Chemical equilibrium. Imperfect gases.

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If you find a mistake, kindly report it to the author :-)
Chemical equilibrium (in gas phase)

Consider a general homogeneous chemical reaction in gas phase

\[ \nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \]

which we rewrite as

\[ \nu_A A + \nu_B B - \nu_C C - \nu_D D = 0 \]

Starting from the expression for \( A \)

\[ dA = -SdT - pdV + \sum_j \mu_j dN_j \]

We introduce extent of reaction \( \xi \):

\[ dN_j = \nu_j d\xi \quad \text{for all } j \]

Convention: \( \nu_j \) of reactants taken with a negative sign.

For constant \( V \) and \( T \) we obtain:

\[ dA = \sum_j \mu_j dN_j = \left( \sum_j \nu_j \mu_j \right) d\xi \]
Chemical equilibrium (in gas phase)

The condition of chemical equilibrium:

\[ 0 = \left( \frac{\partial A}{\partial \xi} \right)_{V,T} = \sum_j \nu_j \mu_j \]

For an ideal gas composed of A, B, C and D:

\[
Q(N_A, N_B, N_C, N_D, V, T) = \sum_{j} \nu_j \mu_j
\]

\[
= Q(N_A, V, T) Q(N_B, V, T) Q(N_C, V, T) Q(N_D, V, T)
\]

\[
= \frac{(q_A(V, T))^{N_A}}{N_A!} \frac{(q_B(V, T))^{N_B}}{N_B!} \frac{(q_C(V, T))^{N_C}}{N_C!} \frac{(q_D(V, T))^{N_D}}{N_D!}
\]

Chemical potential of A . . . using Stirling (\( \ln N! \approx N \ln N - N \))

\[
\mu_A = -k_B T \left( \frac{\partial \ln Q}{\partial N_A} \right)_{N_j \neq A, V, T} = -k_B T \ln \frac{q_A(V, T)}{N_A}
\]
Chemical equilibrium (in gas phase)

Substituting

\[ \mu_A = -k_B T \ln \frac{q_A(V, T)}{N_A} \]

into

\[ \sum_j \nu_j \mu_j = 0 \]

We obtain directly

\[ \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} \]

For an ideal gas \( q = f(T)V \), so we can introduce

\[ K_c(T) = \frac{\rho_C^{\nu_C} \rho_D^{\nu_D}}{\rho_A^{\nu_A} \rho_B^{\nu_B}} = \frac{(q_C/V)^{\nu_C} (q_D/V)^{\nu_D}}{(q_A/V)^{\nu_A} (q_B/V)^{\nu_B}} = \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} V^{-\Delta \nu} \]

where \( \Delta \nu = -\nu_A - \nu_B + \nu_C + \nu_D \)
Equilibrium constants $K_c$ and $K_p$

Using partial pressures $p_j = \rho_j k_B T$, we introduce

$$K_p(T) = \frac{p_C^{\nu_C} p_D^{\nu_D}}{p_A^{\nu_A} p_B^{\nu_B}} = \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} \left( \frac{V}{k_B T} \right)^{-\Delta \nu} = K_c(T) (k_B T)^{\Delta \nu}$$

- $K_c(T)$ and $K_p(T)$ are functions of temperature only
- With expressions for $q(V, T)$ we now have a general framework for predicting equilibrium constants from molecular structure
- From first principles (almost . . . within some limitations):
  - Rigid rotor, harmonic oscillator
  - High temperature – quantum effects are neglected except for vibrations
  - Dilute gases – negligible intermolecular interactions
- Let’s have a look at some examples . . .
Example: association of alkali metal vapours:

\[ 2Na \rightleftharpoons Na_2 \]

\[ K_p(T) = \frac{p_{Na_2}}{p_{Na}^2} = \frac{q_{Na_2}(V, T)}{q_{Na}^2(V, T)} \left( \frac{V}{k_BT} \right) \]

\[ q_{Na}(V, T) = \left( \frac{2\pi m_{Na}k_BT}{\hbar^2} \right)^{3/2} V q_{\text{elec}}(T) \]

\[ q_{Na_2}(V, T) = \left( \frac{2\pi m_{Na_2}k_BT}{\hbar^2} \right)^{3/2} V \frac{8\pi^2 I k_BT}{2\hbar^2} \frac{e^{-\beta \hbar \nu/2}}{1 - e^{-\beta \Theta_v}} \omega_1 e^{D_e/k_BT} \]

\[ K_p(T) = \frac{q_{\text{elec}}(T)}{k_BT} \left( \frac{2\pi m_{Na_2}^2 k_BT}{m_{Na} \hbar^2} \right)^{-3/2} \left( \frac{2\Theta_r}{T} \right)^2 \left( \frac{2\Theta_r T}{e^{-\beta \Theta_v} - 1} \right)^{-1} \omega_1 e^{D_0/k_BT} \]

