

as  $P \rightarrow 0$  and introduce an activity coefficient  $\gamma_f$  defined by,

$$f = P \gamma_f$$

$$\text{then, } \ln \gamma_f = \frac{\rho}{kT} \int_0^1 \int_0^\infty u(r) g(r, \epsilon_f) 4\pi r^2 dr d\epsilon_f -$$

$$\ln \frac{Pv}{NkT} \quad (\text{fluid})$$

• Potential of Mean force and the Superposition Approximation.

For any given configuration  $r_1, \dots, r_N$  of the  $N$  molecules of the system the force acting on particle  $i$ :

$$\therefore F = -m \frac{d^2 x}{dt^2}$$

$$F_\alpha = -\nabla_\alpha U(r_1, \dots, r_N, \epsilon_f)$$

Averaged over all configurations of molecules  $n+1, \dots, N$ , but holding the set of molecules  $1, \dots, n$  fixed at  $r_1, \dots, r_n$

$$\text{i.e. } F_\alpha^{(n)} = -\overline{\nabla_\alpha U}^{(n)}$$

$-\overline{\nabla_\alpha U}^{(n)}$  is the mean force  $F_\alpha^{(n)}$

acting on particle  $\alpha$ .

$$\overline{\nabla_\alpha U} = \frac{\int dr_{n+1} \dots \int dr_N \exp[-\beta U(r_1, \dots, r_N, \epsilon_f)] \nabla_\alpha U}{\int dr_{n+1} \dots \int dr_N [\exp[-\beta U(r_1, \dots, r_N, \epsilon_f)]]}$$

Solvent averaged force between a pair of particles/molecules/atoms.

$$\left\langle \frac{d}{dr_1} [u(r_1, r_N, \epsilon_s)] \right\rangle_{r_1, r_2}$$

$$\int dr_3 \dots \int dr_N \exp[-\beta u(r_1, r_N, \epsilon_s)] \frac{du(r_1, r_N, \epsilon_s)}{dr_1}$$

$$= \frac{\int dr_3 \dots \int dr_N \exp[-\beta u(r_1, r_N, \epsilon_s)]}{\int dr_3 \dots \int dr_N \exp[-\beta u(r_1, r_N, \epsilon_s)]}$$

$$= \frac{k_B T \frac{d}{dr_1} \int dr_3 \dots \int dr_N \exp[-\beta u(r_1, r_N, \epsilon_s)]}{\int dr_3 \dots \int dr_N \exp[-\beta u(r_1, r_N, \epsilon_s)]}$$

$$= k_B T \frac{d}{dr_1} \ln \left[ \int dr_3 \dots \int dr_N \exp[-\beta u(r_1, r_N, \epsilon_s)] \right]$$

$$= k_B T \frac{d}{dr_1} \ln \left[ \frac{N(N-1) \int dr_3 \dots \int dr_N \exp(-\beta u)}{\int dr_1 \int dr_2 \dots \int dr_N \exp(-\beta u)} \right]$$

$$= k_B T \frac{d}{dr_1} \ln \left[ \int g^{(2)}(r_1, r_2, \epsilon_s) \right]$$

$$= k_B T \frac{d}{dr_1} \ln g^{(2)}(r_1, r_2, \epsilon_s)$$

uh  $\frac{2}{3}$ ?

$$= k_B T \frac{d}{dr_1} \ln g^{(2)}(r_1, r_2, \epsilon_s)$$

$$\therefore g(r) = \exp(-\beta \omega(r))$$

$$\ln g(r) = -\beta \omega(r)$$

$$\omega(r) = -kT \ln g(r)$$

$$S_2 = k_B T \frac{d}{dr_1} \ln e^{-\beta \omega(r)}$$

$$= -\frac{d\omega(r)}{dr_1}$$

$\omega(r)$  - Reverse work done by the system

bring back to the distance  $r_{12}$

$$r_1 \xrightarrow[r_{12}-r_1]{r_{12}} r_2$$

Experimental determination of  $g(r)$ .

