# 5. Mean Field Approximations in Statistical Mechanics

## 5.1. Introduction

Equilibrium Ensembles: powerful, general formalism for deriving thermodynamic properties from molecular-level information.

In practice: Exact, analytical solution of this formalism impossible for all by the simplest microscopic models.

Approximations necessary to arrive at closed-form solutions.

One source of difficulty: Need to sum over a very large number of system microstates, or configurations. e.g. $Z(N,V,T) = \sum_{\text{all configs}} \exp[-\beta \mathcal{V}(\text{config.})]$

Mean field approximations: Neglect correlations between different parts of the system at some level, and thus avoid need to consider a multitude of configurations.

Common strategies:

1. Define a variable ("order parameter") that provides a collective description of the configuration (e.g. magnetization, density, concentration). Derive an approximate expression for the Helmholtz or Gibbs energy in terms of the order parameter. Minimize to impose equilibrium.

2. Approximate system of interacting particles by an equivalent system of noninteracting particles subject to an external field. Field represents effects of other particles on given particle ("mean field"). Derive thermodynamics by imposing self-consistency condition: Response that the mean field elicits from a particle must be consistent with the average state of surrounding particles that shape its value.

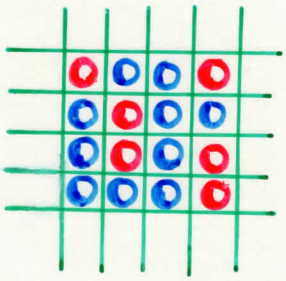
The term "mean field" is used rather loosely to denote a spectrum of approaches, ranging from the most simple-minded to the most sophisticated! Better avoid "mean field," and call approximation by its name (e.g., Bragg-Williams; Quasichemical; Flory; Debye-Hückel, etc.)

In this discussion we will present two examples:

- Bragg-Williams approximation on a lattice, to derive a simple regular solution model for binary systems.

- Derivation of the van der Waals equation of state.

## 5.2. SIMPLE MODEL OF A SUBSTITUTIONAL METALLIC SOLUTION: BRAGG-WILLIAMS APPROXIMATION



N sites

A

B

Energies:

$W_{AA} < 0$

$W_{BB} < 0$

$W_{AB} < 0$

Lattice model

of substitutional solid solution (also used for liquid solutions!)

- Coordination number $z$.
- Sites can be occupied by atoms of metal A or metal B
- No multiple occupancy of sites
- Nearest-neighbor attractive interactions. Characteristic energies $W_{AA}$, $W_{BB}$, $W_{AB}$.

Composition dictated by numbers of atoms $N_A$, $N_B$

$$N_A + N_B = N$$

Mole fractions $x_A = N_A/N$, $x_B = N_B/N$ (5.1)

OBJECTIVE: Derive thermodynamics of mixing: $g^E = g^E(T, x_A)$ ← excess molar Gibbs energy

(phase diagram, activity coefficients, ...)

NOTE: The lattice model we are employing allows no volume change upon mixing: $\Delta V_{mix} = V^E = 0$

Therefore, mixing thermodynamics will be P-independent.

As a consequence, $a^E \equiv g^E$ at any $T, x_A$. (5.2)

Choose to study system at constant $N_A, N_B, T$ (canonical ensemble).

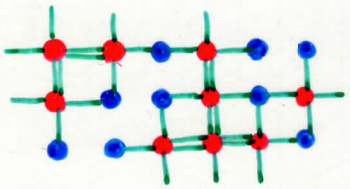
## Simple counting relations.

Let: $N_{AA}, N_{BB}, N_{AB}$ } = { total number of AA, BB, AB nearest neighbor pairs in a given configuration.

Then, $N_A + N_B = N$

$z N_A = 2N_{AA} + N_{AB}$

$z N_B = 2N_{BB} + N_{AB}$ (5.3)



Potential energy of a given configuration:

$$E = N_{AA} w_{AA} + N_{BB} w_{BB} + N_{AB} w_{AB} \overset{(5.3)}{=}$$

$$= \frac{zN_A}{2} w_{AA} + \frac{zN_B}{2} w_{BB} + N_{AB}\left(w_{AB} - \frac{1}{2} w_{AA} - w_{BB}\right) =$$

$$= E_A + E_B + \frac{1}{z} N_{AB}\, \omega \qquad (5.4)$$

$E_A \equiv \frac{zN_A}{2} w_{AA}$ = total potential energy of a pure lattice of $N_A$ atoms.

$E_B \equiv z\frac{N_B}{2} w_{BB}$ = total potential energy of a pure lattice of $N_B$ atoms.

$$\omega = z\left(w_{AB} - \frac{w_{AA}}{2} - \frac{w_{BB}}{2}\right)$$ : INTERCHANGE ENERGY

Total energy change per exchanged atom:

$$\frac{2z w_{AB} - z w_{AA} - z w_{BB}}{2} = \omega$$

Negative Deviations from ideality: $\omega < 0$ (unlike atom interactions more favorable than like atom interactions)

Positive Deviations from ideality: $\omega > 0$ (like atom interactions more favorable than unlike atom interactions)

Typically, for systems interacting through van der Waals forces,

$|w_{AB}| \simeq (|w_{AA}|\,|w_{BB}|)^{1/2}$ (Lorentz-Berthelot rule)

so $\omega = z/2\left(|w_{AA}|^{1/2} - |w_{BB}|^{1/2}\right)^2 = v^*\left[\left(\frac{z}{2v^*}|w_{AA}|\right)^{1/2} - \left(\frac{z}{2v^*}|w_{BB}|\right)^{1/2}\right]^2 =$

$= v^*\left[\left(\frac{|E_A|}{N_A v^*}\right)^{1/2} - \left(\frac{|E_B|}{N_B v^*}\right)^{1/2}\right]^2 = v^*\left[\left(\frac{|E_A|}{V_A}\right)^{1/2} - \left(\frac{|E_B|}{V_B}\right)^{1/2}\right]^2$

or $\omega = v^* (\delta_A - \delta_B)^2$ where $v^*$ = volume occupied by an atom

$|E|/V$ = cohesive energy density

$\delta$ = Hildebrand solubility parameter.

System partition function:

$$Q(N_A, N_B, T) = \sum_{\text{all configs}} \exp(-\beta E_{\text{config.}})$$

$$= \sum_{N_{AB}} g(N_A, N_B, N_{AB}) \exp\left[-\beta \left(E_A + E_B + \frac{N_{AB}}{z} \omega\right)\right] \quad (5.5)$$

$g$: number of configurations containing $N_{AB}$ unlike pairs.

Up to now, formulation is exact.

We want to obviate the need to consider all possible configurations.

## Mean Field Approximation

At equilibrium, far from critical points, $N_{AB}$ for a macroscopic system will be strongly peaked around its average value, $\langle N_{AB} \rangle$.

Substitute $N_{AB}$ in exponential of (1.4.5) by this average value:

$$Q_{MF}(N_A, N_B, T) = \exp\left[-\beta \left(E_A + E_B + \frac{\langle N_{AB} \rangle}{z} \omega\right)\right] \sum_{N_{AB}} g(N_A, N_B, N_{AB}) \quad (5.6)$$

Note that, in doing so, we have thrown away fluctuations in $N_{AB}$.

Now:

$\sum_{N_{AB}} g(N_A, N_B, N_{AB})$ = total number of lattice configurations of $N_A$ A molecules and $N_B$ B molecules on $N$ lattice sites.

$$\sum_{N_{AB}} g(N_A, N_B, N_{AB}) = \frac{N!}{N_A!\, N_B!} \quad (5.7)$$

Then, $$Q_{MF}(N_A, N_B, T) = \frac{N!}{N_A!\, N_B!} \exp\left[-\beta \left(E_A + E_B + \frac{\langle N_{AB} \rangle}{z} \omega\right)\right] \quad (5.8)$$

What is $\langle N_{AB} \rangle$ ?

**Bragg-Williams approximation of random mixing:**
"There is no short-range order apart from that which follows from long-range order".

$$\langle N_{AB} \rangle = N_{AB}^{*} \equiv N_A \cdot z \left( \frac{N_B}{N} \right) \qquad (5.9)$$

- $\langle N_{AB} \rangle$: avg. number of AB nearest-neighbor pairs (indicative of short-range order)
- $N_{AB}^{*}$: denotes random mixture (no energetics)
- $N_A$: number of A molecules
- $z$: number of lattice sites around an A site
- $\frac{N_B}{N}$: fraction of lattice sites occupied by B (long-range order)

"smeared" nearest-neighbor environment, of composition equal to overall composition of the system.

The approximation ignores local composition effects:
In reality, $\omega < 0 \rightarrow \langle N_{AB} \rangle > N_{AB}^{*}$
$\omega > 0 \rightarrow \langle N_{AB} \rangle < N_{AB}^{*}$

Mean-field expression for the partition function:

$$Q_{MF}(N_A, N_B, T) = \frac{N!}{N_A! N_B!} \exp\left[ -\beta \left( E_A + E_B + \frac{N_A N_B}{N} \omega \right) \right] \qquad (5.10)$$

Thermodynamics in the mean field:

$$A(N_A, N_B, T) = -\frac{1}{\beta} \ln Q_{MF}(N_A, N_B, T) =$$

$$= k_B T \left[ N_A \ln\left(\frac{N_A}{N}\right) + N_B \ln\left(\frac{N_B}{N}\right) \right] + E_A + E_B + \frac{N_A N_B}{N} \omega \qquad (5.11)$$

Helmholtz energy of mixing:

$$\Delta A_{mix}(N_A, N_B, T) = A(N_A, N_B, T) - \underbrace{A_A(N_A, T)}_{\text{same as } E_A} - \underbrace{A_B(N_B, T)}_{\text{same as } E_B}$$

(no entropic contribution, A molecules indistinguishable)

$$\frac{\Delta A_{mix}(N_A, N_B, T)}{N} = k_B T \left\{ \frac{N_A}{N} \ln\left(\frac{N_A}{N}\right) + \frac{N_B}{N} \ln\left(\frac{N_B}{N}\right) \right\} + \frac{N_A}{N} \frac{N_B}{N} \omega$$

Molar Helmholtz energy of mixing:

$$\Delta a_{mix}(x_A, T) = \underbrace{RT(x_A \ln x_A + x_B \ln x_B)}_{\Delta a^{id}_{mix}} + \underbrace{N_{Avo}\,\omega}_{\text{call } \omega'}\, x_A x_B \qquad (5.12)$$

or (5.2)

$$a^E(x_A, T) \equiv g^E(x_A, T) = \omega' x_A x_B \qquad (5.13)$$

NOTES:

- Excess Gibbs energy is purely enthalpic:

