

8.08 Statistical Physics II — Spring 2019

Recitation Note 6

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1 Common Problems in Quiz 1 and Psets

There were a lot of confusions in Ginzburg-Landau theory of phase transition.

First, the order parameter and the critical exponent are different. Order parameters (e.g. magnetization) characterize the order of the system. Critical exponents characterize the behavior of thermodynamic properties of the system near the critical point. One of the critical exponents, usually denoted as β , describes the order parameter behavior near the critical point: $\Delta \sim t^\beta$.

Consider the expansion of the GL free energy:

$$F(T, \Delta) = h(T)\Delta + a(T)\Delta^2 + b\Delta^4, \quad (1)$$

where $b > 0$. Δ is the order parameter.

- The coefficients in the GL free energy are smooth function of order parameter and temperature. One of the significant consequences of GL theory is that the order parameter can be a non-smooth function of temperature while the free energy is smooth.
- In the GL theory,
 - Second order phase transition: free energy minimum splitting.
For example, $h(T) = 0$ and $a(T) = a_1(T - T_2)$.
 - First order phase transition: free energy minimum switching.
For example, $h(T) = h_1(T - T_1)$ and $a(T) = -a_0 < 0$. It is important to note $a(T) < 0$ such that there are two minima to switch.
- Although $h(T) = a(T) = 0$ is a legal answer for a system without any phase transition, this system sits at the critical point all the time and is not stable against perturbations. Changing $a(T)$ a little bit (no matter how small) sends the system into a different phase. However, if $a(T) = a_0 > 0$, varying a_0 a little bit (as long as smaller than $|a_0|$) will not send the system into a different phase.

2 Grand Canonical Ensemble

2.1 Properties

Grand canonical ensemble describes a system in contact with a large particle bath and a large heat bath. It is very similar to the canonical ensemble, except that apart from the temperature that characterizes the system in equilibrium with the heat bath, there is another parameter called the “chemical potential” that characterizes the system in equilibrium with the particle bath. In Table 1 we compare all three ensembles we have encountered so far in this course.

In the table, $n \equiv N/V$ is the particle density and isothermal compressibility

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T. \quad (2)$$

According to the fluctuation-response relation, $\kappa_T > 0$.

2.2 Relation with the Canonical Ensemble

The canonical partition function and the grand partition function are related as

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_i e^{-\beta E_i^{(N)}} \quad (3)$$

$$= \sum_{N=0}^{\infty} f^N Z_N, \quad (4)$$

Table 1: Comparison between different ensembles.

	Microcanonical ensemble	Canonical ensemble	Grand canonical ensemble
Canonical variable	U, V, N	T, V, N	T, V, μ
Probability distribution	$P_i = \frac{1}{\Omega}$	$P_i = \frac{1}{Z} e^{-\beta E_i}$	$P_{n,i} = \frac{1}{\Xi} e^{-\beta(E_i^{(n)} - \mu n)}$
Normalization factor	$\Omega = \sum_i 1$	$Z = \sum_i e^{-\beta E_i}$	$\Xi = \sum_n \sum_i e^{-\beta(E_i^{(n)} - \mu n)}$
Thermodynamic potential	$S = k_B \ln \Omega$	$F = -k_B T \ln Z$	$\Omega = -k_B T \ln \Xi$
Thermodynamic quantity		$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$	$\langle E \rangle = -\frac{\partial \ln \Xi}{\partial \beta}$ $\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln \Xi}{\partial \mu}$
Fluctuation		$\langle (\Delta E)^2 \rangle = -\frac{\partial^2 \ln Z}{\partial \beta^2} = N k_B T^2 c_v$	$\langle (\Delta E)^2 \rangle = -\frac{\partial^2 \ln \Xi}{\partial \beta^2} = N k_B T^2 c_v$ $\langle (\Delta N)^2 \rangle = \frac{1}{\beta^2} \frac{\partial^2 \ln \Xi}{\partial \mu^2} = N k_B n \kappa T$
Equilibrium condition		$T_1 = T_2$	$T_1 = T_2, \mu_1 = \mu_2$

where $f = e^{\beta\mu}$ is the fugacity of the system and Z_N is the partition function of the N particle system.

In noninteracting systems, $Z_N = Z^N$ or $Z_N = Z^N/N!$, where $Z \equiv Z_1$ is the single particle partition function. The grand partition function simplifies as

$$\Xi = \begin{cases} \sum_{N=0}^{\infty} f^N Z^N = \frac{1}{1-fZ}, & \text{distinguishable,} \\ \sum_{N=0}^{\infty} f^N \frac{Z^N}{N!} = e^{fZ}, & \text{indistinguishable.} \end{cases} \quad (5)$$

For such systems, we can compute their average particle number:

$$N_0 \equiv \langle N \rangle = \frac{\partial \ln \Xi}{\partial (\beta\mu)} = f \frac{\partial \ln \Xi}{\partial f} = \begin{cases} \frac{fZ}{1-fZ}, & \text{distinguishable,} \\ fZ, & \text{indistinguishable.} \end{cases} \quad (6)$$

