

2. Thermodynamic aspects

Basic definitions:

interaction potential $w(r) \hat{=} \text{pair potential}$

in solvent medium

$\hat{=} \text{potential of mean force}$

relation to the force: $F = -\frac{dw(r)}{dr}$

$w(r)$: also free energy or available energy
(work can be done by the force)

Many body effects / interactions in a solvent medium

Possibilities

① Two solute molecules in a solvent

- solute-solute interaction

- changes in solute-solvent } ΔA when solutes
solvent-solvent } approach each other

→ solute displace solvent molecules,
displace ment work can exceed [free space]
attractive potential, consequence: molecules
repel each other in this medium!!

↑ when no solvent is present!

② perturbation of local solvent ordering or structure by the solute. Associated free energy varies with molecular distance \rightarrow additional ~~force~~ solvation/Structural force

③ Solute-solvent IA: Can change properties of solute molecules
(eg. dipole moment / charge etc.)
 \rightarrow dissociation of acids

④ Cavity formation energy: expended by the medium to accommodate the 'guest molecule'

Solvent medium effects dependent on specific solvent/solute interactions

a specific molecule in a medium

(gas or liquid) has 'cohesive energy'
or 'self energy'

μ_i

(comes from the sum of all interactions with the surrounding molecules, more relevant than $w(r)$). But how are μ_i of an individual molecule and $w(r)$ related.

① gas phase, let $w(r)$ simply be a power law:

$$w(r) = -C/r^n \quad \text{for } r > a \quad (\text{where } n > 3)$$

$$= \infty \quad \text{for } r < a$$

σ = hard sphere diameter

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~~μ^i~~ μ^i may be calculated by summing all the pair potentials over all of space

$$\mu_{\text{gas}}^i = \int_{\sigma}^{\infty} w(r) 4\pi r^2 dr = -4\pi C_6 / (n-3) \sigma^{(n-3)}$$

(see last lecture)

(later used for derivation of the van der Waals equation of state)

Vapor \rightarrow condensed phase: μ^i includes cavity energy

close packing: up to 12 neighbors

molecule introduced in its own liquid phase:

\rightarrow 12 molecules must be separated to form the ~~total~~ cavity (hole)

cost: $6 * w(\sigma)$ (6 bonds holding 12 molecules together)

\rightarrow 12 new bonds are formed when the first molecule is introduced: $12 * w(\sigma)$

\Rightarrow net energy change $\mu_{\text{liq}}^i \approx 6 w(\sigma)$
(half the total interaction energy)

Molar cohesive energy:

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$$U = -N_0 \mu_{\text{liq}}^i \approx -6 N_0 w(\sigma)$$

~~Similar~~ Similar expression can be obtained for U

from $\mu_{\text{gas}}^i = -4\pi C \int (\sigma^{-n-3})$ (see above)

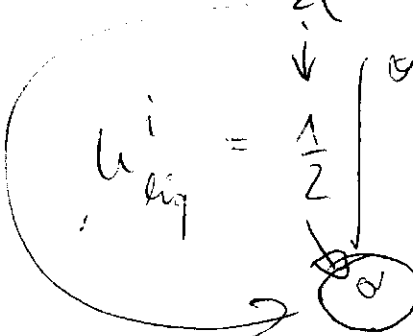
number density of molecules in a (pure) liquid/solid

$$\rho = 1/\text{molecular volume} = 1/[(4\pi/3)(\sigma/2)^3]$$

therefore!

$$U_{\text{liq}}^i = \frac{1}{2} \int w(r) \rho \pi r^2 dr = \frac{-12 C}{(n-3)\sigma^n} \approx \frac{12}{(n-3)} w(\sigma)$$

↑
molecular radius



for van der Waals interaction ($n=6$)

$$\mu_{\text{liq}}^i = 4 w(\sigma) \quad \text{or} \quad U = 4 N_0 w(\sigma)$$

rule of Kump: cohesive energy of a molecule
in liquid or solid: between
4-6 * of pair energy

- Exact calculation difficult because the amount of neighbors can vary between 12 (inert gases) and 4 (water)

- ρ can be a function of r , $\rho = \rho(r)$

Solute molecule in a medium:

simplest case: solute molecules surrounded by 12 solvent molecules of similar sizes have a cohesive energy change on transferring the molecule (solute) from space into medium:

$$\mu_{eq}^i = \left[6 u_{mm}^i - 12 u_{sm}^i \right]$$

↑
↑
 (solvent-solvent) (solvent-molecule)

Separation of six solvent pairs solute interacts with 12 solvent molecules

effective pair potential between two solute molecules:
Change of the sum of their free energies μ^i on approach

The Boltzmann distribution

In phase equilibrium: molecular interaction energies of a molecule has two values μ_1^i and μ_2^i in two planes. Concentrations of these molecules in the two planes (regions) is given by the Boltzmann distribution:

$$X_1 = X_2 \exp\left(-(\mu_1^i - \mu_2^i)/KT\right)$$

which can be also written as

$$\mu_1^i + KT \log_e X_1 = \mu_2^i = KT \log_e X_2 \quad (\text{ideally mixed})$$