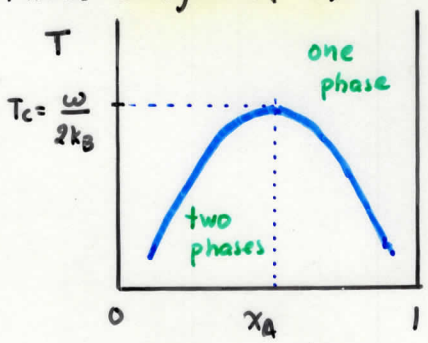
$$h^E(x_A, T) = \frac{\partial(G^E/T)}{\partial(1/T)} = \omega' x_A x_B \Rightarrow s^E = \frac{h^E - g^E}{T} = 0$$

(No deviation from random organization of molecules allowed)

- Solution is regular: $s^E = 0$, $v^E = 0$
- Activity coefficients: $\ln\gamma_A = \frac{\omega}{k_B T} x_B^2$, $\ln\gamma_B = \frac{\omega}{k_B T} x_A^2$ (5.14)

(Two-suffix Margules model)

- Phase diagram ($\omega > 0$ case)




Symmetric, with UCST at $\frac{\omega}{k_B T_c} = 2$

- Infinite dilution activity coefs: $\ln\gamma_B^{\infty} = \frac{\omega}{k_B T}$, $\left.\frac{\partial \ln\gamma_B}{\partial x_B}\right)_{x_B \to 0} = -\frac{2\omega}{k_B T}$

For this model, $\left.\frac{\partial \ln\gamma_B}{\partial x_B}\right)_{x_B \to 0} = -2\ln\gamma_B^{\infty}$

(test for how well the model would fit experimental data for real alloys: See Lupis, C.H.P. Chemical Thermodynamics of Materials, Elsevier: Amsterdam, 1983)

## 5.3. An improved mean field approximation for the lattice: The Quasichemical Approximation.

( Bethe - Peierls approximation for Ising model / Guggenheim approx. for mixtures)

OBJECTIVE: Take into account local composition effects

Exact partition function:

$$Q(N_A, N_B, T) = \sum_{N_{AB}} g(N_A, N_B, N_{AB}) \exp\left[-\beta\left(E_A + E_B + \frac{N_{AB}}{2}\omega\right)\right] \qquad (5.15)$$

$g(N_A, N_B, N_{AB})$: number of configurations containing $N_{AB}$ unlike nearest-neighbor pairs.

BASIC IDEA:

- Develop an approximate expression for $g(N_A, N_B, N_{AB})$
- Using that expression, determine the maximal value of the term $g(N_A, N_B, N_{AB}) \exp\left[-\beta(E_A + E_B + \frac{N_{AB}}{2}\omega)\right]$, and the corresponding value of $N_{AB}$.
- Substitute partition function by its maximum term. (maximum term approximation, justified in the thermodynamic limit, far from critical points).

QUASICHEMICAL APPROXIMATION TO $g(N_A, N_B, N_{AB})$:

Assume random mixing of AB, BA, AA, BB pairs, rather than of monomers (correlations cut off at a higher level).

$$g(N_A, N_B, N_{AB}) = h(N_A, N_B) \frac{(N_{AA} + N_{BB} + N_{AB})!}{N_{AA}!\, N_{BB}!\, \left(\frac{N_{AB}}{2}\right)!\, \left(\frac{N_{AB}}{2}\right)!} = h(N_A, N_B) \frac{\left[\frac{1}{2}z(N_A + N_B)\right]!}{N_{AA}!\, N_{BB}!\, \left[\left(\frac{N_{AB}}{2}\right)!\right]^2}$$

$h(N_A, N_B)$: correction factor, depending on $N_A, N_B$ but not on $N_{AA}, N_{BB}, N_{AB}$

counting relations (5.3)

(5.16)

exact for $\omega = 0$

Correction factor calculated by demanding that (5.16) hold in the case where A, B form a <u>random mixture</u> at the same composition:

$$g(N_A, N_B, N_{AB}^*) = \frac{(N_A+N_B)!}{N_A!\,N_B!} = h(N_A, N_B)\,\frac{\left[\frac{1}{2}z(N_A+N_B)\right]!}{N_{AA}^*!\;N_{BB}^*!\;\left[\left(\frac{N_{AB}^*}{2}\right)!\right]^2} \qquad (5.17)$$

where $N_{AA}^* = \frac{z}{2}\frac{N_A^2}{N_A+N_B}$, $N_{BB}^* = \frac{z}{2}\frac{N_B^2}{N_A+N_B}$, $N_{AB}^* = \frac{z N_A N_B}{N_A+N_B}$

From (5.16), (5.17),

$$g(N_A, N_B, N_{AB}) = \frac{(N_A+N_B)!}{N_A!\,N_B!}\;\frac{(N_{AA}^*)!\;(N_{BB}^*)!\;\left[\left(\frac{1}{2}N_{AB}^*\right)!\right]^2}{\left(\frac{z}{2}N_A - \frac{N_{AB}}{2}\right)!\left(\frac{zN_B}{2} - \frac{N_{AB}}{2}\right)!\left[\left(\frac{1}{2}N_{AB}\right)!\right]^2} \qquad (5.18)$$

expressed solely in terms of constants and $N_{AB}$

Search for the value $\langle N_{AB}\rangle$ that maximizes the partition function term $g(N_A, N_B, N_{AB})\exp\left[-\beta\left(E_A+E_B+\frac{N_{AB}}{z}\omega\right)\right]$ and for the associated values $\langle N_{AA}\rangle$, $\langle N_{BB}\rangle$, obtainable from the counting relations (5.3), leads to the interesting result:

$$\frac{\left(\frac{1}{2}\langle N_{AB}\rangle\right)^2}{\langle N_{AA}\rangle\,\langle N_{BB}\rangle} = \exp\left(-2\beta\,\frac{\omega}{z}\right) \qquad (5.19)$$

Eq. (5.19) can be viewed as a condition for "chemical equilibrium" for the "reaction"

$$AA + BB \rightarrow AB + BA \qquad \text{"}\Delta G^{\circ}\text{"} = N_{Avo}\left(2\omega_{AB} - \omega_{AA} - \omega_{BB}\right) = \frac{2}{z}\omega N_A$$

The origin of the name "quasichemical approximation" lies in this observation.

Using the maximum term approximation, the mixture thermodynamics can be deduced. (see J.M. Prausnitz et al., <u>Molecular Thermodynamics of Fluid-Phase Equilibria</u>).

## 5.4. Derivation of the van der Waals Equation of State

Johannes Diderik van der Waals; Ph.D. Thesis, Leiden, 1873. Nobel Prize 1910.

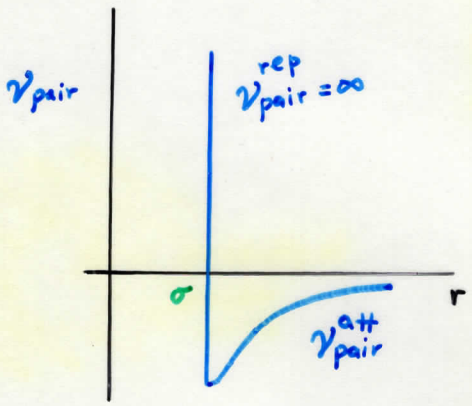
Starting Point:

$$P = -\left.\frac{\partial A}{\partial V}\right)_{T,N} = k_B T \left.\frac{\partial \ln Z}{\partial V}\right)_{T,N} \qquad (5.39)$$

$$Z(N,V,T) = \int \exp\left[-\beta \mathcal{V}(\underline{r}_1, \ldots, \underline{r}_N)\right] d^3r_1 \ldots d^3r_N \qquad (5.38)$$

Pairwise additivity approximation:

$$\mathcal{V}(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \mathcal{V}_{pair}(|\underline{r}_i - \underline{r}_j|) \equiv \sum_{i<j} \sum \mathcal{V}_{pair}(r_{ij}) \qquad (5.20)$$



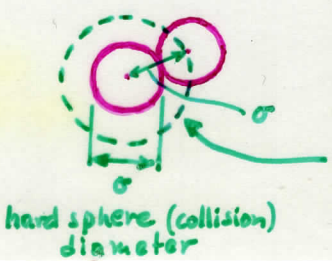

Insights of van der Waals:

- Pair potential consists of a harshly repulsive and a smooth attractive part.
- Fluid structure governed mainly by harsh repulsive forces.

Potential considered for derivation of vdW equation of state:

$$\mathcal{V}_{pair}(r) = \begin{cases} \mathcal{V}_{pair}^{rep}(r) = \infty, & r \le \sigma \\ \mathcal{V}_{pair}^{att}(r), & r > \sigma \end{cases} \qquad (5.21)$$

← hard sphere of diameter $\sigma$




hard sphere (collision) diameter

"excluded volume": centers of other molecules cannot come into sphere of radius $\sigma$ around given molecule.

Configurational Integral:

$$Z(N,V,T) = \int \exp\left[-\beta \mathcal{V}^{rep}(\underline{r}_1,\dots,\underline{r}_N)\right] \exp\left[-\beta \mathcal{V}^{att}(\underline{r}_1,\dots,\underline{r}_N)\right] d^3r_1 \dots d^3r_N \qquad (5.22)$$

$\mathcal{V}^{rep}$: $\sum_{i<j}\sum \mathcal{V}^{rep}_{pair}(r_{ij})$ ; $\mathcal{V}^{att}$: $\sum_{i<j}\sum \mathcal{V}^{att}_{pair}(r_{ij})$

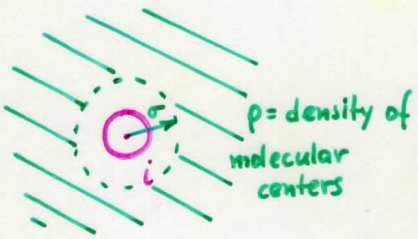
## Mean field treatment of attractive interactions:

Substitute configuration-dependent term $\mathcal{V}^{att}(\underline{r}_1,\dots,\underline{r}_N)$ by an average term

$$\mathcal{V}^{att}(\underline{r}_1,\underline{r}_2,\dots,\underline{r}_N) = \mathcal{V}^{att}_{MF} = \frac{1}{2}\sum_{i=1}^{N} \mathcal{V}^{att}_{MF,i} \qquad (5.23)$$

$\mathcal{V}^{att}_{MF,i}$: mean attractive potential energy felt by molecule $i$ due to its interactions with all other molecules in the system.

$\frac{1}{2}$: corrects for doublecounting of pairwise attractive interactions.