- We get \( K_p(1000 \, \text{K}) = 0.50 \, \text{atm}^{-1} \) (experiment: 0.47 atm\(^{-1}\))
More examples in textbook

- Isotopic exchange reactions – cancellation of terms due to Born-Oppenheimer approximation
  \[ \text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD} \]
  \[ \text{CH}_4 + \text{DBr} \rightleftharpoons \text{CH}_3\text{D} + \text{HBr} \]

- Reaction of diatomic and polyatomic molecules
  \[ \text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI} \]
  \[ \text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O} \]

- Reaction with hindered rotation
  \[ \text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6 \]

- Individual project: \( K_p(T) \) of some other gas phase reaction(s).
Results of examples from the textbook

Lines are calculations, points experimental data.

$\log_{10} K$ vs. $1000/T \ [K^{-1}]$

- $C_2H_4$
- $HD$
- $H_2O$
- $Na_2$
Imperfect (real) gases.

- Ideal gas approximation is good **only** at low densities (pressures):
  \[
  \lim_{\rho \to 0} p(T) = \rho k_B T
  \]

- At higher densities, intermolecular interactions gain importance

- Classical Hamiltonian
  \[
  H(p, q) = \sum_{j=1}^{N} \frac{1}{2m_j} \left( p_{x,j}^2 + p_{y,j}^2 + p_{z,j}^2 \right) + U(x_1, y_1, z_1, \ldots, x_N, y_N, z_N)
  \]

- Configuration integral

  \[
  Z_N = \frac{Z_N}{\Lambda^{3N} N!}, \quad Z_N = \int \cdots \int e^{-\beta U(q)} (dq)^{3N}
  \]

  For an ideal gas \( U = 0 \):
  \[
  Z_N = V_N; \quad Q = \frac{q}{N!}, \quad q = f(T) V \Rightarrow pV = N k_B T
  \]
Virial expansion

- Correction to deviations from ideal behaviour
- Power series of the form
  \[ \frac{p}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \ldots \]
- Systematic: two-particle collisions, three-particle collisions, etc.
- Second, third and higher virial coefficients
- Specific constants for a particular gas
- Depend only on temperature
- Objective: Obtain \( B_j(T) \) in terms of interaction potentials \( U(r) \)
- Joseph Mayer, Maria Mayer \( \approx 1940s \)
Virial expansion from the grand partition function

- Grand partition function

\[ \Xi(\mu, V, T) = \sum_{N=0}^{\infty} Q(N, V, T) \lambda^N, \quad \text{where} \quad \lambda = e^{\beta \mu} \]

\[ \Xi(\mu, V, T) = 1 + \sum_{N=1}^{\infty} Q_N(V, T) \lambda^N \]

where \( Q_N(V, T) = Q(N, V, T) \)

- Characteristic function of the grandcanonical ensemble

\[ pV = k_B T \ln \Xi \]

- Define a new activity \( z \) proportional to density as \( \rho \to 0 \)

\[ \frac{N}{V} = -\frac{k_B T}{V} \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T} = \frac{\lambda}{V} \left( \frac{\partial \ln \Xi}{\partial \lambda} \right)_{V,T} \xrightarrow{\lambda \to 0} \frac{\lambda Q_1}{V} = z \]
Virial expansion from the grand partition function

- Grand partition function

\[ \Xi(\mu, V, T) = 1 + \sum_{N=1}^{\infty} \left( \frac{Q_N(V, T) V^N}{Q_1^N} \right) z^N \]

where \( z = \frac{\lambda Q_1}{V} \)

- We define \( Z_N \) (which later turns to be the configuration integral):

