Thermodynamics and Statistical mechanics I.

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Contents

LECTURE 1
Thermodynamics. Entropy. LL 9

1.1. Thermodynamics. Entropy.

- Introduction
- Work vs Heat, separation of time scales, chaotic vs collective motion.
- Many particles – impossible to solve – but energy, momentum and ang. momentum are conserved
- Macroscopic/thermodynamic **state** variables, P pressure, V volume, T temperature, E internal energy,... Energy E is a function of a state and can be express through other variables of state, for example $E(P, V)$. Each given macroscopic state has a specific energy **in equilibrium**. The macroscopic variables do not provide complete description of the microscopic state!
- Energy conservation

$$dE = \text{đ}\mathcal{A} + \text{đ}Q, \text{where}$$

  $\mathcal{A}$ work done on the system. Collective.
  Q heat transferred to the system. Chaotic.
  I note that dE is a differential, but $\text{đ}\mathcal{A}$ and $\text{đ}Q$ are not. (**Remark:** There are two notions that are sometimes confused: (i) A function is not differentiable, (ii) something is not a differential of a function. (i) means that there is a function, but it is not smooth enough, (ii) means that there is no function at all.) The distinction is that E depends only on a given state and does not depend on how the system got in to that state, while $\text{đ}\mathcal{A}$ and $\text{đ}Q$ depend on the path the system took to get to a given state.
- Work is $\text{đ}\mathcal{A} = -PdV$. The total work which is done by the system, when system went from a state 1 to a state 2 along a path Γ is given by $\mathcal{A} = \int_\Gamma P dV$. The value of this integral depends on path Γ and is equal to the area under the path Γ on $P - V$ diagram. In particular the work done during a cyclic process (system returns to the state it started from) is not zero, but the total change of energy of the system is zero!
- $P - V$ diagrams and calculation of work. Work is path dependent. Change of energy does not depend on path. Energy is a function of state!
- How to calculate $\text{đ}Q$? We somehow need to characterize the chaotic part of the energy. What do we know about it? 1. It is irreversible in the sense that two types of marbles mix in a jar by steering but cannot be unmixed by steering in the opposite direction. 2. A disturbed system goes back to equilibrium. Hypotheses: There is a function of state S for a system (it is called entropy) which can only increase and is at maximum when the system is at equilibrium (at given say P and V). Naturally if such function exist, then e^S (or any other monotonic function of S) will have the same property. So we impose one more condition. The entropy S is additive. It means that the entropy of a system equals to sum of the entropies of its subsystems.
    In summary:
  - Entropy is a function of state.

- When the system equilibrates by its own dynamics at fixed thermodynamical variables the entropy increases. For given thermodynamical variables of the system the entropy is at maximum at equilibrium.
- Entropy is additive.
- The existence of this function has large consequence and is central for thermodynamics.
- Entropy is a function of state! The change of entropy does not depend on the path.
- Notions of work and heat do not make sense without specifying the path. Consequences in language: A system can **transfer** heat (a system cannot **have** heat). A system can **do** work (a system cannot **have** work). A system has energy. A system has entropy.

1.2. Mathematical remark

- Difference between "not differentiable function" and "not a differential".
- "not differentiable function" is a function that is not smooth enough.
- If we work with functions of only one variable, then any expression of the form $f(x)dx$ is a differential of some function $F(x)$, meaning $dF(x) = f(x)dx$.
- If we work with functions of two variables, then the same is not true: not every expression of the form

(1.1) $$g_1(x, y)dx + g_2(x, y)dy$$

  is a differential of some function $G(x, y)$. For example an expression $0dx + xdy$ is not a differential.
- To see what are the condition for a form (1.1) to be a differential let's write a differential of a function $G(x, y)$, $dG = \frac{\partial G}{\partial x}dx + \frac{\partial G}{\partial y}dy$, comparing this to (1.1) we find that $g_1 = \partial G/\partial x$ and $g_2 = \partial G/\partial y$, then we see that $\partial g_1/\partial y = \partial^2 G/\partial y \partial x = \partial^2 G/\partial x \partial y = \partial g_2/\partial x$.
- So in order for (1.1) to be a differential we must have

(1.2) $$\frac{\partial g_1(x, y)}{\partial y} = \frac{\partial g_2(x, y)}{\partial x}$$

- This is locally necessary and sufficient condition.

LECTURE 2
Temperature. Macroscopic motion. LL 9,10,13,14

2.1. Entropy

Hypothesis: for macrosystems there exists a **function of state** called entropy such that.

    1 If the system is not in equilibrium entropy increases.
    2 In equilibrium it has a maximum value.
    3 It is additive.

  The existence of such a function has important consequences.

2.2. Temperature. LL 9.

Here I will define temperature. Our intuition about temperature tells us that

  (a) in equilibrium temperature of a system is the same throughout the system,
  (b) if we touch a hot body, we feel warmth $\rightarrow$ energy is transferred from hot to cold.

- If we consider a macro system and split it in N subsystems in such a way, that each subsystem is still a macro system, then total entropy $S = \sum_a S_a$.
- Consider a system in equilibrium. Consider it as if it consists of two macroscopic subsystems. Each subsystem is also at equilibrium. The total energy is $E = E_1 + E_2$. The total entropy of the system is $S = S_1(E_1) + S_2(E_2)$. Lets find an extremum (maximum) of S as function of E_1, at fixed E. As the total system is at equilibrium the entropy is at maximum, so $\frac{\partial S}{\partial E_1} = 0$, on the other hand $\frac{\partial S}{\partial E_1} = \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}$, so we find $\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$. This is correct for all and any subsystems. So we conclude, that

$$\left(\frac{\partial S}{\partial E}\right)_V = \text{const. throughout the system} = \frac{1}{T},$$

  So T can be (is) called temperature. Here is why:
- Consider two bodies at different temperatures T_1 and T_2. Let's put them into contact. The total entropy will start to increase, $dS/dt \geq 0$, but $dS/dt = dS_1/dt + dS_2/dt = (\partial S_1/\partial E_1)_V dE_1/dt + (\partial S_2/\partial E_2)_V dE_2/dt$, as $dE_2/dt = -dE_1/dt$ we find

$$\frac{dS}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\frac{dE_1}{dt} \geq 0$$

3

There are two cases: $T_1 > T_2$, then $dE_1 < 0$ – the body 1 looses energy, the body 2 gains, or $T_1 < T_2$, then $dE_1 > 0$ – the body 2 looses energy, the body 1 gains. In both cases the energy goes from a hot body to the cold one! exactly as it should be with temperature according to our intuition.

In summary we see that $\left(\frac{\partial E}{\partial S}\right)_V = T$, and $dE = -PdV + đQ$. If the volume is kept fixed, then $(\partial E/\partial S)_V = đQ/dS = T$, so $đQ = TdS$ and we find

$$(2.1) \qquad\qquad dE = -PdV + TdS$$

Rearranging this equation we write

$$(2.2) \qquad\qquad dS = \frac{1}{T}dE + \frac{P}{T}dV$$

Intuitively, pressure in gas in equilibrium should be the same throughout the volume of the gas. Let's see that it is indeed so. Consider gas isolated in a cylinder. Let's imagine that there is a membrane separating the total volume into two $V = V_1 + V_2$. The membrane can move. The total entropy of the system is $S = S_1(E_1, V_1) + S_2(E - E_1, V - V_1)$ we showed that if we maximize this entropy with respect to E_1, then the condition ensures that the temperature is constant through the whole system. Now let's maximize the entropy with respect to V_1.

$$0 = \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} - \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2} \qquad \text{but according to (2.2) } (\partial S/\partial V)_E = P/T, \text{ so} \qquad \frac{P_1}{T_1} = \frac{P_2}{T_2}.$$

As $T_1 = T_2$ we have $P_1 = P_2$.

2.3. Macroscopic motion. LL 10

Again, our intuition tells us that an isolated body in equilibrium cannot have internal macroscopic motions, it can only move and rotate as whole.

- Split the body of a bunch of macroscopic subsystems. Let's say, that subsystem a is at point $\mathbf{r}_a$ and has total energy E_a and momentum $\mathbf{P}_a$. The total momentum and total angular momentum of the body are conserved:

$$\sum_a \mathbf{P}_a = \text{const.}, \qquad \sum_a \mathbf{r}_a \times \mathbf{P}_a = \text{const.}$$

- The entropy S_a depends only on the internal energy $E_a - K_a(\mathbf{P}_a)$, where $K_a(\mathbf{P}_a)$ is the kinetic energy of the subsystem and can be written as $S_a(E_a - K_a(\mathbf{P}_a))$. The total entropy of the whole system is $S = \sum_a S_a(E_a - K_a(\mathbf{P}_a))$.
- We need to find an extremum (maximum) of the total entropy with respect to all $\mathbf{P}_a$ keeping the constraints.
- This is done by Lagrange's method, by introducing two vector Lagrange's multipliers $\mathbf{a}$ and $\mathbf{b}$ and finding the maximum of the function $\tilde{S} = S + \mathbf{a} \cdot \sum_a \mathbf{P}_a + \mathbf{b} \cdot \sum_a \mathbf{r}_a \times \mathbf{P}_a$ with respect to all $\mathbf{P}_a$ as unconstrained variables. So we have

$$0 = \frac{\partial \tilde{S}}{\partial \mathbf{P}_b} = -\frac{\partial S_b}{\partial E_b}\frac{\partial K_b(\mathbf{P}_b)}{\partial \mathbf{P}_p} + \mathbf{a} + \mathbf{b} \times \mathbf{r}_b = -\frac{1}{T}\mathbf{v}_a + \mathbf{a} + \mathbf{b} \times \mathbf{r}_b.$$

Notice, that $\mathbf{a}$, $\mathbf{b}$, and T are the same for all and every subsystem. If we now introduce two vectors $\mathbf{u} = T\mathbf{a}$, and $\mathbf{\Omega} = T\mathbf{b}$, then we write

$$\mathbf{v}_b = \mathbf{u} + \mathbf{\Omega} \times \mathbf{r}_b, \quad \text{for any } b$$

So the only allowed microscopic potion of a body in equilibrium is motion with constant velocity and constant rotation as whole. No internal macroscopic motion is possible in equilibrium.