For the calculation of $\mathcal{V}^{att}_{MF,i}$:

Consider centers of all other molecules as constituting a "smeared" background of uniform density $\rho$ at all distances $\sigma \le r < \infty$

This treatment ignores any two-body correlations at distances $r \gtrsim \sigma$

$$\mathcal{V}^{att}_{MF,i} = \int_{\sigma}^{\infty} \underbrace{4\pi r^2 dr\, \rho}_{\text{number of molecules in spherical shell between } r \text{ and } r+dr \text{ from center of } i.}\ \mathcal{V}^{att}_{pair}(r) \qquad (5.24)$$

From (5.22) to (5.24):

$$Z(N,V,T) = \exp\left[-\frac{\beta N}{2}\int_{\sigma}^{\infty} 4\pi r^2 dr\, \rho\, \mathcal{V}^{att}_{pair}(r)\right] \int \exp\left[-\beta \mathcal{V}^{rep}(\underline{r}_1,\dots,\underline{r}_N)\right] d^3r_1 \dots d^3r_N \qquad (5.25)$$

or

$$Z(N,V,T) = Z^{aff}(N,V,T)\; Z^{rep}(N,V) \qquad (5.26)$$

where $$Z^{aff}(N,V,T) = \exp\left[-\beta \frac{N^2}{V} 2\pi \int_\sigma^\infty V_{pair}^{aff}(r)\, r^2 dr\right] \qquad (5.27)$$

$$Z^{rep}(N,V) = \int \underbrace{\exp\left[-\beta V^{rep}(\underline{r}_1,\dots,\underline{r}_N)\right]}_{\text{either 0 or 1}} d^3\underline{r}_1 \dots d^3\underline{r}_N = \int d^3\underline{r}_1 \dots d^3\underline{r}_N \qquad (5.28)$$

all non-overlapping configurations of N hard spheres in volume V.

## Approximate Calculation of $Z^{rep}(N,V)$

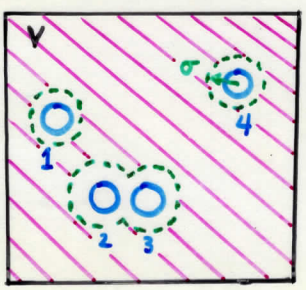
- $Z^{rep}$ can be written as a product of "free volumes", available for addition of the 1st, 2nd, ..., $N^{th}$ particle:

$$Z^{rep}(N,V) = \int d^3r_1 \; \frac{\int_{\text{no overlap}} d^3r_1\, d^3r_2}{\int d^3r_1} \; \frac{\int_{\text{no overlap}} d^3r_1\, d^3r_2\, d^3r_3}{\int_{\text{no overlap}} d^3r_1\, d^3r_2} \cdots \frac{\int_{\text{no overlap}} d^3r_1\, d^3r_2 \dots d^3r_N}{\int_{\text{no overlap}} d^3r_1\, d^3r_2 \dots d^3r_{N-1}} = \prod_{i=1}^{N} V_f^{(i)} \qquad (5.29)$$

$V_f^{(1)}$ $V_f^{(2)}$ $V_f^{(3)}$ ... $V_f^{(N)}$

where

$V_f^{(i)}$ = volume available for adding the center of an $i^{th}$ hard sphere into a nonoverlapping configuration of (i-1) hard spheres in a total volume V so that a non-overlapping configuration of i spheres is created, averaged over all possible nonoverlapping configurations of (i-1) spheres.




e.g. $V_f^{(5)}$ = volume of shaded region (inside V, outside all excluded volumes) averaged over all nonoverlapping configurations of 1, 2, 3, 4.

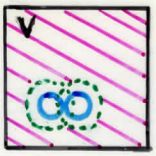
Let $V_e = \frac{4}{3}\pi\sigma^3$ (excluded volume of one sphere) (5.30)

Clearly, $V_f^{(1)} = V$

$V_f^{(2)} = V - V_e$

van der Waals approximation for $V_f^{(i)}$: $V_f^{(i)} = V - (i-1)V_e$ (5.31)

- Approximation (5.31) underestimates $V_f^{(i)}$, as it fails to recognize that the excluded volume spheres of particles 1, 2, ..., i-1 may actually overlap.




e.g. For the configuration on the left, the volume available for addition of a third particle is greater than $V - 2V_e$.

- Approximation (5.31) ignores three-body and higher correlations between particles. (All that is accounted for is two-body exclusion).

- Approximation (5.31) becomes satisfactory at low densities:

$$N V_e << V \quad , \text{ or } \quad \rho V_e << 1 \qquad (5.32)$$

We will assume that condition (5.32) is fulfilled in our analysis.

Combining (5.29) with the approximation (5.31), we obtain:

$$Z^{rep}(N,V) = \prod_{i=1}^{N} [V - (i-1)V_e] = V^N \prod_{i=1}^{N} \left[1 - (i-1)\frac{V_e}{V}\right], \text{ or}$$

$$\frac{Z^{rep}(N,V)}{V^N} = \left[1 - \frac{V_e}{V}\right]\left[1 - 2\frac{V_e}{V}\right] \cdots \left[1 - (N-1)\frac{V_e}{V}\right] \qquad (5.33)$$

In view of the condition (5.32), we can expand the product in eq 5.33 and retain only the first order term in $\frac{V_e}{V}$:

$$\frac{Z^{rep}(N,V)}{V^N} \simeq 1 - \left[\frac{V_e}{V} + 2\frac{V_e}{V} + \cdots + (N-1)\frac{V_e}{V}\right] = 1 - \frac{V_e}{V}\left[1+2+\cdots+(N-1)\right] =$$

$$= 1 - \frac{V_e}{V}\cdot\frac{(N-1)N}{2} \simeq 1 - \frac{V_e}{V}\frac{N^2}{2} = 1 - \frac{NV_e}{2V}N \simeq \left(1 - \frac{NV_e}{2V}\right)^N \quad (5.34)$$

where the last substitution is again justified by (5.32).

Our final result for the $Z^{rep}$ term can be written:

$$Z^{rep}(N,V) = V^N\left(1 - \frac{NV_e}{2V}\right)^N = V^N\left(1 - \frac{N}{V}\cdot\frac{2}{3}\pi\sigma^3\right)^N \quad (5.35)$$

Now, introduce the notation:

$$a = -2\pi N_{Avo}^2 \int_\sigma^\infty v_{pair}^{att}(r)\, r^2\, dr \quad (5.36)$$

$$b = N_{Avo}\frac{2}{3}\pi\sigma^3 = N_{Avo}\, 4V_{HS} = N_{Avo}\frac{V_e}{2} \quad (5.37)$$

molecular hard sphere volume

molecular excluded volume

Equations (5.26), (5.27), (5.35) to (5.37) give:

$$Z(N,V,T) = \exp\left(+\beta a \frac{N^2}{V N_{Avo}^2}\right) V^N \left(1 - \frac{Nb}{V N_{Avo}}\right)^N \quad (5.38)$$

or $$\ln Z(N,V,T) = N\ln V + N\ln\left(1 - \frac{Nb}{VN_{Avo}}\right) + \frac{1}{k_BT}\, a\, \frac{N^2}{VN_{Avo}}$$

Using (4.22),

$$P = k_BT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} = k_BT\left[\frac{N}{V} + \frac{N^2 b}{V^2 N_{Avo}}\frac{1}{1 - \frac{Nb}{VN_{Avo}}} - \frac{1}{k_BT}\, a\, \frac{N^2}{V^2 N_{Avo}^2}\right]$$

(5.39)

Realizing that $\frac{V N_{Avo}}{N} = v$, molar volume of the fluid, we obtain from (5.39)

$$P = RT\left[\frac{1}{v} + \frac{b}{v^2}\,\frac{1}{1-\frac{b}{v}}\right] - \frac{a}{v^2} = \frac{RT}{v}\cdot\frac{1}{1-\frac{b}{v}} - \frac{a}{v^2} = \frac{RT}{v-b} - \frac{a}{v^2},$$

or

$$\boxed{\left(P + \frac{a}{v^2}\right)(v-b) = RT} \qquad \text{vdW EOS} \qquad (5.40)$$

NOTES

- Although quantitatively inexact, the van der Waals equation unified all experimental knowledge of fluid behavior at the time of its development by
  - accounting for deviations from the ideal gas law.
  - predicting gas-liquid equilibrium and the existence of a critical point.
  - providing support to the molecular hypothesis.

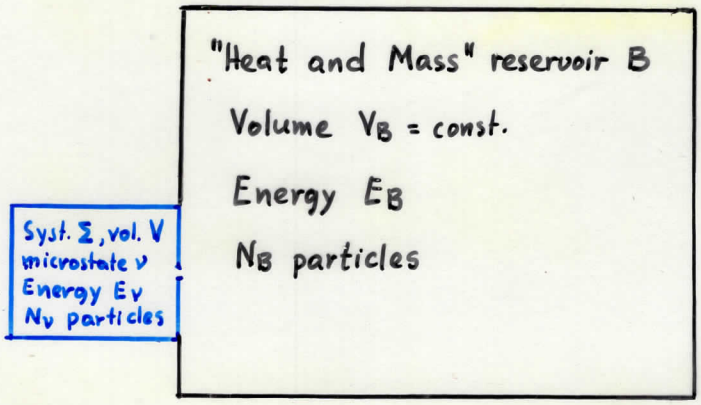
- The concept of short-range repulsive and long-range attractive forces between molecules, and the idea that fluid structure is dictated by the former, are very important. In a sense, van der Waals introduced the first perturbation theory, using the hard-sphere fluid as a reference fluid.

- Much more accurate equations of state exist today for hard-sphere fluids than the one obtained from the van der Waals equation for $a = 0$.

# 6. THE GRAND CANONICAL ($\mu VT$) ENSEMBLE

Statistical microscopic representation of an open system of given volume, capable of exchanging energy and particles with its surroundings.

## 6.1. Derivation of the Probability Density from Microcanonical Ensemble




System

$\Sigma' = \Sigma + B$ $\quad B >> \Sigma$

at constant

$N_{\Sigma'} = N + N_B$ $\quad$ N fluctuates

$V_{\Sigma'} = V + V_B$ $\quad$ V const.

