Freie Universität Berlin
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Statistical Physics and Thermodynamics (SS 2017)

Problem sheet 12

Hand in: Friday, July 14 during the lecture

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

1. Virial expansion (8 points)

The pressure $P = (\beta V)^{-1} \ln \mathcal{Z}(\mu, V, T)$, with $\mathcal{Z}(\mu, V, T)$ being the grand-canonical potential, can be written as a power series

$$\beta P = \sum_{l=1}^{\infty} \left(\frac{z}{\lambda_T^3} \right)^l b_l, \tag{1}$$

with the fugacity being $z = \exp[\mu/k_B T]$ and $\beta = (k_B T)^{-1}$. The first three coefficients are given by

$$\begin{aligned} b_1 &= (\lambda_T^3/V) Z_1 \\ b_2 &= (\lambda_T^6/V)(Z_2 - Z_1^2/2) \\ b_3 &= (\lambda_T^9/V)(Z_3 - Z_1 Z_2 + Z_1^3/3), \end{aligned}$$

in terms of the partition sum

$$Z_N(V, T) = \frac{1}{N!} \prod_j^N \int \frac{d^3 q_j}{\lambda_T^3} \exp\left[- \sum_{k>l}^N \beta w (q_k - q_l) \right].$$

a) Write the particle number

$$N = \frac{1}{\beta} \frac{\partial (\ln \mathcal{Z}(\mu, V, T))}{\partial \mu}$$

as a power series in z/λ_T^3. **(2 points)**

b) Invert the power series of $c = N/V$ to obtain z/λ_T^3 in terms of c up to the third order. Give the first three coefficients in terms of V, λ_T and Z_N. **(3 points)**

c) Insert the power series for z/λ_T^3 into the power series of the pressure (Eq. 1) to obtain the first three terms of the pressure in powers of the density c. **(3 points)**

2. Joule-Thomson process (8 points)

The Joule-Thomson process refers to one way of adiabatically expanding a gas. The system involved consists of two gas reservoirs, labeled 1 and 2, held at different pressures $P_1 > P_2$ by two pistons, and connected by a throttle valve. The gas flows from the reservoir with pressure P_1 to the reservoir with pressure P_2, while P_1 and P_2 are held constant by the moving pistons.

a) Consider a volume of gas V_1 from reservoir 1 being pushed through the throttle to a volume V_2 in reservoir 2. Show that the total enthalpy $H = U + PV$ of the entire system is conserved during this process. **(2 points)**

b) Show that the Joule-Thomson coefficient $\mu_{\mathrm{JT}} = (\partial T/\partial P)_H = (T(\partial V/\partial T)_P - V)/C_P$, with $C_P = (\partial H/\partial T)_P$. **(3 points)**

c) The sign of the Joule-Thomson coefficient determines whether a pressure reduction leads to a cooling or a heating of the gas. Calculate the inversion curves, $T = T_i(V)$ and $P = P_i(T)$, defined by $\mu_{\mathrm{JT}} = 0$ for the Van der Waals-gas. **(3 points)**

Remark: Adiabatic expansion can be performed in multiple ways, and the resulting temperature change depends on the exact procedure.

3. Bimodal curves of the Van der Waals gas (4 points)

The reduced (universal) Van der Waals equation of state is given by

$$\tilde{P} = \frac{8\tilde{T}}{3\tilde{V} - 1} - \frac{3}{\tilde{V}^2}.$$

In this exercise, we approximate the bimodal curves around the critical point ($\tilde{P} = \tilde{V} = \tilde{T} = 1$).

a) Expand the Van der Waals equation around the critical point using $\tilde{T} = \tilde{t} + 1$, $\tilde{P} = \tilde{p} + 1$ and $\tilde{V} = \tilde{v} + 1$, where $\tilde{t}$, $\tilde{p}$ and $\tilde{v}$ are small deviations from the critical point. Write down the pressure deviation $\tilde{p}$ including terms up to and including the third order in $\tilde{t}$ and $\tilde{v}$. **(2 points)**

b) The temperatures and volumes around the critical point which satisfy the Maxwell construction follow a power law $\tilde{v} \propto |\tilde{t}|^{\beta}$. Derive the exponent β for which the Maxwell construction is satisfied, which means that the integral $\int \tilde{p}(\tilde{t}, \tilde{v}) d\tilde{v}$ vanishes for a given $\tilde{p}_0$.
Hint: Note that the antisymmetric terms ($\tilde{v}$, $\tilde{v}^3$...) create the characteristic shape of the $\tilde{p}(\tilde{t}, \tilde{v})$ curve around the critical point. **(2 points)**