Sample Solutions Exercise 10

Exercise 10.1: Equation of State (4P)

Let us consider a thermodynamical system for which the entropy is given by

$$H(E,V,N) = (EVN)^\alpha$$

with an exponent $\alpha > 0$.

(a) Determine the temperature, the pressure, and the chemical potential. (1P)

(b) For which value of α are the results obtained in (a) physically reasonable? (1P)

(c) With (b), compute the chemical potential as a function of (T,V,N). (1P)

(d) With (b), compute the pressure as a function of (T,V,N). Sketch qualitatively an isothermal line (a line of constant T,N) in a P-V diagram. (1P)

Sample Solution

(a) The conjugate thermodynamical quantities are given by (1P)

$$T = \left(\frac{\partial H}{\partial E}\right)^{-1}_{N,V} = \frac{E}{\alpha\,(EVN)^\alpha}\,,$$

$$P = T\left(\frac{\partial H}{\partial V}\right)_{E,N} = \frac{E}{V}\,,$$

$$\mu = -T\left(\frac{\partial H}{\partial N}\right)_{E,V} = -\frac{E}{N}.$$

(b) The conjugate quantities have to be intensive. P and μ are always intensive. T is intensive if and only if $\alpha = \frac{1}{3}$. (1P)

(c) For $\alpha = 1/3$ the first equation of state reads $E = \frac{(T^3VN)^{1/2}}{3\sqrt{3}}$. Inserting this into the last equation of state $\mu = -E/B$ gives (1P)

$$\mu(T,V,N) = -\frac{T^{3/2}V^{1/2}}{3\sqrt{3}N^{1/2}}.$$

(d) Similarly, we get (1P)

$$P(T,V,N) = \frac{N^{1/2}T^{3/2}}{3\sqrt{3}V^{1/2}}.$$

Hence $P(V) \propto V^{-1/2}$. Looks like a hyperbola.

Exercise 10.2: Expansion coefficient and compressibility (2P)

Express the *isobaric expansion coefficient* $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}$ as well as the the *isothermal compressibility* $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}$ as second derivatives of the appropriate thermodynamic potential.

Sample Solution

In both cases the thermodynamic state variables are (T,P,N), hence we have to work with the Gibbs free energy $G(T,P,N)$ with the differential (1P)

$$\mathrm{d}G = \frac{\partial G}{\partial T}\,\mathrm{d}T + \frac{\partial G}{\partial P}\,\mathrm{d}P + \frac{\partial G}{\partial N}\,\mathrm{d}N = -H\,\mathrm{d}T + V\,\mathrm{d}P + \mu\,\mathrm{d}N$$

which tells us that $V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$. This implies (1P)

$$\alpha = \frac{1}{V}\left(\frac{\partial^2 G}{\partial P \partial T}\right)_N, \qquad \kappa = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_{P,N}.$$

Exercise 10.3: Free energy of a perturbed system (6P)

A classical system in thermal equilibrium with a heat bath at temperature T is described by an energy function $E^{(0)} : \Omega^{\mathrm{sys}} \to \mathbb{R} : s \to E_s^{(0)}$. Let $Z^{(0)} = \sum_s e^{-\beta E_s^{(0)}}$ be the partition sum of the system.

(a) Assume that the energy function is perturbed by $E_s^{(0)} \to E_s = E_s^{(0)} + \lambda E_s^{(1)}$ with $\lambda \ll 1$. Compute the corresponding partition sum $Z(\lambda)$ as a power series in λ. (2P)

(b) What is the mathematical meaning of $Z(\lambda)$? Hint: Try to compute $\frac{\mathrm{d}^n}{\mathrm{d}\lambda^n} Z(\lambda)\big|_{\lambda=0}$ (1P)

(c) Prove the general statement that in the canonical ensemble the free energy $F = E - TH$ (more precisely: $\langle F\rangle = \langle E\rangle - T\langle H\rangle$) is given by $F = -T\ln Z$. (1P)

(d) Apply (c) to (a),(b) in order to compute $F(\lambda)$ as a power series in λ up to second order. What is the mathematical meaning of $F(\lambda)$? (2P)

Sample Solution

(a) In the canonical ensemble the partition sum reads $Z^{(0)} = \sum_s e^{-\beta E_s^{(0)}}$, where $\beta = 1/T$ is the inverse temperature and the sum runs over all system configurations $s \in \Omega^{\mathrm{sys}}$. In the unperturbed case, the expectation value of an arbitrary random variable X is given by

$$\langle x\rangle_0 = \frac{1}{Z^{(0)}} \sum_s e^{-\beta E_s^{(0)}} x_s.$$

Setting $x_s = e^{-\beta\lambda E_s^{(1)}} = 1 - \beta\lambda E_s^{(1)} + \mathcal{O}(\lambda^2)$ we simply get

$$Z(\lambda) = \sum_s e^{-\beta E_s} = \sum_s e^{-\beta(E_s^{(0)} + \lambda E_s^{(1)})} = Z^{(0)} \left\langle e^{-\beta\lambda E^{(1)}} \right\rangle_0$$

$$\Rightarrow \quad Z(\lambda) = Z^{(0)} \left\langle \sum_{n=0}^{\infty} \frac{(-\beta\lambda E^{(1)})^n}{n!} \right\rangle_0 = Z^{(0)} \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} \left\langle (-\beta E^{(1)})^n \right\rangle_0 .$$

(b) We have

$$Z(\lambda) = Z^{(0)} \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} m_n = Z^{(0)} \, M(\lambda)$$

where $m_n = \left\langle (-\beta E^{(1)})^n \right\rangle_0$, thus $Z(\lambda)$ may be interpreted as the moment-generating function $M(\lambda)$ of the perturbation $-\beta E^{(1)}$ multiplied by $Z^{(0)}$.

(c) We start with the definition of the Shannon entropy

$$H = -\sum_s P_s \ln P_s = -\frac{1}{Z} \sum e^{-\beta E_s} \ln \frac{e^{-\beta E_s}}{Z}$$

$$= \frac{1}{Z} Z \ln Z + \frac{\beta}{Z} \sum_s e^{-\beta E_s} E_s = \ln Z + \beta \langle E \rangle .$$

This implies

$$\ln Z = H - \beta E = -\beta(E - TH) = -\beta F \quad \Rightarrow \quad F = -T \ln Z$$

(d) Writing down the free energy we realize that

$$F(\lambda) = -T \ln Z(\lambda) = -T \ln Z^{(0)} - T \ln \sum_{n=0}^{\infty} \frac{\lambda^n}{n!} m_n = F^{(0)} - T \, K(\lambda) \, ,$$

where $K(\lambda)$ is the cumulant-generating function of the perturbation $-\beta E^{(1)}$. The zeroth cumulant is always zero, the first one is the mean, and the second cumulant is the variance. Thus we can conclude that

$$F(\lambda) = F^{(0)} - \frac{1}{\beta} \sum_{n=1}^{\infty} \frac{\lambda^n}{n!} \kappa_n$$

$$\Rightarrow \quad F(\lambda) = F^{(0)} + \lambda \langle E^{(1)} \rangle_0 - \frac{\beta\lambda^2}{2} \left\langle \left(E^{(1)} - \langle E^{(1)} \rangle \right)^2 \right\rangle + \mathcal{O}(\lambda^3) .$$

So the free energy is basically the cumulant-generating function of $-\beta E^{(1)}$.

$(\Sigma = 12\text{P})$