 2) *Thermodynamics*: work, heat, energy, entropy, processes, equilibria, non-equilibrium thermodynamics.
- 3) **Statistical thermodynamics**: postulates, ensembles, partition functions, thermodynamic quantities
- 4) **Statistics**: probability, averages, variance, covariance, tests, analysis, trends

### Classical Mechanics

1) Equations  $\vec{F} = m \frac{d^2\vec{r}}{dt^2}; \quad v(t) - v(0) = \frac{1}{m} \int_0^t F(x,y,z,t') dt'$  ; is  
 $r(t) - r(0) = \int_0^t v(t') dt'$

2)  $\vec{r}' \text{ vs } t'$  a trajectory of the particle

Newton laws, Lagrange's and Hamiltonian's equations, equivalent forms for Newton's laws

Inter particle interaction  $\vec{F} = -Gm_1m_2\hat{r}/r^2$  only attractive!

### Quantum Mechanics

1)  $\Delta x \Delta p_x \geq \hbar/2; i\hbar \frac{\partial \psi(r,t)}{\partial t} = H\psi(r,t)$ ; solve the equation subject to boundary conditions

Note  $i = \sqrt{-1}$ , phase factor important in time evolution; derivation of intermolecular forces

## Thermodynamics

- 1)  $\Delta E = q + w$ ,  $\Delta S = q_{rev}/T$ ,  $S = \int_0^T \frac{C_p}{T} dT$ ,  $S(0) \rightarrow 0$  others  $f^{\text{th}}$  H, A, G,  $\mu_i$ ,  $K_{eq}$ ,  $\partial S/\partial t$  (non-eq. thermodynamics entropy production)

## Statistical Mechanics

- 3) 1) principle of equal a priori probabilities,  $p(E_1) = p(E_2)$  if  $E_1 = E_2$ ; see  $p(\text{head}) = p(\text{tail})$  if both faces are "equal"

- 2) Ensemble average = time average

→ Ensemble, partition function, thermodynamics  $Q = \sum_i e^{-\beta E_i}$ ,  $\beta = 1/k_B T$ ,  $\langle E \rangle = -\partial \ln Q / \partial \beta$

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

Input to st. thermo      Molecular energy levels, inter molecular forces.

$$\text{Time Av } \langle D \rangle_t = \lim_{t \rightarrow \infty} \frac{1}{t} \int D(t') dt'$$

$$\text{For discrete measurements, } \frac{1}{n} \sum_{i=1}^n D_i$$

i.e. Average speeds of molecules, Average energies, .. very difficult to measure

*Ensemble*: A large imaginary collection of systems with identical macroscopic parameters s. a.

N, V, E or N, V, T but different microscopic arrangements

Micro canonical ensemble



N, V, E

$$\text{Total energy of a member} = \sum n_i \epsilon_i$$

$n_i$  = no. of molecules with energy  $\epsilon_i$

$\epsilon_i$  measured w. r. t some reference z p e.

Each member isolated cannot exchange heat with surroundings.

Total energy E can be obtained in many ways

Eg. If  $N = 20$ , and  $E = 20\epsilon$  and molecular energies are  $\epsilon, 2\epsilon, 3\epsilon, \dots$

Then  $(\overset{1}{0'} \overset{1}{\epsilon'} \overset{1}{2 \epsilon'} \overset{1}{3 \epsilon'} \overset{1}{4 \epsilon'} \overset{2}{5 \epsilon'} \overset{0}{6 \epsilon'} \dots \dots 0)$  and  $W = \frac{20!}{1!2!3!..}$

$(0, 0, \dots, \overset{1}{20 \epsilon})$  are  $W = \frac{20!}{20!}$

Two possible arrangements given above giving  $E = 20\epsilon$

The no. of ways of achieving the above configurations is given by

$$W = \frac{N!}{n_1!n_2!\dots n_i!}$$

For large N, W increases very rapidly

W = weight of a configuration

Among many conceivable configurations, which is the most probable?

To find  $W_{\max}$ , use  $\ln W$

$$d(\ln W) = \sum_i \left( \frac{\partial \ln W}{\partial n_i} \right) dn_i \tag{1}$$

But all  $n_i$  s are not independent, as

$$\sum n_i = N = \text{constant} \text{ and } \sum \epsilon_i n_i = E = \text{constant}$$

$$\left. \begin{array}{l} \sum dn_i = 0 \\ \sum \epsilon_i dn_i = 0 \end{array} \right\} \begin{array}{l} - 2 \\ - 3 \end{array} \text{Constraints}$$

Use Lagrange's method of undetermined multipliers

$$d \ln W = \sum_i \frac{\partial \ln W}{\partial n_i} dn_i + \alpha \sum dn_i - \beta \sum \epsilon_i dn_i$$

