Notes for Lecture 15

Phase transitions

In the previous lecture, we have considered the Bose gas problem, and have noted that it contains the physics of *condensation*, the Bose-Einstein condensation. We will discuss more on the BEC, which will be used as a nice pathway to general discussions on phase transitions.

15.1 BEC

We learned that a Bose gas is fascinating. Without any particle-particle interaction, it leads to a phase transition! The origin of this strange behavior is the Bose statistics, which we *can* interpret as providing an effectively attractive interaction between particles (Secs. 10.6, 12.4).

Even without any interaction, it leads to a non-analytic thermodynamic function and a phase transition! In this sense, a BEC is one of those quantum effects that humans have a hard time grasping in general. The origin of this strange behavior is simply the Bose statistics, which we *can* interpret as providing an effectively attractive interaction between particles (Sec. 13.4).

15.1.1 BEC transition

The core results regarding the BEC transition have been given in Sections 14.1.4 and 14.1.6, while the core derivation has been given in Section 14.1.5. What we found was that the chemical potential gets pinned at 0 in the BEC phase, and the "order parameter" $\frac{n(0)}{N}$ turns on in this phase. Near the phase boundary, this order parameter vanishes while $n(0) \gg 1$.

From now on, we will use the expressions "above the BEC transition" and "below the BEC transition" in the following sense, to convey the meaning in terms of the temperature or the density, as we discovered in the last lecture.

$$\text{above the BEC transition:} \quad n\lambda^3 < \zeta(3/2) \approx 2.612 \tag{15.1}$$

$$\text{below the BEC transition:} \quad n\lambda^3 > \zeta(3/2) \approx 2.612 \tag{15.2}$$

Note that the transition can be controlled by volume as well as temperature (Section 14.1.6).

15.1.2 Pressure, Energy, Heat Capacity

Let us evaluate E and P for a Bose gas. The expressions Eqs. 14.14 and 14.15, which are copied here, are still valid, since the energy and the pressure are contributed only by excited states.

$$E = \frac{3}{2}\frac{k_BT}{\lambda^3}\, g_{5/2}(z)\, V$$

$$P = \frac{k_BT}{\lambda^3}\, g_{5/2}(z)$$

Above the BEC transition, the fugacity z will gradually decrease below 1, approaching the classical limit as $n\lambda^3 \to 0$. Below the BEC transition, where $z = 1$, we get

$$\frac{E}{V} = \frac{3}{2}\frac{k_BT}{\lambda^3}\,\zeta(5/2) \qquad \zeta(5/2) \approx 1.341 \tag{15.3}$$

$$\frac{C_V}{V} = \frac{15}{4}\frac{k_B}{\lambda^3}\,\zeta(5/2) \qquad \text{since } \lambda \propto T^{-1/2} \tag{15.4}$$

Since $\lambda = h/\sqrt{2\pi m k_B T}$, this means the following.

> In the BEC phase, P, E/V and C_V/V are functions of T only.

And

$$\frac{E}{V},\ P \propto T^{5/2} \quad \text{and} \quad \frac{C_V}{V} \propto T^{3/2} \tag{15.5}$$

Why this behavior? The reason can be found by considering what it means to have $\mu = 0$. Just like in the phonon and photon problems (LN 11), $\mu = 0$ means that the particle number is not an independent variable. As other independent variables are adjusted, particles are thermally generated "out of the vacuum," and subsequently the particle number is dependent on other variables such as T and V. Here, the "vacuum" refers to the ground state at zero temperature. In the case of the photon problem, it can be taken as the true vacuum. In the case of the phonon, it is the ground state of the crystal. In the case of the BEC, the "vacuum" is the fully condensed state. And "particles" are used to mean excitations relative to the ground state. These are *not* gimmicky definitions of vacuum and particles at all. They are the most physical definitions of what vacuum and particles really mean.

