

CHM328S: Modern Physical Chemistry
Problem Set 4: Non-Ideal Gases

Notes:

- This fourth problem set is due on Thursday, March 26, 2009.
- Note the following useful relations:
 - * For a pure state: $dG = Vdp - SdT$ and $G = n\mu$.
 - * $\int_{-\infty}^{\infty} e^{-\frac{1}{2}ax^2} dx = \sqrt{\frac{2\pi}{a}}$
 - * $\log(1+x) \approx 1+x$ if x is small
 - * $e^x \approx 1+x$ if x is small

1. Consider n moles of a (pure) gas in a container of volume V at temperature T . For such a system, the pressure can be written as a so-called virial expansion:

$$pV = nRT \left[1 + \frac{B(T)}{V_m} + \mathcal{O}(V_m^{-2}) \right],$$

where $B(T)$ is the *first virial coefficient*, $V_m = V/n$ is the molar volume, and $\mathcal{O}(V_m^{-2})$ denotes terms proportional to V_m^{-2} that are negligible for dilute gases.

- (a) Derive from the virial expansion that

$$V_m = \frac{RT}{p} \left[1 + \frac{B(T)p}{RT} + \mathcal{O}(V_m^{-2}) \right].$$

- (b) Prove that at constant temperature, the differential of the chemical potential may be written as $d\mu = V_m dp$.
 - (c) Derive that the difference in chemical potential between states with different pressures p and p_0 equals

$$\mu(p, T) - \mu(p_0, T) = RT \ln \frac{p}{p_0} + B(T)(p - p_0) + \mathcal{O}(V_m^{-2}).$$

2. Consider a classical system of N point particles in a square box of size $L \times L \times L$ and at temperature $T = 1/(k_B\beta)$. In classical statistical mechanics, the partition sum is

$$Q = \frac{1}{h^{3N} N!} \int e^{-\beta H(\mathbf{r}_i, \mathbf{p}_i)} d\Gamma, \quad (1)$$

where:

- $\mathbf{r}_i = (x_i, y_i, z_i)$ denotes the position vector of particle i ,
- $\mathbf{p}_i = (p_{xi}, p_{yi}, p_{zi})$ denotes its momentum vector,

- h is Planck's constant (introduced only to make Q dimensionless),
- H gives the energy of the system as a function of all positions and momenta,
- and $\int d\Gamma$ is a short-hand notation for the integrals:

$$\int d\Gamma = \int d\mathbf{r}_1 d\mathbf{p}_1 \int d\mathbf{r}_2 d\mathbf{p}_2 \cdots \int d\mathbf{r}_N d\mathbf{p}_N$$

(where in turn $\int d\mathbf{r}_i = \int_0^L dx_i \int_0^L dy_i \int_0^L dz_i$ and $\int d\mathbf{p}_i = \int_{-\infty}^{\infty} dp_{xi} \int_{-\infty}^{\infty} dp_{yi} \int_{-\infty}^{\infty} dp_{zi}$).

- (a) Let H be given by the energy of an ideal gas, i.e.

$$H(\mathbf{r}_i, \mathbf{p}_i) = \sum_{i=1}^N \frac{1}{2m} (p_{xi}^2 + p_{yi}^2 + p_{zi}^2),$$

show that then

$$Q = \frac{q^N}{N!},$$

and show that in this expressions, the classical molecular partition sum q equals

$$q = \frac{1}{h^3} \int d\mathbf{r} d\mathbf{p} e^{-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)}.$$

- (b) Show by evaluating the expression for q that

$$q = L^3 \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2}.$$

- (c) How does this relate to the quantum mechanical partition sum of an ideal gas (translational part only) that we found in class?

3. Consider again the classical partition sum defined in equation (1) on the previous page, but now with

$$H(\mathbf{r}_i, \mathbf{p}_i) = H^{(0)}(\mathbf{r}_i, \mathbf{p}_i) + H^{(1)}(\mathbf{r}_i, \mathbf{p}_i)$$

where $H^{(1)}(\mathbf{r}_i, \mathbf{p}_i)$ can be assumed to be small.

- (a) Derive that

$$Q = Q_0 \times \left(1 - \frac{\beta}{Q_0} \int H^{(1)}(\mathbf{r}_i, \mathbf{p}_i) \frac{e^{-\beta H^{(0)}(\mathbf{r}_i, \mathbf{p}_i)}}{N! h^{3N}} d\Gamma \right),$$

where Q_0 is the partition sum of the system with only $H^{(0)}$.

Let us define

$$W = \frac{1}{Q_0} \int H^{(1)}(\mathbf{r}_i, \mathbf{p}_i) \frac{e^{-\beta H^{(0)}(\mathbf{r}_i, \mathbf{p}_i)}}{N! h^{3N}} d\Gamma.$$

- (b) Compute the Helmholtz free energy A in terms of Q_0 and W .
- (c) Indicate how this analysis might be used to find the first virial coefficient $B(T)$ of question 1.