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

- And rewrite \( \Xi \) in terms of \( Z_N \):

\[ \Xi(\mu, V, T) = 1 + \sum_{N=1}^{\infty} \left( \frac{Z_N(V, T)}{N!} \right) z^N \]

as a power series in \( z \)
Virial expansion from the grand partition function

- Assume that pressure can be expressed as a power series in $z$:

$$\frac{p}{k_B T} = \sum_{j=1}^{\infty} b_j z^j$$

- Expand $\Xi = \exp(pV/k_BT)$ as a power series

$$\Xi = \exp\left(\frac{pV}{k_B T}\right) = \exp\left(V \sum_{j=0}^{\infty} b_j z^j\right) = \sum_{k=0}^{\infty} \frac{1}{k!} \left(V \sum_{j=0}^{\infty} b_j z^j\right)^k$$

$$= 1 + V(b_1 z + b_2 z^2 + \cdots) + \frac{V^2}{2} (b_1^2 z^2 + 2b_1 b_2 z^3 + \cdots) + \cdots$$

- Compare with

$$\Xi(\mu, V, T) = 1 + \sum_{N=1}^{\infty} \left(\frac{Z_N(V, T)}{N!}\right) z^N = 1 + Z_1 z + \frac{Z_2}{2!} z^2 + \cdots$$

and collect like powers of $z$ to obtain $b_j$ in terms of $Z_N$.
Virial expansion from the grand partition function

\[ b_1 = (1!V)^{-1}Z_1 = 1 \]
\[ b_2 = (2!V)^{-1}(Z_2 - Z_1^2) \]
\[ b_3 = (3!V)^{-1}(Z_3 - 3Z_2Z_1 + 2Z_1^3) \]
\[ b_4 = (4!V)^{-1}(Z_4 - 4Z_3Z_1 - 3Z_2^3 + 12Z_2Z_1^2 - 6Z_1^4) \]
\[ \ldots \]

- Each \( b_j \) involves integrals with at most \( j \) particles
- Let’s express \( p \) in terms of \( \rho \):

\[
\rho = \frac{N}{V} = \frac{\lambda}{V} \left( \frac{\partial \ln \Xi}{\partial \lambda} \right)_{V,T} = \frac{z}{V} \left( \frac{\partial \ln \Xi}{\partial z} \right)_{V,T} = \frac{z}{k_B T} \left( \frac{\partial p}{\partial z} \right)_{V,T}
\]
- Using \( p = k_B T \sum_{j=1}^{\infty} b_j z^j \), we obtain

\[
\rho = \sum_{j=1}^{\infty} j b_j z^j = b_1 z + 2b_2 z^2 + 3b_3 z^3 + \cdots
\]
Virial expansion from the grand partition function

• We (formally) rewrite \( z \) in terms of \( \rho \):
  \[
  z = \sum_{j=1}^{\infty} a_j \rho^j \quad \leftrightarrow \quad \rho = \sum_{j=1}^{\infty} j b_j z^j = b_1 z + 2 b_2 z^2 + 3 b_3 z^3 + \cdots
  \]

• Collecting like powers of \( z \), we determine the coefficients \( a_j \):
  \[
  a_1 = b_1 = 1 \quad z = \rho - 2 b_2 \rho^2 + (8 b_2^2 - 3 b_3) \rho^3 + \cdots
  \\
  a_2 = -2 b_2 \quad z^2 = \rho^2 - 4 b_2 \rho^3 + \cdots
  \\
  a_3 = -3 b_3 + 8 b_2^2 \quad z^3 = \rho^3 + \cdots
  \]

• General procedure for all powers exists but we omit it

• To obtain \( p \) in terms of \( \rho \) we now substitute for \( z \) in
  \[
  \frac{p}{k_B T} = \sum_{j=1}^{\infty} b_j z^j = b_1 z + b_2 z^2 + \cdots = \rho - 2 b_2 \rho^2 + b_2 \rho^2 + \cdots
  \]
Virial expansion from the grand partition function

- Which yields the desired **virial expansion**

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

where

\[ B_2(T) = -b_2 = -(2V)^{-1}(Z_2 - Z_1^2) \]
\[ B_3(T) = 4b_2^2 - 2b_3 \]
\[ = -(3V)^{-2}\left(V(Z_3 - 3Z_2Z_1 + 2Z_1^3) - 3(Z_2 - Z_1^2)^2\right) \]
\[ \ldots \]