Therefore, in the BEC state, the excitations are "extracted from vacuum" by simply taking bosons out of the BEC. This is why the chemical potential is zero. As long as the "reserve" – the BEC – does not run out, it acts as a source from which finite temperature excitations can be extracted. And the number of excitations N_e that can be extracted will be higher, the higher the temperature is. How this number scales as a function of T depends on what the dispersion relation is. $N_e \propto k_T^d \propto \omega_T^{d/\alpha} \propto T^{d/\alpha}$ if $\omega \propto k^\alpha$, d is the dimensionality of space, and $\omega_T (\sim k_B T/\hbar)$ and k_T are the energy and momentum scales, respectively, of thermal generated particles[1]. Thus, the total energy is given by $E \sim T^{1+d/\alpha}$. This explains why we got $E/V \propto T^{5/2}$, since $d = 3$ and $\alpha = 2$ in the above example. This will lead to the power law signature in the heat capacity

$$C_V \propto T^{3/2} \tag{15.6}$$

Note that, from Eq. 15.4, $C_V/N = k_B \frac{15}{4}\frac{\zeta(5/2)}{\zeta(3/2)} \approx 1.93$ at $T = T_c$. Therefore, the heat capacity overshoots the classical value $C_V/N = 1.5$ at $T = T_c$. Above T_c, the heat capacity decreases. The heat capacity is continuous at T_c, since $g_{3/2}(z)$ is a continuous function. However, C_V cannot be analytic at T_c, due to the non-analyticity of $g_m(z)$ at $z = 1$; C_V shows a cusp singularity at T_c (cf. Fig. T7.4).

For the same reason, we can conclude that P and E are not only continuous across the transition but so are their first T-derivatives.

15.1.3 Isotherm

It is interesting to consider isotherms $P = P(V)$. It is novel that we already have a phase transition, recognizable from the isotherms. Let us figure out how the isotherm behaves above the transition point and below. We expect that the isotherm behave

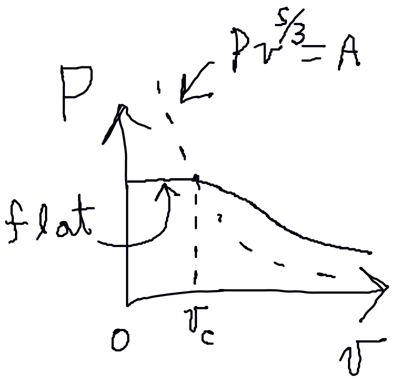
---

[1] These important arguments are much like those equally important ones at the end of Secs. 11.1.4 and 13.1.4. Especially, note that ω_{max}, k_{max} of Sec. 11.1.4 correspond to ω_T, k_T here, respectively. These notations can be exchanged freely.

differently above and below. The boundary curve can be computed by rewriting the BEC condition $n\lambda^3 = \zeta(3/2)$, using Eq. 14.15, as

$$Pv^{5/3} = \frac{h^2}{2\pi m}\frac{\zeta(5/2)}{\zeta(3/2)^{5/3}} \tag{15.7}$$

where $v \equiv V/N = 1/n$. On the left hand side of this boundary, the isotherm is flat, since P is a function of T only, below the BEC transition. So, $dP/dv = 0$ in the BEC phase. It is left for your exercise to show that dP/dv also vanishes when v approaches v_c from above the BEC transition. So, the isotherm looks like the following figure.



Qualitatively, this isotherm has some similarity to the physical isotherm for gas-liquid transition, e.g. the one that can be deduced from the van der Waals equation of state (Homework 5). The similarity is only partial, though. The isotherm in the current case does not have the pure liquid phase where P goes up as v goes up. The reason for this is that the "liquid phase" in the current case is the BEC, which is in fact a zero volume liquid within this simple theory. Also, note that the compressibility is infinite below the BEC transition, since $dP/dV = 0$. Both these results are due to the simplifying assumption of no interaction. In reality, however weakly the molecules interact, the hard core repulsion cannot be ignored, and these behaviors will change.