The form of the total entropy $S = \sum_a S_a(E_a - K_a(\mathbf{P}_a))$ also tells us that $S_a(E)$ is a monotonically increasing function of it's argument, otherwise the maximum of the entropy would correspond to the minimum of the argument, or all subsystem's a energy is kinetic energy, so the whole system consists of a bunch of subsystems that are flying away (total momentum is conserved) from each other. This monotonic increase means that $T > 0$.

Remark: So far everything is very general. Nowhere above I used any information about the system, what it consists of and so on... In order to describe a particular system we need two equations, say equation of state $T(P, V)$ and say $E(V, S)$.

3.1. Examples

3.1.1. Ideal Gas

The equation of state for the ideal gas is $PV = RT$. Let's try to find what we can figure out about its energy. Using (2.2) $dS = \frac{1}{T}dE + \frac{P}{T}dV$ we find

$$dS = \frac{1}{T}dE + \frac{R}{V}dV, \quad \text{so we see } (\partial S/\partial E)_V = 1/T \text{ and } (\partial S/\partial V)_E = R/V$$

Then we see

$$\left(\frac{\partial 1/T}{\partial V}\right)_E = \frac{\partial^2 S}{\partial V \partial E} = \frac{\partial^2 S}{\partial E \partial V} = \left(\frac{\partial R/V}{\partial E}\right)_V = 0$$

If we have the temperature as a function of volume and energy $T(V,E)$, then solving the equation $T = T(E,V)$ with respect to E we find energy $E(T,V)$. But we have just shown that T does not depend on V at fixed E, so we find that E does not depend on volume at constant temperature, so energy is a function of temperature only.

So the equation of state for an ideal gas demands that $E = f(T)$, where f is some function. Then for the entropy we find

$$dS = f'(T)\frac{dT}{T} + R\frac{dV}{V}$$

On the other hand

$$C_V = \left(\frac{đQ}{dT}\right)_V = \left(\frac{TdS}{dT}\right)_V = f'(T), \qquad dS = C_V(T)\frac{dT}{T} + R\frac{dV}{V}$$

3.1.2. Energy a function of temperature only.

Let's consider an opposite situation: We know that the energy depends only on temperature: $E = E(T,V) = E(T)$, what can we say about the equation of state? From (2.2) $dS = \frac{1}{T}dE + \frac{P}{T}dV$ we find that we must have

$$\left(\frac{\partial P/T}{\partial E}\right)_V = \left(\frac{\partial 1/T}{\partial V}\right)_E = 0$$

As temperature as function of E and V does not depend on V. Now we see that

$$\frac{1}{T}\left(\frac{\partial P}{\partial E}\right)_V - \frac{P}{T^2}\left(\frac{\partial T}{\partial E}\right)_V = 0$$

$$\frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V \frac{dT}{dE} = \frac{P}{T^2}\frac{dT}{dE}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T}$$

$$P = g(V)T$$

This can be verified experimentally. Measuring P as function of T, and extracting slope as a function of V.

3.2. Thermodynamic Potentials. LL 14, 15

There are four (for fixed number of particles) thermodynamic potentials: energy, enthalpy (heat function), free energy (Helmholtz free energy), and thermodynamic potential (Gibbs free energy). All four are function of state. (that is the origin of the name potential, like potential energy is a function of coordinates.)

   • **Energy.** We know one thermodynamic potential, energy. It's differential is

(3.1) $$dE = -PdV + TdS$$

   We see, that proper variables for energy are V and S. We see that the change of energy equals heat for a constant volume process and equals minus work for a process without heat exchange. Comparison of dE with the differential definition gives:

(3.2) $$\left(\frac{\partial E}{\partial V}\right)_S = -P, \qquad \left(\frac{\partial E}{\partial S}\right)_V = T$$

   • **Enthalpy.** As E, P, and V are all state variables, we can define another state variable $W = E + PV$ which is called enthalpy. It's differential is

(3.3) $$dW = TdS + VdP, \qquad W = E + PV.$$

   The proper variables for enthalpy are S and P. It's change equals to amount to heat for a process at constant pressure. Again we see

(3.4) $$\left(\frac{\partial W}{\partial P}\right)_S = V, \qquad \left(\frac{\partial W}{\partial S}\right)_P = T$$

   • **Free energy.** Free energy is defined as $F = E - TS$. It's differential is

(3.5) $$dF = -SdT - PdV, \qquad F = E - TS$$

   The proper variables are T and V. It's change at constant temperature is work (with a minus sign). Again we see

(3.6) $$\left(\frac{\partial F}{\partial V}\right)_T = -P, \qquad \left(\frac{\partial F}{\partial T}\right)_V = -S$$

- **Thermodynamic potential.** Thermodynamic potential is defined as $\Phi = E - TS + PV$. Its differential is

$$(3.7) \qquad d\Phi = -S\,dT + V\,dP, \qquad \Phi = E - TS + PV$$

The proper variables are T and P. Again we see

$$(3.8) \qquad \left(\frac{\partial \Phi}{\partial P}\right)_T = V, \qquad \left(\frac{\partial \Phi}{\partial T}\right)_P = -S$$

These four potentials, E, W, F, and Φ are related to each other and can be expressed through each other. Let's imagine, that we know free energy as function of its proper variables: $F(T, V)$. Then first we notice, that the first of equations (3.6) is just the equation of state and gives P as function of V and T. The second of the equations (3.6) gives entropy as function of V and T, $S = S(V, T)$. We then can solve this equation and find $T(V, S)$. Then energy is given by $E(S, V) = F(T(S, V), V) + ST(S, V)$.

3.3. Relation between derivatives. LL 16

All four E, W, F, and Φ are the functions of state, right from their differentials we can read

$$(3.9) \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \qquad \text{from } E \ (3.1)$$

$$(3.10) \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P, \qquad \text{from } W \ (3.3)$$

$$(3.11) \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \qquad \text{from } F \ (3.5)$$

$$(3.12) \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \qquad \text{from } \Phi \ (3.7)$$

LECTURE 4
Relation between measurables.

4.1. Maxwell Relations

$$(4.1) \qquad dE = TdS - PdV, \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V,$$

$$(4.2) \qquad dW = TdS + VdP, \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P,$$

$$(4.3) \qquad dF = -SdT - PdV, \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,$$

$$(4.4) \qquad d\Phi = -SdT + VdP, \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.$$

4.2. Measurables

Entropy, as well as all the potential themselves are not directly measurable in an experiment. However, in experiment we can determine what is called **equation of state** – an equation connecting P, V, T, as these three variables can be measured directly. It is also possible to measure specific heat and responses: the specific heat is defined as how much heat we need to put into system to change the system's temperature by 1 degree or $C = \frac{\mathrm{d}Q}{dT} = T\frac{dS}{dT}$, compressibility is defined as $\beta = -\frac{1}{V}\frac{\partial V}{\partial P}$, thermal expansion coefficient $\alpha = \frac{1}{V}\frac{\partial V}{\partial T}$. All these coefficients depend on the process that we employ for the measurement. It is customary (the easiest to measure) to define

$$(4.5) \qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$(4.6) \qquad \beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S, \qquad \beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$(4.7) \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

They are not independent from each other.

4.3. Dependence of the heat capacity on volume or pressure.

The equation of state defines the dependence of the heat capacity on volume and pressure, but not on temperature. Lets calculate them

• The dependence of C_V on volume:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left.\frac{\partial}{\partial V}\right|_T\left.\frac{\partial}{\partial T}\right|_V S = -T\left.\frac{\partial}{\partial V}\right|_T\left.\frac{\partial}{\partial T}\right|_V\left.\frac{\partial}{\partial T}\right|_V F = -T\left.\frac{\partial^2}{\partial T^2}\right|_V\left(\frac{\partial F}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

The last derivative can be calculated from the equation of state.

• The dependence of C_V on pressure:

$$\left(\frac{\partial C_V}{\partial P}\right)_T = \left(\frac{\partial C_V}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V\left(\frac{\partial V}{\partial P}\right)_T = -\beta_T V T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

4.4. Mathematical remark. Jacobians.

A Jacobian of two functions $u(x, y)$ and $v(x, y)$ of two variables x and y is defined as

(4.8)
$$\frac{\partial(u, v)}{\partial(x, y)} = \text{Det}\begin{vmatrix} \partial u/\partial x & \partial u/\partial y \\ \partial v/\partial x & \partial v/\partial y \end{vmatrix}$$

Then it is clear that

$$\frac{\partial(u, y)}{\partial(x, y)} = \left(\frac{\partial u}{\partial x}\right)_y, \qquad \frac{\partial(u, v)}{\partial(x, y)} = -\frac{\partial(u, v)}{\partial(y, x)}, \qquad \frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(t, s)}\frac{\partial(t, s)}{\partial(x, y)}$$

(It is a good exercise to prove these properties.)

LECTURE 5
Relation between measurables. Joule-Thomson process.

5.1. Relation between measurables

One can design experiments to measure different responses:

- One can measure $(\partial P/\partial T)_V$ – this is what blows up overheated boiler. However, it will not be an independent measurement.

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial(P,V)}{\partial(T,V)} = \frac{\partial(P,V)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(T,V)} = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T = \frac{\alpha}{\beta_T}$$

- One can compress a gas without supplying any heat and measure the change of temperature:

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial(T,S)}{\partial(V,S)} = \frac{\partial(T,S)}{\partial(T,V)}\frac{\partial(T,V)}{\partial(V,S)} = -\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial T}{\partial S}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V \frac{-T}{T\left(\frac{\partial S}{\partial T}\right)_V} = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V$$

- A relation involving β_S is obtained in the following way

$$\beta_S = -\frac{1}{V}\frac{\partial(V,S)}{\partial(P,S)} = -\frac{1}{V}\frac{\partial(V,S)}{\partial(V,T)}\frac{\partial(V,T)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(P,S)} = -\frac{1}{V}\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial S}\right)_P = \beta_T C_V/C_P$$

- We can also calculate the relation between C_V and C_P.

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = T\frac{\partial(S,P)}{\partial(T,P)} = T\frac{\partial(S,P)}{\partial(T,V)}\frac{\partial(T,V)}{\partial(T,P)} =$$

$$T\left[\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial P}{\partial V}\right)_T - \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial P}{\partial T}\right)_V\right]\left(\frac{\partial V}{\partial P}\right)_T = C_V - T\left[\left(\frac{\partial P}{\partial T}\right)_V\right]^2 \left(\frac{\partial V}{\partial P}\right)_T$$

where I used (4.3). Now using the $(\partial P/\partial T)_V = \alpha/\beta_T$ calculated before we find

(5.1)
$$C_P - C_V = TV\frac{\alpha^2}{\beta_T}$$

5.2. Joule-Thomson process. LL 18

A very interesting phenomena occurs at so called Joule-Thomson process. Let's take a thermally isolating wall with a small hole in it (or a porous wall). On the left from the wall the gas is at a constant pressure P_1 and temperature T_1, on the right gas is at the constant pressure P_2, what is the temperature on the right?

