**Imperfect gases**

\[ Q(N,V,T) = \frac{1}{N!h^{3N}} \int \ldots \int e^{-\beta H} dp_1 \ldots dp_N dr_1 \ldots dr_N \]

Integration over momenta

\[ Q(N,V,T) = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N \]

\[ Z_N = \int \ldots \int e^{-\frac{U_N}{kT}} dr_1 dr_2 \ldots dr_N \]

Non-ideal behavior

\[ \frac{p}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \ldots \]

Higher coefficients—too complicated
It is not suitable for condense phase, high orders would be required

\[ B_2(T) = -b_2 = -\frac{Z_2 - Z_1^2}{2!V} \]

\[ B_3(T) = 4b_2^2 - 2b_3 = -\frac{1}{3V^2} \left[ V Z_3 - 3Z_2Z_1 + 2Z_1^3 - 3 \right] \]

\[ Z_2 - Z_z^2 \]

http://test.sdsu.edu/testhome/index.html
**Liquids**

Completely different than gases ⇒ different approach required

**Example – argon in gas and liquid phase**

\[ r_{vdW} = 188 \text{ pm} \]
\[ m = 39.95 \text{ g/mol} \]
\[ \rho_l = 1430 \text{ g/L} \]
\[ \rho_g = 1.784 \text{ g/L} \]

<table>
<thead>
<tr>
<th></th>
<th>Density (g/L)</th>
<th>mol/L</th>
<th>Molecules /L</th>
<th>V(Ar) %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas</strong></td>
<td>1.784</td>
<td>0.045</td>
<td>2.69*10^{22}</td>
<td>0.075</td>
</tr>
<tr>
<td><strong>Liquid</strong></td>
<td>1430</td>
<td>35.795</td>
<td>2.16*10^{25}</td>
<td>60.00</td>
</tr>
</tbody>
</table>

**Gas**

Virial expansion

**Liquid**

Pair distribution function

Introducing correlation function \( g^{(2)} \)
- \( g^{(2)} \) can be obtained from diffractional analysis
- TD variable can be expressed as a function of \( g^{(2)} \)
**Distribution function**

\((N,V,T)\)

Probability that molecule 1 is in \(v\ dr_1\) around \(r_1\) … \(N\ v\ dr_N\) around \(r_N\)

\[ P^{(N)}(r_1,\ldots,r_N)dr_1\ldots dr_N = \frac{e^{-\beta U_N} dr_1\ldots dr_N}{Z_N} \]

Probability that molecule 1 is in \(dr_1\) around \(r_1\), ..., \(n\) in \(dr_n\) around \(r_n\) and other molecules are anywhere:

\[ P^{(n)}(r_1,\ldots,r_n)dr_1\ldots dr_n = \int \ldots \int e^{-\beta U_N} dr_{n+1}\ldots dr_N \frac{dr_1\ldots dr_N}{Z_N} \]

Probability that any molecule is in \(dr_1\) around \(r_1\), ..., \(n\) in \(dr_n\) around \(r_n\) and other molecules are anywhere:

\[ \rho^{(n)}(r_1,\ldots,r_n) = \frac{N!}{(N-n)!} P^{(n)}(r_1,\ldots,r_n) \]

\(\rho^{(1)}\)

The simplest distribution function

- Crystal – periodic function
- Liquid – a constant

\[ \int \frac{\rho^{(1)}(r_1)dr_1}{V} = \rho^{(1)} = \frac{N}{V} = \rho \]
Molecules are totally independent:

\[ \rho^{(n)}(r_1, \ldots, r_n) = \rho^n \]

\[ \rho^{(n)}(r_1, \ldots, r_n) = \rho^n g^{(n)}(r_1, \ldots, r_n) \]

- Their motion is not correlated
- No interactions
- Non-zero probability to find two molecule at one point
- No phase transitions can occur

„Correlation function“
- It respects the interaction between molecules
- Partial analogy to \textit{ab initio}
Correlation function $g^{(n)}$ – represents non-dependence of molecules

$$
\rho^{(n)}(r_1, \ldots, r_n) = \rho^n g^{(n)}(r_1, \ldots, r_n)
$$

$$
g^{(n)}(r_1, \ldots, r_n) = \frac{V^n N!}{N^n (N-n)!} \int \cdots \int e^{-\beta U_N} dr_{n+1} \ldots dr_N Z_N
$$

$$
= V^n (1 + O(N^{-1})) \int \cdots \int e^{-\beta U_N} dr_{n+1} \ldots dr_N Z_N
$$

$$
g^{(2)}(r_1, r_2) = \frac{V^2 N!}{N^2 (N-2)!} \int \cdots \int e^{-\beta U_N} dr_3 \ldots dr_N Z_N
$$

