Homework 8 Soln

8.1 [Colligative properties]  
(1) A certain amount of substance dissolved in 100 g of benzene causes 1.43 K decrease of the melting point of benzene. The same amount dissolved in 100 g water causes 1.52 K decrease of the melting point of water. The extent of depression of the melting point of water is \( \Delta T = K_w m \) with \( K_w = 2.41 \text{ (K·kg/mol)} \), where \( m \) is molality (mol/kg). For benzene the analogous law reads \( \Delta T = K_b m \), where \( K_b = 5.12 \text{ (K·kg/mol)} \). How can you explain the discrepancy?  

**Soln.** 
The effective molality in water is  
\[
m_w = \frac{\Delta T}{K_w} = \frac{1.52}{2.41} = 0.631.
\]

The effective molality in benzene is  
\[
m_b = \frac{\Delta T}{K_b} = \frac{1.43}{5.12} = 0.280.
\]

Therefore, \( m_w / m_b = 0.631/0.280 = 2.25 \) (that is, there are 2.25 times as many particles in water as in benzene). Probably, the most natural interpretation is that this substance dissociates into (more than) two parts in water (perhaps, ionic dissociation).

(2) When a 5 grams of substance is dissolved in 100 g water, the vapour pressure at 100 °C is reduced by 1.32% (see (3) of Q27.5). Then, what is the melting point of this solution under 1 atm? The cryoscopic constant for water is \( K_w = 1.855 \text{ K·kg/mol} \).  

**Soln.**  
We know  
\[
\frac{|\Delta P|}{P} = x,
\]
so the mole fraction \( x \) is given by  
\[
x = \frac{5}{M}(100/18) = 0.0132.
\]

Therefore, \( M = (18/20)/0.0132 = 68.2 \).  

The molality of the solution is \( = 50/68.2 = 0.733 \text{ mol/kg} \). Therefore, \( \Delta T = 1.855 \times 0.733 = 1.36 \text{ K} \).  

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1In practice, if you wish to use colligative properties, use Wikipedia. Therefore, remember at least the names relevant to the topic: Raoult, Henry, freezing point depression and boiling point elevation, osmotic pressure, vapor pressure depression  
2\( K \) is called the cryoscopic constant.  
3Do not confuse this with 'molarity' mol/liter, which is usually written as \( M \)
8.2 [Gibbs and Poisson]

We know that the canonical partition function reads

$$Z_N = \frac{1}{N!} f^N,$$

(HW7.1)

where $f$ is the one particle canonical partition function. We know why we need $1/N!$, but let us pretend that $Z_N = f^N$. What will happen?

(1) Compute the grand canonical partition function with chemical potential $\mu$, and then find the equation of state $PV = \cdots$. Do you get the ideal gas law?

**Soln.** The grand canonical partition function reads (the origin is at the center of the cube)

$$\Xi = \sum_{n=0}^{\infty} f^n e^{\beta \mu n} = \frac{1}{1 - f e^{\beta \mu}}.$$ 

$fe^{\beta \mu} < 1$ is required for the grand canonical partition function to be well defined, so $\mu$ has an upper bound. However, this itself does not cause any problem (Recall the boson case: $\mu$ cannot exceed the one-particle ground state energy.) Therefore,

$$\beta PV = \log \Xi = -\log(1 - fe^{\beta \mu}).$$

Classically, this is meaningful, because $\mu \ll 0$. Therefore,

$$N = \frac{\partial \log \Xi}{\partial \mu} = \frac{fe^{\beta \mu}}{1 - fe^{\beta \mu}},$$

which implies $fe^{\mu \beta} = N/(1 + N)$. Therefore, the equation of state reads

$$\beta PV = -\log(1 - fe^{\beta \mu}) = -\log(1 - N/(1 + N)) = \log(1 + N).$$

This is quite unphysical, because $PV$ is not extensive. Notice that $\Xi = 1 + N$.\(^4\)

If we assume $f$ as a function of $V$, then $d(\beta PV) = -Ed\beta + \beta PdV + Nd(\beta \mu)$ means (notice that $f' = df/dV = f/V$)

$$P = \left(\frac{\partial PV}{\partial V}\right)_{T,\mu} = -k_B T \frac{fe^{\beta \mu}}{1 - fe^{\beta \mu}} = k_B T \frac{fe^{\beta \mu}}{V} \frac{fe^{\beta \mu}}{1 - fe^{\beta \mu}} = \frac{N k_B T}{V}.$$

Thus nothing seems wrong. What is going on? I have not figured it out yet.