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

4

As all  $n_i$ s are now independent

For the most probable distribution, the coefficient of each  $dn_i$  in (4) is zero

$$\frac{\partial \ln W}{\partial n_i} - \alpha + \beta \epsilon_i = 0$$

5

Use Stirling's approximation  $\ln N! = N \ln N - N$

$$\ln W = \ln N! - \ln (n_1! n_2! \dots)$$

$$= N \ln N - N - \sum_j n_j \ln n_j$$

$$\approx N \ln N - N - \sum_j n_j \ln n_j + \sum_j n_j$$

$$\approx N \ln N - \sum_j n_j \ln n_j$$

6

$$\frac{\partial \ln W}{\partial n_i} = -\ln n_i + 1 \text{ as } n_i \text{ and } n_j \text{ are independent}$$

$$\approx -\ln n_i \text{ as } n_i \text{ are also large}$$

$$\therefore -\ln n_i + \alpha - \beta \epsilon_i = 0 \text{ or } n_i^*, \text{ the most probable of } n_i$$

$$n_i^* = \exp(\alpha - \beta \epsilon_i)$$

7

$$\text{But } \sum n_i^* = N = \sum_i e^\alpha e^{-\beta \epsilon_i}$$

8

$$\therefore e^\alpha = N / \sum e^{-\beta\epsilon_i} \quad 9$$

From 7 and 9 
$$\frac{n_i^*}{N} = p_i = \frac{e^{-\beta\epsilon_i}}{\sum e^{-\beta\epsilon_i}} \quad 10$$

**Molecular partition function:**

$$q = \sum e^{-\beta\epsilon_i}, \quad \epsilon_i \approx \text{molecule energy states}$$

If  $i^{\text{th}}$  level has degeneracy  $g_i$ , then

$$q = \sum g_i e^{-\beta\epsilon_i}, \text{sum over levels}$$

eg: linear heteronuclear diatomic ( $\epsilon_j = hcBJ(J + 1)$ ;  $J = 0, 1, 2 \dots$ ;  $B = \text{rotational constant in cm}^{-1}$ )

e.g.  $B_{\text{HCl}^{35}} = 10.6 \text{ cm}^{-1}$

$B_{\text{H}_2} = 60.84 \text{ cm}^{-1}$

$J^{\text{th}}$  level is  $(2J+1)$  fold degenerate

(e.g. p level in H atom is 3 fold degenerate)

Distinguish between levels and states

$$\left. \begin{array}{l} 2p \dots \\ 2s \dots \\ 1s \dots \end{array} \right\} 3 \text{ levels, but 5 states}$$

$$q = \text{sum over states} = \sum_{j=0}^{\infty} (2J + 1) e^{-\beta hcBJ(J+1)}$$

Last lecture microcanonical ensemble N, V, E

T varies between systems.

T determined by the most probable distribution or distribution with maximum weight,  $W^*$

$$\frac{n_i}{N} = \frac{e^{-\beta \epsilon_i}}{q} = p_i ; \text{ plot } \ln p_i \text{ Vs } \epsilon_i \text{ to get slope} = -\beta$$

Canonical ensemble N, V, T fixed for each member.

Example

- 1) Imagine several 1 liter cells of water in a swimming pool
  - 2) Single 1 liter cell in the pool at different times
- Here  $E_i$  varies from member to member

What is  $p(E_i) = p_i$ , the probability that a given member with energy  $E_i$  ?

$p_i$  = fraction of members of the ensemble with energy  $E_i$

Construct ensemble as follows


$N$  = total no. of members of the ensemble

$n_i$  = no. of members with energy  $E_i$

$\sum n_i E_i = E$  total ensemble energy , fixed

$\sum n_i = N = \text{fixed}$

$W$  = wt .of the distribution  $n_0, n_1, \dots$

$W = \frac{N!}{\prod_i n_i!}$ , maximize  $W$  subject to the two constraints as in the earlier case

$$\frac{n_i^*}{N} = p_i = \frac{e^{-\beta E_i}}{\sum e^{-\beta E_i}} \text{ canonical probability} = \text{fraction of members with energy } E_i$$

= probability of finding a system with energy  $E_i$

Alternatively consider the role of the reservoir

$E_{\text{total}} - E_i$  = energy of reservoir

Consider an ensemble of such systems with different  $E_i$

We wish to calculate  $p_i = p(E_i)$  of the system

$p(E_i) \propto W'(E_{\text{total}} - E_i)$  = no. of ways in which the reservoir can accommodate energy  $E_i$

$$p(E_i) = C W'(E_{\text{total}} - E_i), C = \text{constant}$$

All members with  $E = E_i$  equally probable principle of equal a priori probability

Since  $E_i \ll E_{\text{total}}$ , expand  $\ln W'$  as

$$\ln W'(E_{\text{total}} - E_i) = \ln W'(E_{\text{total}}) - \underbrace{\left( \frac{\partial \ln W'}{\partial E} \right)_{E_t} \cdot E_i}_{\text{depends on } E_t \text{ \& reservoir}} + \dots$$

$$\text{Let } \beta = + \frac{\partial \ln W'}{\partial E}$$

$$\ln W'(E_{\text{total}} - E_i) = \ln W'(E_{\text{total}}) - \beta E_i$$

$$W'(E_{\text{total}} - E_i) = W' E_{\text{total}} e^{-\beta E_i}$$

## 13 Classical Limit

$dx dp_x \sim h$ , minimum volume of phase space ( $q, p$ )