Spherical molecules – $g^{(2)}$ depends only on the distance $r_{12}$: $g^{(2)}(r_{12}) = g^{(2)}(r)$

Probability of finding the second molecule in $dr$ around $r$ from the first molecule

$$
\int_0^\infty \rho g(r) 4\pi r^2 dr = N - 1 \approx N
$$

Radial distribution function

$g(r)$ ... Factor that gives local density from density
The radial distribution function of a fluid of molecules obeying a Lennard-Jones 6-12 potential from molecular dynamics calculations. $T^\infty = kT/s$ and $\rho^\infty = \sigma^3 \rho$.

$$\int_0^\infty \rho g(r)4\pi r^2 \, dr = N - 1 \approx N$$

$g(r)$ ... Factor that gives local density from density

$r \to 0 \ldots g(r) \to 0$

$r \to \infty \ldots g(r) \to 1$
Assuming pair-representability in potential energy

\[ U_N(r_1, \ldots, r_N) = \sum_{i<j} u(r_{ij}) \]

All TD functions can be expressed as a function of \( g(r) \)

Radial distribution function can be obtained from diffraction experiments for liquids kapalin:

Scattering through an angle \( \theta \)

\[ P(\theta) \propto \sum_i \sum_j \frac{\sin(sr_{ij})}{sr_{ij}} = \int_0^\infty 4\pi r^2 g(r) \frac{\sin(sr)}{sr} dr \]

Inter-atomic distances \( r_{ij} \) changes continuously

\[ s = (4\pi / \lambda) \sin(\theta / 2) \]

Fourier transformation

\[ P(\theta) \propto \int_0^\infty 4\pi r^2 \left( g(r) - 1 \right) \frac{\sin(sr)}{sr} dr + \int_0^\infty 4\pi r^2 \frac{\sin(sr)}{sr} dr \]

= 0

\[ P(\theta) \propto \int [g(r) - 1] e^{isr} dr \]
\[ P(\theta) \propto \int [g(r) - 1] e^{i\sigma r} dr \times \rho \]

\[ h(s) = \rho \int h(r) e^{i\sigma r} dr \]

„Structure factor“

TD functions of liquids from diffraction analysis !!!

\[ h(r) = (g(r) - 1) \quad \text{... Goes to 0 for large } r \]
Three different pair-distribution functions – X-ray gives only their superposition and it cannot be simply decomposed.

Combination of X-ray and neutron diffraction for H2O and D2O gives enough data for decomposition.

http://www.isis.stfc.ac.uk/groups/disordered-materials/database/
Imperfect gases

Accounting for inter-molecular interactions – consider monoatomic gas for simplicity

\[ Q_N \frac{V,T}{N!} = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N = \frac{Z_N}{N! A^{3N}} \]

\[ Q_N = \frac{1}{N!} \left( \frac{Q_1}{V} \right)^N Z_N \]

Integration over momenta

\[ H = \frac{1}{2m} \sum_{n=1}^{N} p_{x_n}^2 + p_{y_n}^2 + p_{z_n}^2 + U \ x_1, y_1, \ldots, z_N \]

\[ Q(N,V,T) = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N \]

\[ Z_N = \int \cdots \int e^{-U_N/kT} \, dr_1 \, dr_2 \cdots dr_N \]

Expression for E, p, \( \mu \) must be found
(Others can be obtained from these)

Holds in classical limit
(for monoatomic gas)
TD functions in terms of $g(r)$

$$Q_N = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2}$$

$$Z_N = \frac{Z_N}{N! A^{3N}}$$

$$\bar{E} = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$\bar{E} = \frac{3}{2} NkT + kT^2 \left( \frac{\partial \ln Z_N}{\partial T} \right)_{N,V} = \frac{3}{2} NkT + \bar{U}$$

$$\bar{U} = \frac{\int \cdots \int U e^{-\beta U} dr_1 dr_N}{Z_N}$$

Pair representation – all contributions are equivalent:

$$\bar{U} = \frac{N(N-1)}{2} \left[ \int \cdots \int u(r_{12}) e^{-\beta U} dr_1 dr_N \right] = \frac{N(N-1)}{2} \int \int u(r_{12}) \left[ \int \cdots \int e^{-\beta U} dr_3 dr_N \right] dr_1 dr_2$$

