The Thermodynamics of Linear Fluids and Fluid Mixtures by Pekař & Samohýl

Exercise 1 to section 4.8.

Show that ideal mixture defined by (4.437) is generally different from a simple mixture.

Try to answer before continuing reading.

The partial free energy of constituent α is independent of densities of other constituents in the mixture of simple fluids. This was demonstrated by equation (4.412) and its derivation:

$$g_{\alpha} = \hat{g}_{\alpha}(T, \rho_{\alpha}).$$

If (4.172) and (4.292) are introduced into the definition of ideal mixture we obtain:

$$g_{\alpha}M_{\alpha} = M_{\alpha}g_{\alpha}^{\bullet}(T,P) + RT\ln(Mw_{\alpha}/M_{\alpha}).$$

Substitution from (4.187) gives

$$g_{\alpha}M_{\alpha} = M_{\alpha}g_{\alpha}^{\bullet}(T,P) + RT\ln[(M\rho_{\alpha}/\rho M_{\alpha})].$$

Taking into account (4.187) we see that the resulting expression for g_{α} is not function $\hat{g}_{\alpha}(T, \rho_{\alpha}) - P_{\alpha}$ is generally a function of ρ (and T) and ρ still remains in this expression.

Note. Some (other) demonstration was given also in Rem. 27 (p. 239).