Proportionality factor  $h^3$  for each particle

$N$  particles  $h^{3N}$

$$Q \rightarrow q^N / N!$$

$$Q = \sum_i e^{-\beta E_i} = \frac{1}{N! h^{3N}} \int dq^N dp^N e^{-\beta H(p,q)}$$

$$= Q_{cl}, \text{ the classical limit of } Q \text{ as } h \rightarrow 0; \sum_i \rightarrow \frac{1}{h^{3N} N!} \int dp^N \int dq^N$$

$$\text{Recall also, } q_{tr} = \left( \frac{2\pi m k T}{h^2} \right)^{3/2}$$

$$q_r = \frac{8\pi^2 I k T}{h} \text{ and } q_v = \frac{kT}{h\nu}$$

Quantum partition functions, i.e

Partition functions and averages in terms of operators and wave functions

$$Q = \sum e^{-\beta E_i}, \quad \langle M \rangle = \frac{\sum M_j e^{-\beta E_j}}{Q}$$

$\mathcal{H}$  = hamiltonian,  $E_j$  : eigenvalues and  $\psi_j$ : normalized eigenfunctions of  $\mathcal{H}$

$$\mathcal{H}\psi_j = E_j\psi_j; \quad \mathcal{H}^n\psi_j = E_j^n\psi_j$$

$$e^{-\beta\mathcal{H}}\psi_j = \left( \sum_{n=0}^{\infty} \frac{(-\beta)^n \mathcal{H}^n}{n!} \right) \psi_j$$

$$= \frac{\sum (-\beta)^n E_j^n \psi_j}{n!} = e^{-\beta E_j} \psi_j$$

$$e^{-\beta E_j} = \int \psi_j^* e^{-\beta\mathcal{H}} \psi_j d\tau$$

$$Q = \sum_j e^{-\beta E_j} = \sum_j \int \psi_j^* e^{-\beta\mathcal{H}} \psi_j d\tau; \quad d\tau = d\vec{r}^N$$

Generally  $(e^{-\beta\mathcal{H}})_{ij} = \int \psi_i^* e^{-\beta\mathcal{H}} \psi_j d\tau$ , a matrix element  $ij$  of the operator  $e^{-\beta\mathcal{H}}$

$$Q = \sum_j (e^{-\beta E_j})_{ii} = \text{Tr}(e^{-\beta\mathcal{H}}), \text{ the trace}$$

Trace is independent of the basis function  $\psi_j$  i.e. if  $\psi_j$  are replaced by  $\phi_j = \sum_n a_{jn} \psi_n$

$$\text{Where } a_{jn} = \int \psi_n^* \phi_j d\tau$$

1

$$\phi_j \text{ normalized, i.e. } \sum_j a_{jk}^* a_{jl} = \delta_{kl} \quad \sum_n a_{jn}^* a_{jn} = 1$$

$\psi_j$ s can be expressed in terms of  $\phi_t$ s too

$$\psi_s = \sum_t b_{st} \phi_t, \quad b_{st} = \int \phi_t^* \psi_s d\tau = a_{ts}^* \text{ From (1) } * = \text{complex conjugate}$$

$$\therefore \sum_n b_{jn}^* b_{jn} = \sum_n a_{nj}^* a_{nj} = 1$$

$$\text{Now } \int \phi_j^* e^{-\beta\mathcal{H}} \phi_j d\tau$$

$$= \sum_j \sum_m \sum_n a_{jm}^* a_{jn} e^{-\beta E_n} \underbrace{\int \psi_m^* \psi_n d\tau}_{\delta_{mn}}$$

$$= \sum_j \sum_n a_{jn}^* a_{jn} e^{-\beta E_n} = \sum_n e^{-\beta E_n} = Q$$

Independent of the orthonormal basis  $\phi_n$

$$(1) \int \phi_j^* \phi_l d\tau = \sum_n \sum_m \int a_{jn}^* a_{lm} \psi_n^* \psi_m d\tau$$

$$= \sum_n \sum_m a_{jn}^* a_{lm} \delta_{nm} = \sum_n a_{jn}^* a_{ln} = \delta_{jl}$$

If  $\hat{M}$  is the operator for variable M,  $M_{jj} = M_j = \int \psi_j^* \hat{M} \psi_j d\tau$

$$\begin{aligned} \sum_j M_j e^{-\beta E_j} &= \sum_j e^{-\beta E_j} \int \psi_j^* \hat{M} \psi_j d\tau = \sum_j \int \psi_j^* \hat{M} e^{-\beta E_j} \psi_j d\tau = \sum_j \int \psi_j^* \hat{M} e^{-\beta \mathcal{H}} \psi_j d\tau \\ &= \sum_j (\hat{M} e^{-\beta \mathcal{H}})_{jj} = T_r(\hat{M} e^{-\beta \mathcal{H}}) \end{aligned}$$

$$\therefore \langle M \rangle = \frac{\sum_j M_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \frac{T_r(\hat{M} e^{-\beta \mathcal{H}})}{T_r(e^{-\beta \mathcal{H}})}$$