$E_{\Sigma'} = E + V_B$ $\quad$ E fluctuates

Specification of a microstate for $\Sigma$ entails specifying N and E
Consider system $\Sigma$ being in particular state $\nu$, characterized by $N_\nu$, $E_\nu$

Number of microstates accessible to total system under these conditions is $\Omega_B (N_{\Sigma'} - N_\nu, V_B, E_{\Sigma'} - E_\nu)$, or, for brevity, $\Omega_B (N_{\Sigma'} - N_\nu, E_{\Sigma'} - E_\nu)$

Total system $\Sigma'$ is isolated, therefore described by the microcanonical ensemble. All the microstates of $\Sigma'$ are equiprobable, each with probability $\dfrac{1}{\Omega_{\Sigma'}(N_{\Sigma'}, V_{\Sigma'}, E_{\Sigma'})}$

Probability that $\Sigma$ will be in state $\nu$ is

$$P_\nu = \frac{\Omega_B (N_{\Sigma'} - N_\nu, E_{\Sigma'} - E_\nu)}{\Omega_{\Sigma'}(N_{\Sigma'}, V_{\Sigma'}, E_{\Sigma'})} = \text{Const. } \Omega_B (N_{\Sigma'} - N_\nu, E_{\Sigma'} - E_\nu) \qquad (6.1)$$

Using the fact that B is much larger than $\Sigma$,

$$P_\nu = \text{Const.}\ \Omega_B(N_{\Sigma'}, E_{\Sigma'}) \exp\left[\ln\Omega_B(N_{\Sigma'}-N_\nu, E_{\Sigma'}-E_\nu) - \ln\Omega_B(N_{\Sigma'}, E_{\Sigma'})\right] =$$

$$= \text{Const}' \exp\left[-E_\nu \left.\frac{\partial \ln\Omega_B}{\partial E_B}\right)_{N_B=N_{\Sigma'}, V_B} - N_\nu \left.\frac{\partial \ln\Omega_B}{\partial N_B}\right)_{E_B=E_{\Sigma'}, V_B}\right] \quad (6.2)$$

Now (microcanonical ensemble formalism)

$$\left.\frac{\partial \ln\Omega_B}{\partial E_B}\right)_{N_B, V_B} = \frac{1}{k_B T_B} \quad \text{(4.5)}$$

← temperature

Also, set

$$\left.\frac{\partial \ln\Omega_B}{\partial N_B}\right)_{E_B, V_B} = \frac{1}{k_B}\left.\frac{\partial S_B}{\partial N_B}\right)_{E_B, V_B} = -\frac{\mu_B}{k_B T_B} \quad (6.3)$$

← chemical potential per particle.

{ NOTE: Eq. (6.3) is consistent with thermodynamics: For a 1-component system, $dU = TdS - PdV + \mu dn \Rightarrow \left.\frac{\partial S}{\partial n}\right)_{U,V} = -\frac{\mu}{T}$. The chemical potential of statistical mechanics is absolute, rather than relative, and expressed per molecule, rather than per mole }

The quantities $T_B$, $\mu_B$ characterize the reservoir.

Setting $T_B = T = \frac{1}{k_B \beta}$, $\mu_B = \mu$, the probability distribution becomes

$$P_\nu^{\mu VT} = \text{const}' \exp\left[-\beta E_\nu + \beta \mu N_\nu\right], \text{ or}$$

Probability $$P_\nu^{\mu VT} = \frac{\exp\left[-\beta E_\nu + \beta\mu N_\nu\right]}{\Xi(\mu, V, T)} \quad (6.4)$$

where $$\Xi(\mu, V, T) = \sum_\nu \exp\left[-\beta E_\nu + \beta\mu N_\nu\right] \quad (6.5)$$

GRAND PARTITION FUNCTION

↑ summation over all numbers of particles $N_\nu$ and for all energy states for each $N_\nu$.

## Classical Formulation:

Microstate specified as $N, \underset{\sim}{q}^N, \underset{\sim}{p}^N$.

Probability density

$$\rho^{\mu VT}(\underset{\sim}{q}^N, \underset{\sim}{p}^N) = \frac{1}{\Xi(\mu,V,T)} \frac{1}{h^{3N} N!} \exp\left[-\beta \mathcal{H}(\underset{\sim}{q}^N, \underset{\sim}{p}^N, N) + \beta\mu N\right] =$$

$$= \frac{1}{\Xi(\mu,V,T)} \frac{1}{h^{3N} N!} z^N \exp\left[-\beta \mathcal{H}(\underset{\sim}{q}^N, \underset{\sim}{p}^N, N)\right] \quad (6.6)$$

where Grand Partition Function is

$$\Xi(\mu,V,T) = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int_{\substack{\text{all phase space} \\ \text{accessible to} \\ N \text{ particles}}} d^{3N}q \; d^{3N}p \; \exp\left[-\beta \mathcal{H}(\underset{\sim}{q}^N, \underset{\sim}{p}^N, N) + \beta\mu N\right] =$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{h^{3N} N!} \int_{\substack{\text{all phase space} \\ \text{accessible to} \\ N \text{ particles}}} d^{3N}q \; d^{3N}p \; \exp\left[-\beta \mathcal{H}(\underset{\sim}{q}^N, \underset{\sim}{p}^N, N)\right] =$$

$$= \sum_{N=0}^{\infty} z^N \, Q(N,V,T) \quad (6.7)$$

↳ canonical partition function

and $z = \exp(\beta\mu)$, "activity" (compare $\mu - \mu^\circ = RT \ln a$) (6.8)

## 6.2. Connection with Thermodynamics

Definition: $\Omega(\mu, V, T) = -k_B T \ln \Xi(\mu, V, T)$ : GRAND POTENTIAL

In a homogeneous system,

$$-PV = \Omega(\mu, V, T) = -k_B T \ln \Xi(\mu, V, T) \qquad (6.9)$$

[ Makes sense: Maximum term approximation on (6.7) gives

$-k_B T \ln \Xi(\mu,V,T) = -k_B T N \ln z - k_B T \ln Q(\langle N\rangle, V, T) = -N\mu + A = -G + A = -PV$ ]

Average number of particles in the system:

$$\langle N\rangle_{\mu VT} = \sum_\nu P_\nu^{\mu VT} N_\nu = z \left.\frac{\partial \ln \Xi}{\partial z}\right)_{V,T} = k_B T \left.\frac{\partial \ln \Xi}{\partial \mu}\right)_{T,V} \qquad (6.10)$$

Eliminating $\mu$ between (6.9) and (6.10), one obtains an equation of state.

Gibbs energy: $G = \langle N\rangle \mu = \langle N\rangle k_B T \ln z = k_B T \left.\frac{\partial \ln \Xi}{\partial \ln \mu}\right)_{T,V}$ (6.11)

Helmholtz energy: $A = G - PV = \langle N\rangle \mu - k_B T \ln \Xi = k_B T \left[\left.\frac{\partial \ln \Xi}{\partial \ln \mu}\right)_{T,V} - \ln \Xi\right]$ (6.12)

Formulation for a multicomponent system : n components

$N = N_1 + N_2 + \cdots + N_n$

$N, N_1, \ldots, N_n$ fluctuating ; $\mu_1, \ldots, \mu_n$ fixed

$$\rho^{\mu_1 \mu_2 \cdots \mu_n VT}(\underset{\sim}{r}^N, \underset{\sim}{p}^N, N_1, N_2, \ldots, N_n) = \frac{1}{\Xi(\mu_1, \mu_2, \ldots, \mu_n, V, T)} \frac{e^{-\beta \mathcal{H}(\underset{\sim}{r}^N, \underset{\sim}{p}^N, N_1, N_2, \ldots, N_n) + \beta(\mu_1 N_1 + \mu_2 N_2 + \cdots + \mu_n N_n)}}{h^{3N} N_1! N_2! \cdots N_n!} \qquad (6.13)$$

where

$$\Xi(\mu_1, \mu_2, \ldots, \mu_n, V, T) = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \cdots \sum_{N_n=0}^{\infty} \frac{1}{h^{3N} N_1! N_2! \cdots N_n!} \int d^{3N}r \, d^{3N}p \exp\left[-\beta \mathcal{H}(\underset{\sim}{r}^N, \underset{\sim}{p}^N, N_1, \ldots, N_n) + \beta(\mu_1 N_1 + \cdots \mu_n N_n)\right]$$

## 6.3. Density Fluctuations in the Grand Canonical Ensemble

Variance in number of particles in a one-component system. (All averages at constant $\mu, V, T$):

$$\langle (\delta N)^2 \rangle \equiv \langle (N - \langle N \rangle)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 \qquad (6.14)$$

From eq (6.10): $\langle N \rangle = k_B T \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{T,V}$ (6.15)

hence

$$\left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{1}{\beta} \left( \frac{\partial^2 \ln \Xi}{\partial \mu^2} \right)_{T,V} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \left[ \frac{1}{\Xi} \left( \frac{\partial \Xi}{\partial \mu} \right)_{T,V} \right]_{T,V} =$$

$$= \beta \left[ \frac{1}{\beta^2 \Xi} \left( \frac{\partial^2 \Xi}{\partial \mu^2} \right)_{\beta,V} - \left\{ \frac{1}{\beta \Xi} \left( \frac{\partial \Xi}{\partial \mu} \right)_{\beta,V} \right\}^2 \right] \qquad (6.16)$$

Now, $\Xi = \sum_\nu \exp[-\beta E_\nu + \beta \mu N_\nu]$, so $\frac{1}{\Xi} \left( \frac{\partial^2 \Xi}{\partial \mu^2} \right)_{\beta,V} = \beta^2 \frac{\sum_\nu N_\nu^2 \exp[-\beta E_\nu + \beta \mu N_\nu]}{\sum_\nu \exp[-\beta E_\nu + \beta \mu N_\nu]}$

or $\frac{1}{\beta^2} \frac{1}{\Xi} \left( \frac{\partial^2 \Xi}{\partial \mu^2} \right)_{\beta,V} = \langle N^2 \rangle \qquad (6.17)$

Using (6.15) and (6.17) in (6.16), we obtain

$$\left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \beta \left[ \langle N^2 \rangle - \langle N \rangle^2 \right] \qquad (6.18)$$

The left-hand side of (6.18) can be obtained from classical thermodynamics:

$$\left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{N_{Avo}^2}{\left[ \frac{\partial (\mu N_{Avo})}{\partial \left( \frac{\langle N \rangle}{N_{Avo}} \right)} \right]_{T,V}} = \frac{N_{Avo}^2}{\left( \frac{\partial (-s\,dT + v\,dP)}{\partial n} \right)_{T,V}} = \frac{N_{Avo}^2}{v \left( \frac{\partial P}{\partial n} \right)_{T,V}} = - \frac{N_{Avo}^2 \left( \frac{\partial V}{\partial P} \right)_{T,n}}{v \left( \frac{\partial V}{\partial n} \right)_{T,P}}$$

$$= - \frac{N_{Avo}^2}{V} \frac{n \left( \frac{\partial V}{\partial P} \right)_T}{V} = \frac{\langle N \rangle^2}{V n} \underbrace{\left[ - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \right]}_{\kappa_T}$$

or $$\left.\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = \frac{\langle N\rangle^2}{V}\kappa_T \qquad (6.19)$$

$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_T$ = ISOTHERMAL COMPRESSIBILITY

