Homework 8

Due on April 11 (W by midnight),\(^1\) 2018 to sblkrsh2@illinois.edu. If you use pdf, you can submit your draft to me for comments: if before 18:00 of April 8 (Sun), 2018, I guarantee to respond (fairly quickly); after that (but before April 11) I may (try if you wish).

As usual, HW is treated as a learning device, so do not hesitate to ask me any question, and also you may discuss with each other (after your individual efforts).

8.1 [Colligative properties]\(^2\)

(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 \(K_w = 2.41 \text{ (K·kg/mol)}\),\(^3\) where \(m\) is molality (mol/kg).\(^4\) 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?

(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 \(K_w = 1.855 \text{ K·kg/mol}\).

8.2 [Gibbs and Poisson]

We know that the canonical partition function reads

\[
Z_N = \frac{1}{N!} f^N, \quad \text{(HW7.1)}
\]

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?

(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?

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

\(^1\)The homework cycle will be Tu to W, but hopefully, the problems will be posted by Monday Noon.

\(^2\)In 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.

\(^3\)\(K\) is called the cryoscopic constant.

\(^4\)Do not confuse this with ‘molarity’ mol/liter.
boundary square?

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

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.]

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

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

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

Assuming that the system is in a sufficiently large box of volume \(V\) use

\[ \langle r | p \rangle = \frac{1}{\sqrt{V}} e^{i p r/\hbar}. \] (HW7.2)

and introducing the continuum approximation,

\[ \sum_p \approx \frac{V}{\hbar^3} \int dp, \] (HW7.3)

show that

\[ Z = \frac{1}{\hbar^6} \int dr_1 dr_2 \int dp dp' e^{-\beta (p^2 + p'^2)/2m}[1 \pm \Re \exp(i (p - p') \cdot (r_1 - r_2)/\hbar)]. \] (HW7.4)
(3) Rewrite $Z$ in the following form

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

(HW7.5)

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