Defining the density operator  $\hat{\rho}$  as

$$\hat{\rho} = \frac{e^{-\beta \mathcal{H}}}{T_r(e^{-\beta \mathcal{H}})}$$

The matrix elements of  $\hat{\rho}$  are the density matrix or the elements of the density matrix

$$\langle M \rangle = T_r(\hat{M} \hat{\rho})$$

As  $\hbar \rightarrow 0$  (the classical limit)

$$\langle M \rangle = \frac{\int \dots \int dp dq M(p,q) e^{-\beta \mathcal{H}(p,q)}}{\int \dots \int dp dq e^{-\beta \mathcal{H}(p,q)}}$$

Now we need to prove that

$$Q = \sum_j e^{-\beta E_j} \text{ becomes, as } \hbar \rightarrow 0 \quad \frac{1}{N! h^{3N}} \int \dots \int e^{-\beta H} d\vec{p}_1, \dots, d\vec{p}_N, d\vec{q}_1, \dots, d\vec{q}_N$$

## 14

$$Q = \sum_j \int \phi_j^* e^{-\beta \mathcal{H}} \phi_j d\tau \quad (1)$$

Derivation due to Kirkwood

$$\mathcal{H} = K + U = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + U(\vec{r}_1, \dots, \vec{r}_N)$$

To write (1) as an integral over  $p_s$  and  $q_s$ , use eigenfunctions of the momentum ( $\hat{p}$ ) operator

$$-i\hbar \vec{\nabla}; \quad p_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

$$u(\vec{p}_1, \vec{p}_2, \dots, \vec{r}_1, \dots, \vec{r}_N) = \exp \left[ \frac{i}{\hbar} \sum_{k=1}^N \vec{p}_k \cdot \vec{r}_k \right]; \quad -i\hbar \vec{\nabla}_i u = \vec{p}_i u$$

Express  $\phi_j$ s in terms of  $u_j$  i.e. expand  $\phi_j$  in terms of  $u$

$$\phi_j(\vec{r}_1 \dots \vec{r}_N) = \int \int A_j(\vec{p}_1, \dots, \vec{p}_N) e^{\frac{i}{\hbar} \sum p_k \cdot r_k} d\vec{p}_1 \dots d\vec{p}_N \quad (2)$$

We will avoid symmetry properties of  $\phi_j$  which give the factor  $N!$ ;  $\phi_j$  eigenfunctions of  $\mathcal{H}$

(2) gives  $\phi_j$  as a FT of  $A_j(\vec{p}_1, \dots, \vec{p}_N)$ . The inverse FT gives A

$$A_j(\vec{p}_1, \dots, \vec{p}_N) = \frac{1}{(2\pi\hbar)^{3N}} \int \dots \int \phi_j(\vec{r}_1, \dots, \vec{r}_N) e^{-\frac{i}{\hbar} \sum p_k \cdot r_k} d\vec{r}_1 \dots d\vec{r}_N \quad (3)$$

Use (2) in (1)

$$Q = \sum_j \int \dots \int \phi_j^*(\vec{r}_1, \dots, \vec{r}_N) A_j(\vec{p}_1, \dots, \vec{p}_N) e^{-\beta\mathcal{H}} e^{\frac{i}{\hbar} \sum p_k \cdot r_k} d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N$$

Express  $A_j$  using (3). Use  $r'_1, r'_2 \dots$  to distinguish between  $r_1$  &  $r'_1$  variables

$$Q = h^{-3N} \int \dots \int \left\{ \sum_j \phi_j^*(\vec{r}_1, \dots, \vec{r}_N) \phi_j(\vec{r}'_1, \dots, \vec{r}'_N) \right\} e^{-\beta\mathcal{H}} e^{\frac{i}{\hbar} \sum p'_k \cdot r'_k} e^{\frac{i}{\hbar} \sum p_k \cdot r_k} d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N d\vec{r}'_1 \dots d\vec{r}'_N \quad (4)$$

Properties of FTs and  $\delta$  functions  $g(k) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx$

$f(x)$ : Single valued, finite no. of finite discontinuities, maxima and minima and  $\int_{-\infty}^{\infty} |f(x)|^2 dx = \text{finite}$

$$f(x) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} g(k) e^{ikx} dk, \quad f(x), g(k) \text{ an FT pair}$$

$$\text{In 3d, } V(\vec{k}) = (2\pi)^{-3/2} \iiint_{-\infty}^{\infty} V(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} d\vec{r}$$

$$V(\vec{r}) = (2\pi)^{-3/2} \iiint_{-\infty}^{\infty} V(\vec{k}) e^{i\vec{k} \cdot \vec{r}} d\vec{k}$$

$$\int_{-\infty}^{\infty} \delta(x-a) \phi(x) dx = \phi(a)$$

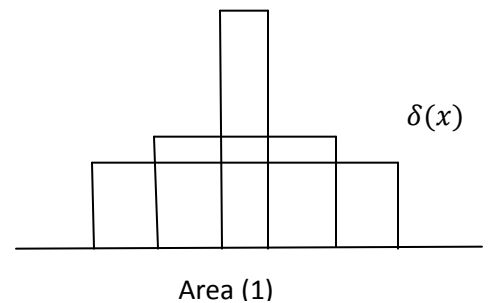
$$\int_{-\infty}^{\infty} \delta(x) dx = 1$$

