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Statistical Physics and Thermodynamics (SS 2018)

Problem sheet 8

Hand in: Friday, June 22 during the lecture

http://www.physik.fu-berlin.de/en/einrichtungen/ag/ag-netz/lehre/

1 Grand potential and Gibbs-Duhem relation (11 points)

The thermodynamic properties of a system are described by thermodynamic potentials. Which potential one uses depends on the physical situation. For example, for a system with constant particle number N and volume V coupled to a heat reservoir with temperature T, the Helmholtz free energy $F(T, V, N)$ is typically approximate.

We now allow for particle exchange with a reservoir (with chemical potential μ). To derive the corresponding thermodynamic potential, one performs a Legendre transformation on $F(T, V, N)$ to eliminate N in favor of the chemical potential μ. This is done as follows:

1. One calculates
$$\mu(T, V, N) = \left[\frac{\partial F(T, V, N)}{\partial N}\right]_{T,V}, \tag{1}$$
and solves this equation for N to obtain $N(T, V, \mu)$.
2. One uses the result from step one to calculate the Legendre transform
$$\Omega(T, V, \mu) = F[T, V, N(T, V, \mu)] - \mu\, N(T, V, \mu). \tag{2}$$

a) In the lecture, we showed that the Helmholtz free energy of an ideal gas is given by
$$F(T, V, N) = N k_{\mathrm{B}} T \left[\ln\left(\lambda^3 \frac{N}{V}\right) - 1\right], \tag{3}$$
with the thermal wavelength $\lambda = h/\sqrt{2\pi m k_{\mathrm{B}} T}$, where h is the Planck constant and m the mass of a gas particle. Explicitly perform the Legendre transfomation for the ideal gas to show that you recover the grand canonical potential,
$$\Omega(T, V, \mu) = -k_{\mathrm{B}} T \frac{V}{\lambda^3} \exp\left(\frac{\mu}{k_{\mathrm{B}} T}\right), \tag{4}$$
which was derived in the lecture using the grand canonical partition function. **(3 points)**

b) Show that $N(T, V, \mu)$ derived from $\Omega(T, V, \mu)$ is the same expression you obtained in a) from $F(T, V, N)$. **(1 point)**

c) Show that in general (i.e. for a general Helmholtz free energy, and not just for the ideal gas considered in task a),
$$\mathrm{d}\Omega = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu. \tag{5}$$
(2 points)
Hint: Start from eq. (2), where Ω is expressed as a function of (T, V, μ). Then use the definition of the total differential, $\mathrm{d}\Omega = (\partial\Omega/\partial T)_{V,\mu}\mathrm{d}T + (\partial\Omega/\partial V)_{T,\mu}\mathrm{d}V + (\partial\Omega/\partial\mu)_{T,V}\mathrm{d}\mu$, the chain rule and the fact that because of $\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N$ you know the partial derivatives of $F(T, V, N)$, to derive eq. (5).

d) There cannot be a thermodynamic potential which only has the intensive variables (T, p, μ) as independent variables. This follows from the Gibbs-Duhem relation,

$$0 = S\mathrm{d}T - V\mathrm{d}p + N\mathrm{d}\mu, \tag{6}$$

which states that the three intensive variables (T, p, μ) of a 1-component system are related. In the lecture, you derived this relation from the grand canonical potential. Derive this relation from the Gibbs free energy $G(T, p, N)$.

Proceed as follows:

1. In analogy to part c), use the definition of the Legendre transform to show that $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N$. **(2 points)**
2. Show that if a (continously differentiable) function $f(x)$ is homogeneous, i.e. $f(\alpha x) = \alpha f(x)$ (for all $\alpha \in (0, \infty)$), then it fulfills the Euler relation
$$f(x) = x\frac{\partial f(x)}{\partial x}. \tag{7}$$
(1 point)
3. Use the Euler relation to show that $G = \mu N$ (which of the variables (T, p, N) corresponds to x from the Euler relation?), so that $\mathrm{d}G = N\mathrm{d}\mu + \mu\mathrm{d}N$. **(1 point)**
4. Put 1. and 3. together to obtain the Gibbs-Duhem relation. **(1 point)**

2 Formation of hydrogen in the early universe (9 points)

After the Big Bang, which took place 13.8 billion years ago, it took another 377,000 years until the first neutral atoms formed. In this exercise we use our knowledge of the grand canonical ensemble to obtain a rough estimate for the stability of hydrogen. Consider the combination reaction for hydrogen

$$\mathrm{p}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{H},$$

where p^+ are protons of mass m_p, e^- are electrons of mass m_e and H is the hydrogen atom of mass m_H. All particles are in thermodynamic equilibrium in a volume V and you can consider all species as an ideal gas.

a) Since the individual particle numbers are not conserved, we work in the grand canonical ensemble. Write down the grand-canonical potential $\Omega_\mathrm{p}(T, V, \mu_\mathrm{p})$ for the protons, $\Omega_\mathrm{e}(T, V, \mu_\mathrm{e})$ for the electrons and $\Omega_\mathrm{H}(T, V, \mu_\mathrm{H})$ for the hydrogen atoms. **(1 point)**

b) For given T, V, μ_p, μ_e, μ_H calculate the respective number of particles $\langle N_\mathrm{p}\rangle \equiv N_\mathrm{p}$, $\langle N_\mathrm{e}\rangle \equiv N_\mathrm{e}$ and $\langle N_\mathrm{H}\rangle \equiv N_\mathrm{H}$ **(1 point)**

c) Assume that in a single reaction $\mathrm{p}^+ + \mathrm{e}^- \to \mathrm{H}$, the energy $\Delta\mu = \mu_H - \mu_p - \mu_e$ is released and calculate the law of mass action. **(1 point)**

d) Using your result from c), assuming charge neutrality $N_\mathrm{p} = N_\mathrm{e}$ as well as that the total number of particles is conserved, $N = N_\mathrm{H} + N_\mathrm{p} + N_\mathrm{e}$, express the equilibrium density of free electrons, $c_\mathrm{e} = N_\mathrm{e}/V$, in terms of the total particle density $c = N/V$. **(1 point)**

e) Is the relative concentration of electrons, c_e/c, a monotonic function of c or does it have extrema? What is the value of c_e/c in the limits of low and high total particle density? Draw a schematic plot of c_e/c as a function of c. Furthermore, calculate the total particle density c at which exactly half of the hydrogen is dissociated, given by the condition $c_\mathrm{H}/c = 1/2$. **(4 points)**

f) Based on these results check whether matter in the universe mostly existed as subatomic particles (protons and electrons) or as neutral atoms (hydrogen) in the following epochs.

Epoch	*Time*	*Temperature*
Photon epoch	10 s	10^9 K
Recombination	380 ka	4000 K
Dark ages	150 Ma	60 K

Use that the ionization energy of hydrogen is $\Delta\mu = 13.6\,\mathrm{eV}$ and assume for simplicity that the total particle density $c = 5.4 \times 10^9\, m^{-3}$ is constant in all epochs.