

Ch/ChE 164 Winter 2024

Homework Problem Set #4

Due Date: Thursday, February 15, 2024 @ 11:59pm PT

For all problems, please consider reasonable simplifications of your final results.

1

1. (15 pts.) (Adapted from Callen). Consider a mixture of two non-identical monatomic ideal gases.

1.1

- Starting from the expression for the grand canonical partition function and taking the limit of small fugacity, show that the canonical partition function Z is factorizable and

$$Z = Z_1 Z_2 = \frac{1}{N_1!} q_1^{N_1} \frac{1}{N_2!} q_2^{N_2}$$

(You may wish to use the occupancy representation $|n_1 m_1, n_2 m_2 \dots\rangle$, where n_1 denotes occupancy of energy level 1 of gas 1, and m_1 denotes occupancy of energy level 1 of gas 2, etc.).

First, I will say that an individual partition function for each molecule is given by:

$$Z_i = \sum_{n_i} e^{-\beta \epsilon_i n_i} \quad (1)$$

The occupations of the first and second gases are given by:

$$n_1, n_2, \dots \quad (2)$$

$$m_1, m_2, \dots \quad (3)$$

The number of particles in the first and second gases are given by:

$$N_1 = \sum_i n_i \quad (4)$$

$$N_2 = \sum_i m_i \quad (5)$$

Total energy of the first and second gases are given by:

$$U_1 = \sum_i n_i \epsilon_i \quad (6)$$

$$U_2 = \sum_i m_i \epsilon_i \quad (7)$$

Their sum is

$$U = U_1 + U_2 = \sum_i n_i \epsilon_i + \sum_i m_i \epsilon_i \quad (8)$$

The grand canonical partition function is given by:

$$\Xi = \sum_{\nu} e^{-\beta(U_{\nu}) + \beta\mu N_1 + \beta\mu N_2} \quad (9)$$

Adding the various sums to the exponent gives:

$$\Xi = \sum_{\nu} e^{-\beta \sum_i n_i \epsilon_i - \beta \sum_i m_i \epsilon_i + \beta\mu^{(1)} \sum_i n_i + \beta\mu^{(2)} \sum_i m_i} \quad (10)$$

where $\mu^{(1)}$ and $\mu^{(2)}$ are the chemical potentials of the first and second gases, respectively. We can factor this in two separate sums each over the individual molecule:

$$\Xi = \sum_n e^{-\beta \sum_i n_i \epsilon_i + \beta\mu^{(1)} \sum_i n_i} \sum_m e^{-\beta \sum_i m_i \epsilon_i + \beta\mu^{(2)} \sum_i m_i} \quad (11)$$

In

1.2

The sum over the states can be written as a product of sums over the states of the first and second gases:

- Compute the entropy and show that (comparing to the entropy of the two separate gases) there is an entropy of mixing of the form

$$S_{\text{mixing}} = (-x_1 \log x_1 - x_2 \log x_2) Nk$$

where N is the total number of particles. Look at Callen pg. 393 ch 18

2

2. In class we derived the heat capacity of the Fermi gas at low temperature by an intuitive argument, which $C_v \sim NkO(T/T_F)$. Here we will derive the precise form and constants (adapted from Callen).

Denote the Fermi-Dirac distribution at temperature T as $f(\epsilon, T)$ and the (temperature dependent) chemical potential by μ (note this is not the Fermi energy ϵ_F except when $T = 0$). We will first derive a general result for an integral of the form (Sommerfeld expansion)

$$I \equiv \int_0^\infty \phi(\epsilon) f(\epsilon, T) d\epsilon = \int_0^\mu \phi(\epsilon) d\epsilon + \frac{\pi^2}{6} (kT)^2 \phi'(\mu) + \frac{7\pi^4}{360} (kT)^4 \phi'''(\mu) + \dots$$

a) (10 pts.) Integrate I by parts, and let $\Phi \equiv \int_0^\epsilon \phi(\epsilon') d\epsilon'$. Then expanding $\Phi(\epsilon)$ in a power series in $\epsilon - \mu$ to third order, deduce The fd distribution is given by:

$$f(\epsilon, T) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \quad (12)$$

where $\beta = 1/kT$. The number of particles is a sum over all states α :

