

8.08 Statistical Physics II — Spring 2019

Recitation Note 7

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1 Common Problems in Psets

There are two common problems with Taylor expansion.

- When the improper integral is absolutely convergent, one is free to switch the order of integration and Taylor expansion. In this way, there is no need to resort to special functions if only leading order behavior is of interest. For example, we encounter the following integral in pset 4:

$$\int_0^{2\pi} d\theta e^{-\beta(-6Jm \cos \theta)}. \quad (1)$$

Near the phase transition point, m is small, and so does the exponent (as long as β is finite). Therefore, to keep the lowest order of the temperature dependent term:

$$\int_0^{2\pi} d\theta e^{-\beta(-6Jm \cos \theta)} \approx \int_0^{2\pi} d\theta (1 + 6Jm\beta \cos \theta + 18J^2m^2\beta^2 \cos^2 \theta) = 2\pi(1 + 9J^2m^2\beta^2). \quad (2)$$

In this way, there is no need to know any knowledge about Bessel functions.

- In Taylor expansion, one always neglect small terms, not the other way around. Functions such as $e^{-\Delta/k_B T}$ cannot be Taylor expanded around $T = 0$. Note that although it is possible to do Laurent expansion around $T = 0$ as

$$\exp\left(-\frac{\Delta}{k_B T}\right) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{\Delta}{k_B T}\right)^n, \quad (3)$$

such expansions are usually unhelpful physically because one cannot simply keep the first order term.

Dimensionless integral means a integral whose integrand is dimensionless. If the integral range does not depend on parameters in the problem, the dimensionless integral is usually just a constant. For example, we encounter the following integral in pset 6:

$$\int_{-\infty}^{+\infty} d\delta n e^{-Nb\delta n^4/k_B T}, \quad (4)$$

which is not dimensionless because δn has the dimension of density. Since every exponent is dimensionless, we can change the variable

$$x = \left(\frac{Nb}{k_B T}\right)^{1/4} \delta n. \quad (5)$$

x is now dimensionless, and

$$\int_{-\infty}^{+\infty} d\delta n e^{-Nb\delta n^4/k_B T} = \left(\frac{Nb}{k_B T}\right)^{-1/4} \int_{-\infty}^{+\infty} dx e^{-x^4}. \quad (6)$$

$\int_{-\infty}^{+\infty} dx e^{-x^4}$, now a dimensionless integral, is just a constant which is often unimportant (one can also evaluate the integral, which is $2\Gamma(5/4) \approx 1.81$). By doing the change of variable in this way, it is clear how does the integral scale with N and T , which is often the behaviors that are of interest.

2 Equivalence of Ensembles

In recitation 3, we have already seen the equivalence of the microcanonical ensemble and the canonical ensemble. Here we show the equivalence of the canonical ensemble and the grand canonical ensemble. To be concrete, we still use the absorption of classical ideal gas as the example.

Consider a surface with M (distinguishable) locations to host (classical monoatomic) gas molecules. Each location can host at most one gas molecule. The binding energy of the gas molecule on the surface is $-u < 0$. A molecule

vibrates as a harmonic oscillator when it is trapped on the surface and it is fair to neglect the interaction between the trapped molecules. The goal is to compute the number of particles absorbed on the surface n as a function of number of locations M , pressure P and temperature T .

In the following, we derive $\mu \sim n$ relations using both ensembles.

- Canonical ensemble approach. The partition function of the absorbed gas is

$$Z_n = \binom{M}{n} Z_{\text{har}}^n e^{\beta u n}. \quad (7)$$

The free energy is

$$F = -k_B T \ln Z_n = -u n + k_B T [n \ln n + (M - n) \ln(M - n) - n \ln Z_{\text{har}}], \quad (8)$$

where we have used the Stirling's approximation and neglected n independent terms. The chemical potential is

$$\mu = \frac{\partial F}{\partial n} = -u - k_B T \ln Z_{\text{har}} + k_B T \ln \left(\frac{n}{M - n} \right). \quad (9)$$

- Grand canonical ensemble approach. The grand partition function of each site is

$$\Xi_1 = 1 + e^{-\beta(-u-\mu)} Z_{\text{har}}. \quad (10)$$

The grand partition function for the gas on the surface is

$$\Xi = \Xi_1^M = \left(1 + e^{-\beta(-u-\mu)} Z_{\text{har}} \right)^M. \quad (11)$$