Combining (6.18), (6.19):

$$\langle (\delta N)^2\rangle \equiv \langle (N-\langle N\rangle)^2\rangle = k_B T \frac{\langle N\rangle^2}{V}\kappa_T \text{ , or}$$

an intensive thermodynamic property

$$\frac{\langle (\delta N)^2\rangle^{1/2}}{\langle N\rangle} \equiv \frac{\langle (N-\langle N\rangle)^2\rangle^{1/2}}{\langle N\rangle} = \frac{[\langle N^2\rangle - \langle N\rangle^2]^{1/2}}{\langle N\rangle} = \left(\frac{RT}{v}\kappa_T\right)^{1/2}\cdot\frac{1}{\langle N\rangle^{1/2}}$$

(compressibility equation) (6.20)

CONCLUSIONS from (6.20)

- $\kappa_T > 0$ for a thermodynamically stable system.
- The ratio $\frac{\langle (\delta N)^2\rangle^{1/2}}{\langle N\rangle}$ vanishes in the thermodynamic limit:
  The distribution of N values becomes extremely peaked at $\langle N\rangle$, and the grand canonical ensemble formalism yields the same results as canonical ensemble.
- Fluctuation in molecular density $\rho$: $\langle (\delta\rho)^2\rangle^{1/2} = \rho\left(\frac{k_B T}{V}\kappa_T\right)^{1/2}$ (6.21)
  At the critical point of a substance, $\kappa_T \to \infty$
  Density fluctuations from point to point in a fluid become unbounded.
  This causes a pure substance to become turbid at the critical point.
  (CRITICAL OPALESCENCE)

[ Explanation: Rayleigh scattering: $\frac{I(\theta)}{I_0} = \frac{\pi^2 V^2 \langle (\delta\epsilon)^2\rangle}{2\lambda^4}\frac{(1+\cos^2\theta)}{R^2}$ ← variance of dielectric constant

But $\frac{\epsilon-1}{\epsilon+2} = A\rho$ (Clausius-Mosotti) $\Rightarrow$ $\langle (\delta\epsilon)^2\rangle = \frac{(\epsilon-1)^2(\epsilon+2)^2}{9}\cdot\frac{\langle (\delta\rho)^2\rangle}{\rho^2}$

Hence $\frac{\dot{E}_{scattered}}{I_0} = \int \frac{I(\theta)}{I_0} R^2 \sin\theta\, d\theta\, d\phi = \frac{8\pi^3}{27\lambda^4} k_B T (\epsilon-1)^2(\epsilon+2)^2 V \kappa_T$ ]

# 6.4. Application of the Grand Canonical Ensemble: DERIVATION OF THE BET ADSORPTION ISOTHERM FOR MULTILAYER ADSORPTION.

References:

Brunauer, S.; Emmett, P.H.; Teller, E. J. Am. Chem. Soc. 1938, 60, 309.

Hill, T.L. Statistical Mechanics, Mc Graw-Hill, 1956, Appendix 4.

Hill, T.L. J. Chem. Phys. 1946, 14, 263, 268.

## The BET Equation

System: Gas/solid surface. Gas adsorbs on surface, forming multiple molecular layers.

Isotherm: An expression for the adsorbed amount as a function of ambient gas pressure, at given temperature.

$$\frac{c}{c_m} = \frac{b\,(P/P_s)}{\left(1-\frac{P}{P_s}\right)\left(1-\frac{P}{P_s}+b\,\frac{P}{P_s}\right)} \qquad (P<P_s) \qquad (6.22)$$

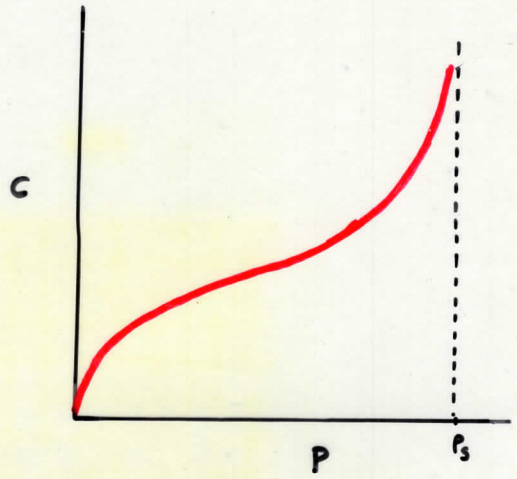
$c$: adsorbed amount per unit mass sorbent, mol/g

$c_m$: adsorbed amount that would correspond to full coverage of the surface by a monolayer.

$P$: gas-phase pressure

$P_s$: vapor pressure of saturated liquid sorbate at the prevailing temperature.

General shape of the isotherm:




(Type II in Brunauer classification)

Utility in calculating specific surface areas of porous solids:

- Perform measurements of sorbed amount using a nonpolar gas ($N_2$, Ar) at liquid nitrogen temperatures, over a range of pressures $0.05 < \frac{P}{P_s} < 0.35$

- Plot experimental results in the form:

$$\frac{P}{c\,(P_s - P)} \quad \text{versus} \quad \frac{P}{P_s}$$

According to BET isotherm, plot should be linear:

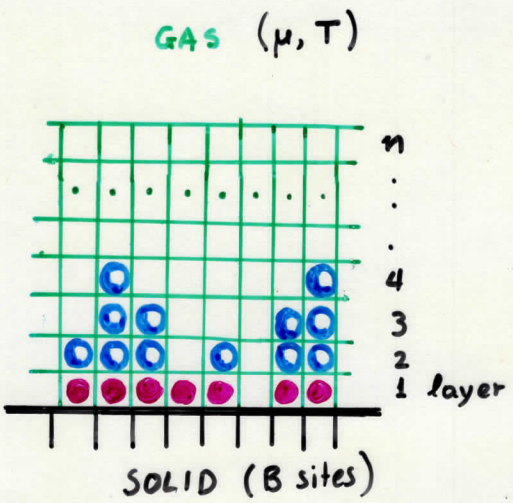
$$\frac{P}{c\,(P_s - P)} = \frac{1}{c_m b}\left[(b-1)\left(\frac{P}{P_s}\right) + 1\right] \qquad (6.23)$$

- Obtain $c_m$, $b$ from slope and intercept.

- Knowing the surface area occupied by a molecule of the gas, translate $c_m$ (mol sorbate / g sorbent) into a specific surface area ($cm^2$ internal + external surface / g sorbent).

Absolute specific surface areas can be determined to within 20% by this method.

## Model Assumptions.




1. Surface consists of an array of identical sorption sites.
2. Gas molecules can adsorb directly on the surface to form the first layer. Gas molecules can also adsorb on top of adsorbed gas molecules, to form layers 2, ..., n. (We will assume for the moment that up to $n$ layers can be formed).
3. There is no lateral interaction between sorbed molecules in layer 1, apart from the requirement that no two molecules can occupy the same sorption site. In the statistical mechanical formulation, all molecules in the 1st layer can be modelled as independent entities, each with its own partition function $q_1$.
4. Molecules in layers 2, ..., n form a phase which is similar to a saturated liquid at temperature T. They, too, can be treated in the formulation as independent entities, each with its own partition function $q_L$. The quantity $q_L$ is the same for all layers 2, ..., n.
5. The pressure is sufficiently low that the gas phase can be treated as ideal. If the sorbate molecules have internal structure, they are characterized by an internal partition function $q_G^{int}$.

## Formulation

Treat the problem in the Grand Canonical Ensemble (particularly convenient for sorption applications).

- Let gas chemical potential be $\mu$.

  Note: (connection with gas-phase pressure)

$$\mu = k_B T \ln\left(\frac{\rho_G \Lambda^3}{q_G^{int}}\right) = k_B T \ln\left(\frac{P\Lambda^3}{k_B T\, q_G^{int}}\right) \qquad (4.45)$$

- By virtue of phase equilibrium, chemical potential must be $\mu$ throughout the adsorbed phase.

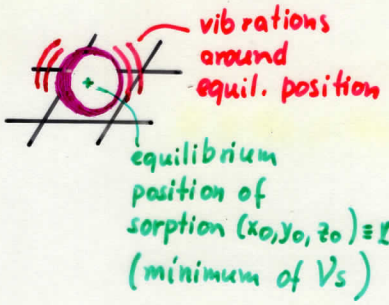
- Focus on a section of the surface containing B sites.

- Adsorbed phase has given spatial extent $(B, n)$, chemical potential, and Temperature. Grand Canonical Ensemble applicable.

### What goes into the partition function $q_1$ ?

- For molecules with internal structure, contributions from vibrational motion of bonds and bond angles, torsional and overall rotational motion. (what goes into $q_G^{int}$. Values of these contributions in the sorbed state may be quite different from gas phase).
- Potential energy of adsorptive (surface-molecule) interaction.
- Contributions from center of mass vibration around equilibrium position of sorption (uninhibited translation on surface no longer possible).

e.g. For spherical (structureless) molecule kept to a site by a solid-molecule potential $\mathcal{V}_s(\underline{r})$




Sorption potential around equilibrium position $(x_0, y_0, z_0)$ is well approximated by the expression

$$\mathcal{V}_s = \mathcal{V}_{s,0} + \underbrace{\left.\frac{\partial \mathcal{V}_s}{\partial \underline{r}}\right|_{\underline{r}_0} \cdot (\underline{r} - \underline{r}_0)}_{0 \text{ (potential function has a minimum at } \underline{r}_0)} + \frac{1}{2}\left.\frac{\partial^2 \mathcal{V}_s}{\partial x^2}\right|_{\underline{r}_0}(x-x_0)^2 + \frac{1}{2}\left.\frac{\partial^2 \mathcal{V}_s}{\partial y^2}\right|_{\underline{r}_0}(y-y_0)^2 + \frac{1}{2}\left.\frac{\partial^2 \mathcal{V}_s}{\partial z^2}\right|_{\underline{r}_0}(z-z_0)^2$$

Hamiltonian consists of potential energy $\mathcal{V}_{s,0} < 0$ plus three independent harmonic oscillator Hamiltonians, with frequencies

$$\omega_x = \sqrt{\frac{1}{m}\left.\frac{\partial^2 \mathcal{V}_s}{\partial x^2}\right|_{\underline{r}_0}}, \quad \omega_y = \sqrt{\frac{1}{m}\left.\frac{\partial^2 \mathcal{V}_s}{\partial y^2}\right|_{\underline{r}_0}}, \quad \omega_z = \sqrt{\frac{1}{m}\left.\frac{\partial^2 \mathcal{V}_s}{\partial z^2}\right|_{\underline{r}_0}}$$

Partition function of molecule sorbed in layer 1:

$$q_1 = \exp\left(-\beta \mathcal{V}_{s,0}\right) \frac{\exp\left(-\beta\hbar\frac{\omega_x}{2}\right)}{1-\exp\left(-\beta\hbar\omega_x\right)} \cdot \frac{\exp\left(-\beta\hbar\frac{\omega_y}{2}\right)}{1-\exp\left(-\beta\hbar\omega_y\right)} \cdot \frac{\exp\left(-\beta\hbar\frac{\omega_z}{2}\right)}{1-\exp\left(-\beta\hbar\omega_z\right)} \qquad (6.24)$$

[ If vibration frequencies are low enough compared to $\frac{k_B T}{\hbar}$, then $q_1 = \exp\left(-\beta \mathcal{V}_{s,0}\right) \cdot \left(\frac{k_B T}{\hbar}\right)^3 \cdot \frac{1}{\omega_x \omega_y \omega_z}$, in the classical limit ]

Similarly, partition function $q_L$ reflects local environment in one of the layers sorbed on top of the first layer.