Expression for $E$, $p$, $\mu$ must be found (Others can be obtained from these)
\[ \bar{U} = \frac{N(N-1)}{2} \int \cdots \int u(r_{12}) e^{-\beta U} \ dr_1 dr_N \]

\[ = \frac{N(N-1)}{2} \int \int u(r_{12}) \left[ \int \cdots \int e^{-\beta U} \ dr_3 \ldots dr_N \right] \ dr_1 dr_2 \]

\[ \rho^{(2)}(r_1, r_2) = N(N-1) \int \cdots \int e^{-\beta U_N} \ dr_3 \ldots dr_N \]

\[ \bar{U} = \frac{1}{2} \int \int u(r_{12}) \rho^{(2)}(r_1, r_2) \ dr_1 dr_2 \]

\[ \rho^{(n)}(r_1, \ldots, r_n) = \rho^n g^{(n)}(r_1, \ldots, r_n) \]

\[ \bar{U} = \frac{N^2}{2V} \int_0^\infty u(r) g(r) 4\pi r^2 \ dr \]

\[ \frac{E}{NkT} = \frac{3}{2} + \frac{\rho}{2kT} \int_0^\infty u(r) g(r, \rho, T) 4\pi r^2 \ dr \]
\[-p = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} \]

\[Q_N(V,T) = \frac{1}{N!} \left( \frac{2\pi mkT}{\hbar^2} \right)^{3N/2} \]

\[Q_N = \frac{Z_N}{N! A^{3N}} \]

Only \(Z_N\) depends on \(V\)

\[\bar{p} = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} = kT \left( \frac{\partial \ln Z_N}{\partial V} \right)_{N,T} \]

Assuming that for large \(V\) the pressure does not depend on the container shape – use a cube of volume \(V\).

\[Z_N = \int \ldots \int e^{-U_N/kT} \, dr_1dr_2\ldots dr_N = \int_0^{V^{1/3}} \ldots \int_0^{V^{1/3}} e^{-\beta U} \, dx_1dy_1dz_1\ldots dx_Ndy_Ndz_N \]

Substitution – introduction of fractional coordinates

\[x^c_A = V^{1/3} x^c_A \]

\[Z_N = V^N \int_0^1 \int_0^1 e^{-U_N/kT} \, dx_1^c\ldots dz^c_N \]

\(Z_N\) is a function of volume, and even \(U_N\) depends on volume:
Assuming that interaction energy can be express as a sum of pair interactions:

\[
U_N = \sum_{i=1}^{N} \sum_{j>i}^{N} u(r_{ij})
\]

\[
r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2} = V^{1/3} [(x'_i - x'_j)^2 + (y'_i - y'_j)^2 + (z'_i - z'_j)^2]^{1/2}
\]

\[
Z_N = V_N \int_0^1 \int_0^1 e^{-U_N / kT} dx_1 ... dz_N
\]

\[
Z_N = V_N \int_0^1 \int_0^1 \exp \left\{ -\beta \sum_{i=1}^{N} \sum_{j>i}^{N} u(V^{1/3}, x'_i, ..., z'_N) \right\} dx'_1 ... dz'_N
\]

\[
\left( \frac{\partial Z_N}{\partial V} \right)_{N,T} = \frac{N}{V} Z_N - \frac{V}{kT} \int_0^1 \int_0^1 \left( \frac{\partial U}{\partial V} \right) \exp \left\{ -\beta \sum_{i=1}^{N} \sum_{j>i}^{N} u(V^{1/3}, x'_i, ..., z'_N) \right\} dx'_1 ... dz'_N
\]

\[
\left( \frac{\partial U}{\partial V} \right)_{N,T} = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{du(r_{ij})}{dV} \frac{dr_{ij}}{dV} = \frac{1}{3V} \sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij} \frac{du(r_{ij})}{dr_{ij}}
\]

\[
\frac{dr_{ij}}{dV} = \frac{1}{3V^{2/3}} \left[ (x'_i - x'_j)^2 + (y'_i - y'_j)^2 + (z'_i - z'_j)^2 \right] = \frac{1}{3V} r_{ij}
\]
\( x'_i \rightarrow x_i \)

\( u(r_{12}) \) is the same as any other term \( \rightarrow \frac{1}{2}N(N-1) \) terms