- **\( B_j(T) \)** consists of integrals with at most \( j \) particles
- With increasing \( j \), the equations increase in complexity
Comments on the virial expansion

- General recipe for corrections to non-ideality of gases
- Converges quickly at low pressures
  - First term suffices for $p \lesssim 10$ atm
  - Second term suffices for $p \lesssim 100$ atm
- Further terms are needed at high pressures
- Not utilisable in liquid or solid phase
- The expansion may not exist at all, e.g. for $U(r) \sim r^{-n}$, $n \leq 3$

Table 12–1. The contribution of the first few terms in the virial expansion of $p/\rho kT$ for argon at 25°C

<table>
<thead>
<tr>
<th>$p$ (atm)</th>
<th>$p/\rho kT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1 + B_2 \rho + B_3 \rho^2 + \text{remainder}$</td>
</tr>
<tr>
<td>10</td>
<td>$1 - 0.00064 + 0.00000 + \cdots (+0.00000)$</td>
</tr>
<tr>
<td>100</td>
<td>$1 - 0.06754 + 0.02127 + \cdots (-0.00036)$</td>
</tr>
<tr>
<td>1000</td>
<td>$1 - 0.38404 + 0.68788 + \cdots (+0.37232)$</td>
</tr>
</tbody>
</table>

Virial coefficients in the classical limit

- We now show that in the classical limit $Z_N$ from the preceding derivations is indeed the configuration integral

- After integration over momenta we have

$$Q_1(V, T) = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V = \frac{V}{\Lambda^3}$$

- Earlier we have derived a classical expression for $Q$ with the configuration integral $Z_N$, which we now rewrite in terms of $Q_1$:

$$Q_N(V, T) = \frac{Z_N}{N!\Lambda^{3N}} = \frac{1}{N!} \left( \frac{Q_1}{V} \right)^N Z_N$$

- The last expression is identical to how we introduced symbol $Z_N$ in the preceding derivations (without assumptions about its form)
The second virial coefficient

- First three configuration integrals

\[ Z_1 = \int dr_1 = V, \quad Z_2 = \iiint e^{-\beta U(r_1, r_2)} dr_1 dr_2 \]

\[ Z_3 = \iiint e^{-\beta U(r_1, r_2, r_3)} dr_1 dr_2 dr_3 \]

- The second virial coefficient

\[ B_2(T) = -\frac{1}{2V} (Z_2 - Z_1^2) = -\frac{1}{2V} \iiint (e^{-\beta U(r_1, r_2)} - 1) dr_1 dr_2 \]

- Assume that \( U \) depends just on separation: \( U_2 = u(r_{12}) \)

- Reasonable for monatomic or spherically symmetric particles

- Generalization to non-spherical molecules: separation and mutual orientation.
The Mayer function

Substitution: \( r_{12} = r_2 - r_1 \):

\[
B_2(T) = -\frac{1}{2V} \int \int (e^{-\beta U(r_1, r_2)} - 1) \, dr_1 \, dr_2
\]

\[
= -\frac{1}{2V} \int dr_1 \int (e^{-\beta U(r_{12})} - 1) \, dr_{12} = 2\pi \int (e^{-\beta U(r_{12})} - 1) \, r^2 \, dr
\]

We introduce the Mayer function

\[
f_{ij} = f(r_{ij}) = e^{-\beta u(r_{ij})} - 1
\]

to express \( B_2(T) \) as

\[
B_2(T) = 2\pi \int f_{12} r^2 \, dr
\]

- All virial coefficients can be conveniently expressed in terms of \( f_{ij} \).
Three particle interaction potential

\[ U(r_1, r_2, r_3) = u(r_{12}) + u(r_{13}) + u(r_{23}) + \Delta_3 \]

- \( \Delta_3 \) is the deviation from pairwise additivity (we neglect it)

