**Exercise Problems - Week 9**

# Statistical Mechanics and Thermodynamics

SoSe 2018

June 11, 2018

JGU Mainz - Institut für Physik

## Choose 4 of the 6 problems below. Each problem is worth 12 points.

### Problem 1

1. Making use of expression
$$p \propto \exp\left\{-\frac{\Delta E - T\Delta S + P\Delta V}{k_B T}\right\}$$
and expansion of the quantity $\Delta E$ around equilibrium value show that
$$p \propto \exp\left\{-\frac{\Delta T\Delta S - \Delta P\Delta V}{2k_B T}\right\}.$$

2. Using the results of p.1 calculate
   a) $\overline{(\Delta S)^2}$; $\overline{(\Delta P)^2}$; $\overline{(\Delta S\Delta P)}$.
   b) $\overline{(\Delta V)^2}$; $\overline{(\Delta T)^2}$; $\overline{(\Delta V\Delta T)}$.

3. Using the results of p.2 show that
   a) $\overline{(\Delta S\Delta T)} = k_B T$;
   b) $\overline{(\Delta P\Delta V)} = -k_B T$;
   c) $\overline{(\Delta P\Delta T)} = k_B T^2 C_V^{-1}(\partial P/\partial T)_V$ ;
   d) $\overline{(\Delta S\Delta V)} = k_B T(\partial V/\partial T)_P$.

### Problem 2

In the expression for the probability distribution function
$$p \propto \exp\left\{-\frac{\Delta T\Delta S - \Delta P\Delta V}{2k_B T}\right\}.$$
we can choose $E$ and $V$ as "independent variables". However, $E$ and $V$ are not statistically independent variables, as $\overline{(\Delta V\Delta E)} \neq 0$. Show that
$$\overline{(\Delta V\Delta E)} = \kappa_B T\left\{T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T\right\}.$$
Using probability function for the variables $\Delta E$ and $\Delta V$, calculate $\overline{(\Delta E)^2}$, $\overline{(\Delta V)^2}$.

### Problem 3

Consider a system of $N$ noninteracting particles in a volume $V$ at an absolute temperature $T$. The single particle energy states are described by $\epsilon_i = \hbar^2 k_i^2/2m$. For convenience, assume that the $k_i$ are determined by periodic boundary conditions.

1. Show that the mean pressure $\bar{P}$ of the system is given quite generally in terms of the average kinetic energy $E$ by
$$\overline{P} = \frac{2\overline{E}}{3V}$$
independent of whether the particles obey classical, Fermi-Dirac, or Bose-Einstein statistics.

2. Show that the dispersion in pressure of this system, $\overline{(\Delta P)^2} = \overline{(P - \overline{P})^2}$ , is given by
$$\overline{(\Delta P)^2} = \frac{2k_B T^2}{3V}\left(\frac{\partial \overline{P}}{\partial T}\right)_{N,V}$$
.

## Problem 4

1. For a general (non-ideal) gas, derive the formula

$$dE = nC_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV.$$

$C_V$ is the constant-volume specific heat, assumed here to be a constant, and $n$ denotes the number of moles of gas. You may want to use the Maxwell relation,

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V .$$

2. For the van-der-Waals equation of state,

$$\left( P + \frac{n^2 a}{V^2} \right) (V - b) = nRT,$$

derive a specific form for $dE$ given above. $C_V$ is again a constant (valid, presumably, over a limited temperature range).

3. Find, for the van-der-Waals gas, the constant-pressure specific heat $C_P(T, V)$, using your result from the previous part. Note that $C_P$ is not a constant, but show that it reduces to the expected form for the ideal gas case.

## Problem 5

Derive the van der Waals equation of state assuming that the interaction potential between the particles in a gas is

$$u(r) = \begin{cases} \infty, & \text{for } r < r_0 \\ -\overline{u}, & \text{otherwise} \end{cases}$$

where

$$\overline{u} = cN/V$$

Here $N/V$ is the number of particles per unit volume, and $c$ is a constant. (First evaluate the classical partition function $Z$, and then use it to find pressure $P$.) Give physical interpretation of your finite answer (the van der Waals equation), and show that it reduces to the correct result when $u(r) = 0$.

## Problem 6

Consider a classical system of $N$ point particles of mass $m$ in a volume $V$ at temperature $T$. The particles interact through a two-body repulsive central potential

$$\phi(r) = \phi_0 \left( \frac{r_0}{r} \right)^n$$

where $\phi_0 > 0, r_0 > 0,$ and $n > 0$.

1. Calculate the partition function $Z(T, V)$ for this system and show explicitly that $Z(T, V) = Z_0(T, V) q(TV^{n/3})$, where $Z_0$ is the ideal gas partition function and the function q(x) (which you can not express in a closed form!) depends on T and V only through $x = TV^{n/3}$.

2. Given the result of the previous part, show that the internal energy $U$ and the pressure $P$ are related as $U = U_0 + \frac{3}{n} (P - P_0) V$ , where the subscript 0 refers to n the ideal gas.

3. What is the potential $\phi(r)$ as $n \to \infty$? Explain the result obtained in the previous part in this limit. Is it correct?