# Grand Partition Function

Let $N_1, N_2, \ldots, N_n$ the number of molecules in the 1st, ..., $n^{th}$ layer.
(These fluctuate, in response to a fixed chemical potential $\mu$)
For all physically acceptable configurations,

$$0 \leq N_n \leq N_{n-1} \leq \cdots \leq N_2 \leq N_1 \leq B$$ (a molecule must sit on something!)

## Grand Partition Function:

$$\Xi(\mu, B, n, T) = \sum_{N_1=0}^{B} \sum_{N_2=0}^{N_1} \sum_{N_3=0}^{N_2} \cdots \sum_{N_n=0}^{N_{n-1}} \left\{ \frac{B!}{(B-N_1)!\, N_1!} \frac{N_1!}{(N_1-N_2)!\, N_2!} \cdots \frac{N_{n-1}!}{(N_n-N_{n-1})!\, N_n!} \times \right.$$

(6.25)

$$\left. \times\, q_1^{N_1}\, q_L^{N_2+\cdots+N_n} \exp\left[(N_1+N_2+\cdots+N_n)\beta\mu\right] \right\}$$

- $\frac{B!}{(B-N_1)!\, N_1!}$: ways of arranging $N_1$ noninteracting molecules in B lattice sites
- $\frac{N_1!}{(N_1-N_2)!\, N_2!}$: ways of arranging $N_2$ non-interacting molecules on $N_1$ molecules
- $q_1^{N_1}$: each independent molecule in layer 1 contributes its individual partition function, $q_1$
- $q_L^{N_2+\cdots+N_n}$: each independent molecule in one of the layers 2, ..., n contributes its individual partition function, $q_L$
- $\exp\left[(N_1+N_2+\cdots+N_n)\beta\mu\right]$: chemical potential is everywhere $\mu$

$\Xi(\mu, B, n, T)$ can be calculated analytically!

Call $q_L \exp(\beta\mu) = x$ (6.26)

$$\frac{q_1}{q_L} = \lambda$$

$$\Xi(\mu, B, n, T) = \sum_{N_1=0}^{B} \sum_{N_2=0}^{N_1} \cdots \sum_{N_n=0}^{N_{n-1}} \frac{B!}{(B-N_1)!\, N_1!} \frac{N_1!}{(N_1-N_2)!\, N_2!} \cdots \frac{N_{n-1}!}{(N_n-N_{n-1})!\, N_n!} (\lambda x)^{N_1} x^{N_2+\cdots+N_n} \qquad (6.27)$$

Do the innermost summation first:

$$\sum_{N_n=0}^{N_{n-1}} \frac{N_{n-1}!}{(N_n-N_{n-1})!\, N_n!} x^{N_n} = \sum_{N_n=0}^{N_{n-1}} \binom{N_{n-1}}{N_n} x^{N_n} = (1+x)^{N_{n-1}}$$ Binomial Theorem

Do the summation over $N_{n-1}$ next:

$$\sum_{N_{n-1}=0}^{N_{n-2}} \frac{N_{n-2}!}{(N_{n-2}-N_{n-1})!\, N_{n-1}!} \underbrace{\frac{x^{N_{n-1}} (1+x)^{N_{n-1}}}{[x(1+x)]^{N_{n-1}}}} = [1+x(1+x)]^{N_{n-2}} = [1+x+x^2]^{N_{n-2}}$$

. . .

Summation over $N_2$ will give:

$$\sum_{N_2=0}^{N_1} \frac{N_1!}{(N_1-N_2)!\, N_2!} x^{N_2} \left(1+x+x^2+\cdots+x^{n-2}\right)^{N_2} = \left(1+x+x^2+\cdots+x^{n-1}\right)^{N_1}$$

Do the outermost summation last:

$$\Xi(\mu, B, n, T) = \sum_{N_1=0}^{B} \frac{B!}{(B-N_1)!\, N_1!} (\lambda x)^{N_1} \left(1+x+x^2+\cdots+x^{n-1}\right)^{N_1} = \left[1+\lambda x\left(1+x+\cdots+x^{n-1}\right)\right]^B,$$

or

$$\Xi(\mu, B, n, T) = \left[1 + \lambda x \left(\frac{1-x^n}{1-x}\right)\right]^B \qquad (6.28).$$

The average number of adsorbed molecules at equilibrium can be found as:

$$\langle N \rangle \equiv \langle N_1 + N_2 + \cdots + N_n \rangle = k_B T \left.\frac{\partial \ln \Xi}{\partial \mu}\right)_{B,n,T} = \frac{1}{\beta} \left.\frac{\frac{\partial \ln \Xi}{\partial x}}{\frac{1}{\beta}\frac{\partial x}{x}}\right)_{B,n,T} = x \left.\frac{\partial \ln \Xi}{\partial x}\right)_{B,}$$

or $\langle N \rangle = x B \left[1 + \lambda x \left(\frac{1-x^n}{1-x}\right)\right]^{-1} \lambda \frac{n x^{n+1} - (n+1) x^n + 1}{(1-x)^2}$, or

$$\frac{\langle N \rangle}{B} = \frac{\mathcal{J} x \left[ 1 - (n+1) x^n + n x^{n+1} \right]}{(1-x)\left(1 - x + \mathcal{J} x - \mathcal{J} x^{n+1}\right)} \qquad (6.29)$$

Eq (6.29) is really an adsorption isotherm. By definition, we can identify

$$\frac{\langle N \rangle}{B} = \frac{c}{c_m} \qquad (6.30)$$

($c$: adsorbed amt.; $c_m$: adsorbed amt. corresponding to full monomolecular coverage.)

As regards the quantity $x$, in order to give it a tangible interpretation we think as follows:

Consider the average number of molecules in the first layer, $\langle N_1 \rangle$. From the form of the grand partition function, eq (6.27), we have:

$$\langle N_1 \rangle = \mathcal{J} \cdot \frac{1}{\Xi} \left( \frac{\partial \Xi}{\partial \mathcal{J}} \right)_{x,B} = \mathcal{J} \left( \frac{\partial \ln \Xi}{\partial \mathcal{J}} \right)_{x,B}$$

Substituting from (6.28), we obtain:

$$\frac{\langle N_1 \rangle}{B} = \frac{\mathcal{J} x \left(1 - x^n\right)}{1 - x + \mathcal{J} x - \mathcal{J} x^{n+1}} \qquad (6.31)$$

Combining (6.29) and (6.31),

$$\frac{\langle N \rangle}{\langle N_1 \rangle} = \frac{1 - (n+1)x^n + n x^{n+1}}{(1-x)\left(1 - x^n\right)}$$

Consider, now, the system as the gas-phase pressure tends towards the saturation pressure $P_s$. In that limit, all layers will be filled with saturated liquid, and therefore

As $P \to P_s$, $\dfrac{\langle N \rangle}{\langle N_1 \rangle} = n \overset{(6.29,6.31)}{\Rightarrow} 1-(n+1)x^n + nx^{n+1} = n\left(1-x-x^n+x^{n+1}\right) \Rightarrow$

$$\Rightarrow 1-(\cancel{n}+1)x^n + \cancel{nx^{n+1}} = n - nx - \cancel{nx^n} + \cancel{nx^{n+1}} \Rightarrow$$

$$\Rightarrow 1-x^n = n(1-x) \Rightarrow (1-x)\left[1+x+\cdots+x^{n-1}-n\right] = 0$$

Now, the only possible real solution to the above equation is $x=1$. Therefore, we conclude:

As $P \to P_s$, $x \to 1$. (6.32)

Recall, now, that, by eq (6.26), (4.45):

$$x = q_L \cdot \frac{P\Lambda^3}{k_B T q_G^{int}} \tag{6.33}$$

Taking the limit (6.32), eq (6.33) gives:

$$1 = q_L \frac{P_s \Lambda^3}{k_B T q_G^{int}} \Rightarrow q_L = \frac{k_B T q_G^{int}}{P_s \Lambda^3} \tag{6.34}$$

Thus, we managed to attribute a concrete meaning to the partition function $q_L$. Combining (6.33) and its limiting form, eq (6.34), we obtain immediately:

$$x = \frac{P}{P_s} < 1. \tag{6.35}$$

In view of eq (6.30), (6.35), eq (6.29) can be recast into the form:

$$\frac{c}{c_m} = \frac{\alpha\left(\frac{P}{P_s}\right)\left[1-(n+1)\left(\frac{P}{P_s}\right)^n + n\left(\frac{P}{P_s}\right)^{n+1}\right]}{\left(1-\frac{P}{P_s}\right)\left[1-\frac{P}{P_s}+\alpha\frac{P}{P_s}-\alpha\left(\frac{P}{P_s}\right)^{n+1}\right]} \quad ; \quad \alpha = \frac{q_1 P_s \Lambda^3}{k_B T q_G^{int}} \tag{6.36}$$

(BET equation for adsorption limited to n layers)

Furthermore, if we let the number of layers $n \to \infty$, we obtain from (6.36) the simpler equation

$$\frac{c}{c_m} = \frac{b\,(P/P_s)}{\left(1-\frac{P}{P_s}\right)\left(1-\frac{P}{P_s}+b\,\frac{P}{P_s}\right)} \quad ; \quad b \equiv \lambda = \frac{q_1 P_s \Lambda^3}{k_B T\, q_G^{int}} \qquad (6.22)$$

which is the BET equation we stated at the beginning of this example!

Note that we have managed to arrive at a molecular interpretation of b. [Compare (6.22), (6.24)]. The coefficient b is a function of temperature. For a structureless (spherical) sorbate, it is shaped by the surface-sorbate energetics and the mass of the sorbate molecule. If the sorbate has internal degrees of freedom, perturbations in these degrees of freedom upon sorption also affect b.

For $n=1$, the general equation (6.36) reduces to

$$\frac{c}{c_m} = \frac{b\,(P/P_s)}{1+b\,(P/P_s)} \quad ; \quad b \equiv \lambda = \frac{q_1 P_s \Lambda^3}{k_B T\, q_G^{int}} \qquad (6.37)$$

which is the Langmuir isotherm for monolayer adsorption.