- Influence of the third particle on interactions between 1 and 2

\[ B_3(T) = 4b_2^2 - 2b_3 \]

\[ = -(3V)^{-1} \left( (Z_3 - 3Z_2Z_1 + 2Z_1^3) - 3V^{-1} (Z_2 - Z_1^2)^2 \right) \]

\[ Z_3 = \iiint (1 + f_{12})(1 + f_{23})(1 + f_{13}) \, dr_1 \, dr_2 \, dr_3 = V^3 + \]

\[ + \iiint (f_{12}f_{13}f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12} + f_{13} + f_{23}) \, dr_1 \, dr_2 \, dr_3 \]

\[ Z_1Z_2 = V \iint (1 + f_{12}) \, dr_1 \, dr_2 = \iiint (1 + f_{12}) \, dr_1 \, dr_2 \, dr_3 \]
Third virial coefficient in terms of $f_{ij}$

$$B_3(T) = -(3V)^{-1} \left( (Z_3 - 3Z_2 Z_1 + 2Z_1^3) - 3V^{-1}(Z_2 - Z_1^2)^2 \right)$$

- Permutation of identical particles in the classical limit:

  $$Z_1 Z_2 = \iiint (1 + f_{12}) dr_1 dr_2 dr_3 = V^3 + \iiint f_{12} \, dr_1 dr_2 dr_3$$
  $$= \iiint (1 + f_{13}) dr_1 dr_2 dr_3 = \iiint (1 + f_{23}) dr_1 dr_2 dr_3$$

  $$2Z_1^3 = 2 \iiint dr_1 dr_2 dr_3 = 2V^3$$

- Then the first term of $B_3(T)$ simplifies to

  $$Z_3 - 3Z_1 Z_2 + 2Z_1^3 = \iiint (f_{12} f_{13} f_{23} + f_{12} f_{13} + f_{12} f_{23} + f_{13} f_{23}) dr_1 dr_2 dr_3$$
Third virial coefficient in terms of $f_{ij}$

- Apply the same procedure to the second term, $3V^{-1}(Z_2 - Z_1^2)^2$

$$Z_1^2 = \int\int dr_1 dr_2, \quad Z_2 = \int\int (1 + f_{12}) dr_1 dr_2$$

$$Z_2 - Z_1^2 = \int\int f_{12} dr_1 dr_2 = V \int f_{12} dr_{12}$$

$$V^{-1}(Z_2 - Z_1^2)^2 = V \int f_{12} dr_{12} \int f_{13} dr_{13} = \int\int\int f_{12} f_{13} dr_1 dr_{12} dr_{13}$$

$$= \int\int\int f_{12} f_{13} dr_1 dr_2 dr_3 = \int\int\int f_{13} f_{23} dr_1 dr_2 dr_3 = \int\int\int f_{12} f_{23} dr_1 dr_2 dr_3$$

- Finally $B_3(T)$ simplifies to

$$B_3(T) = -(3V)^{-1} \left( (Z_3 - 3Z_2 Z_1 + 2Z_1^3) - 3V^{-1}(Z_2 - Z_1^2)^2 \right)$$

$$= -\frac{1}{3V} \int\int\int f_{12} f_{13} f_{23} \, dr_1 dr_2 dr_3$$
Summary of virial coefficients in terms of $f_{ij}$

- First and second:
  
  $$B_2(T) = -\frac{1}{2V} \int \int f_{12} \, dr_1 \, dr_2$$  
  
  $$B_3(T) = -\frac{1}{3V} \int \int \int f_{12} f_{13} f_{23} \, dr_1 \, dr_2 \, dr_3$$

  where

  $$f_{ij} = e^{-\beta u(r_{ij})} - 1$$

- Higher virial coefficients increasingly complex
- Can be conveniently derived with the help of graph theory
- If you are interested, read the textbook for more details
- When we know $u(r_{ij})$, we can evaluate $B_j(T)$
  - Analytically for some simple forms of $u(r_{ij})$
  - Numerically in other cases
Hard models for $u(r_{ij})$

Hard sphere (HS)

$$u(r) = \begin{cases} 
\infty & \text{for } r < \sigma \\
0 & \text{for } r > \sigma 
\end{cases}$$

- Analytically tractable $B_j(T)$
- Useful for fundamental studies
- Generalizable to non-spherical shapes (see Boublík’s book)

Square well (SW)

$$u(r) = \begin{cases} 
\infty & \text{for } r < \sigma \\
-\varepsilon & \text{for } \sigma < r < \lambda\sigma \\
0 & \text{for } r > \lambda\sigma 
\end{cases}$$

- Short-range repulsion – excluded volume
- Short-range attraction – Van der Waals interactions

![Graph showing the potential functions for HS and SW with parameter $\lambda = 1.5$.]
Soft sphere models for $u(r_{ij})$

Asymptotic result for dispersion interaction:

$$u(r) \overset{r \to \infty}{=} -C_6 r^{-6}$$

Soft potentials of the form

$$u(r) = C_n \left( \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^6 \right)$$

The Lennard-Jones (LJ) potential

$$u_{LJ}(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)$$

Exponent 12 has been introduced for numerical convenience.

