Freie Universität Berlin
Fachbereich Physik
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Statistical Physics and Thermodynamics (SS 2018)

Problem sheet 10

Hand in: Friday, July 6th during the lecture

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

1 Extremal properties of the grand canonical potential (5 points)

Consider a system at constant volume, denoted as system 1, that can exchange particles and heat with a reservoir (grand canonical ensemble). Note that you have seen a similar calculation in the lecture.

a) By which variables is the grand canonical ensemble defined? **(1 point)**

b) Split the entropy $S_{\text{tot}}(U, V, N)$ of the total system (system 1 plus the reservoir) into a contribution from system 1 and a contribution from the reservoir. **(1 point)**

c) Obtain the total differential dS for the reservoir from the first law of thermodynamics. **(1 point)**

d) Expand the entropy function of the reservoir around U, V, N. **(1 point)**

e) Use your previous results to show that the grand canonical potential $\Omega_1(\mu, V, T)$ is minimized for system 1. **(1 point)**

2 Maximal efficiency of a heat engine I (4 points)

In the following, we will derive the maximal efficiency η for an arbitrary cyclic process operating between two heat reservoirs T_1, T_2 with $T_1 > T_2$ from the second law of thermodynamics. Assume ΔQ_1 and ΔQ_2 to be the amounts of heat taken from the hot and cold reservoirs. Note that $\Delta Q_1 > 1$ and $\Delta Q_2 < 0$.

a) Express the efficiency η of the cycle in terms of ΔQ_1 and ΔQ_2. **(1 point)**

b) How does the entropy of each reservoir change in one cycle? What is hence the total entropy change of the two reservoirs after one cycle? **(1 point)**

c) Use the second law of thermodynamics to obtain an upper bound for η and compare to the efficiency η_C of the Carnot process. **(2 points)**

3 Maximal efficiency of a heat engine II (5 points)

In this exercise, we want to show in a different way that the Carnot cyclic process has the maximally possible efficiency. We consider therefore an arbitrary heat engine X with unknown efficiency η_X. We use the mechanic work ΔW done by the system X to operate a Carnot heat pump I_{C} to pump back the heat from the cold to the hot reservoir, see Fig. 1.

Assume that ΔQ_1 is the amount of heat absorbed by the heat engine X from the hot reservoir during one cycle.

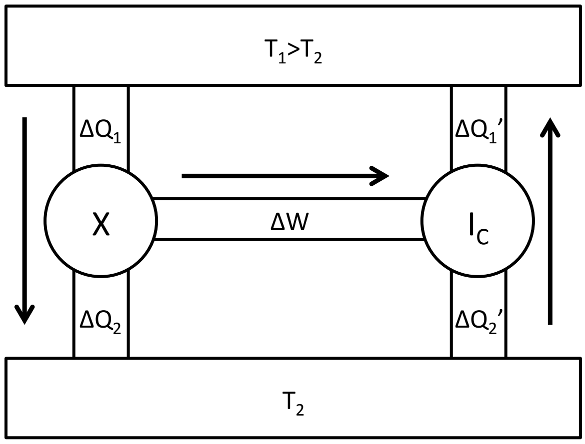

Figure 1: Visualization of the setup for exercise 3.

a) Calculate $\Delta Q_2 < 0$, which is the amount of heat transferred to the cold reservoir by X, $\Delta Q_1'$, i.e. the amount of heat transferred by the system I_C to the hot reservoir and $\Delta Q_2'$, which denotes the heat taken by I_C from the cold reservoir. Express your results in terms of ΔQ_1, η_X and $\eta_C = 1 - T_2/T_1$. **(3 points)**

b) Conclude that $\eta_X \leq \eta_C$ by regarding the direction of the total heat flux. **(2 points)**

4 Phase coexistence at constant volume (6 points)

For the entire problem, assume coexistence of two phases (referred to as 1 and 2) in the N, V, T ensemble.

a) Realize that the Helmholtz free energy $F_i(N_i, V_i, T)$ for each phase can be written as $F_i = V_i f(N_i/V_i, T)$. **(1 point)**

b) Obtain an expression for the total Helmholtz free energy $F_\text{tot}(N_1, N_2, V_1, V_2, T)$ in terms of your result from (a). **(1 point)**

c) Minimize $F_\text{tot}(N_1, N_2, V_1, V_2, T)$ with respect to the free parameters N_1 and V_1 to show that

$$f'(N_1/V_1, T) = f'(N_2/V_2, T) = \frac{f(N_1/V_1, T) - f(N_2/V_2, T)}{N_1/V_1 - N_2/V_2}. \tag{1}$$

Hint: How do V_2 and N_2 depend on V_1 and N_1? **(2 points)**

d) Consider two individual phases at equilibrium characterized by functions $F(V)$ as shown in Fig. 2. Use your result from (c) to argue how the function $F(V)$ will look at phase coexistence and constant temperature. Note that the correct result is often referred to as *common tangent construction.* **(1 point)**

e) Draw a typical $P - V$ diagram at fixed temperature for a system undergoing a phase transition. **(1 point)**

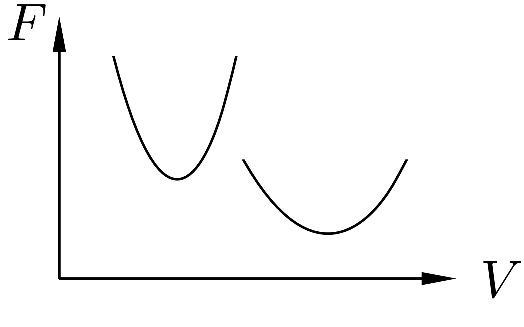

Figure 2: $F - V$ diagram with two different phases.