There is a steady flow of the gas through the hole. Let's assume that the difference $P_1 - P_2$ is small. We then need to calculate $\left(\frac{\partial T}{\partial P}\right)_{\text{JT}}$, where JT stands for Joule-Thomson process. We now need to characterize the JT process in thermodynamical terms. Let's note:

• The process is irreversible as there is friction in the whole, so the entropy of the gas is not conserved.
• There is no heat coming to the system, so $\delta A = dE$, which means, that work is a function of state and does not depend on the process.

Let's take a volume V_1 of the gas on the left, the total internal energy of this gas is E_1. After all gas in that volume have gone trough the hole the gas takes the volume V_2, its internal energy is E_2. The total work which is done on the gas is $P_1V_1 - P_2V_2$. This work must be equal to the change of energy, so $P_1V_1 - P_2V_2 = E_2 - E_1$. It means that the enthalpy

$$W = P_1V_1 + E_1 = P_2V_2 + E_2$$

is conserved! So we just need to calculate $\left(\frac{\partial T}{\partial P}\right)_W$:

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{\partial(T,W)}{\partial(P,W)} = \frac{\partial(T,W)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(P,W)} = -\left(\frac{\partial W}{\partial P}\right)_T\frac{1}{C_P} =$$

$$-\frac{1}{C_P}\left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right] = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] = \frac{1}{C_P/V}[T\alpha - 1]$$

Notice three facts.

First, $C_P/V = c_p$ is just specific heat per unit volume, so there is no dependence on some volume which is not defined anywhere in the problem.

Second, for the ideal gas $T\alpha = 1$, so the JT effect does not produce a change in the temperature.

Third, in general $T\alpha$ can be either larger or smaller then one, moreover $T\alpha - 1$ may change sign as a function of temperature. So it means that a gas can either heat up or cool down in the process. The latter case is commonly used in refrigerators.

We also can calculate the change of the entropy of the gas. Using $dW = TdS + VdP|_{JT} = 0$ we find:

$$\left(\frac{\partial S}{\partial P}\right)_W = -\frac{V}{T}$$

LECTURE 6
Maximum work.

6.1. Maximum work. LL 19

Consider an isolated system in equilibrium. If all the processes inside are reversible, then $dS = 0$. It means that $đA = dE$, so dA is a full differential. It also means that if the system after some process returned to the same state, the total work done by the system is zero.

Consider an isolated system, which consists of several subsystems. Each subsystem is at equilibrium, but the subsystems are not at equilibrium with each other. We want to know how much work it is possible to extract from such system while its subsystems equilibrate with each other. We are interested only in the work due to the equilibration process. In particular we consider the volume of the system in the final state to be the same as in the initial state. (Otherwise the system can just expand by a reversible process).

It is clear, that the work done by the system depends on how the equilibrium is reached. The final state (its energy, entropy, etc) will also depend on the process. The initial total energy of the system is E_0, and the entropy is S_0, The total energy in the final state E depends on the total entropy of the final state (the final state itself depends on the process). As the system is isolated, the total work done by the system must be equal to the change of energy:

$$R = E_0 - E(S)$$

Now let's find the maximum of the work R as the function of the entropy of the final state. For that we take the derivative of the above with respect to the entropy of the final state S:

$$\frac{\partial R}{\partial S} = -\frac{\partial E}{\partial S} = -T < 0$$

So it is a monotonically decreasing function. It means that in order to maximize the work entropy of the final state must be as small as possible. During any process the entropy cannot decrease. So the smallest possible entropy is the initial total entropy of the system.

It means that in order to extract the maximal work out of the equilibration process the subsystems should be equilibrated in a reversible process – process at constant entropy.

More precisely what we proved is the following:

If there exist such a process of equilibration of the two subsystems which keeps the total entropy constant, then this process is the process which allows us to extract the maximum possible work.

   Now we need to show that such a process does *exist*. To find such a process we first consider a simple equilibration process when the two subsystems are brought in a direct contact. So we have two subsystems at different temperatures T_1 and T_2, with say $T_2 > T_1$, and we bring them into contact. During a small time the first one is getting energy δE, and the second loosing the same energy. So the entropy of the first subsystem changes by $\delta E/T_1$, while the second subsystem looses $\delta E/T_2$. The total increase of the entropy is $\delta S = \delta E(1/T_1 - 1/T_2) > 0$. So this is irreversible process which leads to the increase of the total entropy.

   In order to equilibrate the two subsystems at constant total entropy we need to use a third subsystem "working medium". Here I describe a process we can use to equilibrate the two subsystems cold one (temperature T_1) and hot one (temperature T_2) at constant total entropy. Subsystems 1 and 2 do not change their volume and hence do not do any work. All work will be done by the "working medium". We then do the following

- Initially medium is at the temperature T_2.
- We bring it in contact with the subsystem 2, and suck some small energy δE_2 from the hot subsystem to the medium. As the subsystem 2 never does any work its entropy in this process has decreased by $\delta S = \delta E_2/T_2$,
- We now thermally isolate the working medium. While it is isolated, we bring the medium down to temperature T_1 (by, say, changing its volume). No change of the entropy occurs.
- We bring the medium to a contact with the cold body. We transfer some energy δE_1 from the medium to the cold body. The amount of energy δE_1 is chosen such that the cold body gets the entropy δS – the entropy the hot system has lost before, as subsystem 1 also never does any work the energy we need to transfer is $\delta E_1 = T_1 \delta S = \frac{T_1}{T_2}\delta E_2$. As the temperatures of the medium and the cold systems are the same, the cold system's entropy increases by the same amount δS. The total entropy of the system stays unchanged.
- We again isolate the medium and bring its temperature back to T_2. Again, no change of entropy occurs.

This is what is called "Carnot cycle". At the end of this cycle, the medium has exactly the same entropy and temperature as at the beginning. So it is at the same state and its energy has not changed. The cold subsystem gained exactly the same amount of entropy as the hot lost, so the total entropy of the whole system is unchanged. The energy the hot body have lost is δE_2, the energy the cold body gained is $\delta E_1 = \frac{T_1}{T_2}\delta E_2$. The total system is isolated, so the conservation of energy tells us that the work which is done by the system is

$$\delta R = \delta E_2 - \delta E_1 = \frac{T_2 - T_1}{T_2}\delta E_2$$

The efficiency of this engine is then

$$\eta = \frac{\delta R}{\delta E_2} = \frac{T_2 - T_1}{T_2}$$

This is the theoretical very best one can get from any engine. (Don't forget, T is absolute temperature.)

Thermodynamic inequalities.

7.1. Thermodynamic stability and thermodynamic inequalities. LL 21

The stability of any system can be understood in either one of the two equivalent ways: a) The system is stable if the minimal work required to change its state is positive. b) The system is stable if after a small perturbation it returns back to the initial state.

The difference between a mechanical and a thermodynamical systems is in the fact that the thermodynamical body must be considered as coupled to a heat bath.

Let's take a large (very large) isolated macroscopic system at equilibrium at temperature T_0 and pressure P_0. Let's take a part (small, but macroscopic) of this system and call it body, the rest of the system is called medium or thermal bath. The bath is large, so no changes of the body affects it. In all processes then we can consider T_0 and P_0 to be constant.

(a) Let's calculate how much work needed to be done to make a disturbance to the body. Let's assume that the disturbance changed the entropy of the body by δS and its volume by δV. The whole system is isolated, so there is no heat transferred to the system as a whole. Then the work done must be equal to the change of the total energy of the system $\delta R = \delta E + \delta E_0$ (subscript 0 refers to the heat bath/medium) For the medium we can write $\delta E_0 = T_0 \delta S_0 - P_0 \delta V_0$, where the temperature and the pressure of the medium T_0 and P_0 stay constant in the process (notice, that this cannot be said about the body. Me make no assumption on how the body changes), so $\delta R = \delta E + T_0 \delta S_0 - P_0 \delta V_0$. The total volume of the system is constant, so $\delta V_0 + \delta V = 0$, which means $R = \delta E + T_0 \delta S_0 + P_0 \delta V$. We know that the work is minimal when the total change of entropy is zero, so $\delta S + \delta S_0 = 0$, or $\delta R_{min} = \delta E - T_0 \delta S + P_0 \delta V$. So we see, that the minimal work required to take the system out of equilibrium is

$$\delta R_{min} = \delta E - T_0 \delta S + P_0 \delta V = \delta(E - T_0 S + P_0 V).$$

The minimal work must be positive, or the system will not be stable, so the stability condition is that

(7.1) $\quad E - T_0 S + P_0 V \quad$ is at minimum, or $\quad \delta E - T_0 \delta S + P_0 \delta V \geq 0 \quad$ for any δV and δS.

(b) Let's see what happens to the body after a disturbance. After the disturbance the body will equilibrate with the bath. Lets calculate the change of the body energy in

the equilibration process. The change of energy is equal to the heat transferred from the medium $-T_0\delta S_0$, plus the work done by the media $P_0\delta V_0$, where δV_0 and δS_0 are changes of the volume and the entropy of the media/bath. So $\delta E = -T_0\delta S_0 + P_0\delta V_0$. On the other hand the $\delta V_0 = -\delta V$ — the change of the body's volume. As the process is not necessarily reversible, then $\delta S + \delta S_0 \geq 0$. So we have $\delta E + P_0\delta V = -T_0\delta S_0 \leq T_0\delta S$, or $\delta(E + P_0V - T_0S) \leq 0$ during the equilibration. So during the equilibration the quantity $E + P_0V - T_0S$ is always decreasing and is, then, at minimum in equilibrium. We then come back to the condition (7.1).

The two ways to make this argument show, that whether we consider the process of kicking the body out of equilibrium with the bath, or we consider the process of equilibration of the body with the bath we have the same result.