For more model potentials see e.g. Boublík, Chapter 4.1

- Finite derivatives for all $r$
- Upon compression, particles can come closer than $\sigma$
Second virial coefficient for hard potentials

**Hard sphere**

\[
B_2(T) = -2\pi \lim_{u \to 0} \left( \int_{0}^{\sigma} (e^{-\beta u} - 1)r^2 dr + \int_{\sigma}^{\infty} (e^{0} - 1)r^2 dr \right)
\]

\[
= \frac{2}{3} \pi \sigma^3 = b_0
\]

**Square well**

\[
B_2(T) = -2\pi \lim_{u \to 0} \left( \int_{0}^{\sigma} (e^{-\beta u} - 1)r^2 dr + \int_{\lambda \sigma}^{\infty} (e^{0} - 1)r^2 dr \right)
\]

\[
+ \int_{\sigma}^{\lambda \sigma} (e^{\beta \varepsilon} - 1)r^2 dr
\]

\[
= \frac{2}{3} \pi \sigma^3 \left( 1 - (\lambda^3 - 1)(e^{\beta \varepsilon} - 1) \right)
\]

\[
= b_0 \left( 1 - (\lambda^3 - 1)(e^{\beta \varepsilon} - 1) \right)
\]
Second virial coefficient for LJ potential

\[ B_2(T) = -2\pi \int_0^\infty \left( e^{-\beta u_{\text{LJ}}(r)} - 1 \right) r^2 \]

Introduce reduced variables:

\[ T^* = \frac{k_B T}{\varepsilon}, \quad x^* = \frac{x}{\sigma}, \quad B_2^*(T) = \frac{B(T)}{b_0}, \quad \text{where } b_0 = \frac{2}{3} \pi \sigma^3 \]

To rewrite the integral

\[ B_2^*(T^*) = -3 \int_0^\infty \left( \exp \left( -\frac{4}{T^*} (x^{-12} - x^{-6}) \right) - 1 \right) x^2 \, dx \]

Which can be written as (see Boublík, without derivation)

\[ B_2^*(T^*) = -\sum_{j=0}^{\infty} \frac{2^{j+1/2}}{4^j j!} \Gamma \left( \frac{2j - 1}{4} \right) T^{*- (2j+1)/4} \]

Padé approximant:

\[ B_2^*(T^*) \approx \frac{\sqrt{2}}{T^{*1/4}} \frac{1.18163 - 2.23086 T^{*-1/2} + 0.08095 T^{*-1}}{1 - 0.4606 T^{*-1/2}} \]

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Lecture 6: Chemical equilibrium. Imperfect gases.
Remarks on $B_2(T)$ for various potentials

- Analytical results for few cases – step potentials
- Numerically straightforward determination for any well-behaved potential
- Well behaved means decaying faster than $r^{-3}$
- $B_2^*(T^*)$ and higher virial coefficients are available in tables
- Molecular parameters ($\varepsilon$, $\sigma$, \ldots) are tabulated for a number of molecules and potentials
- For a given potential, $B_j^*(T^*)$ is a universal function for all molecules
- Individual project: compare expressions for $B_2(T)$ for different potentials with experimental data
Some examples

Figure 12–4. The solid line is the reduced virial coefficient for the Lennard-Jones 6–12 potential as a function of the reduced temperature $T^*$. Experimental data of a number of substances are also given. (From J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids. New York: Wiley, 1954.)
Some examples

\[ B_3^* = \frac{B_3}{\hbar^2} \]

\[ T^* \]

