Problem Set 9	
Statistical Mechanics	
summer 2024	

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Problem 23: Adsorption

There are N_o adsorption sites on a surface. $N(\leq N_o)$ of the sites are occupied by adsorbed molecules. The latter do not interact with each other. Show that the chemical potential of the adsorbed molecules is given by

$$\mu = k_B T \ln \frac{N}{(N_o - N)q(T)} ,$$

where q(T) is the molecular partition function. As usual you can assume that N_o , N as well as $N_o - N$ are large numbers.

(4 points)

Problem 24: Partition function of a relativistic gas

(a) Obtain the (classical) partition function $Q_{NV,T}$ of a ultra-relativistic gas of N point-like particles obeying the energy-momentum relation $\epsilon = pc$. Here c is the speed of light.

(4 points)

(b) Show that

$$PV = \frac{1}{3}E$$
 and $E = 3Nk_BT$.

(4 points)

Problem 25: Open one-state system

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(a) Obtain the equation of state for an open one-state system, i.e. $P = P(\rho, T)$ with $\rho = N/V$, for Bosons and Fermions. Neglect any interaction aside from the statistical interaction between the particles.

(4 points)

(b) Plot the pressure at constant temperature and constant volume vs. density in both cases.

(2 points)

Problem 26: Flory's equation of state

Flory's equation of state,

$$\frac{bP}{k_BT} = -\frac{1}{2}\frac{\epsilon_o}{T}\varphi^2 - \ln(1-\varphi) ,$$

is one of many equations of state akin to the van der Waals equation for gases and liquids. Here b the volume of the molecules and $\varphi = bN/V$ is the so-called volume fraction. $\epsilon_o(>0)$ is a parameter, which ensures the attractive interaction between the molecules.

(a) Show that at Flory's equation of state approaches the ideal gas law in the limit $N/V \rightarrow 0$.

(3 points)

(b) Define the quantities $e_o = k_B \epsilon_o / b$ and $t = k_B T / b$. If t/e_o is smaller than a certain number c, Flory's equation of state also exhibits a van der Waals loop. Determine c and make sketches of $bP/(k_B \epsilon_o)$ vs. ϕ for $t/e_o = c, c \pm 0.03$.

(3 points)

(c) Calculate the second virial coefficient $B_2(T)$ and sketch B_2/b vs. T/ϵ_o .

(2 points)

(d) Calculate the critical point, i.e. φ_c and T_c .

(3 points)