

### 3.31 Fugacity: Definition and relation to residual function

We will now discuss the fugacity as a parameter to describe the behavior of real gases/fluids. Actually the underlying concept is quite general in materials science since the fugacity  $f$  can be interpreted as an "effective pressure" much the same as e.g. effective masses are used to describe properties of real (non-free) electrons. First we have to find the pressure dependency of the Gibbs potential for a perfect gas. At constant temperature we have

$$dG_m(T, p) = V_m dp \quad \text{i.e.} \quad G_m^{ideal}(T, p) = G_m^{ideal}(T, p_0) + \int_{p_0}^p V_m dp = G_m^{ideal}(T, p_0) + RT \ln \frac{p}{p_0} \quad (3.78)$$

For a real gas/fluid we just assume the same functionality but replace the pressure by the fugacity, i.e.

$$G_m(T, p) = G_m(T, p_0) + \int_{p_0}^p V_m dp = G_m^{ideal}(T, p_0) + RT \ln \frac{f}{f_0} = G_m^{ideal}(T, p_0) + RT \ln \frac{p}{p_0} + RT \ln \gamma \quad (3.79)$$

For the last equality we have used the definition of a fugacity coefficient  $\gamma = f/p$ . One chooses standard condition  $p_0$  for which (all) real systems behave ideally, so for  $p \rightarrow p_0$

$$G_m(T, p_0) = G_m^{ideal}(T, p_0) \quad \text{and} \quad p_0 = f_0 \quad (3.80)$$

which allows to write the residual Gibbs potential as

$$\begin{aligned} G_m^{res}(T, p) &= G_m(T, p) - G_m^{ideal}(T, p) = RT \ln \frac{f}{p} = RT \ln \gamma \\ &= \int_0^p \left( V_m - \frac{RT}{p} \right) dp \end{aligned} \quad (3.81)$$

i.e.

$$\begin{aligned} \gamma &= \exp \left( \frac{1}{RT} \int_0^p \left( V_m - \frac{RT}{p} \right) dp \right) \quad \text{with} \quad V_m = \frac{ZRT}{p} \\ \Rightarrow \gamma &= \exp \left( \int_0^p \frac{Z-1}{p} dp \right) \end{aligned} \quad (3.82)$$

so the fugacity (coefficient) is directly related to the compression factor  $Z = 1 + B'p + C'p^2 + \dots$ . Fig. 3.10 summarizes the results:

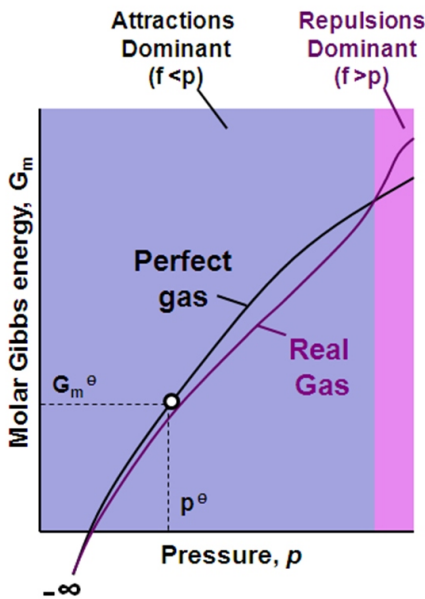


Figure 3.10: Gibbs potential for a perfect and a real gas.

- For  $p \rightarrow 0$  a real gas has the same  $G$  as a perfect gas, both states coincide.
- For intermediate  $p$ , the attractive forces are dominant, resulting in less escaping power, i.e.  $f < p$  and  $Z < 1$ .
- At high  $p$ , the repulsive forces are dominant, leading to more escaping power, i.e.  $f > p$  and  $Z > 1$ .

As an example for fugacity values the following table shows the experimental results for  $N_2$  at 273 K:

|                  |         |        |       |      |
|------------------|---------|--------|-------|------|
| $p / \text{atm}$ | 1       | 10     | 100   | 1000 |
| $f / \text{atm}$ | 0.99955 | 9.9560 | 97.03 | 1839 |