Also the marginal distribution of the particle number:

$$P_N = \sum_j P_{N,j} = \begin{cases} (fZ)^N (1-fZ) = \left(\frac{N_0}{1+N_0}\right)^N \frac{1}{1+N_0} \sim \text{Geometric}\left(\frac{1}{1+N_0}\right), & \text{distinguishable,} \\ \frac{(fZ)^N}{N!} e^{-fZ} = \frac{N_0^N}{N!} e^{-N_0} \sim \text{Poisson}(N_0), & \text{indistinguishable.} \end{cases} \quad (7)$$

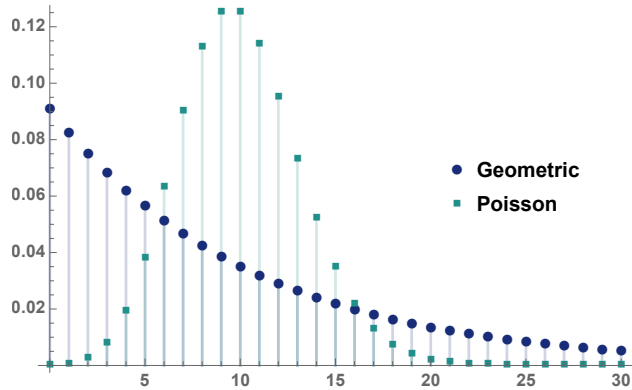


Figure 1: Probability mass function of geometric distribution and mean distribution with mean 10.

Both marginal distributions have mean N_0 . The variance of distinguishable case is $N_0(N_0 + 1) \sim N_0^2$ while the variance of the indistinguishable case is N_0 .

The variance of the distinguishable case is not consistent with the fluctuation-response relation (which requires $\text{Var}(N) \sim N_0$), because the geometric distribution is problematic—the most probable particle number is always at zero, and is not peaked at the mean N_0 . In this case, we cannot use saddle point approximation in the thermodynamic limit, and the logarithm of the grand partition function does not reduce to the grand potential¹. This is another example that statistical mechanics fails to reproduce thermodynamics.

The indistinguishable case is well-behaved. Consider a large box of classical ideal gas. By treating a small volume of the gas as the system and the remaining part as the particle bath, the above result states that the particle number in the small volume obeys Poisson distribution.

¹If you are not sure what this means, see section 1.2 *Partition Function and Helmholtz Free Energy* in the first recitation note.

3 Absorption of Classical Ideal Gas

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 .

We can treat classical ideal gas (system 1) and gas molecules on the surface (system 2) as two systems in equilibrium. At equilibrium, $T_1 = T_2 = T$ and $\mu_1 = \mu_2$.

We first compute the chemical potential of classical ideal gas. We already know the free energy of the classical ideal gas

$$F_1 = k_B T N \left[\ln \left(\frac{N \lambda_T^3}{V} \right) - 1 \right], \quad (8)$$

where $\lambda_T = (2\pi\hbar^2/mk_B T)^{1/2}$. The chemical potential is

$$\mu_1 = \frac{\partial F_1}{\partial N} = k_B T \ln \left(\frac{P \lambda_T^3}{k_B T} \right), \quad (9)$$

where we have used the equation of state of classical ideal gas $pV = Nk_B T$. The reason why we can compute chemical potential using the canonical ensemble is the same as the reason why we can compute temperature using the microcanonical ensemble². In the thermodynamic limit, all three ensembles are equivalent. We are free to use whichever is convenient as long as we correctly identifying $S \sim T$ and $N \sim \mu$ relation.

We then compute the chemical potential of the absorbed gas. We already know the partition function of a quantum harmonic oscillator is $Z_{\text{har}} = [2 \sinh(\beta\varepsilon/2)]^{-1}$, where ε is the intrinsic frequency of the oscillator. The partition function of the absorbed gas is

$$Z_n = \binom{M}{n} Z_{\text{har}}^n e^{\beta u n}. \quad (10)$$

The free energy is

$$F_2 = -k_B T \ln Z_n = -u n + k_B T [n \ln n + (M - n) \ln(M - n) - n \ln Z_{\text{har}}], \quad (11)$$

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

$$\mu_2 = \frac{\partial F_2}{\partial n} = -u - k_B T \ln Z_{\text{har}} + k_B T \ln \left(\frac{n}{M - n} \right). \quad (12)$$

Equate Eq. (9) and (12), we have

$$\frac{n}{M} = \left[1 + \frac{2k_B T}{P \lambda_T^3} \exp \left(-\frac{u}{k_B T} \right) \sinh \left(\frac{\varepsilon}{2k_B T} \right) \right]^{-1}. \quad (13)$$

As a sanity check, it is not hard to see $0 \leq n/M \leq 1$.

First we study the pressure dependence. As pressure increases, n/M also increases. Especially, when P is small, $n/M \sim P$. In the $P \rightarrow \infty$ limit, the $n/M \rightarrow 1$.

We then study the temperature dependence. Since we are working with classical ideal gas, the zero temperature limit is invalid. The intermediate temperature range is complicated due to the coexistence of many temperature scales. At large T limit, $\exp(-u/k_B T) \sim 1$, $\sinh(\varepsilon/2k_B T) \sim \varepsilon/2k_B T$. Therefore, $n/M \sim T^{-3/2}$, i.e., n/M decreases with increasing the temperature.

²If you are not sure what this means, see section 1 *Equivalence of Ensembles* in the third recitation note.