This can be proved by the definition of the grand partition function:

$$\Xi = \sum_{n=0}^M \sum_i e^{-\beta(E_n^{(i)} - \mu n)} \quad (12)$$

$$= \sum_{n_1, \dots, n_M=0}^1 \sum_{i_1, \dots, i_M} \exp \left[-\beta \left(\sum_{k=1}^M E_{n_k}^{(i_k)} - \mu \sum_{k=1}^M n_k \right) \right] \quad (13)$$

$$= \prod_{k=1}^M \sum_{n_k=0}^1 \sum_{i_k} \exp \left[-\beta \left(E_{n_k}^{(i_k)} - \mu n_k \right) \right] \quad (14)$$

$$= \prod_{k=1}^M \Xi_k \quad (15)$$

$$= \Xi_1^M. \quad (16)$$

The key of the above proof is the independence of the sites, namely $E_n^{(i)} = \sum_{k=1}^M E_{n_k}^{(i_k)}$. If you are not sure how we get Eq. (14) from (13), try the simplest example where $M = 2$:

$$(Z_0^{(1)} + Z_1^{(1)})(Z_0^{(2)} + Z_1^{(2)}) = \underbrace{Z_0^{(1)} Z_0^{(2)}}_{n=0} + \underbrace{Z_0^{(1)} Z_1^{(2)} + Z_1^{(1)} Z_0^{(2)}}_{n=1} + \underbrace{Z_1^{(1)} Z_1^{(2)}}_{n=2}. \quad (17)$$

The above proof is generally true even if the summation of n_k takes from 0 to ∞ , as long as different sites are non-interacting.

The number of absorbed gas molecules is

$$n = \frac{\partial \ln \Xi}{\partial(\beta \mu)} = M \frac{e^{\beta(u+\mu)} Z_{\text{har}}}{1 + e^{\beta(u+\mu)} Z_{\text{har}}}. \quad (18)$$

$n \propto M$ because each site is independent. By the linearity of the expectation, $\langle n \rangle = \langle \sum_{i=1}^M n_i \rangle = \sum_{i=1}^M \langle n_i \rangle = M \langle n_1 \rangle$ we indeed reach the same result.

One can check that Eq. (9) and (18) are equivalent. In this particular example, both approaches are equally simple. However, in the example in the pset, this is not the case.

A surface has N_s sites which can adsorb 1 or 2 atoms. It costs no energy to adsorb 1 atom or 2 atoms. The surface is in contact with a gas of the atoms.

- Canonical ensemble approach.

$$Z_n = \sum_{n_1+2n_2=n} \binom{N_s}{n_1} \binom{N_s-n_1}{n_2}, \quad (19)$$

then

$$\mu = \frac{\partial F}{\partial N}, \quad (20)$$

However, the summation in the partition function is difficult to perform (although doable with great care).

- Grand canonical ensemble approach.

$$\Xi_1 = 1 + e^{\beta\mu} + e^{2\beta\mu}. \quad (21)$$

Since sites are independent, the total grand partition function is

$$\Xi = \Xi_1^{N_s} = (1 + e^{\beta\mu} + e^{2\beta\mu})^{N_s}. \quad (22)$$

Then

$$\langle n \rangle = \frac{\partial \ln \Xi}{\partial (\beta\mu)}, \quad (23)$$

which is much simpler.

Keep in mind the above simplification is only true when different sites are non-interacting.

3 Bose-Einstein Distribution

Bose-Einstein distribution is very similar to the chemical potential of molecules on a surface.

1. Different sites on the surface are non-interacting.
2. Each site can host infinite number of gas molecules, instead of 0, 1 or 2, which reflects the nature of bosons. (In fact, if each site can only host 0 or 1 molecule, we will get the so called Fermi-Dirac distribution, which we will study later in this course. This reflects the Pauli exclusion principle of fermions.)
3. The “site” becomes the “momentum”: $n_i \rightarrow n_{\mathbf{k}}$.
4. The molecules on each site only has a site-dependent binding energy $\varepsilon_{\mathbf{k}}$. Other than that, the molecules on each site are non-interacting: $E_{n_{\mathbf{k}}}^{(i_{\mathbf{k}})} = n_{\mathbf{k}}\varepsilon_{\mathbf{k}}$.

In this way,

$$\Xi_{\mathbf{k}} = \sum_{n=0}^{\infty} e^{-\beta n(\varepsilon_{\mathbf{k}}-\mu)} = \frac{1}{1 - e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}}, \quad (24)$$

and the occupation number of bosons with a specific momentum:

$$\langle n_{\mathbf{k}} \rangle = \frac{\partial \ln \Xi_{\mathbf{k}}}{\partial (\beta\mu)} = \frac{1}{e^{\beta(\varepsilon_{\mathbf{k}}-\mu)} - 1}. \quad (25)$$

This is the so-called Bose-Einstein distribution.