FT of  $\delta(x)$

$$(2\pi)^{-1/2} \int_{-\infty}^{\infty} \delta(x) e^{-iux} dx = (2\pi)^{-1/2}$$

$$\delta(x) = (2\pi)^{-1} \int e^{iux} dx$$

$$\text{In 3d, } (2\pi)^{-3/2} \iiint_{-\infty}^{\infty} e^{-i\vec{k} \cdot \vec{r}} \delta(\vec{k}) d\vec{k} = (2\pi)^{-3/2}$$



$$\delta(\vec{k}) = \delta(k_x)\delta(k_y)\delta(k_z) = (2\pi)^{-3} \iiint_{-\infty}^{\infty} e^{i\vec{k}\cdot\vec{r}} d\vec{r}$$

In spherical coordinates, and for functions depending on  $|\vec{r}|$  and  $|\vec{k}|$

$$V(\vec{k}) = (2\pi)^{-3/2} \iiint_{-\infty}^{\infty} V(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} d\vec{r}$$

$$d\vec{r} = dx dy dz = r^2 \sin \theta dr d\theta d\phi$$

$$\vec{k}\cdot\vec{r} = kr \cos \theta$$

$$V(\vec{k}) = (2\pi)^{-3/2} \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} dr \sin \theta dr d\theta d\phi r^2 e^{-ikr \cos \theta} V(|\vec{r}|)$$

Integration over  $\phi$  gives  $2\pi$ . Integration over  $\theta$  gives,

$$V(|\vec{k}|) = \left(\frac{2}{\pi}\right)^{1/2} \int_0^{\infty} V(|\vec{r}|) \frac{r \sin(kr)}{k} dr$$

A single integral for f's depending only on r

$$\text{For even } f(x), \int_{-\infty}^{\infty} f(x) dx = 2 \int_0^{\infty} f(x) dx$$

$$\text{For odd } f(x), \int_{-\infty}^{\infty} f(x) dx = 0$$

$$e.g. f(x) = (x^2 + a^2)^{-1}$$

$$\phi(k) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} \frac{e^{-ikx}}{x^2 + a^2} dx$$

$$e^{-ikx} = \cos kx - i \sin kx$$

$$\phi(k) = 2(2\pi)^{-1/2} \int_{-\infty}^{\infty} \frac{\cos kx}{x^2 + a^2} dx = \left(\frac{\pi}{2}\right)^{1/2} a^{-1} e^{-k|\alpha|}$$

$$\text{FT of } e^{-\lambda x^2} = (2\lambda)^{-1/2} e^{-\frac{k^2}{4\lambda}}$$

$$\text{Since } \int_{-\infty}^{\infty} f(x) x \delta(x) dx = 0, \quad x \delta(x) = 0$$

$$\text{And } -\delta(x) = x \delta'(x), \quad |||^{ly} \delta(ax) = a^{-1} \delta(x)$$

$$\delta(x') = \lim_{\sigma \rightarrow 0} \frac{1}{(2\pi\sigma^2)^{1/2}} e^{-(x-\bar{x})^2/2\sigma^2}$$

$$x' = x - \bar{x}$$

$$\psi(x) = \sum_k a_k u_k(x)$$

$$a_k = \int u_k^*(x) \psi(x) dx$$

$$\psi(x) = \int [\sum_k \int u_k^*(x') u_k(x)] \psi(x') dx'$$

$$\Rightarrow \delta(x - x') = \sum_k u_k^*(x') u_k(x)$$

## 15

Generalizing to N dimensions

$$\sum_j \phi_j^*(\vec{r}_1 \dots \vec{r}_N) \phi_j(\vec{r}'_1 \dots \vec{r}'_N) = \delta(r_1 - r'_1) \dots \delta(r_N - r'_N)$$

Using in (4) earlier

$$Q = h^{-3N} \int \dots \int e^{-\frac{i}{\hbar} \sum \vec{p}_k \cdot \vec{r}_k} e^{-\beta \mathcal{H}} e^{\frac{i}{\hbar} \sum \vec{p}_k \cdot \vec{r}_k} d\vec{p}_1 \dots d\vec{p}_N d\vec{r}_1 \dots d\vec{r}_N \quad (1)$$

$\mathcal{H}$  Contains  $\nabla_i^2$  and does not commute with  $\exp(\{\pm \frac{i}{\hbar} \sum \vec{p}_k \cdot \vec{r}_k\})$

Eq (1) above is a phase space integral except we have  $\mathcal{H}$  in place of H

Kirkwood's suggestion

$$e^{-\beta \mathcal{H}} e^{-\frac{i}{\hbar} \sum \vec{p}_k \cdot \vec{r}_k} = e^{-\beta H} e^{-\frac{i}{\hbar} \sum \vec{p}_k \cdot \vec{r}_k} w(\vec{p}_1 \dots \vec{r}_N, \beta) = F((\vec{p}_1 \dots \vec{r}_N, \beta)$$

$$\therefore Q = h^{-3N} \int \dots \int d\vec{p}_1 \dots d\vec{p}_N e^{-\beta H} w(\vec{p}_1 \dots \vec{r}_N)$$

As  $\hbar \rightarrow 0, w \rightarrow 1$ , the classical limit except for the N! term in the denominator

