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SoSe 05

Set 8
6/6/05

T IV: Thermodynamik und Statistik
(Prof. E. Frey)

Problem set 8

Problem 8.1 *Volume fluctuations*

Relate the first four cumulants of the volume in the pressure ensemble (NPT-ensemble) to the volume V and the isothermal compressibility κ_T

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N},$$

starting from the expansion of the free enthalpy $G(T, P, N)$ in powers of the pressure (Problem 5.4). Evaluate the probability distribution of the volume for an ideal gas and compare your results obtained via the cumulant method to the one from the compressibility.

Problem 8.2 *Thermodynamic identities*

Prove the following thermodynamic relations

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}, \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V, \qquad \left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P.$$

Here C_P, C_V denote the specific heat at constant pressure and volume, respectively, and κ_T, κ_S the isothermal and adiabatic compressibility.

Problem 8.3 *functional determinant*

Show that the following identity holds

$$\frac{\partial(T, S)}{\partial(P, V)} = 1,$$

a) by evaluating explicitly the functional determinant.
b) by considering closed paths for reversible processes in the T-S and P-V plane, repsectively.

Problem 8.4 *Gibbs-Duhem*

Derive the first law of thermodynamics

$$df = -sdT - Pdv\,,$$

for the free energy per particle $f(T,v) = F(T, V = Nv, N)/N$ from the corresponding law for the free energy F. Here $s = S/N$ and $v = V/N$ are the entropy resp. volume per particle. Use the extensivity and derive as a byproduct the Gibbs-Duhem relation $F = \mu N - PV$, i.e. $f = \mu - Pv$.

Problem 8.5 *Legendre transformation*

Evaluate the free energy density $f = \mathrm{e} - Ts$ for the system of uncoupled quantum harmonic oscillators as the Legendre transform of the energy density $\mathrm{e}(s)$. Here the entropy density in the microcanonical ensemble reads

$$s(\mathrm{e}) \quad = \quad k_B \frac{\mathrm{e} + \hbar\omega/2}{\hbar\omega} \ln \frac{\mathrm{e} + \hbar\omega/2}{\hbar\omega} - k_B \frac{\mathrm{e} - \hbar\omega/2}{\hbar\omega} \ln \frac{\mathrm{e} - \hbar\omega/2}{\hbar\omega}$$

and the temperature is defined as $1/T = (\partial s/\partial \mathrm{e})$. Eliminate e and s from the free energy density and express f in terms of the temperature.

Problem 8.6 *Bogoliubov's inequality* (5 pts)

This problem requires some knowledge on quantum mechanics. For two density matrices ρ, ρ' [i.e, with eigenvalues between zero and unity only, and $\mathsf{Tr}\rho = \mathsf{Tr}\rho' = 1$] show the following inequality

$$\mathsf{Tr}\left[\rho'\left(\ln\rho - \ln\rho'\right)\right] \leq 0\,.$$

It is convenient to introduce respective eigenstates and to use the completeness relation

$$\rho = \sum_n |n\rangle \rho_n \langle n|\,, \qquad \sum_n |n\rangle\langle n| = \mathbf{1}\,,$$

and the estimate $\ln x \leq x - 1$. Apply the inequality to derive the upper bound

$$F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$$

for the free energy F corresponding to $\rho = \exp(\beta F - \beta\mathcal{H})$ in terms of a known system $\rho_0 = \exp(\beta F_0 - \beta\mathcal{H}_0)$. Here $\langle\cdot\rangle_0$ denotes canonical averaging with respect to ρ_0.