Statistical Mechanics WS 2013/14 Sheet 7

Please hand in your solutions (in pairs) before the Monday lecture.

Problem 1 : The Clausius-Clapeyron Equation (10 points)

Consider a system comprising N molecules at constant temperature T and constant pressure p. The molecules *coexist* in gas-liquid phases (N_g gas molecules with a volume V_g, and N_l liquid molecules with a volume V_l) in the system.

a) (2 points) Write down the Clausius-Clapeyron equation in terms of the above notations and the latent heat $\mathcal{L}$. Explain in one sentence what does this equation describe physically.

b) (4 points) Suppose that the small temperature change ΔT changes the pressure by $\Delta p = \alpha \rho_l$ where ρ_l is the number density of molecules in the liquid phase. Express ρ_l in terms of the above notations.

c) (4 points) Suppose that the system is initially in (T_0, p_0), and $\rho_l = \gamma p/(k_B T)$, and the gas phase is assumed to be ideal. Calculate the pressure p.

Problem 2 : Solid-Gas Phase (20 points)

Consider molecules *coexist* in gas-solid phases (N_g gas molecules in $V_g \approx V$, and N_s solid molecules in V_s) in the system.

a) (10 points) Express N_g in terms of z_g and z_s. Here, z_g and z_s are single-molecule partition functions for the gas and solid phases, respectively. Assume the thermodynamic limit, and that gas molecules are indistinguishable while solid molecules are distinguishable.

b) (10 points) In three-dimension, regarding the gas as ideal gas, and the solid as quantum harmonic oscillators with an additive absorption energy $-\epsilon$ per molecule, calculate the number of the gas molecules.

Problem 3 : The Joule-Thomson Coefficient (20 points)

a) (2 point) Write down the Joule-Thomson coefficient μ_{JT} in terms of the thermal expansion coefficient α, T, C_p and V. What does this coefficient describe physically? Express in one sentence.

b) (4 point) Calculate μ_{JT} for the ideal gas. Explain the result in one sentence.

c) (4 points) Calculate μ_{JT} for the van der Waals gas.

d) (10 points) Suppose that we can use the Morse potential given as $V(r) = \epsilon\left[e^{-2(r-\sigma)/\sigma} - 2e^{-(r-\sigma)/\sigma}\right]$ for a diatomic molecular gas (where r is the radial distance between molecules, σ is the diameter of a molecule, and ϵ denotes some units of energy), and assuming that the total mean energy per a molecule $\langle E\rangle$ is proportional to the mean energy for a pair of the molecules: $\langle E\rangle = \langle E_{\text{pair}}\rangle N/2$. Calculate μ_{JT}. Use the excluded volume term from the van der Waals gas.

Problem 4 : The Virial Coefficients (30 points)

I. Consider a hard core potential ($V(r) = \infty,\ r \le \sigma$ and otherwise zero) for gas molecules with a diameter σ.

a) (5 points) Calculate the second virial coefficient.

b) (10 points) Calculate the third virial coefficient.

II. Consider a potential for a gas,

$$V(r) = \begin{cases} \infty & ,\ 0 < r < \sigma \\ -\epsilon & ,\ \sigma < r < b \\ 0 & ,\ b < r < \infty. \end{cases} \tag{1}$$

a) (5 points) Calculate the second virial coefficient.

b) (10 points) Calculate the Joule-Thomson coefficient using this second virial coefficient.