*Figure 12–6. The reduced third virial coefficient for the Lennard-Jones potential. The experimental values have been reduced using values of \( \varepsilon \) and \( \sigma \) determined by fitting the second virial coefficient to experimental data. The nonspherical molecules (carbon dioxide and ethylene) deviate markedly from the calculated curve. Also the light gases (hydrogen, deuterium and helium) exhibit different behavior because of quantum effects. (From R. B. Bird, E. L. Spotz, and J. O. Hirschfelder, *J. Chem. Phys.* 18, 1395, 1950.)*

The law of corresponding states

If the interaction potential is of the form

\[ U(r_{ij}) = \sum_{i,j} u(r_{ij}) = \sum_{i,j} \varepsilon \phi(r_{ij}/\sigma) \]

Then the configuration integral is

\[ Z_N = \sigma^{3N} \int \ldots \int \exp \left( -\frac{\varepsilon}{k_B T} \sum_{i,j} \phi \left( \frac{r_{ij}}{\sigma} \right) \right) d\left( \frac{r_1}{\sigma^3} \right) \ldots d\left( \frac{r_N}{\sigma^3} \right) \]

\[ = \sigma^{3N} f \left( T^*, \frac{V}{\sigma^3}, N \right) \]

- Reduced energy, distance and volume: \((\varepsilon/k_B T), (r/\sigma), (V/\sigma^3)\)
- In the reduced form the result is dimensionless.
- Universal for all molecules interacting via the same form of \(U(r_{ij})\)
- Independent of parameters \(\varepsilon\) and \(\sigma\)
The law of corresponding states

\[ \frac{A}{N k_B T} = -\frac{1}{N} \ln \mathcal{Q} = -\frac{1}{N} \ln \frac{Z_N}{N! \Lambda^{3N}} = -\frac{1}{N} \ln \frac{Z_N}{N!} + 3 \ln \Lambda \]

- \(A/Nk_B T\) is intensive, so it is a function of \(\nu = V/N\) and \(T\)
- \(N^{-1} \ln(Z_N/N!)/N\) is also intensive and a function of \(\nu\) and \(T\) only

\[ \frac{Z_N}{N!} = \frac{\sigma^{3N}}{N!} f\left(T^*, \frac{V}{\sigma^3}, N\right) = \sigma^{3N} \left(g\left(T^*, \frac{\nu}{\sigma^3}\right)\right)^N \]

- \(g\) is another universal function for a given form of \(U(r)\)

\[ Q(N, V, T) = \left(\frac{\sigma^3 g(k_B T/\varepsilon, \nu/\sigma^3)}{\Lambda^3}\right)^N \]

\[ p = k_B T \left(\frac{\partial Q}{\partial V}\right)_{N,T} = \frac{k_B T}{N \sigma^3} \left(\frac{\partial Q}{\partial (\nu/\sigma^3)}\right)_{N,T} = \frac{k_B T}{\sigma^3} \left(\frac{\partial \ln g}{\partial (\nu/\sigma^3)}\right)_{N,T^*} \]
The law of corresponding states

We rewrite our last result as

\[ \frac{pv}{k_B T} = \frac{v}{\sigma^3} \left( \frac{\partial \ln g}{\partial (v/\sigma^3)} \right)_{N,T^*} \]

- \( g \) is a universal function for the given form of \( U(r_{ij}) \)
- \( pv/k_B T \) is a universal function of \( \varepsilon^* = \varepsilon/k_B T \) and \( v^* = v/\sigma^3 \)
- Can be generalized to include polar molecules and quantum effects
- From the law of corresponding states for LJ potential:

\[ T_c^* \approx 1.3 \Rightarrow \varepsilon \approx \frac{3}{4} k_B T_c, \quad \frac{v_c}{\sigma^3} \approx 2.7 \Rightarrow b_0 = \frac{2\pi \sigma^3}{3} \approx \frac{3}{4} v_c \]

where \( T_c \) and \( V_c \) are critical temperature and critical volume
Figures from McQuarrie: Statistical Mechanics, University Science Books (2000)
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<th>$p_c$(atm)</th>
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<th>$V_c/N\sigma^3$</th>
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Figure 12-7. Comparison of observed and calculated values of the third virial coefficient of argon. Solid lines include a nonadditivity correction; dashed lines show a portion of the additive third virial coefficient curve. (From Sherwood and Prausnitz, J. Chem. Phys. 41, 429, 1964.)