from x-ray

$$\lambda \sim 10^{-8} \text{ cm}$$

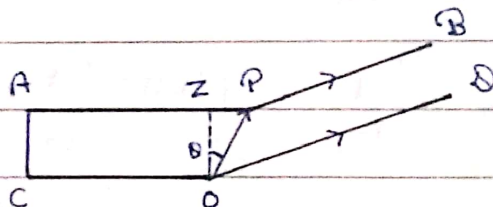
$$E = E_0 e^{i(kx - \omega t)}$$

$$k = k \cdot \hat{e}$$

Unit vector

$$E = E_0 \cos(kx - \omega t) + \text{Integration Part}$$

Phase fraction



$$k_0 = k' \hat{e}_0 \rightarrow \text{Incident beam}$$

$$k = k \hat{e} \rightarrow \text{Scattered beam}$$

$$APB \sim CD$$

$$e^{i\phi} - e^{\phi}$$

$$S_0, E(B) = E(D) e^{i(e_0 - e)\phi}$$

$$= E(D) e^{-i\phi}$$

$$\therefore \phi = e - e_0$$

$$\therefore E(S) = A \sum_{i=1}^N e^{-i\phi_i}$$

$$I(D) = |E_S|^2 = E_S \times E_S^*$$

$$= A^2 \sum_{i=1}^N e^{i\phi_i} \sum_{j=1}^N e^{-i\phi_j}$$

$$I(\theta) = A^2 N S(\theta)$$

$$N S(\theta) = \sum_{i=1}^N e^{i\theta r_i} \sum_{j=1}^N e^{-i\theta r_j}$$

$$= \sum_{i=1}^N (\cos \theta r_i + i \sin \theta r_i)$$

$$\sum_{j=1}^N (\cos \theta r_j - i \sin \theta r_j)$$

$$= N + \sum_{i \neq j} \sum_{j=1}^N e^{i\theta R_{ij}}$$

$$R_{ij} = r_i - r_j$$

$$S(\theta) = 1 + \rho \int e^{i\theta R} g(R) dR$$

↓  
Fourier transformation of  $g(R)$ .

$$\therefore h(R) = g(R) - 1$$

Pair Co-Relation function.

$$S(\theta) = 1 + \rho \int e^{i\theta R} [h(R) + 1] dR$$

$$= 1 + \rho \int e^{i\theta R} h(R) dR + \rho \int e^{i\theta R} dR$$

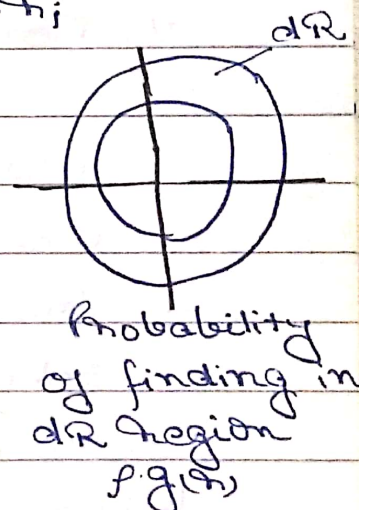
↓  
Fourier transformation

$$= 1 + \rho h(\theta) + \rho (2\pi)^3 \delta(R)$$

$$\delta k = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} e^{ikR} dR$$

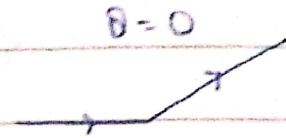
$$S(\theta) = 1 + \rho h(\theta)$$

↓  
Neglect  $\rho (2\pi)^3 \delta(R)$



if incident beam and scattered beam is same direction or coincide.

So,  $S(q) = 1 + \rho h(h)$



Simulation:

- (i) Monte Carlo Simulation (MC)  
(Metropolis Algorithm)
- (ii) Molecular dynamics (MD)

(i) Monte Carlo Simulation:

The Metropolis algorithm generates a Markov chain of state. A Markov chain satisfies the following conditions

- a. The outcome of each trial depends only upon the preceding trial and not upon any previous trials.
- b. Each trial belongs to a finite set of possible outcomes.

Condition 'a' provides a clear distinction b/w the Molecular dynamics and Monte Carlo methods. For in a MC simulation all of the states are connected in time. Suppose the system is in a state  $m$ . We denote the probability of moving to the state  $n$  as  $\pi_{mn}$ . The various  $\pi_{mn}$  can be considered to constitute an  $N \times N$  matrix  $\pi$  (the transition