

4. Volume dependence of the internal energy for various equations of state

In this exercise it should be investigated how the internal energy for some equations of state $f(p, V, T) = 0$ with reversible changes of state depends on the volume V .

- (a) In the following we consider the internal energy U as a function of the temperature T and the volume V and denote with $dS = \delta Q/T = \frac{1}{T} dU + \frac{p}{T} dV$ the change in entropy S . Derive the relation from the integrability criterion for the complete differential dS

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p.$$

(2 Points)

- (b) How does the internal energy $U(T, V)$ for the ideal gas $pV = NkT$ or for the van der Waals gas

$$\left(p + \frac{\alpha}{(V/N)^2}\right) \left(\frac{V}{N} - 4v_0\right) = kT$$

depend on the volume?

(2 Points)

- (c) What is the relationship between pressure p and temperature T for the equation of state of a gas in which the internal energy U only depends on the temperature, but not on the volume?

(1 Point)

5. Cooling with the help of the Carnot cycle

The Carnot cycle discussed in the lecture can be used to cool the colder reservoir of temperature $T_1 < T_2$ by doing mechanical work $-L > 0$ on the system in a reversible manner (analogous to the lecture, L is the work done by the system). In contrast to the lecture, the isotherms and adiabats of the cycle are not clocked clockwise ($A \rightarrow B \rightarrow D \rightarrow C \rightarrow A$), but counterclockwise ($A \rightarrow C \rightarrow D \rightarrow B \rightarrow A$).

Repeat the reasoning from the lecture in the event that the Carnot cycle is run through counterclockwise. Then, based on the adiabatic expansion of the ideal gas, show that the amount of heat Q_1 that is withdrawn from the colder reservoir is given by the equation

$$Q_1 = \frac{(-L)}{\frac{T_2}{T_1} - 1}.$$

(3 Points)

6. Thermodynamic potentials und Maxwell Relations

Thermodynamic potentials are functions from which all thermodynamic quantities can be derived. The prerequisite for this is that the correct variables (natural variables) are used for the respective thermodynamic potential. In addition to the internal energy U , there are further thermodynamic potentials, of which we will describe the enthalpy H , the free energy F , the free enthalpy G , the great potential Ω and finally the Helmholtz free potential Consider energy A .

- (a) The change in the internal energy $U(S, V, \vec{H})$ of a body with a magnetic moment \vec{M} in a homogeneous external magnetic field is \vec{H}

$$dU = T dS - p dV - \vec{M} d\vec{H} = T dS - p dV - \sum_i M_i dH_i \quad (1)$$

for a constant number of particles. Based on the free energy $F(T, V, \vec{H})$, we define the so-called Helmholtz free energy $A = A(T, V, \vec{M})$ via

$$A = F + \vec{M} \cdot \vec{H} = F + \sum_i M_i H_i. \quad (2)$$

Based on the equations (1) and (2), derive the follow relations

$$\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_{V, H_i} &= T, & \left(\frac{\partial U}{\partial V}\right)_{S, H_i} &= -p, & \left(\frac{\partial U}{\partial H_i}\right)_{S, V, H_k \neq H_i} &= -M_i, \\ \left(\frac{\partial A}{\partial T}\right)_{V, M_i} &= -S, & \left(\frac{\partial A}{\partial V}\right)_{T, M_i} &= -p, & \left(\frac{\partial A}{\partial M_i}\right)_{T, V, M_k \neq M_i} &= H_i, \end{aligned}$$

and thus prove the Maxwell relations

$$\begin{aligned} \left(\frac{\partial M_i}{\partial V}\right)_{S, H_k} &= \left(\frac{\partial p}{\partial H_i}\right)_{S, V, H_k \neq H_i}, & \left(\frac{\partial M_i}{\partial S}\right)_{V, H_k} &= -\left(\frac{\partial T}{\partial H_i}\right)_{S, V, H_k \neq H_i}, \\ \left(\frac{\partial H_i}{\partial V}\right)_{T, M_k} &= -\left(\frac{\partial p}{\partial M_i}\right)_{T, V, M_k \neq M_i}, & \left(\frac{\partial H_i}{\partial T}\right)_{V, M_k} &= -\left(\frac{\partial S}{\partial M_i}\right)_{T, V, M_k \neq M_i}. \end{aligned}$$

(2 Points)