Integration splitted into integration over coordinates of 1 and 2 and on other coordinates

\[
\frac{p}{kT} = \left( \frac{\partial \ln Z_N}{\partial V} \right)_{N,T} = \frac{N}{V} - \frac{N(N-1)}{Z_NkT6V} \int_0^\infty \int_0^\infty dr_1dr_2r_{12} \frac{du(r_{12})}{dr_{12}} \int_0^\infty \ldots \int_0^\infty \exp -\beta u \ dr_3...dr_N
\]

\[
\rho^{(2)} = \rho^2 g^{(2)} = \rho^2 \frac{V^2N!}{N^2(N-2)!} \frac{1}{Z_N} \int_3^N \int_3^N \exp -\beta u \ dr_3...dr_N
\]

\[
\rho^2 \frac{V^2N!}{N^2(N-2)!} \sim \frac{N^2}{V^2} V^2 = N^2
\]

\[
\left( \frac{\partial \ln Z_N}{\partial V} \right)_{N,T} = \frac{N}{V} - \frac{1}{6Vkt} \int_V \int r_{12} \frac{du(r_{12})}{dr_{12}} \rho^{(2)} \ r_1, r_2 \ dr_1dr_2
\]

\[
\frac{p}{kT} = \rho - \frac{\rho^2}{6kT} \int_0^\infty ru'(r)g(r)4\pi r^2dr
\]

„Pressure equation“

Holds for both liquids and gases
Expanding \( g(r,\rho, T) \) over the density – virial coefficients can be obtained
Expression for $E$, $p$, $\mu$ must be found (Others can be obtained from these)

\[
\left( \frac{\partial A/T}{\partial 1/T} \right)_{N,V} = E
\]

\[\xi \in (0,1)\]

“coupling parameter“ .... Switching on/off the interaction

\[\xi u(r_{i,j})\]

Switching the interaction between molecules $1$ and $j$

\[
U = \sum_{j=2}^{N} \xi u(r_{i,j}) + \sum_{2 \leq i < j \leq N} u(r_{ij})
\]

Addition/deletion of molecules from the system

molecule „1“ is in the system just partially ($\xi$)

Radial distribution function depends on $\xi$.

\[g(r, \rho, T; \xi)\]

\[
\mu = \left( \frac{\partial \ln A}{\partial N} \right)_{V,T}
\]

For large $N$

\[
\mu = A(N,V,T) - A(N-1,V,T)
\]

\[
A(N,V,T) = -kT \ln Q
\]

\[
Q_{N V,T} = \frac{Z_{N}}{N! \Lambda^{3N}}
\]

\[-\frac{\mu}{kT} = \ln \frac{Z_{N}}{Z_{N-1}} - \ln N - \ln \Lambda^{3}\]

\[-\frac{A}{kT} = \ln Z_{N} - \ln N! - 3N \ln \Lambda\]
\[-\frac{\mu}{kT} = \ln \frac{Z_N}{Z_{N-1}} - \ln N - \ln \Lambda^3\]

Express as a function of $\xi$

\[
\ln \frac{Z_N}{Z_{N-1}} = \ln \frac{Z_N}{Z_N} = 1 \quad \text{and} \quad \ln \frac{Z_N}{Z_N} = 0
\]

Integration over $dr_1$

\[
Z_N \quad \xi = 1 = Z_N
\]

\[
Z_N \quad \xi = 0 = VZ_{N-1}
\]

\[
\ln \frac{Z_N}{Z_{N-1}} = \ln V + \int_0^1 \left( \frac{\partial \ln Z_N}{\partial \xi} \right) d\xi
\]

\[
Z_N \quad \xi = \int \ldots \int e^{-\beta U_N} \xi \; dr_1dr_2...dr_N
\]

\[
U \quad r_1,..., r_N, \xi = \sum_{j=2}^N \xi u \; r_{1j} + \sum_{2 \leq i < j \leq N} u \; r_{ij}
\]

\[
\frac{\partial Z_N}{\partial \xi} = -\frac{1}{kT} \int \ldots \int e^{-\beta U_N} \xi \left[ \sum_{j=2}^N u(r_{1j}) \right] dr_1...dr_N
\]

\[
\frac{\partial \ln Z_N}{\partial \xi} = -\frac{1}{NkT} \int \int u(r_{12}) \rho^{(2)} \; r_1, r_2 \; dr_1dr_2 = -\frac{\rho}{kT} \int_0^\infty u(r) g(r; \xi) 4\pi r^2 dr
\]

\[
\frac{\mu}{kT} = \ln \rho \Lambda^3 + \frac{\rho}{kT} \int_1^\infty \int u(r) g(r; \xi) 4\pi r^2 dr d\xi
\]
We need an expression for $g(r)$