15.1.4 Latent heat

In any case, note that the BEC transition is the first order, just like the gas liquid transition (cf. Homework 5). One can ask what the latent heat is. We can start from the Clausius-Clapeyron equation,

$$\left.\frac{dP}{dT}\right|_{coexistence} = \frac{\Delta S}{\Delta V} \tag{15.8}$$

Since the BEC is the zero volume liquid, we see that $\Delta V = V_c - 0 = V_c$ where V_c is the volume at the transition. Putting $\Delta S = L/T_c$, we get

$$\left.\frac{dP}{dT}\right|_{coexistence} = \frac{L}{T_c N v_c} \tag{15.9}$$

Since $P \propto T^{5/2}$ as we found above, below the BEC transition, i.e. in the coexistence region, we get $\left.\frac{dP}{dT}\right|_{coexistence} = \frac{5}{2}\frac{P}{T}$. At T_c, we get $P = n_c k_B T_c \frac{\zeta(5/2)}{\zeta(3/2)}$ (from Eq. 14.15 and the BEC condition). Thus, we get

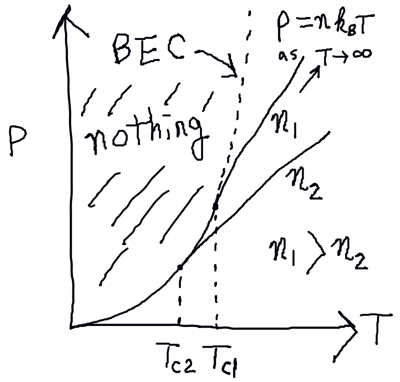
$$\frac{L}{N} = \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)} k_B T_c \approx 1.28\, k_B T_c \tag{15.10}$$

15.1.5 Phase diagram

Let us ponder what the implied P–T phase diagram is within this theory. Recognizing that the BEC phase below T_c is the coexistence phase within the framework of the normal gas-liquid phase transition, we see that

$$P = \frac{k_B T}{\lambda^3}\zeta(5/2) \tag{15.11}$$

valid for the BEC phase marks a curve in the $P - T$ phase diagram. The difference from the normal-gas liquid phase diagram is that this curve does *not* end at a critical point[2], since the latent heat never vanishes at any finite T_c. In other words, the volume of the BEC is always zero, and therefore it is not possible to raise the temperature and equalize the volumes of the gas and the molecule.



---

[2] Note that here in the discussion of BEC, we are using the symbols T_c, v_c, and n_c, etc., to mean transition temperature, volume, density, etc., *not* to mean critical temperature, volume, density.

The $P-T$ phase diagram is sketched above. Out of the BEC phase, the gas phase emerges at T_c, which is higher when the density is higher. As we saw above, the temperature derivative at T_c is continuous. So, the right hand side of the BEC phase curve is the gas phase. The left hand side of the BEC phase? That is not physically accessible within this simple theory. If the particle interactions are taken into account, then this region defines the BEC phase with a finite compressibility.

15.1.6 Macroscopic quantum phenomenon

At low temperature or at high density, the BEC can form, i.e., a macroscopic occupation of the zero energy level leads to a condensation of the system to a new phase.

This sort of expression – an occupation of a quantum energy level by a macroscopic number of bosons – has been said so many times in the literature (scientific or pseudo/meta-scientific) and so it feels a bit hackneyed, but it is important that *you* know what the expression *really* means. The first step of understanding this expression is this simple exercise.

Exercise Using a quantum many body wave function, show to yourself that if any number of bosons occupy the same one particle quantum state (with the wave function $\psi(\vec{x},t)$) then the wave function for any boson must be considered *exactly* the same ($\psi(\vec{x},t)$) with no room for any uncertainty in the relative phase. Namely, all bosons occupying the same one particle quantum level have the same phase.

This result is the so-called *phase coherence* of bosons occupying the same one particle state. In a BEC, a *macroscopic* number of bosons occupy a one-particle quantum level. It is a *macroscopic quantum phenomenon*, in the sense that not just one particle but a collection of a huge number of particles is described by a single one-particle wave function $\psi(\vec{x},t)$ corresponding to the quantum level occupied. Let us stop to think about the meaning of this. In quantum mechanics, we learn that a particle is a wave and vice versa. Then we learn that if you collect a lot of particles the classical mechanics and the classical particle emerge – the quantum mechanics is gone and so is the wave function $\psi(\vec{x},t)$. A possibility of a macroscopic quantum phenomenon means that this is not the only consequence when many particles are amassed. At low temperature or high density, even a macroscopic (read, infinite) number of fundamental particles can act as a quantum object! For this reason, the single particle wave function ψ, normalized to the BEC density, is the so-called **order parameter** of a superfluid, a superconductor, or, indeed, a BEC[3]. The condensate fraction, which

---

[3] More rigorously, but with the same physical content, the order parameter is the ensemble average of the field *operator* $\hat{\psi}$ in the many body theory.

was taken as the order parameter in the previous lecture, is the magnitude squared for ψ, divided by N.