W contains quantum corrections to the classical partition function

$$\frac{\partial F}{\partial \beta} = \frac{\partial}{\partial \beta} e^{-\beta \mathcal{H}} e^{\frac{i}{\hbar} \sum \vec{p}_k \cdot \vec{r}_k}$$

$$\frac{\partial}{\partial \beta} [1 - \beta \mathcal{H} + \beta^2 \mathcal{H}^2 \dots] e^{\frac{i}{\hbar} \sum \vec{p}_k \cdot \vec{r}_k} = \mathcal{H} F,$$

Bloch differential equation with the boundary condition  $F(\beta=0) = e^{\frac{i}{\hbar} \sum \vec{p}_k \cdot \vec{r}_k}$

To solve, expand w in powers of  $\hbar$

$$w(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N, \vec{r}_1 \dots \vec{r}_1, \beta) = \sum_{i=0}^{\infty} \hbar^i w_i(\vec{p}_1 \dots \vec{r}_N, \beta)$$

Solving

$$\omega_0 = 1$$

$$\omega_1 = \frac{-i\beta^2}{2m} \sum_j \vec{p}_j \cdot \nabla_j U$$

$$\omega_2 = \frac{-\beta^2}{2m} \nabla^2 U + \beta^3 \dots - \beta^4 \dots$$

Alternatively in evaluating trace  $\{\langle \vec{p} | e^{-\beta \mathcal{H}} | \vec{p} \rangle\}$  if  $(\beta \mathcal{H})^n | \vec{p} \rangle = (\beta E_p)^n | \vec{p} \rangle$ , which is valid in the classical limit.

But this is not valid. e.g.

$$\begin{aligned}
 -(\beta \mathcal{H})^2 | p \rangle &= \beta^2 \mathcal{H} \mathcal{H} | p \rangle = \beta^2 \mathcal{H} E_p | p \rangle \\
 &= \beta^2 \mathcal{H} \left\{ \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + U_N \right\} | \vec{p} \rangle \\
 &= \beta^2 E_p \left| \vec{p} \right\rangle - \sum_{i=1}^{3N} \frac{\beta^2 \hbar^2}{2m_i} \frac{\partial^2}{\partial q_i^2} U_N \left| \vec{p} \right\rangle \\
 &= \left\{ \beta^2 E_p^2 - \frac{1}{4\pi} \sum_{i=1}^{3N} \Lambda_i^2 \beta \frac{\partial^2}{\partial q_i^2} U_N \right\} | p \rangle
 \end{aligned}$$

$$\Lambda_i = \frac{h}{\sqrt{2\pi m k_B T}}, \text{ The de Broglie thermal wavelength}$$

$\therefore$  Classical limits holds when  $\Lambda_i$  and/or  $\frac{\partial^2}{\partial q_i^2} U_N$  are very small

$\Lambda_i$  should be smaller than the mean particle separation.

Examples:

liquid	$T_t(K)$	$\Delta(\text{\AA})$ at $T_t$	$\Lambda/a$	$\theta_{rot}/T_t$
H <sub>2</sub>	14.05	3.3	0.97	6.1
Ne	245	0.78	0.26	
CH <sub>4</sub>	90.7	0.46	0.12	0.083
N <sub>2</sub>	63.3	0.42	0.11	0.046
CCl <sub>4</sub>	250	0.09	0.017	0.001

Phase diagram of a monatomic species

Liquids exists between  $T_t$  and  $T_c$

$$\frac{K_N}{V_N} \sim 1, \quad T^* = k_B T / \epsilon \sim 1, \quad \rho^* = \frac{N \sigma^3}{V} \sim 1$$

Classical Liquids: Momenta integrated out.

## 16

### Phase space trajectories

N particle system (in volume V),  $\vec{r}_1 \dots \vec{r}_N$  and  $\vec{p}_1 \dots \vec{p}_N$  or  $\vec{r}^N$  and  $\vec{p}^N$  are its coordinates and momenta.

Notation  $\vec{r}^N \equiv \{\vec{r}_1 \dots \vec{r}_N\}$

Given the initial conditions, equations of motion (EOM) determine systems evolution

$$\dot{\vec{p}}_i = \frac{d\vec{p}_i}{dt} = \vec{F}_i = -\frac{\partial U_N}{\partial \vec{r}_i} + \vec{F}_i$$

$$\vec{p}_i(t) = \vec{p}_i(0) + \int_0^t \vec{F}_i(t') dt', \quad i = 1, \dots, N$$

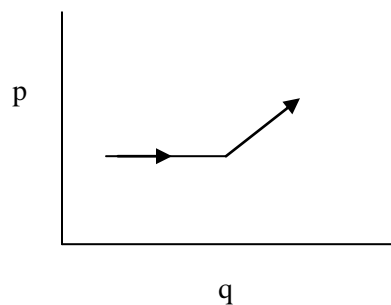
$$\vec{r}_i(t) = \vec{r}_i(0) + \int_0^t \frac{\vec{p}_i(t')}{m_i} dt'$$

Phase or phase point  $\Gamma = \{\vec{r}_1 \dots \vec{r}_N, \vec{p}_1 \dots \vec{p}_N\}$

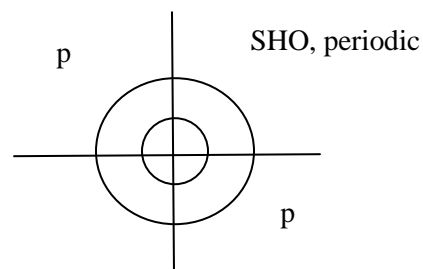
6N variables:

As t changes,  $\Gamma$  changes. System evolution is represented as a phase space trajectory.

e.g.



