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

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

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

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

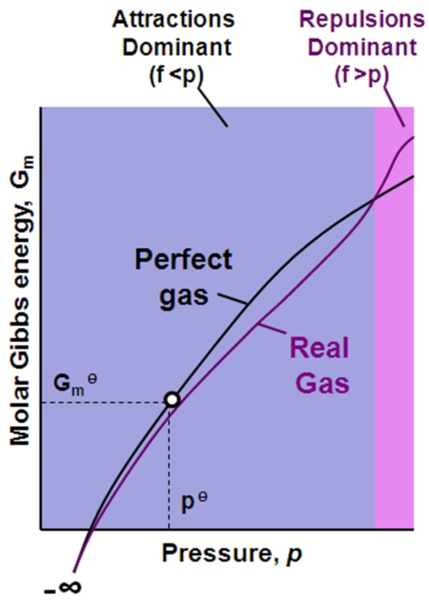

Figure 3.10: Gibbs potential for a perfect and a real gas.

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 $p \to p_0$

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

which allows to write the residual Gibbs potential as

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

i.e.

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

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

- For $p \to 0$ 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 / atm	1	10	100	1000
f / atm	0.99955	9.9560	97.03	1839