15.2 Theory of phase transition

We have seen an example of a phase transition, now, and we will see more – such as the gas-liquid transition. Let us, then, approach the phase transition from a somewhat more general perspective.

15.2.1 Ising model

We start from a simple model, the Ising model. In this model, a lattice of spins are considered. In free space, or highly symmetric crystal (e.g. a cubic crystal), the interaction between two spins, say $\vec{S}_1$ and $\vec{S}_2$, would be described by the Heisenberg model, $-J\vec{S}_1 \cdot \vec{S}_2$, where $J > 0$ means a ferromagnetic interaction and $J < 0$ means an anti-ferromagnetic interaction. However, in a low symmetry crystal, the spin-spin interaction can be strongly direction dependent, and it can happen that within certain ranges of temperatures the spin interaction can be approximated as "Ising-like," namely the interaction between two spins can be approximated as $-JS_{1,z}S_{2,z}$. For simplicity, we will also assume that the spin is 1/2. In such a case, rewriting $S_{i,z} = \hbar\sigma_{i,z}/2$ $(i = 1, 2)$[4], redefining J to absorb $\hbar^2/4$, and dropping the subscript z for the Pauli matrix σ, we get, for the whole crystal,

$$\mathcal{H}_{int} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j \tag{15.12}$$

where $\langle i, j\rangle$ means a unique nearest neighbor pair[5] of i and j, and σ_i is the Pauli matrix (σ_z) for site i. Note that the site index i (j) is a compound index, consisting of more than one integer for a crystal, if the spatial dimension is higher than 1. The Hamiltonian above defines the so-called spin 1/2 *Ising model.* Clearly, the best basis to work with is the set of eigenstates for σ_i. Thus, σ_i can be considered a number, ± 1 depending on which local eigenstate at site i is considered.

---

[4] Note that the sign convention used here follows that of a positive g for the spin moment (LN 8, page 9). $\mu_z = \mu_B \sigma_z$ is the magnetic moment per spin. So, S_z $(= \frac{\hbar}{2}\sigma_z)$ must be interpreted as the *negative* spin. However, in many statistical physics books, you will find this convention only silently implied, if at all. This is presumably because what is ultimately important is the magnetic moment, μ_z, not the spin.

[5] It goes without saying that the nearest neighbor interaction can be generalized to include the next nearest neighbor and so on. Here, we treat this simplest model only, for clarity.

If the spin system is subjected to a magnetic field, $\vec{H} = H\hat{z}$, then the full Hamiltonian becomes

$$\mathcal{H} = -\mu_B H \sum_i \sigma_i - J \sum_{\langle i,j \rangle} \sigma_i \sigma_j \tag{15.13}$$

where μ_B is the Bohr magneton ($\mu_B \equiv e\hbar/(2m_e c) = 5.789 \times 10^{-9}$ eV/gauss).

The partition function is given by

$$X = \sum_{\{\sigma_i=-1,1\}} \exp\left[\beta\mu_B H \sum_i \sigma_i + \beta J \sum_{\langle i,j \rangle} \sigma_i \sigma_j\right] \tag{15.14}$$

where the first sum is over all possible combinations of $\sigma_i = -1, 1$ for all i's.