Free particle subjected to an external force



Features of phase space trajectories (these are not particle coordinate trajectories in time)

- 1) Constants of motion do not change along a phase space trajectory (PST)
- 2) Isolated system moves in a small part of PST along which the constants of motion are fixed
- 3) Ergodic hypothesis: A trajectory passes through every point in phase space consistent with the constants of motion
- 4) After how much time will the system return to the original or the initial phase point  
Poincarre recurrence time.

For periodic system, it is well defined. For others it could be too large.

e.g. A beaker of water.  $10^{40}$  years?

Dynamical variables  $B(\Gamma)$  completely determined by the phase point  $\Gamma$ .

$\left(\frac{\partial B}{\partial t}\right)_\Gamma = 0$ . We can obtain  $\langle B \rangle_{t_e}$ , or  $\bar{B}$

$$\frac{dB}{dt} = \sum_{i=1}^N \left( \frac{\partial B}{\partial \vec{p}_i} \vec{p}_i + \frac{\partial B}{\partial \vec{q}_i} \vec{q}_i \right)$$

Use Hamilton's equations (equivalent to Newton's Laws or Lagrange's EOM)

$$H = \sum_i \frac{p_i^2}{2m} + U_N(\vec{r}_1 \dots \vec{r}_N)$$

$$\frac{\partial H}{\partial \vec{p}_i} = \vec{q}_i; \quad \frac{\partial H}{\partial \vec{q}_i} = -\vec{p}_i$$

$$\therefore \frac{dB}{dt} = \sum_{i=1}^{3N} \left( \frac{\partial B}{\partial q_i} \frac{\partial H}{\partial p_i} + \frac{\partial B}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = \{B, H\}$$

*a poisson Bracket*

If  $B$  is a constant of motion,  $\{B, H\} = \{H, B\} = 0$

Quantum mechanical analogy

$$B \rightarrow \hat{B}, \langle \hat{B} \rangle = \int \psi^* \hat{B} \psi d\tau$$

$$\hat{B} = \frac{d}{dt} \hat{B} = \frac{i}{\hbar} [\hat{B}, \hat{H}] = \frac{i}{\hbar} [\hat{B}H - \hat{H}B], \text{ a commutator Bracket}$$

Heisenberg equation of motion

A more compact form of  $\frac{dB}{dt}$  is

$$\frac{dB}{dt} = i\mathcal{L}B, \mathcal{L} = i \sum_i^{3N} \left( \frac{\partial B}{\partial q_i} \frac{\partial H}{\partial p_i} + \frac{\partial B}{\partial p_i} \frac{\partial H}{\partial q_i} \right)$$

Solution  $\widehat{B}(t) = e^{-\frac{it}{\hbar}\widehat{H}} \widehat{B}(0) e^{\frac{it}{\hbar}\widehat{H}}$

A (be) ‘fore’ part and an ‘after’ part

For a general variable that depends on  $\Gamma$  as well as  $t$ , as in  $C(\Gamma, t)$

$$\frac{dC}{dt} = \left( \frac{\partial C}{\partial t} \right)_{\Gamma} + \left( \frac{\partial C}{\partial \Gamma} \right)_{t} = \left( \frac{\partial C}{\partial t} \right)_{\Gamma} + i\mathcal{L}C$$

$\mathcal{L}$  = Liouville operator

Liouville equation: Basic equation for an non-equilibrium stat mech

$\mathbb{N}$  = no. of systems in the canonical ensemble of  $N$  particles

At  $t = t_0$ , a perturbation is applied.

We want to study the evolution. Different members (of the ensemble)

Execute different PSTs

$$f(\Gamma, t) \delta\Gamma = f(\{\vec{p}^N\}, \{\vec{q}^N\}, t) \delta\vec{p}_1 \dots \delta\vec{p}_N \dots \delta\vec{q}_N$$

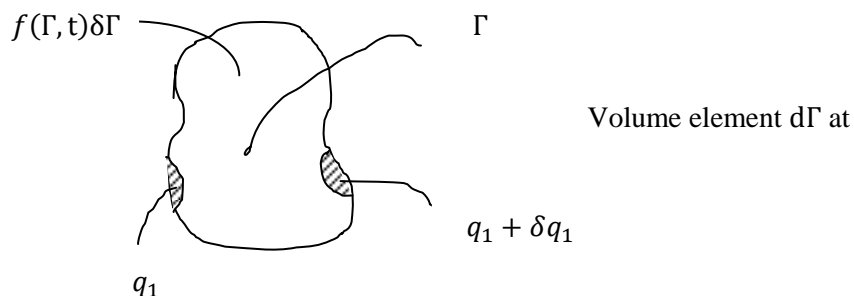
= fraction of members of the ensemble at  $\Gamma$  in a volume element  $\delta\Gamma$

