Problem set 7

Due April 23, 2025

1. Derive the expression for the heat capacity of a two-state system with degeneracies of of the ground and excited states $g_\circ$ and g_1, respectively energy of the ground state equal to 0 and the energy of the excited state equal to ε, respectively, by using (i) the formula based of energy variance and (ii) by taking the energy derivative in temperature. Both ways must give the same result.

2. Starting from the expression of the Boltzmann-averaged energy of an ideal monoatomic gas composed of N point-like particles

$$E = \frac{3}{2} N k_B T$$

   derive the formula for its heat capacity at constant volume (C_V).

3. Based on the expression for C_V derive the expression for the standard deviation of the average energy (σ_E) for an ideal monoatomic gas and for the relative standard deviation of energy (σ_E/E). Compute σ_E/E for 1 picomol (10^{-12} mol) of an ideal gas and comment on the obtained value.

   The relationship between energy variance (σ_E^2) and C_V is

$$\sigma_E^2 = k_B T^2 C_V$$

   Please note that you need either to do atom- and not mol-based calculations or bring the formula to the form in which per-mol quantities can be used.

4. Based on the equation of state of an ideal gas (the Clapeyron equation) and the relatioship between the variance of density and isothermal compressibility coefficient (κ)

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial p} = \frac{V}{k_B T \rho^2}\sigma_\rho^2$$

   with

$$\rho = \frac{N}{V}$$

where N is the number of atoms, V is the volume and p is the pressure, derive the expression for the relative standard deviation of density, σ_ρ/ρ and show that this quantity is independent of pressure. Calculate σ_ρ/ρ for for 1 picomol of an ideal gas and comment on the obtained value.

Please note that you need either to do atom- and not mol-based calculations or bring the formula to the form in which per-mol quantities can be used.