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

Page 179, equation (4.148) on page 177

A slightly modified proof¹ of (4.148) is given using the definition of chemical potential (4.161). The entropy inequality is modified using (4.159), (4.161)₂, (4.150), and (4.149). Further, let us fix the nonzero vector \mathbf{u}_{β} and scalar tr \mathbf{D}_{γ} for some constituents β and γ ($\beta, \gamma \in (1, ..., n)$) and substitute these terms with $\lambda \mathbf{u}_{\beta}$ and $\lambda \operatorname{tr} \mathbf{D}_{\gamma}$ in the entropy inequality. The parameter λ is a real number and all other $\mathbf{u}_{\varepsilon}, \operatorname{tr} \mathbf{D}_{\varepsilon}$ are selected to be zeros. Finally, T, ρ_{ε} are selected arbitrarily but fixed, and \mathbf{g} and $\overset{\circ}{\mathbf{D}}_{\varepsilon}$ are set to zero ($\mathbf{g} = \mathbf{o}$ and $\overset{\circ}{\mathbf{D}}_{\varepsilon} = \mathbf{0}$) for all subscripts $\varepsilon = 1, \ldots, n$. In this way, the entropy inequality is modified to:

$$-\sum_{\psi=1}^{n-1} (g_{\psi} - g_n) r_{\psi}^{(0)} + \lambda \left[\rho_{\gamma} (g_{\gamma} - f_{\gamma}) - \sum_{\psi=1}^{n-1} (g_{\psi} - g_n) r_{\psi}^{(\gamma)} - p_{\gamma} \right] \operatorname{tr} \mathbf{D}_{\gamma} + \lambda^2 \left[\zeta_{\gamma\gamma} (\operatorname{tr} \mathbf{D}_{\gamma})^2 + (\nu_{\beta\beta} - \frac{1}{2} r_{\beta}^{(0)}) \mathbf{u}_{\beta}^2 \right] - \lambda^3 \left[\frac{1}{2} r_{\beta}^{(\gamma)} \mathbf{u}_{\beta}^2 \operatorname{tr} \mathbf{D}_{\gamma} \right] \ge 0.$$

This inequality should be valid for arbitrary values of the real parameter λ , the other quantities being constant. At sufficiently high values of λ , the last (cubic) term predominates. This term can have an arbitrary sign; therefore, the expression in it (in brackets) must be zero. This is valid for arbitrary tr \mathbf{D}_{γ} , arbitrary \mathbf{u}_{β} and also the arbitrary indexes γ, β . From this (4.148) follows for arbitrary $T, \rho_1, \ldots, \rho_n$.

¹following the book Samohýl I. *Rational thermodynamics of chemically reacting mixtures.* Praha: Academia 1982 (in Czech).