Now let's consider the whole system in equilibrium. Then if we disturb slightly any subsystem out of equilibrium, then for that subsystem $\delta E + P_0\delta V - T_0\delta S > 0$. Where the temperature and pressure of the subsystem is almost the same as in the bath. we then see that expanding $E(S,V)$ up to the second order in δV and δS the equilibrium condition reads

$$\frac{\partial^2 E}{\partial S^2}(\delta S)^2 + 2\frac{\partial^2 E}{\partial S\partial V}\delta V\delta S + \frac{\partial^2 E}{\partial V^2}(\delta V)^2 > 0$$

for arbitrary δV and δS. It means that

$$\frac{\partial^2 E}{\partial S^2} > 0$$

(7.2) $\quad \mathrm{Det}\begin{pmatrix} \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S\partial V} \\ \frac{\partial^2 E}{\partial S\partial V} & \frac{\partial^2 E}{\partial V^2} \end{pmatrix} = \mathrm{Det}\begin{pmatrix} \frac{\partial}{\partial S}\frac{\partial E}{\partial S} & \frac{\partial}{\partial V}\frac{\partial E}{\partial S} \\ \frac{\partial}{\partial S}\frac{\partial E}{\partial V} & \frac{\partial}{\partial V}\frac{\partial E}{\partial V} \end{pmatrix} = \frac{\partial(\partial E/\partial S, \partial E/\partial V)}{\partial(S,V)} > 0.$

Since $\partial^2 E/\partial S^2 = (\partial T/\partial S)_V = T/C_V$, the first of these conditions means that

$$C_V > 0$$

The second condition is $-\frac{\partial(T,P)}{\partial(S,V)} > 0$. Now we use $\frac{\partial(T,P)}{\partial(S,V)} = \frac{\partial(T,P)}{\partial(T,V)}\frac{\partial(T,V)}{\partial(S,V)} = \left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}\left(\frac{\partial P}{\partial V}\right)_T$, so we get

$$\left(\frac{\partial P}{\partial V}\right)_T < 0, \quad \text{or} \quad \beta_T > 0.$$

This also mean that $C_P = C_V + TV\alpha^2/\beta_T > C_V$.

States that do not satisfy these conditions are unstable.

LECTURE 8
Change of the total entropy. Nernst's theorem.

8.1. Change of the total entropy. LL 20

In this lecture I consider the whole system and calculate the total change of entropy of the whole system after the disturbance on a subsystem — the body. The total entropy of the system is huge and depends on the size of the whole system, which is as large as we want. The change of that huge entropy, however, is small, as the disturbance is small.
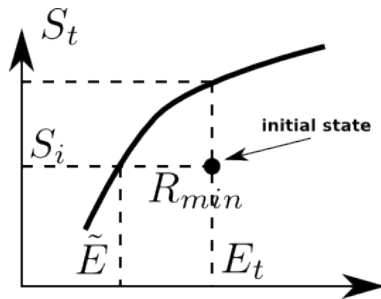
Figure 1. Change of the total entropy.

First, lets consider the whole system at equilibrium. The volume of the whole system is fixed. So the total entropy S_t is a function of the total energy E_t, $S_t(E_t)$. I emphasize, that this function dependence of total entropy on total energy exists only if the whole system is at equilibrium. As the derivative $(\partial S_t)/\partial E_t$ is $1/T_0$ and is positive the function $S_t(E_t)$ monotonically increases, as shown on Fig. 1.

Now we disturbed the body by changing its volume by δV, its entropy by ΔS, and its energy by ΔE. This is our initial state. Thus initially the body is not at equilibrium with the medium, so initially the whole system is not in equilibrium. It will start to equilibrate, and the total entropy will start to grow. The total energy E_t of the system, however, will remain constant. The equilibration will complete when the total entropy will become $S_t = S_t(E_t)$

I want to calculate the difference in the entropy between the non equilibrium initial state and the final equilibrium state.

In the final state of the whole system is in equilibrium. The final entropy of the total system depends on it's final total energy $S_t(E_t)$. Consider our process. Let's start with a non equilibrium state, its energy E_t and entropy S_i. The entropy of this state differs from the final entropy of the equilibrium state by $\Delta S_t = S_i - S_t(E_t)$ (ΔS is negative, as entropy is at maximum in equilibrium) Using the function $S_t(E_t)$ we can find the energy of equilibrium state which has the same entropy as our initial state $S_i = S_t(\tilde{E}) = S_t(E_t + \tilde{E} - E_t) \approx S_t(E_t) + (\partial S_t/\partial E_t)(\tilde{E} - E_t) = S_t(E_t) + \frac{1}{T_0}(\tilde{E} - E_t)$. Now $E_t - \tilde{E}$ is the total change of energy of the whole system at fixed entropy. This change is exactly equal to the minimum work needed to bring the system to the non equilibrium state. So we have $S_i = S_t(E_t) - \frac{1}{T_0}\delta R_{min}$,

or

$$\Delta S_t = S_i - S_t = -\frac{1}{T_0}\delta R_{min} = -\frac{1}{T_0}(\Delta E - T_0\Delta S + P_0\Delta V)$$

(The final entropy S_t is larger then the initial entropy S_i, as initially system is not in equilibrium.)

Notice, that we calculated the change of the entropy of the whole system through the change of the energy, entropy and volume of the smaller disturbed body.

8.2. Nernst's theorem. LL 23

- $C_V > 0$, so energy is monotonic function of temperature.
- At $T = 0$ energy of the whole system as well as all its subsystems is at minimum.
- It means that whole system is at its quantum mechanical ground state.
- Statistical mechanics interprets entropy as logarithm of statistical weight of the macroscopic state.
- If the ground state is not degenerate, than the whole system is in one state the statistical weight of this state is 1, and its logarithm is 0.
- Thus for the entropy

(8.1) $$S(T,V) \xrightarrow[T\to 0]{} 0, \qquad \forall V$$

This is called Nernst's theorem. Notice, that it assumes that the ground state is not degenerate.

Let's assume, that the entropy at small temperature has the leading term in the form $S(T,V) = A(V)T^a$, where $a > 0$. Then

$$C_V = T(\partial S/\partial T)_V = aA(V)T^a \xrightarrow[T\to 0]{} 0.$$

Using $(\partial P/\partial T)_V = (\partial S/\partial V)_T = A'T^a$ we find the equation of state

$$P = \frac{1}{a+1}A'T^{a+1} + P_0(V),$$

where P_0 is the pressure of the ground state. Using this result we can calculate (discarding higher in T terms) the thermal expansion coefficient

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{A'}{-P_0'}T^a \xrightarrow[T\to 0]{} 0$$

The isothermal compressibility β_T is finite and we find from the equation of state

$$\beta_T = -\frac{1}{V}\frac{1}{P_0'}$$

Then from (5.1) we find that $C_P - C_V = \frac{(A')^2}{-P_0'}T^{2a+1}$. So we see that

$$C_P \propto C_V \propto T^a, \qquad \frac{C_P - C_V}{C_P} \propto T^{a+1}$$

Also as C_P and C_V are almost the same then

$$\beta_S \approx \beta_T$$

Notice, that Joule-Thomson coefficient ($\beta_{JT} = (\partial T/\partial P)_W = \frac{1}{C_P/V}(\alpha T - 1)$) is negative and diverges. So at very low temperatures the Joule-Thomson leads to heating.

Another use of this theorem is that if we measure say $C_P(P,T)$ for small T, then we know the entropy

$$S(P,T) = \int_0^T C_P \frac{dT}{T}$$

The lower limit is zero and there is no additional terms that could in principle depend on pressure. So by this procedure we measure entropy with no ambiguity.

LECTURE 9
Dependence on the number of particles.

9.1. Dependence on the number of particles. LL 24

If there is no long range forces the energy of two identical systems is twice the energy of one. The volume, the number of particles, and the entropy also double, while pressure and temperature does not change. These are differences between intensive and extensive variables.

$$T, P \text{ --- intensive}, \qquad S, V, N \text{ --- extensive}.$$

Notice that in differentials we aways have pairs of one extensive and one intensive quantities T–S and P–V.

It means that if we consider the dependence of a thermodynamic potential on the number of particles, then we must get:

$$E = N f_E(S/N, V/N), \quad F = N f_F(T, V/N), \quad W = N f_W(S/N, P), \quad \Phi = N f_\Phi(T, P).$$

Now if we consider say energy to depend on the number of particles as a an independent variable, then the function $E(S, V, N)$ has a full differential $dE = TdS - PdV + \mu dN$, where μ is called chemical potential and is some function of S, V, and N. This correction is the same for every potential, so we have

$$dE = TdS - PdV + \mu(S, V, N)dN, \qquad \mu(S, V, N) = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

$$dF = -SdT - PdV + \mu(T, V, N)dN, \qquad \mu(T, V, N) = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

$$dW = TdS + VdP + \mu(S, P, N)dN, \qquad \mu(S, P, N) = \left(\frac{\partial W}{\partial N}\right)_{S,P}$$

$$d\Phi = -SdT + VdP + \mu(T, P)dN, \qquad \mu(T, P, N) = \left(\frac{\partial \Phi}{\partial N}\right)_{T,P}$$

From the last equation we find $\mu(T, P) = f_\Phi(T, P)$, so

$$\Phi(T, P, N) = N\mu(T, P)$$

and μ when expressed through variables T and P does not depend on N. It means that μ is intensive and $\mu(T, P) = \mu(S/N, V/N) = \mu(S/N, P) = \mu(T, V/N)$. We also can write, that

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP = -sdT + vdP,$$

where s and v are entropy and volume per particle.

Consider now a new potential $\Omega = F - N\mu$, then

$$d\Omega = -SdT - PdV - Nd\mu$$

On the other hand

$$\Omega = F - N\mu = F - \Phi = -PV$$

The use of the function Ω is in the fact that we can take a subsystem of the whole system as a subsystem of a fixed volume. The number of particles will not be constant in this case, but $d\Omega = -SdT - Nd\mu$, and the number of particles inside the volume can be found as

$$N = -(\partial\Omega/\partial\mu)_{T,V} = V(\partial P/\partial\mu)_{T,V}, \qquad n = N/V = (\partial P/\partial\mu)_T$$

9.1.1. Physical meaning of chemical potential

Let's take a system of fixed volume which has N particles. The energy of the system is $E(N)$. Let's add one extra particle to it by an adiabatic process. The energy of the system will change, and become $E(N + 1)$. This change of energy will be very small in comparison to the total energy of the system. Let's calculate this change of energy. As the adiabatic process keeps the entropy constant we have $dS = 0$, the volume is fixed, so $dV = 0$. We thus have $dE = \mu dN$. As we added only one particle $dN = 1$, so the change of energy of the system is

$$\Delta E = \mu.$$

So the chemical potential is the change of the total energy of the system when we add one more particle.

