# Statistical Mechanics

August 20, 2016

Work 2 (and only 2) of the 3 problems. Please put each problem solution on a separate sheet of paper and your name on each sheet.

## Problem 1

A vertical cylinder contains 500 moles of a monatomic ideal gas and is closed off by a piston of mass 50 kg and a cross-sectional area of $100\,\text{cm}^2$. The whole system is thermally insulated during the entire process described below. Initially, the piston is clamped in position so that the gas occupies a volume of $1\,\text{m}^3$ and is at a temperature of 300 K. The piston is then released, and eventually comes to rest in a final equilibrium position corresponding to some larger volume $V$ of the gas. Neglect any frictional forces which might prevent the piston from sliding freely within the cylinder. Compute:

a.) the number of gas molecules in the cylinder;

b.) the initial pressure of the gas (in units of atm); and

c.) the final pressure of the gas (in units of atm).

d.) Obtain an expression for the work done by the expanding gas in terms of change in volume of the system.

Using the above results, apply the first law of thermodynamics and compute:

e.) the final volume of the gas; and

f.) the final temperature of the gas.

*Hints/Comments:* 1) The final equilibrium position of the piston is reached when the weight of the piston is exactly balanced by the pressure of the gas. 2) Note: the process described above is *not* reversible. 3) Constants: $k_B = 1.381 \times 10^{-23}\,\text{J K}^{-1}$, $N_A = 6.022 \times 10^{23}\,\text{mole}^{-1}$, $g = 9.8\,\text{m s}^{-2}$. Unit Conversion: $1\,\text{atm} = 1.013 \times 10^5\,\text{N m}^{-2}$.

# Problem 2

Consider a classical system of $N$ point particles of mass $m$ in a volume $V$ at temperature $T$. Let $U$ be the internal energy of the system and $P$ the pressure. The particles interact through a two-body central potential

$$\varphi(r_{ij}) = \frac{A}{r_{ij}^n}\,;\;\; A > 0\,;\;\; n > 0\,;\;\; r_{ij} = |r_i - r_j|\,.$$

a.) Show that the internal energy of the system can be expressed as

$$U = aPV + bNk_BT\,;\;\; k_B = \textit{Boltzmann constant}$$

where the coefficients $a$ and $b$ depend on the exponent $n$ in the interaction potential. (Hint: Use scaling arguments such as

$$\varphi(\lambda \cdot r_{ij}) = \frac{1}{\lambda^n}\varphi(r_{ij})$$

to derive the Helmholtz free energy $F$ of the system and the formula for the internal energy given above.)

b.) Determine the dependence of $a$ and $b$ on $n$.

# Problem 3

This question is presented in two parts. Please read carefully.

Part a.)

Label each of the following statements as either true or false and explain why. If a statement is true only under special circumstances then label it false.

i. An irreversible process always raises the entropy of the universe.

ii. An irreversible process always raises the entropy of the system.

iii. A temperature gradient can cause a diffusion flow to occur.

iv. Ohm's law is exactly obeyed by electrolyte solutions.

v. A smaller ion will always have a smaller effective radius in aqueous solution.

vi. If the elapsed time of a diffusion experiment is quadrupled, the root-mean-square distance moved by diffusion molecules is increased by a factor of two.

vii. If a mixture of two proteins of equal density is sedimenting in an ultracentrifuge, and if one protein has twice the molar mass of the other protein, its sedimentation velocity will be half as large as that of the other protein.

viii. The viscosity of a gas increases with increasing temperature while that of a liquid decreases with decreasing temperature.

Part b.)

Assume that a certain sample of air maintained at 25° C contains dust particles all of which are the same size. The diameter of the dust particles is $5.0\,\mu$m and their density is 2500 kg $m^{-3}$.

i. Find the most probable speed, the mean speed, and the root-mean-square speed of the dust particles, treating them as giant molecules.

ii. Assuming that the dust particles are described by a Boltzmann distribution, find the ratio of the concentration of dust particles at a height of 1.00 m to the concentration at a height of 0.00 m.

iii. Find the rate of collisions of one dust particle with other dust particles if their number density is $1.0 \cdot 10^9\,\mathrm{m}^{-3}$.

iv. Find the total rate of collisions per cubic meter of pairs of dust particles.

v. Find the rate of collisions of one dust particle with nitrogen molecules (assume standard temperature and pressure, i.e., 25° C and 1 atm).

vi. Assume that a dust particle is stationary and calculate the rate at which nitrogen molecules strike its surface. Compare your answer with that of part (v.) above.

*Constants and units:* $k_B = 1.381 \times 10^{-23}$ J K$^{-1}$, $1\,\mathrm{atm} = 1.013 \times 10^5$ N m$^{-2}$.