Freie Universität Berlin
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Statistical Physics and Thermodynamics (SS 2017)

Problem sheet 9

Hand in: Friday, June 23 during the lecture

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

1. Maxwell relations (8 points)

In the lecture, the Maxwell relation between $(\partial T/\partial V)_{S,N}$ and $(\partial P/\partial S)_{V,N}$ has been derived from the energy $U(S,V,N)$. We will now derive several more.

a) Write down the total differential of the Helmholtz free energy $F(T,V,N) = U - TS$ in terms of the entropy S, the pressure P and the chemical potential μ. **(1 point)**

b) Derive the Maxwell relation between $(\partial S/\partial V)_{T,N}$ and $(\partial P/\partial T)_{V,N}$. **(2 points)**

c) Write down the total differential of the Gibbs free energy $G(T,P,N) = F + PV$ in terms of the entropy S, the volume V and the chemical potential μ. **(1 point)**

d) Derive the Maxwell relation between $(\partial S/\partial P)_{T,N}$ and $(\partial V/\partial T)_{P,N}$. **(2 points)**

e) Using your results from parts (b) and (d), express $(\partial P/\partial T)_{V,N}$ in terms of the isobaric thermal expansion coefficient $\alpha = (1/V)(\partial V/\partial T)_{P,N}$ and the isothermal compressibility $\kappa_T = -(1/V)(\partial V/\partial P)_{T,N}$. **(2 points)**

2. Derivation of the TdS equations (7 points)

Consider a system with a fixed number of particles N. Being a function of state, the entropy S can be expressed as a function of any pair of variables chosen from P, V and T, leading to three separate expressions for the total differential dS. Starting from $S(T,V)$, one of these expressions has been derived in the lecture: $TdS = C_V dT + (T\alpha/\kappa_T)dV$, with $C_V = (\partial U/\partial T)_V$.

a) Starting from $S(T,P)$, derive that $TdS = C_P dT - \alpha TV dP$, with the heat capacity at constant pressure given by $C_P = (\partial H/\partial T)_P$.
Hint: Derive an expression for the temperature T from the total differential of the enthalpy $H(S,P,N) = U+PV$.
(3 points)

b) Using the two TdS equations given above and starting from $S(P,V)$, derive that $TdS = C_V(\kappa_T/\alpha)dP + (C_P/\alpha V)dV$. **(2 points)**

c) Derive an expression for $C_P - C_V$ in terms of T, V, α and κ_T. **(2 points)**

3. Adiabatic expansion of a Van der Waals gas (5 points)

The thermal equation of state of a Van der Waals gas, which is a gas with interactions between the particles, is given by

$$\left(P + \frac{a}{V^2}\right)(V - b) = N k_B T,$$

with a and b being positive numbers. Consider N gas molecules which expand adiabatically ($TdS = \Delta Q = 0$), going from a volume V_1 to a volume V_2. Initially, the gas has a temperature T_1.

a) From the equation of state and your results of exercise 1(e), calculate (α/κ_T). **(2 points)**

b) Use a suitable relation for TdS from exercise 2 to derive an expression for the final temperature of the gas T_2 in terms of N, b, C_V, k_B, T_1, V_1 and V_2. Recover the expression for an ideal gas by setting $a = b = 0$. Is the final temperature T_2 higher or lower for the Van der Waals gas than it would have been for an ideal gas under the same circumstances? **(2 points)**

c) Calculate $C_P - C_V$ for the Van der Waals gas. Is $C_P - C_V$ higher or lower than for an ideal gas? **(1 point)**