

Übungsblatt 1

[due: May 9]

Problem 1: Entropy of mixing

Calculate the entropy of mixing of two volumes V_A and V_B of an ideal gas of species A and B , respectively, both initially at the same temperature T and pressure P , and with a final volume $V_A + V_B$.

Problem 2: Convexity, concavity and local stability

The equilibrium state of a system is the state of maximum entropy.

a) Show that this statement implies the relation

$$S(E + \delta E, V, N) + S(E - \delta E, V, N) - 2S(E, V, N) \leq 0,$$

which can be derived by considering an energy fluctuation between two subsystems of the same size in thermal contact with each other. More generally,

$$S(E + \delta E, V + \delta V, N) + S(E - \delta E, V - \delta V, N) - 2S(E, V, N) \leq 0,$$

which is the mathematical statement that S is a concave function of its extensive variables.

b) Discuss in which sense the local stability requirements are special cases of the concavity condition,

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_{V,N} \leq 0, \quad \left(\frac{\partial^2 S}{\partial V^2}\right)_{E,N} \leq 0, \quad \left(\frac{\partial^2 S}{\partial E^2}\right)\left(\frac{\partial^2 S}{\partial V^2}\right) - \left(\frac{\partial^2 S}{\partial E \partial V}\right)^2 \leq 0.$$

c) Show that at fixed S, V the equilibrium state of a system is the state of minimum internal energy and that E is a convex function of S and V .

Problem 3: Analyse the stability of a system that is kept at fixed volume but is free to exchange energy and particles with a reservoir. The temperature and chemical potential of the reservoir are not affected by the fluctuations. In particular, show that

$$C_{V,N} \geq 0, \quad \left(\frac{\partial N}{\partial \mu}\right)_{V,S} \geq 0, \quad \frac{C_{V,N}}{T} \left(\frac{\partial N}{\partial \mu}\right)_{V,S} \leq \left(\frac{\partial S}{\partial \mu}\right)_{V,N}^2$$