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SoSe 05

Set 9
6/13/05

T IV: Thermodynamik und Statistik
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Problem set 9

Problem 9.1 *boiling of a liquid*

Starting from the Gibbs free energy, discuss the behavior of the free energy, enthalpy, energy, and entropy as function of their natural variables for paths crossing the first order phase transition from a liquid to a gas.

Problem 9.2 *van der Waals fluid*

Use the empirical equation of state for a van der Waals fluid

$$\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = Nk_BT$$

to find the dependence of the free energy density $f(T, v) = F(T, V, N)/N$ on the volume per particle $v = V/N$. Here a and b are some constants with appropiate units. Determine the free energy density completely by matching to the free energy density

$$f_{id}(T, v) = -k_BT \ln(\lambda^{-3} v)\,, \qquad \lambda = \sqrt{\frac{h^2}{2\pi M k_B T}}$$

of an ideal monatomic gas at large v [Answer: $f(T, v) = -a/v - k_BT \ln[(v - b)\lambda^{-3}]]$. Determine the thermal expansion coefficient $\alpha = V^{-1}(\partial V/\partial T)_P$, the heat capacities C_V and C_P and the compressibilities κ_T, κ_S.

Problem 9.3 *dilute solutions*

Consider a mixture of a solvent and a dilute solute at constant pressure and temperature. The Gibbs free energy fulfills

$$dG = -SdT + V dP + \mu dN + \mu' dN'\,,$$

where μ, μ' are the chemical potentials and N, N' the particle numbers of the solvent and solute, respectively. Using the chemical potential of a dilute solute

$$\mu'(T, P, c) = k_BT\left[\psi'(T, P) + \ln c\right] \qquad c = N'/N$$

derive the dependence of the solvent chemical potential $\mu(T, P, c)$ on the concentration c of the solute. [Answer: $\mu(T, P, c) = \mu_0(P, T) - k_BTc$.]

(a) Consider a container with an immobile semipermeable wall, i.e. permeable for the solvent and impermeable for the solute. Determine the osmotic pressure due to different solute concentrations. Since the concentrations are small, you can expand the chemical potential in powers of the pressure difference.

(b) Discuss the reduction of the vapor pressure by the addition of a low concentration of nonvolatile solute, i.e. the change of the liquid-gas coexistence pressure for fixed temperature. Here the solute is confined to the liquid phase of the solvent.

(c) Derive an equation for the rise of the boiling point of a solvent caused by an infinitesimal addition of a nonvolatile solute at fixed pressure.

(d) Similarly, demonstrate the lowering of the freezing point by adding a small amount of a solute confined to the liquid phase.

Problem 9.4 *symmetric mixture*

A simple model for the concentration dependence of the Gibbs free energy of a symmetric mixture is given by

$$G(T,P,c) = G_0(T,P) + Nk_BTc\ln c + Nk_BT(1-c)\ln(1-c) + Nwc(1-c)\,.$$

Here $N = N_A + N_B$ is the total number of particles, $c = N_A/N$ the concentration of the species A, and $1-c = N_B/N$ the concentration of B molecules. Discuss the dependence of G on the concentration c for different values of the dimensionless number w/k_BT. What happens physically when the shape of G changes?