(2) Find the probability to find $n$ particles in the volume where the average number is $\langle n \rangle$? We know the true distribution: Poisson, see Q28.2. What is a noteworthy difference between what we will get and the Poisson distribution?

**Soln.**

$$P(n) = \frac{1}{\Xi} f^n e^{\beta \mu n} = (1 - fe^{\beta \mu}) f^n e^{\beta \mu n} = \frac{\langle n \rangle^n}{(1 + \langle n \rangle)^{n+1}}.$$ 

\(^4\)You might read the same in (28.52), but this is the major error found for the first time in the book. An official correction will be posted. The correct formula is an exponentiated version.
Notice that there is no peak in contrast to the Poisson distribution. This is probably due to the not reduced weights for larger $N$.

### 8.3 [3D box condensate distribution]

Let us put $N$ ideal bosons in a cube with edge $L = 1$ cm. At some temperature $10^{20}$ particles are in the condensate.

1. What is the number density of the condensate around 2 mm deep from the center of one boundary square?

**Soln.**

The one-particle ground state is the ground state wave function. The normalized ground state wave function is

$$\psi_0 = \left(\frac{L}{2}\right)^{-3/2} \cos\left(\frac{\pi x}{L}\right) \cos\left(\frac{\pi y}{L}\right) \cos\left(\frac{\pi z}{L}\right).$$

The density distribution must be $N_0 \psi_0^2$. Therefore, what is asked is given by (note that the location is 3 mm from the center along the $x$-axis)

$$(8N_0/L^3) \cos^2(0.3\pi) = \left(10^{20}/10^{-6}\right) \times 8 \times 0.59^2 = 2.76 \times 10^{26} \text{ m}^{-3}. $$

2. Do you think what you have seen compatible with the ordinary (statistical) thermodynamics?

**Soln.**

Since the distribution is proportional to $\cos^2(\pi x/L) \cos^2(\pi y/L) \cos^2(\pi z/L)$, over a macroscopic range of order 1 cm, the density distribution is not uniform. You might say if you take the non-condensate into account as well, then the density would be uniform (except very close to the cube boundary), but that is not possible, since $N_0$ can be indefinitely close to $N$. Thus, we must conclude that free particles are unphysical, violating the fourth law. That is, extensive quantities are not really extensive. Why does this happen? Because the particles lack hard cores. Every materials particle contains fermions in it, so every materials particle must have a hard core.

### 8.4 [Effective interactions due to statistics]

We discussed intuitively that particles feel effective attraction under the Bose-Einstein statistics and effective repulsion under the Fermi-Dirac statistics (recall Fig. 28.6). Let us be more quantitative.

To simplify the calculation let us consider a two particle system as a canonical ensemble. Its Hamiltonian is

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m}.$$  

The canonical partition function reads

$$Z = Tr e^{-\beta H}.$$
The trace is over all the system states specified by two momenta [the state ket may be written as $|p, p'\rangle$. To express this ket we introduce one particle states $|p\rangle$ and $|p'\rangle$ (normalized one particle kets).

(1) Write $|p, p'\rangle$ in terms of one particle momentum kets $|p\rangle$ and $|p'\rangle$ for bosons and for fermions (i.e., the two-particle state kets must be symmetric or antisymmetric). You must correctly normalize the kets. You may generically assume two momenta are distinct. [This is a trivial question to prepare the stage.]