$$N = \sum_{\alpha} f(\epsilon_{\alpha}, T) \quad (13)$$

$$I = - \sum_{m=0}^{\infty} \frac{1}{m!} \frac{d^m \Phi(\mu)}{d\mu^m} I_m$$

where $I_m = \int_0^\infty (\epsilon - \mu)^m \frac{df}{d\epsilon} d\epsilon = -\beta^{-m} \int_{-\beta\mu}^\infty \frac{e^x}{(e^x+1)^2} x^m dx$

b) (5 pts.) Show that only an exponentially small error is made by taking the lower limit of integration as $-\infty$, and that then all terms with m odd vanish.

c) (5 pts.) Evaluate the first two non-vanishing terms and show that this agrees with the expansion of I .

d) (10 pts.) Using the result for I , express N in the form of such an integral and obtain an expansion for $N(V, T, \mu)$ in terms of kT/μ (to second order). Verify that $T \rightarrow 0$ yields the relation between N and ϵ_F derived in class.

e) (10 pts.) Invert this relationship to obtain $\mu(T)$ as a function of kT/ϵ_F (to second order) for fixed N .

f) (5 pts.) Similarly obtain an expansion for the internal energy E as a function of kT/μ (to second order).

g) (5 pts.) Substituting in $\mu(T)$ into the energy expansion, obtain an expansion of E in kT/ϵ_F to second order, and thus C_v . Hence see why we skipped the detailed computation in class.

3

3. (20 pts.) Show that for the Bose-Einstein and Fermi-Dirac gas at low density and/or high temperature the equation of state is given by

$$p = kT\rho \left(1 \mp \frac{\rho\Lambda^3}{2^{5/2}} + \dots \right)$$

where $\Lambda = h/\sqrt{2\pi mkT}$ is the thermal de Broglie wavelength, and the upper (lower) sign is for the Bose-Einstein (Fermi-Dirac) gas.

We start with the thermodynamic identity for the pressure p in terms of the grand canonical partition function Ξ :

$$pV\beta = \ln \Xi \tag{14}$$

where $\beta = \frac{1}{kT}$, with k being the Boltzmann constant and T the temperature.

The grand canonical partition function for Bose-Einstein (BE) and Fermi-Dirac (FD) gases are given by:

$$\ln \Xi_{\text{BE}} = \sum_{\nu} \ln (1 - e^{-\beta(\epsilon_{\nu} - \mu)}) \quad (15)$$

$$\ln \Xi_{\text{FD}} = \sum_{\nu} \ln (1 + e^{-\beta(\epsilon_{\nu} - \mu)}) \quad (16)$$

where ϵ_{ν} is the energy of state ν and μ is the chemical potential. We will go through the derivation for the Fermi-Dirac gas and then show how similar steps repeat for the Bose-Einstein gas, noting that a comprehensive derivation was given in lecture 8.

After performing a Taylor expansion to second order in the limit of small fugacity inside of the integral in spherical coordinates for this, we get:

$$\ln \Xi = \frac{V}{\Lambda^3} (2s + 1) f_{5/2}(\zeta) \quad (17)$$

So, we have arrived at:

$$p(T, \mu)\beta = \frac{2s + 1}{\Lambda^3} f_{5/2}(\zeta) \quad (18)$$

where:

$$f_{5/2}(\zeta) = \zeta - \frac{\zeta^2}{2^{5/2}} \quad (19)$$

to the 2nd order. For simplicity, we assume that $s = 0$. But now we want to get rid of the fugacity, and turn it into a density. For this, we can use the virial expansion derived in the notes:

$$\zeta = \Lambda^3 \rho + \frac{(\Lambda^3 \rho)^2}{2^{3/2}} \quad (20)$$

$$p = kT\rho \left(1 + \frac{\rho\Lambda^3}{2^{5/2}} + \dots \right) \quad (21)$$

For the BE case, we will have:

$$g_{5/2}(\zeta) = \zeta + \frac{\zeta^2}{2^{5/2}} \quad (22)$$

so the sign is flipped and we get a final result of:

$$p = kT\rho \left(1 - \frac{\rho\Lambda^3}{2^{5/2}} + \dots \right) \quad (23)$$