Many states, many different regions/phases

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$$\mu_i + kT \ln X_i = \text{const.} \quad \text{for all states } 1, 2, 3, \dots, n$$

⇒ flow of molecules until this is satisfied between these ~~two~~ phases/states

μ = chemical potential (total free energy/molecule)
interaction energy + thermal energy contribution

$k \ln X$ = entropy of confining the molecules:

ideal gas - , configurational,
ideal solution - , translational - ;
dilution - , mixing entropy

X_i = fractions/
volume fractions

$$\text{pure solid: } X_1 = 1 \quad \& \quad \ln X_1 = 0$$

Distribution of molecules and particles in system at equilibrium

- equality of chemical potentials: general starting point in formulating conditions of equilibrium molecularly

Simple case: number density ρ of molecules varies with altitude z

$$\& \quad \mu_i^z + kT \ln \rho_z = \mu_i^0 + kT \ln \rho_0 \Rightarrow \rho_z = \rho_0 \exp(-(\mu_i^z - \mu_i^0)/kT)$$

with $(\mu_2^i - \mu_0^i) = mgz$

$m =$ molecular mass

$g =$ gravitational acceleration

\Rightarrow one obtains the

'barometric distribution law'

$$f_z = f_0 \exp(-mgz/kT)$$

Similarly: charge ions, carrying charge

with ψ_1 and ψ_2 . electric potentials [V]

\Rightarrow in two regions of the system: $e(\psi_2 - \psi_1) =$

$$\mu_2^i - \mu_1^i$$

\Rightarrow Nernst's law $f_z = f_1 \exp(-e(\psi_2 - \psi_1)/kT)$

Interaction energy in both cases arises from externally applied gravitational or electric field

two-phase system: $\mu_2^i - \mu_1^i$: difference due to different intermolecular interactions

- one of the phases: pure liquid / ^{or} pure solid, $\ln X_1 = 0$

$$\mu_1^i = \mu_2^i + kT \ln X_2$$

$$\ln X_2 = X_1 \exp(-(\mu_2^i - \mu_1^i)/kT) = X_1 \exp(-\frac{\Delta\mu^i}{kT})$$

example:

$\mu_2^i =$ energy of molecules in solution

$\mu_1^i =$ " " " " solid, $X_2 =$ solubility

→ These interactions, more generally, ^{can} all contribute.

e.g. two pieces of two different species (chemical),
at different heights, different potential difference:

$$\Rightarrow X_2 = X_1 \exp(-(\Delta \mu^i + e\Delta \varphi + m \cdot g \Delta z) / kT)$$

Van der Waals equation of state

Vapor \rightleftharpoons liquid equilibrium

gas molecules: pair potential $w(r) = -C/r^n$

$$\mu_i^l = \mu_i^{gas} = -4\pi C_f / (n-3) \sigma^{n-3} = A_f$$

$$\text{with } A = 4\pi C / (n-3) \sigma^{n-3} = (\text{const})$$

Molecules of finite size:

$$X_2 = 1 / (v - B) = \rho / (1 - B\rho)$$

v = gaseous volume / molecule

$B = 4\pi\sigma^3/3$ (excluded volume, σ = closest molecular distance)

~~also~~: $X_2 = (1 / (v - B)) = \rho / (1 - B\rho)$

↑
effective density of n -th nonideal gas molecules

$$\Rightarrow \mu = -A_f + kT \ln[\rho / (1 - B\rho)]$$

(complete with temperature-dependent terms)

thermodynamic relations:

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$$\left(\frac{\partial \mu}{\partial P}\right)_T = \bar{V} = \frac{1}{\rho} \quad \text{or} \quad \left(\frac{\partial \rho}{\partial \mu}\right)_T = \left(\frac{\partial \mu}{\partial P}\right)_T \cdot \rho$$

we want it for a gas state equation!!

$$P = \int_0^{\rho} \rho \left(\frac{\partial \mu}{\partial \rho}\right) d\rho = \int_0^{\rho} \left[-A\rho + \frac{kT}{1-B\rho} \right] d\rho$$

$$= \frac{1}{2} A \rho^2 - \frac{kT}{B} \ln(1-B\rho)$$

for $B\rho < 1$ the \ln term can be expanded

(Taylor)

$$\ln(1-B\rho) = -B\rho - \frac{1}{2}(B\rho)^2 + \dots \approx -B\rho(1 + \frac{1}{2}B\rho)$$

$$\approx -B\rho / (1 - \frac{1}{2}B\rho)$$

$$\approx -B / (v - \frac{1}{2}B)$$

so, that: $P = \frac{\frac{1}{2}A}{v^2} + \frac{kT}{v - \frac{1}{2}B}$ or $\left(P + \frac{a}{v^2}\right)(v-b) = kT$

\equiv v.d. Waals equation of state in terms of molecular parameters

$$a = \frac{1}{2} A = 2\pi C / (n-3) \sigma^{n-1} \quad \text{and}$$

$$b = \frac{1}{2} B = 2\pi \sigma^3 / 3 \quad (\text{dependent on size, 'repulsive term'})$$

a, b can be thought to be related to attractive and repulsive forces.

not rigorous or exact, but useful! \rightarrow for describing PVT data