One has to use some approximative expression – still difficult

Different levels of approximations/complications
Kirkwood integral equation (1930)

\[ kT \ln \rho^{(n)}_{1,\ldots,n,\xi} = kT \ln \rho + kT \ln \rho_{N-1}^{(n-1)} + \xi \sum_{j=2}^{n} u(r_{1j}) + \frac{1}{N} \int_{0}^{\xi} \int_{V} u(r_{12}) \rho^{(2)}_{r_1, r_2, \xi} \, dr_1 dr_2 d\xi \]

\[ -\int_{0}^{\xi} \int_{V} u(r_{1,n+1}) \rho^{(n+1)}_{1,\ldots,n,n+1,\xi} \, dr_{n+1} d\xi \]

\[ n=2 \]

\[ -kT \ln g^{(2)}_{1,2,\xi} = \xi u(r_{12}) + \rho \int_{0}^{\xi} \int_{V} u(r_{13}) \frac{g^{(3)}_{1,2,3,\xi}}{g^{(2)}_{1,2,\xi}} - g^{(2)}_{1,3,\xi} \, dr_3 d\xi \]

Cannot be solved without approximations

Coupled equations – hierarchy
To find a solution – they must be uncoupled – approximations.
\[ g^{(n)}(r_1, \ldots, r_n) = e^{-\beta w^{(n)}(r_1, \ldots, r_n)} \quad \text{Definition of function } w \]

\[ -\nabla_j \]

Gradient of \( w^{(n)} \) with respect to the position of molecule \( j \)

\[ -\nabla_j U \]

Force acting on molecule \( j \) for any fixed configuration of molecules 1\ldots N

\[ g^{(2)}(r_1, r_2) = \frac{V^2 N!}{N^2 (N-2)!} \int \cdots \int e^{-\beta U_N} dr_3 \cdots dr_N \]

\[ \int \cdots \int e^{-\beta U} \nabla_j U \ dr_{n+1} \cdots dr_N \]

\[ -\nabla_j w^{(n)} = \frac{\int \cdots \int e^{-\beta U} \nabla_j U \ dr_{n+1} \cdots dr_N}{\int \cdots \int e^{-\beta U} \ dr_{n+1} \cdots dr_N} \], \( j = 1, 2, \ldots, n \)

\[ f_j^{(n)} = -\nabla_j w^{(n)} \quad \text{Mean force acting on molecule } j \text{ averaged over all configurations of other } (n+1, N) \text{ molecules} \]

\[ w^{(n)} \]

Potential that gives the mean force acting on particle \( j \)

\[ w^{(2)}(r_{ij}) \]

"Effective" potential between 2 molecules separated by \( r_{ij} \) averaged over the positions of all other molecules
For low density
\[ w^{(2)}(r) \rightarrow u(r) \]

Hard spheres: \( w^{(2)} \) is attractive even if \( u \) isn’t
Other molecules provides attraction

Pair additivity is assumed
\[
\begin{align*}
    w^{(3)}(1, 2, 3) & \approx w^{(2)}(1, 2) + w^{(2)}(2, 3) + w^{(2)}(1, 3) \\
    g^{(3)}(1, 2, 3) & \approx g^{(2)}(1, 2) g^{(2)}(2, 3) g^{(2)}(1, 3)
\end{align*}
\]

\[
-kT \ln g_{r_{12}, \xi} = \xi u(r_{12}) + \rho \int_0^\xi \int_V u_{r_{13}} g_{1, 3, \xi'} [g_{r_{23}} - 1] dr_3 d\xi'
\]

Kirkwood integral equation

orn-Green-Yvon equation - similar
Percus-Yevick
Hypernetted-chain

Different type of equations
Figure 13-6. (a) Equation of state of hard spheres calculated from the Born-Green-Yvon and Kirkwood integral equations compared with the results of molecular dynamics calculations. $v_0$ is the closest-packing volume, $N\sigma^3/\sqrt{2}$. (b) Equation of state of hard spheres calculated from the HNC and Percus-Yevick integral equations compared with the results of molecular dynamics calculations. (From D. Henderson, *Ann. Rev. Phys. Chem.*, 15, p. 31, 1964.)
Figure 13-11. The radial distribution function from the Percus-Yevick equation for the Lennard-Jones 6-12 potential. (From F. Mandel, R. J. Bearman, and M. Y. Bearman, J. Chem. Phys., 52, p. 3315, 1970.)