Exercise Problems - Assignment 9

Statistical Mechanics and Thermodynamics

WS 2018

Due: 21st Jan 2019

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 ΔE 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 ΔE and ΔV, 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?