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

Minimum of entropy inequality

Some comments:

Consequences of the conditions for the minimum of entropy inequality are analyzed on several places in the book. The general background of this procedure is explained here on the example of model B from pages 43-46. A note on chemical reactions and model A is added at the end.

Entropy inequality is a function of three variables here, $\hat{\Sigma}(V, V, T)$, moreover, it is a non-negative function: $\hat{\Sigma} \geq 0$, see (2.21). Consequently, its minimum is zero: $\hat{\Sigma}|_{\min} = 0$. The equilibrium is defined by (2.28), $\dot{V} = 0$; therefore $\hat{\Sigma}|_{eq} = 0$ by (2.27) and $\hat{\Sigma}|_{\min} \equiv \hat{\Sigma}|_{eq}$ regardless the values of V and T.

Thus we have, in general, a function of three real variables f(x, y, z) which is non-negative and has a minimum (zero value) at y = 0 for arbitrary values of x and z. An example of such a function is $f(x, y, z) = (x + z)^2 y^2$.

Looking for the conditions of the minimum and their consequences we can thus focus on the function of one variable only - y, or rather, \dot{V} . This can be done elegantly by looking, instead of the original function $\hat{\Sigma}(V, \dot{V}, T)$, at a new function of one parameter (variable) $\hat{\Sigma}(\lambda) \equiv \hat{\Sigma}(V, \lambda \dot{V}, T)$, where λ is the new parameter. Then we look for the minimum of the new function at the point $\lambda = 0$ for arbitrary (but fixed) values V, \dot{V}, T . Conditions for the minimum are given by equations (2.29) and (2.30) in the book.

The procedure might be complicated by chemical reactions if we use kinetic equations as *a priori* restrictions, as indicated by equation (2.86) on page 56 for the example of extended model A. Here, for instance, the entropy inequality is not identically zero, as followed by the combination of (2.81)-(2.84), but is in the form of (2.89). This is due to the impossibility to choose \dot{m}_2 arbitrarily because it is determined by the kinetic equation (2.86).