Problem set for “Statistical Thermodynamics”
Due March 28, 2018

Problem I: Adiabatic invariance

Two elastic particles with masses \( m \) and \( M \) \((m < M)\) move along the straight line \( OA \) as shown in Fig. 1. At \( O \) the particle \( m \) is reflected elastically by the wall, and when the particle hits \( M \) they collide elastically as well. Assume that at \( t = 0 \) the particles \( m \) and \( M \) collide at the point with coordinate \( x_1 \) and just before the collision their velocities are \( v_1 \) and \( V_1 \) respectively.

(a) Show that for \( t \to +\infty \) the particles will collide only a finite number of times \( N \). Find this integer.

(b) Let \( t_k \) and \( x_k \) be the time and coordinate of the \( k \)-th collision. Express \( x_k \) through \( t_k \) and the initial data.

(c) Let \( m \ll M \) and suppose that the light particle is moving much faster then \( M \). Find an effective force \( F_{\text{eff}} \) (the “pressure”) exerted on the heavy particle \( M \) as a function of its coordinate.

(d) Explain the result obtained in (c) using the concept of adiabatic invariance.

(e) Find the equation for the adiabatic expansion of the one dimensional monoatomic ideal gas.
Problem II: One dimensional gas with nearest neighbor interactions

Consider $N$ indistinguishable particles of mass $m$ on a segment of length $L$ with nearest neighbor interactions so that the Lagrangian is given by

$$
L_V = \sum_{a=1}^{N} \frac{m_2}{2} - \sum_{a=0}^{N} V(x_{a+1} - x_a), \quad \text{with} \quad V(x) = V(-x),
$$

(1)

where the bounding walls are two immobile particles at

$$x_0 = 0, \quad x_{N+1} \equiv L.$$

The size of the system $L$ is an example of a generalized displacement, so that the statistical integral of the system $Z_N(\beta, L)$ can be treated as a function of two variables $\beta$ and $L$.

(a) Using the convolution theorem for Laplace transform find an analytical representation for

$$Y_N(\beta, P) \equiv \int_0^\infty dL \ Z_N(\beta, L) \ e^{-\beta PL} .$$

(2)

(b) Apply the inverse Laplace transform to find an analytical expression for the statistical integral $Z_N(\beta, L)$.

(c) Using the saddle point method calculate the extensive part of the Helmholtz free energy $F = F(T, L)$ of the system in the thermodynamic limit $N \to \infty$.

(d) Find the Gibbs free energy $G = G(T, P)$ in the thermodynamic limit and obtain the thermodynamic equation of state in the case of an arbitrary potential $V(x)$.

(e) Show that the equation of state obtained in (d) in the case where

$$V(x) = \begin{cases} \infty & |x| < d \\ 0 & |x| > d \end{cases},$$

(3)

coincides with the result of Problem V from HW5.

(e) Find the entropy and the equation of state in the case of the harmonic potential $V(x) = V_0 + \frac{Kx^2}{2}$. How does this relate to the solution of Problem IVb from HW5? Investigate the case of low and high temperatures and show that with increasing temperature, the one dimensional crystal “evaporates” (becomes a gas) without passing through a phase transition.
Problem III: Thermodynamic identity

(a) Let $J$ be the generalized (in the Stat Mech sense) force conjugated to the generalized displacement $\lambda$. Prove the following identity

$$
\left( \frac{\partial T}{\partial J} \right)_\lambda \left( \frac{\partial J}{\partial \lambda} \right)_T \left( \frac{\partial \lambda}{\partial T} \right)_J = -1 .
$$

(b) Express the thermal coefficient

$$
\gamma = \frac{1}{P} \left( \frac{\partial P}{\partial T} \right)_V
$$

through the coefficient of thermal expansion

$$
\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P
$$

and the isothermal compressibility

$$
\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T .
$$

Check the relation for the ideal gas.

Problem IV: Gas entropy

(a) Determine the entropy of a gas which obeys the following conditions

$$
V = V_0 \left( 1 + \alpha(T - T_0) \right) , \quad C_P = \text{const} .
$$

Here $C_P$ is the heat capacity at constant pressure, while $V_0$, $T_0$ and $\alpha$ are some constants.

(b) Suppose the gas from (a) is used as the working substance of a thermal engine running the Carnot cycle. What is the efficiency of this engine?

Problem V: Heat transfer

(a) A body of mass $M$ has a temperature-independent specific heat $c$. If the body is heated reversibly from a temperature $T_i$ to a temperature $T_f$ what is the change in its entropy?

(b) Two such bodies are initially at temperatures of 100 K and 400 K. A reversible engine is used to extract heat from the hotter body as a source to the cooler body as a sink. What is the maximum amount of heat that can be extracted in units of $Mc$?
Problem VI: Leaky balloon

Sometimes helium gas in a low-temperature physics lab is kept temporarily in a large rubber bag at essentially atmospheric pressure. A physicist left a 40-L bag filled with He floating near the ceiling before leaving on a vacation. When she returned, all the helium was gone (diffused through the walls of the bag).

(a) Find the entropy change of the gas. Assume that the atmospheric helium concentration is approximately $5 \cdot 10^{-4} \%$.

(b) What is the minimum work needed to collect the helium back into the bag?

Problem VII: Clausius-Clapeyron relation

The Clausius-Clapeyron relation is a way of characterizing a discontinuous phase transition between two phases of matter of a single constituent. On a pressure-temperature ($P - T$) diagram, the line separating the two phases is known as the coexistence curve. The Clausius-Clapeyron relation gives the slope of the tangent to this curve.

(a) Derive the Clausius-Clapeyron relation for the equilibrium of two phases of a substance.

(b) Consider a liquid or solid phase in equilibrium with its vapor. Show that the vapor pressure follows the equation

$$\ln P = A - \frac{B}{T},$$  \hspace{1cm} (4)

where $A$ and $B$ are some constants.

(c) In the vicinity of the triple point the saturated vapor pressure of carbon dioxide depends on the temperature as in $[4]$. If $P$ is expressed in atmospheres, then for the sublimation process $A = 20.84$ and $B = 4145$ K, and for the vaporization process $A = 15.61$ and $B = 3017$ K. Find:

1. the temperature and pressure at the triple point;
2. the values of the specific latent heats of sublimation, vaporization, and melting in the vicinity of the triple point.
Problem VIII: Applications of thermodynamics to dielectrics

The homogeneous external electric field $\vec{E}$ and the total dipole moment of a body $\vec{P}$ is an example of a generalized displacement and conjugated generalized force pair, so that the total differential of the Helmholtz free energy of an isotropic dielectric is given by

$$dF_{\text{dial}} = -SdT - PdV - \vec{P} \cdot d\vec{E}.$$  

(a) Assuming that the dielectric polarization per unit volume $\vec{P}$ is related to the electric field $\vec{E}$ linearly

$$\vec{P} = \varepsilon_0 \chi \vec{E},$$

find the contribution of the polarization effect to the total Helmholtz free energy. Here $\varepsilon_0$ is the vacuum permittivity and $\chi$ stands for the electric susceptibility.

(b) Determine the electric susceptibility of an ideal gas of molecules with dipole moment $\mu$, placed in a homogeneous external electric field $\vec{E}$.

(c) Determine the heat that is generated as a result of the polarization per unit volume of an isotropic dielectric. Ignore any change of the specific volume of the dielectric.