This change of energy occurs because we have to do work in order to adiabatically add a particle. So in other interpretation the chemical potential is the work which needs to be done in order to adiabatically add a particla to the system.

LECTURE 10
Chemical potential

10.1. Homogeneous functions

A homogeneous function of degree p is a function of N variables $f(x_1, x_2, \ldots, x_N)$, such that for any $\lambda \neq 0$

$$f(\lambda x_1, \lambda x_2, \ldots, \lambda x_N) = \lambda^p f(x_1, x_2, \ldots, x_N).$$

If we differentiate such a function with respect to λ and after differentiation set $\lambda = 1$ we will get

$$\sum_{i=1}^{N} x_i \frac{\partial f}{\partial x_i} = pf.$$

Examples of the homogeneous functions in physics: kinetic energy (classical – degree 2, ultrarelativistic – degree 1) Coulomb energy – degree -1, dipole-dipole energy – degree -3, etc.

10.2. Euler equation

Let's now take a system with entropy S, volume V, and number of particles N. Its energy is $E(S, V, N)$. Let's increase the system by a factor of λ, meaning that $V \to \lambda V$, $N \to \lambda N$, $S \to \lambda S$, then its energy will also increase by the same factor. This is so because the energy $E(S, V, N)$ is an extensive quantity of three extensive variables.

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$$

So $E(S, V, N)$ is a homogeneous function of degree 1.

Taking the derivative with respect to lambda and then set $\lambda = 1$ we get

$$S \left(\frac{\partial E}{\partial S} \right)_{V,N} + V \left(\frac{\partial E}{\partial V} \right)_{S,N} + N \left(\frac{\partial E}{\partial N} \right)_{V,S} = E(S, V, N)$$

or

$$E = ST - PV + \mu N \qquad \text{— Euler equation}$$

Now we take the differential of this relation and find $dE = SdT + TdS - PdV - VdP + \mu dN + Nd\mu$, comparing this with $dE = TdS - PdV + \mu dN$ we find that

$$SdT - VdP + Nd\mu = 0 \qquad \text{— Gibbs-Duhem equation}$$

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Using this we get right away

$$\left(\frac{\partial P}{\partial T}\right)_\mu = \frac{S}{T}, \qquad \left(\frac{\partial P}{\partial \mu}\right)_T = \frac{N}{V} = n, \qquad \left(\frac{\partial \mu}{\partial T}\right)_P = -\frac{S}{N}$$

10.3. Ideal gas

We want to find the chemical potential for ideal gas. The equation of state and energy for the ideal gas are

$$PV = kNT, \qquad E = Nf(T),$$

where $f'(T) = c_V(T)$ (c_V heat capacity per particle. As energy does not depend on volume, or in other words, energy does not depend on interparticle distance, which means that there is no interactions between particles. If c_V as a function of temperature is not a constant the particles have internal structure!)

Euler equation tells us, that we need to find the entropy. We use

$$T\left(\frac{\partial S}{\partial T}\right)_{V,N} = Nc_V, \qquad \left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N} = \frac{Nk}{V}$$

From here we find

$$S(T,V) = N\int^T \frac{c_V(T')dT'}{T'} + Nk\log V + g(N)$$

and using Euler equation and expressing $V = NkT/P$ we find

$$\mu(T,P) = -T\int^T \frac{c_V(T')dT'}{T'} - kT\log(kTN/P) + Tg(N)/N + kT + \int^T c_V(T')dT'$$

However, μ as function of T and P cannot depend on the number of particles. So we must have $g(N) = bN - Nk\log N$, where b is just a constant. So finally

$$\mu(T,P) = -T\int^T \frac{c_V(T')dT'}{T'} - kT\log(kT/P) + \int^T c_V(T')dT' + bT$$

From this expression we find that $P = f(T)e^{\mu/kT}$ and does not depend on volume. Then $(\partial P/\partial \mu)_{T,N} = f(T)e^{\mu/kT}/kT = P/kT = N/V = n$.

Another note: the function $g(N) = -kN\log N \approx k\log\frac{1}{N!}$. This function will appear in Stat. Mech. It in fact has a quantum origin.

LECTURE 11
Equilibrium and chemical potential.

11.1. The meaning of formula $N = -(\partial\Omega/\partial\mu)_{T,V}$.

- The number of particles is not fixed.
- The "instantaneous" number of particles N, or the number of particles in a member of a statistical ensemble fluctuates.
- There is, however, the average number of particles $\langle N \rangle$ — a fixed number.
- The fluctuations are small, and are getting smaller in thermodynamic limit.
- Formula $N = (\partial\Omega/\partial\mu)_{T,V}$ gives an **average** number of particles. The same is true for $N = V(\partial P/\partial\mu)_{T,V}$.

This is a subtle point. When we fix the number of particles N, we do not allow this number to fluctuate. We then need to calculate E, F etc., as functions of the exact number of particles. If we fix a chemical potential we do allow the number of particles to fluctuate, then we can calculate the average number of particles for the given chemical potential.

In particular, lets assume that our quantity of interest $f(N)$ depends on the exact number of particles N in our system. we can measure f in two different ways:

(a) We prepare an ensemble of identical systems each of them with the same number of particles N. This is called **canonical ensemble**. Then me measure f in each of the member of the ensemble and take the average of f over ensemble. The result, of course, will be $f(N)$.

(b) We prepare an ensemble of identical systems each of them with the same chemical potential μ — **grand canonical ensemble**. Then we measure f in each of the member of the ensemble and take the average of f over ensemble. The result will be $F(\mu) = \langle f \rangle_\mu$. We then can measure the average number of particles $\langle N \rangle(\mu)$, and then express μ through $\langle N \rangle$ and write $\tilde{f}(N) = F(\mu(\langle N \rangle))$.

Although in both cases we seem to measure the quantity f as a function of a number of particles, unless f is a linear function of N the two results will be different $f(N) \neq \tilde{f}(N)$!

In thermodynamic limit the fluctuations are small, so thermodynamics ignores this difference.

11.2. Equilibrium

Let's consider a system which consists of two subsystems of volumes V_1 and V_2, energy E_1 and E_2, and number of particles N_1 and N_2. The total number of particles $N_1 + N_2 = N$, the total energy $E = E_1 + E_2$ and the total volume $V = V_1 + V_2$ are all fixed. Now we let the whole system to equilibrate. The total entropy of the system is $S = S_1(N_1, E_1, V_1) + S_2(N_2, E_2, V_2) = S_1(N_1, E_1, V_1) + S_2(N - N_1, E - E_1, V - V_1)$. In equilibrium N_1, N_2, E_1, E_2, V_1, and V_2 must be such that, given the constraints, the entropy of the whole system is at maximum. So we have

$$0 = \left(\frac{\partial S}{\partial E_1}\right)_{V,N} = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1,N_1} - \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2,N_2}.$$

$$0 = \left(\frac{\partial S}{\partial N_1}\right)_{E,V} = \left(\frac{\partial S_1}{\partial N_1}\right)_{E_1,V_1} - \left(\frac{\partial S_2}{\partial N_2}\right)_{E_2,V_2}$$

$$0 = \left(\frac{\partial S}{\partial V_1}\right)_{E,N} = \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1,N_1} - \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2,N_2}$$

We now use

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN,$$

and find

$$T_1 = T_2 = T, \qquad P_1 = P_2 = P, \qquad \mu_1(P,T) = \mu_2(P,T)$$

In equilibrium the temperature, pressure, AND chemical potential are the same everywhere.

11.3. Equilibrium in external field. LL 25

Let's consider a system in an external potential field. The potential energy of a molecule is $u(x, y, z)$. So we need to add this energy to the energy of the gas. If we now consider a small volume ΔV at point (x, y, z) of the gas its energy is increased by $u(x, y, z)N_{\Delta V}$, where $N_{\Delta V}$ is the number of particles in the volume ΔV. The same correction should be added to the thermodynamic potential Φ. Then we can see, that $\mu = \mu_0(P,T) + u(x, y, z)$, where μ_0 is the chemical potential without the potential field. This total chemical potential must be constant across the whole body. So we get

$$\mu(P,T) + u(x, y, z) = const.$$

In particular if temperature is kept constant across the whole system, then taking the gradient of the above equation we find (temperature is constant across the whole system, but pressure is not) $(\partial\mu/\partial P)_T \nabla P = \frac{1}{n}\nabla P = -\nabla u$ or

$$\nabla P = -n\nabla u$$

This equation should be considered together with equation of state ($P = knT$ for ideal gas). As the temperature is taken to be constant we have two equations for two unknown fields P, and n.

12.1. Role of chemical potential. LL 81

Consider a phase transition such as liquid-gas. In some conditions the liquid and gas can coexist in equilibrium. This the equilibrium conditions require that pressure and temperature of both phases are the same. The liquid and the gas consist of the same particles. The numbers of particles in the liquid and in the gas (separately) are not conserved (the sum of the two numbers is conserved) It means that the number of particles in each phase must be found from the condition that the chemical potential of the two phases are equal. If the chemical potential of the first phase is $\mu_1(P,T)$, and that of the second phase is $\mu_2(P,T)$, then the equilibrium condition is

$$\mu_1(P,T) = \mu_2(P,T).$$

This equation defines a line in the $P - T$ plane. This is the phase transition line. For each temperature we have a specific pressure, where transition occurs. This curve, or phase transition line is shown in Fig.2.a.