# 9.1. DISTRIBUTION FUNCTIONS IN CLASSICAL MONATOMIC LIQUIDS

## 9.1.1. n-particle density and n-particle distribution function in the canonical ensemble.

System: Fluid of $N$ molecules in volume $V$ at temperature $T$.

Probability density in configuration space:

$$\rho(\underline{r}_1, \cdots, \underline{r}_N) = \frac{\exp[-\beta V(\underline{r}_1, \cdots, \underline{r}_N)]}{\int \exp[-\beta V(\underline{r}_1, \cdots, \underline{r}_N)]\, d^3\underline{r}_1 \cdots d^3\underline{r}_N} = \frac{1}{Z(N,V,T)} \exp[-\beta V(\underline{r}_1, \cdots, \underline{r}_N)] \tag{9.1}$$

$\rho(\underline{r}_1, \cdots, \underline{r}_N)\, d^3\underline{r}_1 \cdots d^3\underline{r}_N$ = probability of finding particle 1 at position $\underline{r}_1$ to $\underline{r}_1 + d\underline{r}_1$, particle 2 at position $\underline{r}_2$ to $\underline{r}_2 + d\underline{r}_2$, ..., particle $N$ at position $\underline{r}_N$ to $\underline{r}_N + d\underline{r}_N$

Then, $\rho^{1\cdots n}(\underline{r}_1, \cdots, \underline{r}_n) = \int \rho(\underline{r}_1, \cdots, \underline{r}_N)\, d^3\underline{r}_{n+1}\, d^3\underline{r}_{n+2} \cdots d^3\underline{r}_N$ is such that

$\rho^{1\cdots n}(\underline{r}_1, \cdots, \underline{r}_n)\, d^3\underline{r}_1 \cdots d^3\underline{r}_n$ = probability of finding particle 1 at position $\underline{r}_1$ to $\underline{r}_1 + d\underline{r}_1$, ... particle $n$ at position $\underline{r}_n$ to $\underline{r}_n + d\underline{r}_n$.

In practice, we are more interested in expressing the probability of finding <u>a particle</u> at $\underline{r}_1$ to $\underline{r}_1 + d\underline{r}_1$, <u>a particle</u> at $\underline{r}_2$ to $\underline{r}_2 + d\underline{r}_2$, ..., <u>a particle</u> at $\underline{r}_n$ to $\underline{r}_n + d\underline{r}_n$, <u>irrespective of the identities</u> of these particles. The probability density for this is <u>proportional</u> to

$$N(N-1)\cdots(N-n+1)\ \rho^{1\cdots n}(\underline{r}_1, \cdots, \underline{r}_n) = \frac{N!}{(N-n)!}\, \rho^{1\cdots n}(\underline{r}_1, \cdots, \underline{r}_n).$$

$N$ ways of choosing 1st particle; $(N-1)$ ways of choosing 2nd particle; $(N-n+1)$ ways of choosing $n$th particle; $\rho^{1\cdots n}$ probability density for a particular set of $n$ particles to be at $\underline{r}_1$ to $\underline{r}_1 + d\underline{r}_1$, ..., $\underline{r}_n$ to $\underline{r}_n + d\underline{r}_n$.

Thus, we define the n-particle density by

$$\rho_N^{(n)}(\underbrace{\underline{r}_1, \dots, \underline{r}_n}) = \frac{N!}{(N-n)!} \frac{\int \exp[-\beta V(\underline{r}_1, \dots, \underline{r}_N)]\, d^3\underline{r}_{n+1} \cdots d^3\underline{r}_N}{Z(N,V,T)} \qquad (9.2)$$

a function of n positions in space.

$\rho_N^{(n)}(\underline{r}_1, \dots, \underline{r}_n)\, d^3\underline{r}_1 \cdots d^3\underline{r}_n$ $\propto$ (proportionality, not equality!) probability of finding a configuration with a particle located between $\underline{r}_1$ and $\underline{r}_1 + d\underline{r}_1$, a particle located between $\underline{r}_2$ and $\underline{r}_2 + d\underline{r}_2$, ... a particle located between $\underline{r}_n$ and $\underline{r}_n + d\underline{r}_n$

Normalization: $$\int \rho_N^{(n)}(\underline{r}_1, \dots, \underline{r}_n)\, d^3\underline{r}_1 \cdots d^3\underline{r}_n = \frac{N!}{(N-n)!} \qquad (9.3)$$

In the special case of an ideal gas, $V(\underline{r}_1, \dots, \underline{r}_N) = 0$ and $Z(N,V,T) = V^N$. Then,

$$\rho_N^{ig(n)}(\underline{r}_1, \dots, \underline{r}_n) = \frac{N!}{(N-n)!} \cdot \frac{1}{V^n} = \rho^n \frac{N!}{N^n (N-n)!} = \rho^n \left(1 + O\left(\frac{n^2}{N}\right)\right)$$

We define the n-particle distribution function by

$$g_N^{(n)}(\underline{r}_1, \dots, \underline{r}_n) = \frac{\rho_N^{(n)}(\underline{r}_1, \dots, \underline{r}_n)}{\rho^n} \qquad (9.4)$$

$g_N^{(n)}$ measures the extent to which the structure of a fluid deviates from complete randomness (that would prevail in an ideal gas).

## 9.2. n-particle density and n-particle distribution function in the grand canonical ensemble.

In the grand canonical ensemble, the number of particles fluctuates

under constant chemical potential $\mu$, or activity $z = \exp(\beta\mu)$.

The n-particle density is defined by

$$\rho^{(n)}(\underset{\sim}{r}_1, \dots, \underset{\sim}{r}_n) = \sum_{N=n}^{\infty} \frac{N!}{(N-n)!} \int d^3 r_{n+1} \cdots d^3 r_N \; \frac{\exp[-\beta V_N(\underset{\sim}{r}_1, \dots, \underset{\sim}{r}_N) + \beta\mu N]}{N!\, \Lambda^{3N}\, \Xi(\mu, V, T)}$$

↳ from integration of $p^{\mu VT}$ over momentum degrees of freedom of N particles.

or

$$\rho^{(n)}(\underset{\sim}{r}_1, \dots, \underset{\sim}{r}_n) = \frac{1}{\Xi} \sum_{N=n}^{\infty} \frac{\zeta^N}{(N-n)!} \int \exp[-\beta V_N(\underset{\sim}{r}_1, \dots, \underset{\sim}{r}_N)]\, d^3 r_{n+1} \cdots d^3 r_N \qquad (9.5)$$

with $\zeta = \dfrac{\exp(\beta\mu)}{\Lambda^3}$

Normalization:

$$\int \rho^{(n)}(\underset{\sim}{r}_1, \dots, \underset{\sim}{r}_n)\, d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_n = \left\langle \frac{N!}{(N-n)!} \right\rangle \qquad (9.6)$$

↳ grand canonical average

In the special case of an ideal gas,

$$\rho^{ig(n)}(\underset{\sim}{r}_1, \dots, \underset{\sim}{r}_n) = \frac{\sum_{N=n}^{\infty} \frac{\zeta^N}{(N-n)!} V^{N-n}}{\sum_{N=0}^{\infty} \frac{\zeta^N}{N!} V^N} = \zeta^n \overset{(1.3.45)}{=} \left[\frac{\rho\Lambda^3}{\Lambda^3}\right]^n = \rho^n$$

We define the n-particle distribution function by

$$g^{(n)}(\underset{\sim}{r}_1, \dots, \underset{\sim}{r}_n) = \frac{\rho^{(n)}(\underset{\sim}{r}_1, \dots, \underset{\sim}{r}_n)}{\rho^n} \qquad (9.7)$$

## 9.3. The Pair distribution function.

### Definitions

NVT:
$$g_N^{(2)}(\underline{r}_1, \underline{r}_2) = \frac{\rho_N^{(2)}(\underline{r}_1, \underline{r}_2)}{\rho^2} = \frac{N(N-1)}{\rho^2} \frac{\int \exp[-\beta V(\underline{r}_1, \dots, \underline{r}_N)]\, d^3\underline{r}_3 \dots d^3\underline{r}_N}{Z(N,V,T)} \qquad (9.8)$$

μVT:
$$g^{(2)}(\underline{r}_1, \underline{r}_2) = \frac{\rho^{(2)}(\underline{r}_1, \underline{r}_2)}{\rho^2} = \frac{\sum_{N=2}^{\infty} \frac{1}{(N-2)!} \frac{\exp(N\beta\mu)}{\Lambda^{3N}} \int \exp[-\beta V_N(\underline{r}_1, \dots, \underline{r}_N)]\, d^3\underline{r}_3 \dots d^3\underline{r}_N}{\rho^2 \; \Xi(\mu, V, T)} \qquad (9.9)$$

($\rho$: μVT-averaged molecular density.)

### Normalization

$$\int \rho_N^{(2)}(\underline{r}_1, \underline{r}_2)\, d\underline{r}_1 d\underline{r}_2 = \rho^2 \int g_N^{(2)}(\underline{r}_1, \underline{r}_2)\, d^3\underline{r}_1 d^3\underline{r}_2 = N(N-1) \qquad (9.10)$$

$$\int \rho^{(2)}(\underline{r}_1, \underline{r}_2)\, d\underline{r}_1 d\underline{r}_2 = \rho^2 \int g^{(2)}(\underline{r}_1, \underline{r}_2)\, d^3\underline{r}_1 d^3\underline{r}_2 = \langle N(N-1) \rangle = \langle N^2 \rangle - \langle N \rangle \qquad (9.11)$$

### Asymptotic limit at large separations $|\underline{r}_1 - \underline{r}_2| \to \infty$

Structural correlations disappear; structure becomes indistinguishable from that of ideal gas at same density.

$$\lim_{|\underline{r}_1 - \underline{r}_2| \to \infty} g_N^{(2)}(\underline{r}_1, \underline{r}_2) = \frac{\rho_N^{ig(2)}(\underline{r}_1, \underline{r}_2)}{\rho^2} = \frac{\rho^2 \frac{N(N-1)}{N^2}}{\rho^2} = 1 - \frac{1}{N} \qquad (9.13a)$$

$$\lim_{|\underline{r}_1 - \underline{r}_2| \to \infty} g^{(2)}(\underline{r}_1, \underline{r}_2) = \frac{\rho^{ig(2)}(\underline{r}_1, \underline{r}_2)}{\rho^2} = \frac{\rho^2}{\rho^2} = 1 \qquad (9.13b)$$

## Important consequences of the definition of $g(\underline{r}_1, \underline{r}_2)$

$\frac{\rho^2}{N(N-1)}\, g_N^{(2)}(\underline{r}_1, \underline{r}_2)\, d^3r_1\, d^3r_2 =$ Probability of finding a molecule within volume element $\underline{r}_1$ to $\underline{r}_1 + d\underline{r}_1$ and another molecule within volume element $\underline{r}_2$ to $\underline{r}_2 + d\underline{r}_2$.