15.2.2 Lattice gas

Let us take a system of gas and divide the volume so that each volume element is very small. We assume that the volume element is small enough so that the probability that a volume element is occupied by two or more gas molecules is vanishingly small. Thus, we are assuming that each volume element has the volume of the order of the excluded volume $\Omega/2$ (cf. $\Omega = v_0$ in Homework 3.7). Let $n_i = 0, 1$ be the occupancy of each volume element by gas molecule. Thus, the information about the repulsive interaction is encoded in the fact that n_i is limited to 1. Then, we introduce the effect of attractive interaction by introducing the Hamiltonian

$$\mathcal{H}_{int} = -\varepsilon \sum_{\langle i,j \rangle} n_i n_j \tag{15.15}$$

Given this Hamiltonian, the grand partition function is given by

$$Q = \sum_{\{n_i=0,1\}} \exp\left[\beta\mu \sum_i n_i + \beta\varepsilon \sum_{\langle i,j \rangle} n_i n_j\right] \tag{15.16}$$

where the first sum is over all possible combinations of $n_i = 0, 1$ for all i's.

Clearly, Eq. 15.16 is very similar to Eq. 15.14. Upon the transformation

$$\sigma_i = 2n_i - 1 \tag{15.17}$$

we can see that the mapping from the lattice gas problem to the Ising spin problem can be made complete, i.e. Q of the first problem is identical with the X of the second problem, up to a proportionality constant, if ε and μ are taken as appropriate functions of $\mu_B H$ and J. (Exercise: find those functions.)

So, the Ising model is mapped to the lattice gas model, using which the gas-liquid phase transition can be described. Another type of model that the Ising model applies is the binary alloy problem.

15.2.3 Mean field theory

The mean field theory is the general approach in which the interaction between particles is reduced to an effective mean field. Thus, the problem is reduced to a one particle problem, where the effect of the inter-particle interaction is represented by the mean field. The self consistency of the solution must be sought for the following reason. In the mean field approach, one particle is first singled out and then all other particles are considered as mean field generators. However, when the solution for that singled out problem is obtained, then one has to confront the fact that that singled out particle is no special than others. The mean field for anther particle can be calculated similarly due to all other particles that now include the first singled-out particle. The solution for the first singled out particle is enough to directly calculate the mean field on any other particle. This way, a self-consistency check can be done. We will demonstrate this using the Ising model above.

Let us look at the Hamiltonian, Eq. 15.12. What is so difficult about this Hamiltonian? It is the fact that the interaction term involves a product of two dynamical variables $\sigma_i\sigma_j$. One way to think about σ_i is

$$\sigma_i \equiv \overline{\langle\sigma_i\rangle} + \Delta\sigma_i \qquad \Delta\sigma_i \equiv \sigma_i - \overline{\langle\sigma_i\rangle} \tag{15.18}$$

Then, we note that

$$\sigma_i\sigma_j = \overline{\langle\sigma_i\rangle}\,\overline{\langle\sigma_j\rangle} + \overline{\langle\sigma_i\rangle}\Delta\sigma_j + \overline{\langle\sigma_j\rangle}\Delta\sigma_i + \Delta\sigma_i\Delta\sigma_j \tag{15.19}$$

The mean field approximation amounts to ignoring the last term, which is the "correlation term." Or, it can be viewed as ignoring "the second order fluctuation" therm since $\Delta\sigma_i$ is the fluctuation operator, as defined. Then, we get

$$\begin{aligned}\sigma_i\sigma_j &\approx \overline{\langle\sigma_i\rangle}\,\overline{\langle\sigma_j\rangle} + \overline{\langle\sigma_i\rangle}\Delta\sigma_j + \overline{\langle\sigma_j\rangle}\Delta\sigma_i \\ &= \overline{\langle\sigma_i\rangle}\sigma_j + \overline{\langle\sigma_j\rangle}\sigma_i - \overline{\langle\sigma_i\rangle}\,\overline{\langle\sigma_j\rangle} \qquad \text{using } \Delta\sigma_i \equiv \sigma_i - \overline{\langle\sigma_i\rangle}\end{aligned} \tag{15.20}$$

From this expression, it is clear why the neglected term is called the correlation term. With that term neglected, $\overline{\langle\sigma_i\sigma_j\rangle} = \overline{\langle\sigma_i\rangle}\,\overline{\langle\sigma_j\rangle}$, i.e., any two spins are uncorrelated.