Notice, that the Gibbs energy is continuous across the transition. Its derivative, however, needs not be continuous. Phase transitions with the continuous thermodynamic potential, but discontinuous derivatives of the potential is called **first order phase transitions.**

There are couple of consequences of this picture:
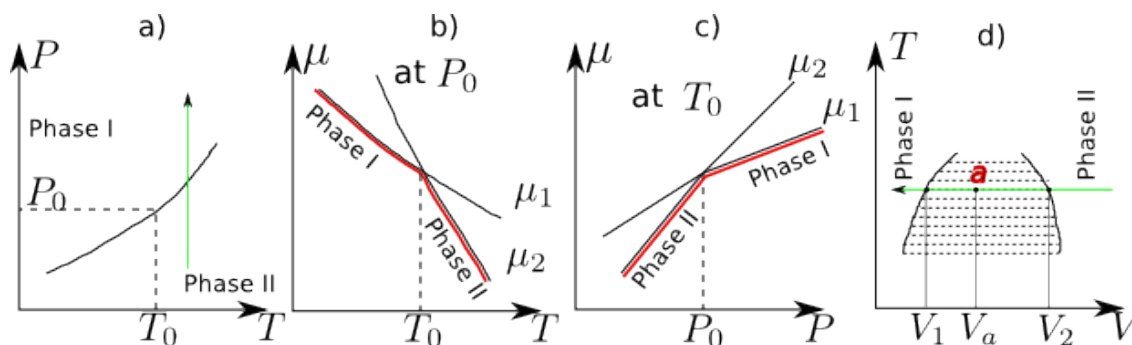
Figure 1. a) $T - P$ phase diagram, b) μ_1 and μ_2 as functions of T at given pressure, c) μ_1 and μ_2 as functions of P at given temperature, d) $V - T$ phase diagram.

- Dew point.
- Flat lower edge of the clouds in the sky.
- Three phases can coexist only at a point — triple point. This point is uniquely defines P_t and T_t.
- It requires very special circumstances for four phases to coexist.
- A line can end at a point (critical point of the water-vapor line) Role of symmetry in brief.

12.2. Discontinuities

Assume that the phase transition is of the first order: then $\mu_1(T, P) = \mu_2(T, P)$ or $\Phi_1(P, T) = \Phi_2(P, T)$ on the transition line. In another words the thermodynamic potential (Gibb's free energy) is continuous function, but its derivatives are discontinuous.

Let's see how μ depends on temperature at fixed pressure. First, we notice, that $(\partial \mu / \partial T)_P = -s < 0$, where s is a specific entropy, which is always positive. So both functions $\mu_{1,2}(P_0, T)$ monotonically decrease with temperature. Also the phase II is a high temperature phase, so we expect it to have a larger specific entropy. The two graphs $\mu_{1,2}(P_0, T)$ must intersect at $T = T_0$. The result is depicted in Fig. 2.b.

From Fig. 2.b it is clear that for the specific entropy $s_1(P, T) = -(\partial \mu_1 / \partial T)_P \neq -(\partial \mu_2 / \partial T)_P = s_2(P, T)$ on the transition line. So the entropy jumps across the transition line.

Now let's see how μ depends on pressure at fixed temperature. As $(\partial \mu / \partial P)_T = v > 0$, where v is the specific volume, both functions $\mu_{1,2}(P, T_0)$ monotonically increase with pressure. We also expect the high temperature phase — phase II — to have larger specific volume. The two graphs $\mu_{1,2}(P, T_0)$ must intersect at $P = P_0$. The result is depicted in Fig. 2.c.

Then analogously, for the specific volume we have $v_1(P, T) = (\partial \mu_1 / \partial P)_T \neq (\partial \mu_2 / \partial P)_T = v_2(P, T)$, so there is also a jump in specific volume see Fig. 2.c.

12.3. Lever rule. LL 81

Now let's look at the transition in $T - V$ diagram. Let's go along $T =$const. line starting from large volume and decreasing the volume as shown on Fig.2.d. At first we will have only phase II. Upon decreasing the volume, at volume V_2 we cross the first solid line at which the transition occurs. This volume $V_2 = Nv_2$, where N is the total number of particles and v_2 is the specific volume of phase II.

Now let's peak the same temperature, but now we start with a very small volume and gradually increase it. At first we have only phase I. At the volume V_1 we hit a transition. Again we have $V_1 = Nv_1$, where N is the total number of particles and v_1 is the specific volume of the phase I.

Notice, that $V_1 < V_2$, as $v_1 < v_2$. So there is a region between V_1 and V_2 which is a coexistence region (shaded region on Fig.2.d. In this region the two phases coexist. The pressure in this region will remain constant (independent of volume at fixed temperature) as whole $T =$const path between the solid lines correspond to one point on the $P - T$ diagram. The mass ratio of the two phases will be changing as we change the volume.

Let's consider a point a on Fig.2.d. At this point the total volume of the system is V_a. Also at this point we have N_1 molecules in phase I, and N_2 molecules in phase II. The total volume of the system then is $N_1 v_1 + N_2 v_2$, and it must be equal to V_a. On the other hand

$v_1 = V_1/N = V_1/(N_1 + N_2)$, and $v_2 = V_2/N = V_2/(N_1 + N_2)$, so we find

$$\frac{N_1}{N_2} = \frac{V_2 - V_a}{V_a - V_1}, \qquad N_1 = N\frac{V_2 - V_a}{V_2 - V_1}, \qquad N_2 = N\frac{V_a - V_1}{V_2 - V_1}$$

This is called *lever rule*.
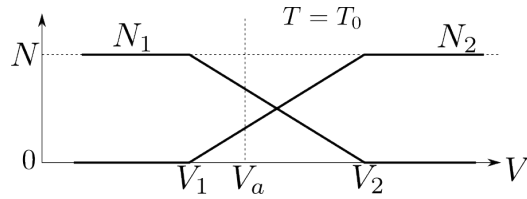
Figure 2. N_1 and N_2 as a function of volume at fixed temperature.

Phase Transitions. Continued.

13.1. Latent heat. LL 81

Let's now go across the transition from phase I to phase II at constant P, by increasing T. The amount of heat we need to supply to the system equals to the change of enthalpy. It is better to consider specific latent heat — the specific heat per molecule. This heat q equals to the change of specific enthalpy w. If we just cross the transition line the pressure and temperature stay the same. But we need to supply the heat which equals to the difference of the enthalpies of the two phases.

$$q = w_2 - w_1.$$

The enthalpy is Gibbs free energy plus TS, the specific enthalpy then is given by $w = \mu + Ts$, where s is the specific entropy. As at the transition point the two chemical potentials equal to each other and the temperature is the same, we get

$$q = T(s_2 - s_1)$$

This can also be obtained from $q = \int T ds$, as T is constant and the process is reversible.

The specific entropy is given by $s = -(\partial \mu / \partial T)_P$. From 2.c we see that the latent heat is not zero, as $s_2 > s_1$ at the transition point (P_0, T_0). Also note, that the finite latent heat is the property of the first order phase transition.
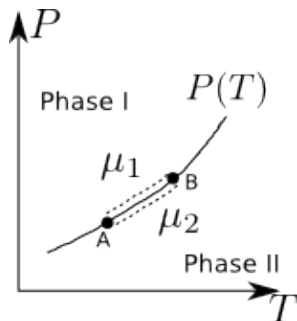
Figure 1.
Clapeyron-Clausius law.

13.2. Clapeyron-Clausius law. LL 82

The chemical potentials of the two phases are the same along the transition line on the $T - P$ diagram. Let's consider two neighboring points A (with coordinates T_A, P_A) and B (with coordinates T_B, P_B). Both points are on the phase transition line. For each point we can write $\mu_1(P_A, T_A) = \mu_2(P_A, T_A)$ and $\mu_1(P_B, T_B) = \mu_2(P_B, T_B)$. If points A and B are close to each other, then $dP = P_B - P_A$ and $dT = T_B - T_A$ are small, then from $\mu_1(P_B, T_B) - \mu_1(P_A, T_A) = \mu_2(P_B, T_B) -$

$\mu_2(P_A, T_A)$ we find

$$\left(\frac{\partial \mu_1}{\partial P}\right)_T dP + \left(\frac{\partial \mu_1}{\partial T}\right)_P dT = \left(\frac{\partial \mu_2}{\partial P}\right)_T dP + \left(\frac{\partial \mu_2}{\partial T}\right)_P dT$$

(Notice, that I never differentiate "across" the transition line!) Using $\left(\frac{\partial \mu}{\partial P}\right)_T = v$, and $\left(\frac{\partial \mu}{\partial T}\right)_P = -s$ (v and s are specific volume and entropy) we find that along the transition line

$$\frac{dP}{dT} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{q}{T(v_2 - v_1)}$$

This is called Clapeyron-Clausius law.
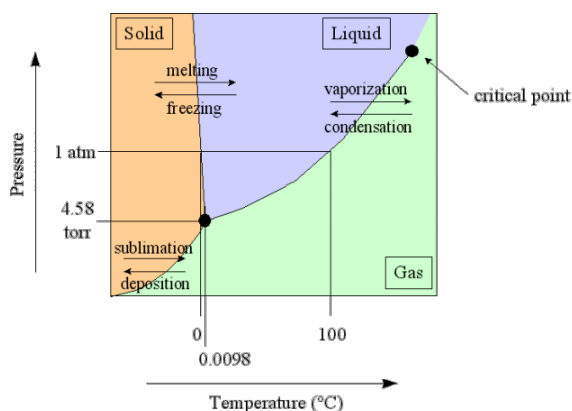
Figure 2. $T - P$ Phase diagram for water.

In particular if the specific volume of the "hot" phase is larger than the specific volume of the "cold" phase (specific volume of the vapor is larger than specific volume of the water) then the derivative is positive and the $P(T)$ transition line goes up — this is the most common situation. The less common is the reverse when the "cold" phase is bulkier than "hot" (ice is bulkier than water). In this case the transition line is going down with increase of temperature.

In some cases the specific volume of the "hot" phases is much larger then the one for the "cold" phase. This is typical for liquid-gas transition away from the critical point. Also, at these temperatures one may neglect the temperature dependence of the latent heat. At these condition the Clapeyron-Clausius law gives $dP/dT = q/Tv_2$. If in addition the gas can be treated as an ideal gas, then $v_2 = T/P$ and we get $dP/P = qdT/T^2$, or $P = P_0 e^{-q/T}$.

On the other hand if the temperature is close to the critical point, then if dP/dT is finite, $q \sim v_2 - v_1 \to 0$.

13.3. Symmetry

Why there can exist the critical point for the liquid-gas transition line, but not for the liquid-solid, or gas-solid?

LECTURE 14
Mixtures.