**Soln.**
We must correctly symmetrize $|p\rangle|p'\rangle$. $+$ is for bosons and $-$ for fermions:

$$|p, p'\rangle = \frac{1}{\sqrt{2}} (|p\rangle|p'\rangle \pm |p'\rangle|p\rangle).$$

(2) The trace in $Z$ may be computed as

$$Z = Tr e^{-\beta H} = \int dr_1 dr_2 \langle r_1 | e^{-\beta H} | r_2 \rangle,$$

$$= \int dr_1 dr_2 \sum_{p,p'} e^{-\beta(p^2+p'^2)/2m} |\langle r_1 | r_2 \rangle| |p,p'\rangle|^2.$$

Assuming that the system is in a sufficiently large box of volume $V$ use

$$\langle r|p \rangle = \frac{1}{\sqrt{V}} e^{ip \cdot r/h}. \quad \text{(HW7.2)}$$

and introducing the continuum approximation,

$$\sum_{p} \simeq \frac{V}{\hbar^3} \int dP, \quad \text{(HW7.3)}$$

show that

$$Z = \frac{1}{h^6} \int dr_1 dr_2 \int dp dp' e^{-\beta(p^2+p'^2)/2m} [1 \pm \text{Re} \exp(i(p-p') \cdot (r_1 - r_2)/h)]. \quad \text{(HW7.4)}$$

**Soln.**

$$Z = \int dr_1 dr_2 \sum_{p,p'} e^{-\beta(p^2+p'^2)/2m} |\langle r_1 | r_2 \rangle| |p,p'\rangle|^2,$$

$$= \int dr_1 dr_2 \sum_{p,p'} e^{-\beta(p^2+p'^2)/2m} \frac{1}{2} |\langle r_1 | p \rangle \langle r_2 | p' \rangle \pm \langle r_1 | p' \rangle \langle r_2 | p \rangle|^2.$$

Explicitly writing the matrix elements, we get

$$Z = \int dr_1 dr_2 \sum_{p,p'} e^{-\beta(p^2+p'^2)/2m} \frac{1}{V^2} [1 \pm \text{Re} \exp(i(p-p') \cdot (r_1 - r_2)/h)],$$

$$= \frac{1}{h^6} \int dr_1 dr_2 \int dp dp' e^{-\beta(p^2+p'^2)/2m} [1 \pm \text{Re} \exp(i(p-p') \cdot (r_1 - r_2)/h)].$$
(3) Rewrite $Z$ in the following form

$$Z = \frac{1}{\hbar^6} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p} d\mathbf{p}' e^{-\beta(p^2+p'^2)/2m+\phi(r_1-r_2)},$$

and find the effective interaction potential $\phi$. Notice that $e^{-\beta \phi}$ is the average of $[\quad]$ in (HW7.4) over both momenta. Show that $\phi$ is an effective repulsive (resp., attractive) potential for fermions (resp., bosons). [Perhaps, try to graph $\phi$.]

**Soln.**

To compute $F$ we need

$$\frac{\int d\mathbf{p} e^{-\beta(p^2/2m)+i\mathbf{p} \cdot \mathbf{r}/\hbar}}{\int d\mathbf{p} e^{-\beta(p^2/2m)}} = e^{-m k_B T r^2/2 \hbar^2}.$$  

Since you do not need the normalization constant, you must be able to guess the form immediately. Do not take the real part first. In any case, the imaginary part vanishes. Therefore,

$$\langle 1 \pm \text{Re} \exp(i(\mathbf{p} - \mathbf{p}') \cdot (\mathbf{r}_1 - \mathbf{r}_2)/\hbar) \rangle _{\mathbf{p}_1, \mathbf{p}_2} = 1 \pm e^{-m k_B T (r_1-r_2)^2/\hbar^2}.$$  

That is,

$$\beta \phi(\mathbf{r}) = -\log[1 \pm e^{-m k_B T (r_1-r_2)^2/\hbar^2}].$$

The graph of $\phi$ looks like the illustration below:

As we expected, the effective interaction is attractive for bosons and repulsive for fermions.

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5In linear calculations as integration, usually it is unwise to separate the real and imaginary part before calculation.