Let us plug in Eq. 15.20 into Eq. 15.12. We get

$$\mathcal{H} = \sum_i \mathcal{H}_i + J \sum_{\langle i,j \rangle} \overline{\langle \sigma_i \rangle}\,\overline{\langle \sigma_j \rangle} \qquad (15.21)$$

$$\mathcal{H}_i \equiv \left(-J \sum_{j = \text{ nn of } i} \overline{\langle \sigma_j \rangle} \right) \sigma_i \qquad (15.22)$$

The 2nd term in $\mathcal{H}$ can be dropped, since it is just a constant. Thus, the problem has effectively become a problem of a single spin (σ_i) in the mean field

$$H_{i,MF} = \frac{J}{\mu_B} \sum_{j = \text{ nn of } i} \overline{\langle \sigma_j \rangle} \qquad (15.23)$$

since the total Hamiltonian is separated into the sum of $\mathcal{H}_i$'s. If there is a real external magnetic field H (Eq. 15.13), then the total field on spin i will be $H_i = H + H_{i,MF}$.

The problem defined by $\mathcal{H}_i = -H_i \mu_B \sigma_i$ is simple. The partition function for σ_i is given by

$$\begin{aligned} X_i &= \exp(\beta H_i \mu_B) + \exp(-\beta H_i \mu_B) \\ &= 2 \cosh(\beta H_i \mu_B) \qquad (15.24) \end{aligned}$$

Therefore, the ensemble average $\overline{\langle \sigma_i \rangle}$ is given by

$$\overline{\langle \sigma_i \rangle} = -\frac{1}{\beta \mu_B} \frac{\partial \log X_i}{\partial H_i} = \tanh(\beta H_i \mu_B) \qquad (15.25)$$

At this point, we will assume a ferromagnetic interaction ($J > 0$), so that $\overline{\langle \sigma_i \rangle}$ is independent of i in equilibrium. Then, define $x \equiv \overline{\langle \sigma_i \rangle}$. The self consistency condition is imposed when one realizes that the field $H_{i,MF} = \frac{J}{\mu_B} z x$ where z is the number of nearest neighbors.[6] Thus, we have the self consistency condition, which reads as

$$x = \tanh\left[\beta\left(Jzx + \mu_B H\right)\right] \qquad (15.26)$$

For the time being, let us consider the $H = 0$ case

$$x = \tanh\left(\beta J z x\right) \qquad (15.27)$$

Clearly, $x = 0$ is a solution to this. However, as we shall see shortly, at low temperatures, the $x = 0$ solution is an unphysical one, and other solutions emerge. How

---

[6] Note that z (or something like it, $\mathbf{z}$) has been used to denote the fugacity in previous lectures. Here, z is simply the coordination number of the lattice. Unfortunately, this is another common usage of the symbol z, and we will use it, as long as it does not conflict with the fugacity.

should we examine to know what the solutions to the above equation are? We can examine the two limits of the right hand side (RHS). First, as $x \to \pm\infty$, the RHS $\to \pm 1$. Second, as $x \to 0$, the RHS $\to \beta J z x$. Third, the derivative of tanh is $1/\cosh^2$, and so the RHS is a monotonically increasing function. These considerations are enough to conclude that the above equation will give three solutions,

$$x = 0, \pm\bar{\sigma} \qquad \text{if} \quad \beta J z > 1 \tag{15.28}$$

namely, if the temperature is low enough or J large enough.

The transition temperature T_c is given by

$$T_c = \frac{Jz}{k_B} \tag{15.29}$$

Thus, this simple Ising model predicts a ferromagnet, providing a simple model why magnets exist if $T < T_c$! This, of course, is a great result, which no semi-classical statistical mechanics can dream of producing (HW 3.5). This *qualitative result* and the ease with which this solution can be obtained like this is the value of the mean field theory. As we shall see, the mean field theory is not so good quantitatively, in general. For instance, for a 2-dimensional square lattice, we get $T_c = 4J/k_B$, while the correct value is $T_c \approx 2.4J/k_B$. The mean field theory that we just covered is called the "Weiss molecular field theory" in the historical context.