14.1. Osmotic pressure. LL 88

Consider a weak solution. It has N solvent and n solute particles, $N \gg n$. Let's denote the chemical potential of the solvent without any solute as $\mu_0(P,T)$. Now consider the solute. It is almost ideal gas, as particles do not interact with each other. So its Gibbs energy can be written as a Gibbs energy of an ideal gas $nTk \log(n) + n\psi(P,T)$. This expression does not take into account the existence of the solvent particles. We can fix it by a simple trick. If we double a number of both solvent and solute particles keeping pressure and temperature constant the Gibbs energy must also double. So the final form of the Gibbs energy is

$$\Phi = N\mu_0(P,T) + nTk \log(n/Ne) + n\psi(P,T) = N\left[\mu_0(P,T) + cTk \log(c/e) + c\psi(P,T)\right],$$

where $c = n/N$ is the solute concentration. So the solvent and solute chemical potentials are

$$\tilde{\mu}_0 = \left(\frac{\partial \Phi}{\partial N}\right)_{P,T,n} = \mu_0(P,T) - Tk\frac{n}{N}, \qquad \mu_1 = \left(\frac{\partial \Phi}{\partial n}\right)_{P,T,N} = Tk \log(n/N) + \psi(P,T),$$

or using the ratio of concentrations

$$\tilde{\mu}_0 = \mu_0(P,T) - cTk, \qquad \mu_1 = Tk \log(c) + \psi(P,T)$$

Let's consider two solutions of the same solute and solvent, but with a different concentrations c_1 and c_2. We assume, that the solutions are separated by the membrane which is permeable for the solvent, but is not permeable to the solute particles. We want to calculate the difference in pressure in the two solutions.

The equilibrium condition requires, that the chemical potential of the solvent in the two solution be equal. Such requirement does not exist for the solute, as it cannot penetrate the membrane and thus is not in equilibrium. The temperature of the solvents must also be equal to each other.

$$\tilde{\mu}_R(P_R,T) = \tilde{\mu}_L(P_L,T), \qquad \mu_0(P_R,T) - c_R kT = \mu_0(P_L,T) - c_L kT$$

If $P_R - P_L$ is not large, then we can write $\mu_0(P_L,T) = \mu_0(P_R,T) + (\partial \mu_0(P,T)/\partial P)_{T,N}(P_L - P_R)$, so

$$(P_L - P_R)\left(\frac{\partial \mu_0}{\partial P}\right)_{T,N} = (c_L - c_R)kT$$

But $(\partial \mu_0(P, T)/\partial P)_{T,N} = (\partial V/\partial N)_{T,P}$. The last expression just tells us by how much the volume of pure solvent changes if we add one more solvent particle to it at constant temperature and pressure. This is just the volume per molecular v of the solvent. So we have

$$\Delta P = (c_L - c_R)kT/v$$

If the right solution does not have any solute particles $c_R = 0$, then

$$\Delta P = c_L kT/v = \frac{nkT}{Nv} = \frac{nkT}{V}$$

Which is very much like the equation of state for the ideal gas.

14.2. Mixture of gases. LL 93

Let's consider a mixture of two ideal gases. Then we have

$$P = P_1 + P_2 = (N_1 + N_2)kT/V = NkT/V$$

The entropy of the mixture is then

$$S = S_1 + S_2 = -N_1 f_1'(T) + N_1 k \log(Ve/N_1) - N_2 f_2'(T) + N_2 k \log(Ve/N_2)$$

As $S = -(\partial F/\partial T)_{V,N_1,N_2}$, we have

$$F = N_1 f_1(T) - N_1 kT \log(Ve/N_1) + N_2 f_2(T) - N_2 kT \log(Ve/N_2) = F_1(T, V) + F_2(T, V)$$

For Gibbs potential it is not so

$$\Phi(P, T, N_1, N_2) = F + PV =$$
$$N_1 f_1(T) + N_1 kT - N_1 kT \log(kTNe/PN_1) + N_2 f_2(T) + N_2 kT - N_2 kT \log(kTNe/PN_2) =$$
$$\Phi_1(P, T, N_1) + \Phi_2(P, T, N_2) + N_1 kT \log(N_1/N) + N_2 kT \log(N_2/N)$$

Let's now take a volume V_1 with the number of particles N_1 of the gas 1 and volume V_2 with the N_2 particles of the gas 2. Let's take V_1 and V_2 such, that the pressure and temperature in the both jars are the same. The total entropy of this system is

$$S_i = -N_1 f_1'(T) + N_1 k \log(V_1 e/N_1) - N_2 f_2'(T) + N_2 k \log(V_2 e/N_2)$$

If we now let the gases mix, the final volume will be $V = V_1 + V_2$, so the final total entropy is

$$S_f = -N_1 f_1'(T) + N_1 k \log((V_1 + V_2)e/N_1) - N_2 f_2'(T) + N_2 k \log((V_1 + V_2)e/N_2)$$

So that the change of the total entropy is $((V_1 + V_2)/V_{1,2} = NkT/N_{1,2}kT = N/N_{1,2})$

$$\Delta S = S_f - S_i = N_1 k \log(N/N_1) + N_2 k \log(N/N_2)$$

So the final entropy is larger then initial! That is why when you mix two types of marbles in a jar you cannot unmix them by steering in the opposite direction. This entropy increase is called entropy of mixing. If the $N_1 = N_2$, then $\Delta S/2N_1 = k \log 2$.

The last result can be understood as follows. Consider a bigger/connected jar. Any microscopic state in the jar consists of $N = N_1 + N_2$ particles. Each particle can be either particle 1, or particle 2. The total number of ways to distribute N_1 particles of N available places disregarding the order is $\frac{N!}{N_1!(N-N_1)!} = \frac{N!}{N_1!N_2!} \approx \frac{N^N}{N_1^{N_1} N_2^{N_2}}$. So in addition to the previous case (gases separately) each state has additional degeneracy. The logarithm of that additional degeneracy is

$$\log W = N_1 \log(N/N_1) + N_2 \log(N/N_2) = \Delta S/k$$

LECTURE 15
Classical statistical mechanics

15.1. Phase space. LL 1

- Phase space of a single particle, Hamilton equations.
- Phase space trajectories. Free particle, oscillator. Perturbed oscillator.
- Two non interacting particles in potential well. Two conservation laws. $4D$ space.
- Interacting particles — collisions. Only one conservation law left – the total energy.
- Phase space of N particle, $2N$ dimensional space. Phase trajectory of a macroscopic system.

Phase trajectory in general is very complicated and unless there are plenty of conservation laws there is no chance to solve the system. Conservation laws are consequences of symmetries. In a not too special (closed) system the only symmetry is the time translation invariance — conservation of the total energy.

15.2. Distribution function. LL 1

- Probability to find our system in a small volume in a phase space $w = \lim_{t \to \infty} \Delta t / t$.
- Probability in canonical ensemble of $\mathcal{N}$ replicas of the same system $w = \lim_{N \to \infty} \Delta \mathcal{N} / \mathcal{N}$.
- The assumption is that these two ways to define the probability are equivalent. What it means is that the system "forgets" its past faster then it returns back to the same small volume of the phase space.
- If the small volume of interest is small enough, then the probability should be proportional to that small volume: $w = \varrho(\mathbf{p}, \mathbf{q}) \mathbf{dp} \mathbf{dq}$. The function $\varrho(\mathbf{p}, \mathbf{q})$ is called the *statistical distribution function.*
- Normalization $\int \varrho(\mathbf{p}, \mathbf{q}) \mathbf{dp} \mathbf{dq} = 1$.
- Average of some quantity $\bar{f} = \int f(\mathbf{p}, \mathbf{q}) \varrho(\mathbf{p}, \mathbf{q}) \mathbf{dp} \mathbf{dq}$ — statistical averaging.

If, by means of $\varrho(\mathbf{p}, \mathbf{q})$, we construct the distribution function of the values of some function $f(\mathbf{p}, \mathbf{q})$, $(\varrho(f) = \int \delta(f - f(\mathbf{p}, \mathbf{q})) \varrho(\mathbf{p}, \mathbf{q}) \mathbf{dp} \mathbf{dq})$ it will be very sharply peaked at the value $\bar{f}$. The peak will become sharper and sharper as we go to the thermodynamic limit.

LECTURE 16
Stat. independence & fluctuations.

16.1. Statistical independence. LL 2

- Interaction is small, (but very important, it leads to equilibrium!)
- For small enough interactions the resulting distribution function in equilibrium is universal (does not depend on interaction).
- Consider two subsystems of a single system.
- They are statistically independent!
- We then have two distribution functions $\varrho_1(\mathbf{p}_1, \mathbf{q}_1)$ and $\varrho_2(\mathbf{p}_2, \mathbf{q}_2)$. The probability to find the system in the volume $\mathbf{dp_1 dq_1 dp_2 dq_2}$ is given by $\varrho_1(\mathbf{p}_1, \mathbf{q}_1)\varrho_2(\mathbf{p}_2, \mathbf{q}_2)\mathbf{dp_1 dq_1 dp_2 dq_2}$.
- So we find

$$\varrho = \varrho_1 \varrho_2 \tag{16.1}$$

- The inverse is also true. If the distribution function has property (16.1), then the two subsystems are statistically independent.

Now if f_1 and f_2 are two physical quantities related to two physical subsystems, then from statistical independence (16.1) we see

$$\overline{f_1 f_2} = \bar{f}_1 \bar{f}_2.$$

16.2. Fluctuations. LL 2

Let's consider some physical quantity $f(\mathbf{q}, \mathbf{p})$. If we measure it in a macrosystem we will find a value very close to the average value $\bar{f}$. The question we want to answer is how close the real value will be to the average? Or what is the typical spread of values of f? Let's imagine, that we can measure $f(\mathbf{q}, \mathbf{p})$ with any accuracy.

We then measure the average value of f: $\bar{f}$. At each measurement we will have a slightly different value of f. We want to know the average deviation of f from $\bar{f}$. So we calculate $\Delta f = f - \bar{f}$. Now it is clear that if we calculate $\overline{\Delta f}$ we will get 0, as Δf can be both positive and negative. We are not, however, interested in the sign of the deviation. So we want to calculate $\overline{(\Delta f)^2}$.

We notice,

$$\overline{(\Delta f)^2} = \overline{f^2 - 2\bar{f}f + \bar{f}^2} = \overline{f^2} - \bar{f}^2$$

The quantity $\sqrt{\overline{(\Delta f)^2}}$ is called *root-mean-square r.m.s. fluctuation* of the quantity f. The quantity $\sqrt{\overline{(\Delta f)^2}}/\bar{f}$ is called relative fluctuation. Notice, that the relative fluctuation is a dimensionless number, so we can judge if it is small or large.