The grand partition function of the total system is

$$\Xi = \prod_{\mathbf{k}} \Xi_{\mathbf{k}} = \prod_{\mathbf{k}} \frac{1}{1 - e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}}, \quad (26)$$

and the total boson number

$$N = \sum_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle = V \int \frac{d^d \mathbf{k}}{(2\pi)^d} \langle n_{\mathbf{k}} \rangle, \quad (27)$$

which determines the $n \sim \mu$ relation. In general this integral cannot be done analytically. Note that V is necessary in the identification $\sum_{\mathbf{k}} \rightarrow V \int d^d \mathbf{k} / (2\pi)^d$ because $\sum_{\mathbf{k}}$ is dimensionless. On the other hand, $d^d \mathbf{k}$ has dimension $[L]^{-d}$. Only $V d^d \mathbf{k}$ is dimensionless.

Here we make several remarks on the chemical potential in Bose-Einstein distribution.

- Typically, $\varepsilon_{\mathbf{k}} \propto k$ or k^2 , and the lowest possible energy a boson can have is zero. Therefore,

$$\langle n_{\mathbf{k}=0} \rangle = \frac{1}{e^{-\beta\mu} - 1} \geq 0. \quad (28)$$

This requires $e^{-\beta\mu} \geq 1$. Since $\beta \geq 0$, chemical potential of bosons must be non-positive $\mu \leq 0$.

- In some cases, such as phonon gas/black-body radiation/harmonic oscillator modes, one is free to create or annihilate bosons and the boson number is not conserved. At thermal equilibrium, the boson number is chosen such that the grand potential is at minimum:

$$\frac{\partial \Omega}{\partial N} = 0, \quad (29)$$

where $\Omega = -k_B T \ln \Xi$. On the other hand,

$$\mu \equiv \frac{\partial \Omega}{\partial N}, \quad (30)$$

by definition. Therefore, in a boson number non-conserving system, the chemical potential is zero.

An equivalent argument is the following. From the first remark we already know $\mu \leq 0$. If $\mu \neq 0$, then it must follow $\mu < 0$. However, this means if the particle number is not-conserved, one can minimize the grand potential by adding particles nonstop, and at equilibrium there will be infinite number of particles, which is not physical.

4 Temperature and Chemical Potential as Lagrange Multipliers

We explicitly derive Bose-Einstein distribution from microcanonical ensemble. The number of different ways of putting $n_{\mathbf{k}}$ particles into $g_{\mathbf{k}}$ degenerate single particle states for Bose particles is (see [this wikipedia page] if you do not know how to count states)

$$\Omega_{\mathbf{k}} = \frac{(n_{\mathbf{k}} + g_{\mathbf{k}} - 1)!}{n_{\mathbf{k}}!(g_{\mathbf{k}} - 1)!}. \quad (31)$$

Then the total entropy the ensemble is

$$S = k_B \ln \Omega = k_B \sum_{\mathbf{k}} \ln \Omega_{\mathbf{k}}. \quad (32)$$

In order to compute the thermodynamic property of the system, we need to maximize the entropy with the constraints of the total energy and the particle number. To do this, we define the Lagrangian and introduce two Lagrange multipliers:

$$L = S + \lambda_1 \left(\sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} n_{\mathbf{k}} - E \right) + \lambda_2 \left(\sum_{\mathbf{k}} n_{\mathbf{k}} - N \right). \quad (33)$$

Note that we have assumed the system is non-interacting by the constraint $E = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} n_{\mathbf{k}}$. By solving $\partial L / \partial n_{\mathbf{k}} = 0$, we have

$$n_{\mathbf{k}} = \frac{g_{\mathbf{k}}}{\exp\left(-\frac{\lambda_1 \varepsilon_{\mathbf{k}} + \lambda_2}{k_B}\right) - 1}. \quad (34)$$

Note that we have used the Stirling's approximation. Note that this already has the same functional form of Bose-Einstein distribution Eq. (25) by identifying

$$\lambda_1 = -\frac{1}{T}, \quad \lambda_2 = \frac{\mu}{T}. \quad (35)$$

Therefore, one can see the temperature and the chemical potential can be interpreted as Lagrange multipliers.

From this point of view, it is natural to see why $\mu = 0$ for particle number non-conserving systems. With no constraint on the particle number, we simply set $\lambda_2 = 0$, which transfers to $\mu = 0$.