## 17

At equilibrium  $f_{eq}(\Gamma, t) = \frac{e^{-\beta H}}{\int e^{-\beta H} d\Gamma}$

$$\int f(\Gamma, t) d\Gamma = 1 \quad \frac{d}{dt} \int f(\Gamma, t) d\Gamma = 0 \quad \text{for a fixed } d\Gamma, \frac{df}{dt} = 0$$

To see this in a volume element,



Time dependence of  $f(\Gamma, t)$  comes about through the time dependence of  $q$  &  $p$

Consider two faces  $\perp^r$  to the  $q_1$  axis at  $q_1$  and  $q_1 + \delta q_1$

$$\text{No. of trajectories entering through } q_1 \text{ in unit time} = \underbrace{\mathbb{N}f(\Gamma, t)\dot{q}_1}_{\text{how } q_1 \text{ changes with time}} \underbrace{\delta q_2 \delta q_3 \dots \delta q_{3N}}_{\text{No. of points in phase space at the area at } q_1}$$

$$\text{No. of points leaving through } q_1 + \delta q_1 = \mathbb{N}f(q_1 + \delta q_1, q_2 \dots p_{3N})\dot{q}_1(q_1 + \delta q_1, q_2 \dots p_{3N})\delta q_2 \dots \delta q_{3N}$$

in unit time

Expand  $f$  and  $\dot{q}_1$  and retain terms linear in  $\delta q_1$

$$= \mathbb{N} \left( f + \frac{\partial f}{\partial q_1} \delta q_1 \right) \left( \dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} \delta q_1 \right) \delta q_2 \dots \delta q_{3N}$$

$$\text{Net flow through the } q_1 \text{ face in unit time} = \mathbb{N} \left( \frac{\partial f}{\partial q_1} \dot{q}_1 + f \frac{\partial \dot{q}_1}{\partial q_1} \right) d \Gamma$$

Net flow through all faces in unit time is

$$= -\mathbb{N} \sum_{i=1}^{3N} \left( \frac{\partial f}{\partial q_i} \dot{q}_i + f \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial f}{\partial p_i} \dot{p}_i + f \frac{\partial \dot{p}_i}{\partial p_i} \right) d \Gamma$$

This equals the net flow/ charge of points in the volume element  $d \Gamma$ , i.e.  $\left( \frac{\partial \mathbb{N}f(\Gamma, t) d \Gamma}{\partial t} \right)_\Gamma$

Use Hamilton's equations

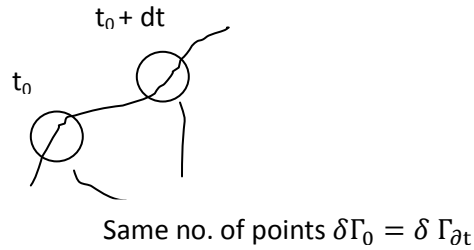
$$\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} = 0$$

$$\therefore \frac{\partial f}{\partial t} = -\sum_{i=1}^{3N} \left( \frac{\partial f}{\partial q_i} \dot{q}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \right) = -\sum_{i=1}^{3N} \left( \frac{\partial f}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = -[f, H]$$

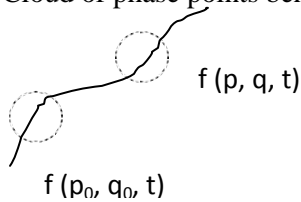
Or  $\frac{df}{dt} = \left( \frac{\partial f}{\partial t} \right)_\Gamma + [f, H] = 0$ , the Liouville equation

Interpolation: Conservation of density in phase space

- Shape of the surface  $\delta\Gamma$  changes with time without changing volume



- Conservation of extension in phase space
- Phase space trajectories never cross
- Cloud of phase points behaves like an incompressible fluid



$$\frac{df^N}{dt} = -\{f^N, H\} = -i\mathcal{L}f^{(N)}$$

$$f(\vec{r}^N, \vec{p}^N, t) = e^{-i\mathcal{L}t} f^N(\vec{r}^N, \vec{p}^N, 0) \text{ while } B(t) = e^{i\mathcal{L}t} B(0)$$

Comparing with rotating a vector vs. rotating the coordinating frame

- Liouville equation reversible in time, like Newton's laws or Schrodinger eq. unlike chemical kinetics, Brownian motion or the Boltzmann equation.

Applications:

- 1) Various approximation schemes originate from Liouville Equation.

Reduced probability density functions (P D Fs)

Ensemble and system interpretation of  $f^N(\vec{r}^N, \vec{p}^N, t)$

Reduced P.D.F

$$f^{(n)}(\vec{r}^n, \vec{p}^n, t) = \frac{N!}{(N-n)!} \int \dots \int f^N(\vec{r}^N, \vec{p}^N, t) d\vec{r}^{N-n} d\vec{p}^{N-n}$$

$$d\vec{r}^{(N-n)} = d\vec{r}_{n+1}, d\vec{r}_{n+1}, \dots, d\vec{r}_N$$

= probability of finding any subset n of N particles at  $\vec{r}_1 \dots \vec{r}_N$  irrespective of the remaining particles.