Freie Universität Berlin
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Statistical Physics and Thermodynamics (SS 2017)

Problem sheet 8

Hand in: Friday, June 16 during the lecture

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

1 Thermodynamic potentials and Gibbs-Duhem relation (11 points)

The thermodynamic properties of a system are described by a thermodynamic potential. 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 used.

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

$$F(T,V,N) = Nk_{\mathrm{B}}T\left[\ln\left(\lambda^3\frac{N}{V}\right) - 1\right], \tag{3}$$

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 in general (i.e. for a general Helmholtz free energy, and not just for the ideal gas considered in task a)),

$$\mathrm{d}\Omega = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu. \tag{5}$$

(3 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)*.*

c) 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 b), 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[1]

$$f(x) = x\frac{\partial f(x)}{\partial x}. \tag{7}$$

   (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 Law of mass action for hydrogen (9 points)

In this exercise you will derive the law of mass action for the reaction

$$\mathrm{H} + \mathrm{H} \rightleftharpoons \mathrm{H}_2.$$

Consider H-atoms (mass m) and H_2-molecules (mass $2m$) in thermodynamic equilibrium in a volume V. Both molecule species can be treated 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 $\Omega_{\mathrm{H}}(T, V, \mu_{\mathrm{H}})$ of the H-atoms and the grand-canonical potential $\Omega_{\mathrm{H}_2}(T, V, \mu_{\mathrm{H}_2})$ of the H_2-molecules. How are the thermal wavelengths λ_{H}, λ_{H_2} related? **(1 point)**

b) For given T, V, μ_{H}, μ_{H_2}, calculate the respective number of particles $\langle N_{\mathrm{H}} \rangle \equiv N_{\mathrm{H}}$, $\langle N_{\mathrm{H}_2} \rangle \equiv N_{\mathrm{H}_2}$. **(1 point)**

c) Assuming that in a single reaction $2\mathrm{H} \to \mathrm{H}_2$, the energy $2\mu_{\mathrm{H}} - \mu_{\mathrm{H}_2} = \Delta\mu$ is released, calculate the equilibrium fraction $(N_{\mathrm{H}}/V)^2/(N_{\mathrm{H}_2}/V)$ in terms of $\Delta\mu$ and $\lambda_{\mathrm{H}} \equiv \lambda$ to obtain the law of mass action. **(1 point)**

d) Using your result from c) and assuming that the total number of particles is conserved, $N = N_{\mathrm{H}} + 2N_{\mathrm{H}_2}$, express the equilibrium density of hydrogen in atomic form, $c_{\mathrm{H}} = N_{\mathrm{H}}/V$, in terms of the total atomic density $c = N/V$. **(1 point)**

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

f) The interstellar medium consists largely of hydrogen at low density $c = 10^7$ m^{-3} at $T = 100$ K, interspersed with clouds of $c = 10^{12}$ m^{-3} at $T = 10$ K. Based on the present calculation, in which form do you expect the hydrogen to be in the two different regions? Use the following constants:

$$\begin{aligned} h &= 6.63 \cdot 10^{-34}\ \mathrm{J\ s} \\ m &= 1.67 \cdot 10^{-27}\ \mathrm{J\ s^2/m^2} \\ k_{\mathrm{B}} &= 1.38 \cdot 10^{-23}\ \mathrm{J/K} \\ \Delta\mu &= 7.24 \cdot 10^{-19}\ \mathrm{J}. \end{aligned}$$

[1] The Euler relation is actually more general, it also holds for functions with vector arguments: If $f(\alpha\vec{x}) = \alpha f(\vec{x})$ (for all $\alpha \in (0, \infty)$), then $f(\vec{x}) = \sum_i x_i(\partial f(\vec{x})/\partial x_i)$. But we will only need the one-dimensional special case here.

Comment: In fact, the hydrogen in the low-density regions of the interstellar space exists mainly in atomic form due to photodissociation under the influence of UV light. For details, see: Stecher and Williams, The Astrophysical Journal, Vol. 149, L29 (1967). (**1 point**)