↖ normalization factor

Let $\mathcal{A}(\underline{r}_i, \underline{r}_j)$ be any function of the positions of two molecules in a fluid.

Then, the canonical ensemble average

$$\left\langle \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} \mathcal{A}(\underline{r}_i, \underline{r}_j) \right\rangle = \rho^2 \int d^3r_1 \int d^3r_2\, \mathcal{A}(\underline{r}_1, \underline{r}_2)\, g_N^{(2)}(\underline{r}_1, \underline{r}_2) \qquad (9.12)$$

↑ doublecounting allowed
Average consists of $N(N-1)$ equal terms

(IMPORTANT RELATIONSHIP FOR THE TRANSFORMATION OF ENSEMBLE AVERAGES)

- In a homogeneous medium, structure is the same around any point.

$g_N^{(2)}(\underline{r}_1, \underline{r}_2)$ and $g^{(2)}(\underline{r}_1, \underline{r}_2)$ depend only on relative position vector $\underline{r}_1 - \underline{r}_2$:

(no dependence on this)

$$g^{(2)}(\underline{r}_1, \underline{r}_2) = g^{(2)}(\underline{r}_1, \underline{r}_1 + \underline{r}_2 - \underline{r}_1) \equiv g^{(2)}(\underline{r}_2 - \underline{r}_1) \equiv g^{(2)}(\underline{r}_{12}) \quad \text{(HOMOG.)} \quad (9.14)$$

- In an isotropic medium, structure depends on the magnitude, but not on the direction of the intermolecular separation vector (spherical symmetry):

(intermol. separation)

$$g_N^{(2)}(\underline{r}_1, \underline{r}_2) \equiv g(|\underline{r}_2 - \underline{r}_1|) = g(r_{12}) = g(r) \quad \text{(ISOTR.)} \quad (9.15)$$

## A Physical interpretation

DEF: $\dfrac{\rho^2}{N(N-1)}\, g_N^{(2)}(\underline{r}_1, \underline{r}_2)\, d^3r_1\, d^3r_2$ = Probability of finding a molecule at $\underline{r}_1$ to $\underline{r}_1 + d\underline{r}_1$, and another molecule at $\underline{r}_2$ to $\underline{r}_2 + d\underline{r}_2$

In homogeneous fluid, probability of finding molecule at $\underline{r}_1$ to $\underline{r}_1 + d\underline{r}_1$ is $d^3r_1 / V = d^3r_1 / \int d^3r_1$

$$\frac{\rho^2}{N(N-1)} \frac{g_N^{(2)}(\underline{r}_1, \underline{r}_2)\, d^3r_1\, d^3r_2}{d^3r_1 / V} = \text{Probability of finding a molecule at } \underline{r}_2 \text{ to } \underline{r}_2 + d\underline{r}_2, \text{ provided a molecule has been placed at } \underline{r}_1 \text{ to } \underline{r}_1 + d\underline{r}_1$$

$$\frac{\rho^2(N-1)}{N(N-1)} \quad \frac{g_N^{(2)}(\underline{r}_1,\underline{r}_2)\, d^3r_1\, d^3r_2}{d^3r_1/V} =$$ Expected number of molecules in volume element $\underline{r}_2$ to $\underline{r}_2 + d\underline{r}_2$, provided a molecule has been placed at $\underline{r}_1$ to $\underline{r}_1 + d\underline{r}_1$.

⇓

Use $N/V = \rho$, $d^3r_1\, d^3r_2 = d^3r_1\, d^3r_{12}$ :

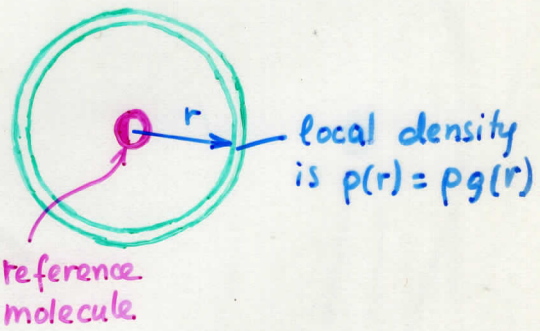
$\rho\, g_N^{(2)}(\underline{r}_1,\underline{r}_2)\, d^3r_{12}$ = Expected number of molecules in volume element $\underline{r}_{12}$ to $\underline{r}_{12} + d\underline{r}_{12}$ of the fluid, defined relative to position $\underline{r}_1$, provided there is a molecule at $\underline{r}_1$

⇓

$\rho\, g_N^{(2)}(\underline{r}_1,\underline{r}_2)$ = Expected density (number of molecules per unit volume in volume element $\underline{r}_{12}$ to $\underline{r}_{12} + d\underline{r}_{12}$ around position $\underline{r}_1$, where there is a molecule.

In isotropic fluid,

$\rho(r) \equiv \rho\, g(r)$ = Local density of molecules within a spherical shell of radius r to r+dr, centered at a given molecule in the fluid, and averaged over all configurations.




(9.16)

## An alternative interpretation

$\frac{\rho^2}{N(N-1)}\, g_N^{(2)}(\underline{r}_1, \underline{r}_2)\, d^3\underline{r}_1\, d^3\underline{r}_2$ = Probability of finding a molecule at $\underline{r}_1$ to $\underline{r}_1 + d\underline{r}_1$, and a molecule at $\underline{r}_2$ to $\underline{r}_2 + d\underline{r}_2$

$\Downarrow$

$\frac{\rho^2}{N(N-1)} \int d^3\underline{r}_1 \int_{r<|\underline{r}_{12}|<r+dr} d^3\underline{r}_{12}\, g_N^{(2)}(\underline{r}_1, \underline{r}_2)$ = Probability of finding a pair of molecules at distance r to r+dr from each other.

$\Downarrow$

(isotropic system)

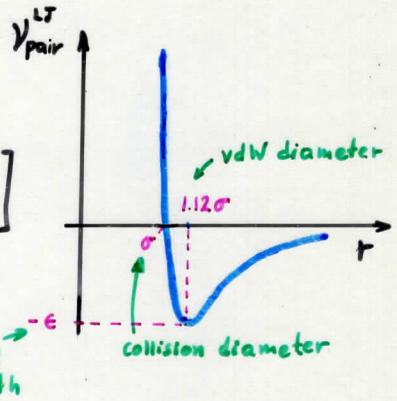
$$\frac{\rho^2}{N(N-1)}\, V \int_{r<r_{12}<r+dr} d^3\underline{r}_{12}\, g_N^{(2)}(r_{12}) = \frac{\rho}{N-1} \int_r^{r+dr} 4\pi r_{12}^2\, dr_{12}\, g_N^{(2)}(r_{12}) =$$

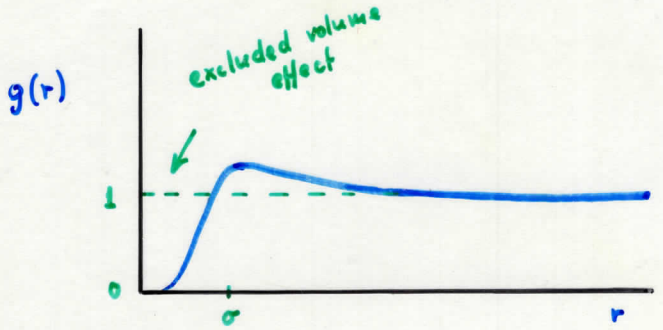
$$= \frac{\rho}{N-1}\, 4\pi r^2\, dr\, g(r) = \underline{\frac{N}{N-1} \cdot \frac{1}{V}\, 4\pi r^2 g(r)\, dr}$$

Probability of finding a pair of molecules at distance r to r+dr from each other. (9.17)

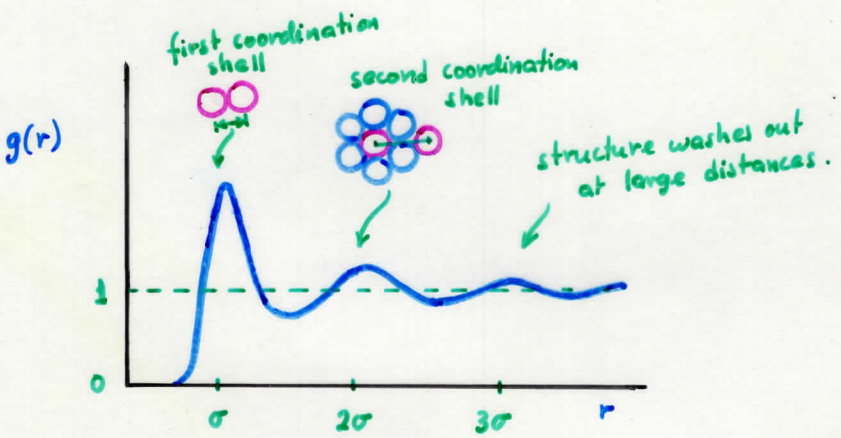
# Typical behavior of g(r)

e.g. Lennard-Jones fluid, $v_{pair}^{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

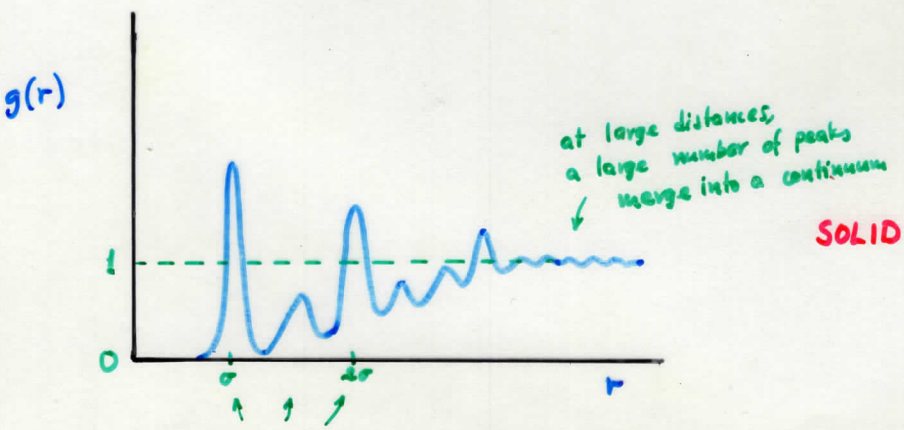



GAS — Very little structure




LIQUID — Short-range order




SOLID

Long-range order
e.g. in fcc crystal peaks expected at $r/\sigma = 1.12$, $r/\sigma = 1.58$, $r/\sigma = 2.24$,

sharp peaks, due to regular arrangement of atoms in crystal lattice