16.3. Mathematical remark. Gaussian integrals.

We need to calculate the integrals

$$\int_{-\infty}^{\infty} e^{-ax^2/2}dx \qquad \text{and} \qquad \int_{-\infty}^{\infty} e^{-ax^2/2+bx}dx$$

They are called Gaussian integrals. We see that

$$\left(\int_{-\infty}^{\infty} e^{-ax^2/2}dx\right)^2 = \int_{-\infty}^{\infty} e^{-a(x^2+y^2)/2}dxdy = 2\pi\int_{0}^{\infty} e^{-ar^2/2}rdr = \frac{2\pi}{a}$$

So

$$\int_{-\infty}^{\infty} e^{-ax^2/2}dx = \sqrt{2\pi/a}$$

And then completing the square in the second integral we find

$$\int_{-\infty}^{\infty} e^{-ax^2/2+bx}dx = e^{b^2/2a}\sqrt{2\pi/a}$$

LECTURE 17

17.1. Fluctuations of additive observables. LL 2

We will also consider only additive quantities. Such as f for whole system is a sum of fs for all subsystems – typical examples are energy, volume, entropy, magnetization, etc. We first want to measure the average f

- Consider a large macrosystem.
- Split it into large number N of subsystems, each is still a macrosystem.
- For each subsystem we can measure the average $\bar{f}_i$ and r.m.s. fluctuation $\overline{(\Delta f_i)^2}$ of f in each subsystem.
- Consider now the whole system. The average value of f in the whole system is

$$\bar{f} = \int f(\mathbf{p}, \mathbf{q}) \varrho(\mathbf{p}, \mathbf{q}) \mathbf{dp} \mathbf{dq} = \int \left(\sum_i f_i(\mathbf{p_i}, \mathbf{q_i}) \right) \prod_i \varrho(\mathbf{p_i}, \mathbf{q_i}) \mathbf{dp_i} \mathbf{dq_i} = \sum_i \bar{f}_i.$$

The r.m.s. fluctuation of f in the whole system is

$$\overline{(\Delta f)^2} = \overline{\left(\sum_i \Delta f_i \right)^2} = \sum_i \overline{(\Delta f_i)^2} + \sum_{i \neq j} \overline{\Delta f_i} \, \overline{\Delta f_j} = \sum_i \overline{(\Delta f_i)^2}$$

So we found that if we have N subsystems, then $\bar{f} \propto N$, and $\overline{(\Delta f)^2} \propto N$. So the relative fluctuation is

$$\frac{\sqrt{\overline{(\Delta f)^2}}}{\bar{f}} \propto \frac{1}{\sqrt{N}}.$$

Each of the subsystems must be a macrosystem on its own and could not be made very small. The number of such macrosystems is, however proportional to the total number of particles. The above formula then shows that the relative fluctuation of a macrosystem decreases with the increase of the system size.

17.2. Distribution function of additive observable.

We want to calculate the distribution function of the additive observable. We split our large macrosystem on a large number N macroscopic subsystems. Then we write

$$\varrho(f) = \int \delta(f - f(\mathbf{p}, \mathbf{q}))\varrho(\mathbf{p}, \mathbf{q})d\mathbf{p}d\mathbf{q} = \int \delta(f - \sum_i f_i(\mathbf{p}_i, \mathbf{q}_i)) \prod_i \varrho_i(\mathbf{p}_i, \mathbf{q}_i)d\mathbf{p}_i d\mathbf{q}_i =$$

$$\int \int \frac{d\lambda}{2\pi} e^{i\lambda(f - \sum_i f_i(\mathbf{p}_i, \mathbf{q}_i))} \prod_i \varrho_i(\mathbf{p}_i, \mathbf{q}_i)d\mathbf{p}_i d\mathbf{q}_i = \int \frac{d\lambda}{2\pi} e^{i\lambda f} \prod_i \int e^{-i\lambda f_i(\mathbf{p}_i, \mathbf{q}_i)} \varrho_i(\mathbf{p}_i, \mathbf{q}_i)d\mathbf{p}_i d\mathbf{q}_i \approx$$

$$\int \frac{d\lambda}{2\pi} e^{i\lambda f} \prod_i \int \left(1 - i\lambda f_i(\mathbf{p}_i, \mathbf{q}_i) - \frac{\lambda^2}{2} f_i^2(\mathbf{p}_i, \mathbf{q}_i)\right) \varrho_i(\mathbf{p}_i, \mathbf{q}_i)d\mathbf{p}_i d\mathbf{q}_i =$$

$$\int \frac{d\lambda}{2\pi} e^{i\lambda f} \prod_i \left(1 - i\lambda \overline{f_i} - \frac{\lambda^2}{2}\overline{f_i^2}(\mathbf{p}_i, \mathbf{q}_i)\right) \approx \int \frac{d\lambda}{2\pi} e^{i\lambda f} \prod_i e^{-i\lambda \overline{f_i} - \frac{\lambda^2}{2}\left(\overline{f_i^2} - \overline{f_i}^2\right)} =$$

$$\int \frac{d\lambda}{2\pi} e^{i\lambda f} e^{-i\lambda \overline{f} - \frac{\lambda^2}{2}\overline{(\Delta f)^2}} = \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{\overline{(\Delta f)^2}}} e^{-(f - \bar{f})^2/2\overline{(\Delta f)^2}}$$

- In this calculation $\lambda \sim 1/\sqrt{N}$. It is the largeness of N that allowed us to keep only two terms in the exponent.
- This small parameter is what allowed us to find the full distribution function $\varrho(f)$ of an additive observable f without any knowledge of the distribution function $\varrho(\mathbf{p}, \mathbf{q})$. The distribution $\varrho(f)$ depends on only two parameters $\bar{f}$ and $\sqrt{\overline{(\Delta f)^2}}$.
- Due to the smallness of $1/\sqrt{N}$, the distribution $\varrho(f)$ is sharply peaked at $f = \bar{f}$.

LECTURE 18
Liouville's theorem.

18.1. Liouville's theorem. LL 3

Let's consider large number $\mathcal{N}$ of identical systems. Each system consists of N molecules and have the same pressure and temperature. Let's take a $2 \times 3N$ dimensional phase space and plot a point for each of $\mathcal{N}$ systems in it at some moment of time. With time each of these points will move through the phase space. The motions of this points are very complicated, each is governed by the same Hamiltonian $\mathcal{H}(\mathbf{p}, \mathbf{q})$. Let's consider the point number i, then

$$\dot{\mathbf{q}}_i = \frac{\partial \mathcal{H}(\mathbf{p}_i, \mathbf{q}_i)}{\partial \mathbf{p}_i}, \qquad \dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}(\mathbf{p}_i, \mathbf{q}_i)}{\partial \mathbf{q}_i}$$

(the systems do not interact with each other) These are $6N$ equations in $6N$ dimensional space for each point.

The number of systems $\mathcal{N}$ is large. So what we will see is a density of points/systems $\varrho(\mathbf{p}, \mathbf{q})$ at each point $\mathbf{p}, \mathbf{q}$ of the in $6N$ dimensional space. Instead of watching evolution of each system's coordinates ($\mathbf{p}_i(t)$ and $\mathbf{q}_i(t)$) with time we will watch an evolution of the density of points/systems at each point of the phase space.

Consider an element of volume $\mathbf{dpdq}$ at a point $\mathbf{p}, \mathbf{q}$ of the phase space. The number of systems inside this volume is $\varrho(\mathbf{p}, \mathbf{q}, t)\mathbf{dpdq}$. The points/systems cannot appear or disappear, so the number of points in this element of volume can only change by points/systems coming in or out of this volume.

This is very analogous to the hydrodynamics with $\varrho(\mathbf{p}, \mathbf{q})$ is the density of compressible liquid, and the velocity of liquid given by $\vec{v} = (\dot{\mathbf{p}}, \dot{\mathbf{q}})$. The continuity equation then reads $\dot{\varrho} = -\text{div}(\varrho \vec{v})$ or in our notations

$$\dot{\varrho} = -\frac{\partial}{\partial \mathbf{p}}(\varrho \dot{\mathbf{p}}) - \frac{\partial}{\partial \mathbf{q}}(\varrho \dot{\mathbf{q}})$$

Using the Hamiltonian equations We then have

$$\dot{\varrho} + \dot{\mathbf{p}}\frac{\partial \varrho(\mathbf{p}, \mathbf{q})}{\partial \mathbf{p}} + \dot{\mathbf{q}}\frac{\partial \varrho(\mathbf{p}, \mathbf{q})}{\partial \mathbf{q}} = -\varrho(\mathbf{p}, \mathbf{q})\left(\frac{\partial \dot{\mathbf{p}}}{\partial \mathbf{p}} + \frac{\partial \dot{\mathbf{q}}}{\partial \mathbf{q}}\right) = -\varrho(\mathbf{p}, \mathbf{q})\left(-\frac{\partial}{\partial \mathbf{p}}\frac{\partial \mathcal{H}(\mathbf{p}, \mathbf{q})}{\partial \mathbf{q}} + \frac{\partial}{\partial \mathbf{q}}\frac{\partial \mathcal{H}(\mathbf{p}, \mathbf{q})}{\partial \mathbf{p}}\right) = 0$$

So we have

$$\frac{d\varrho}{dt} = 0$$

In other words the distribution of the systems is conserved by the motion. This is Liouville's theorem.

18.2. Significance of energy. LL 4

The Liouville's theorem shows that the density, or distribution function is conserved along the trajectories. So it is another conservation law. Let's now imagine, that the whole system consists of two subsystems. Then the statistical independence (16.1) shows that

$$\log \varrho = \log \varrho_1 + \log \varrho_2$$

This means that $\log \varrho$ is an additive conserved quantity. From classical mechanics we know that there are only seven such quantities: energy, three components of momentum, and three components of angular momentum. So we have for each subsystem.

$$\log \varrho_a = \alpha_a + \beta E_a(\mathbf{p}, \mathbf{q}) + \boldsymbol{\gamma} \cdot \boldsymbol{P_a}(\mathbf{p}, \mathbf{q}) + \boldsymbol{\delta} \cdot \boldsymbol{M_a}(\mathbf{p}, \mathbf{q}),$$

where β, $\boldsymbol{\gamma}$, and $\boldsymbol{\delta}$ are the same for all subsystems.

   In a situation when momentum and angular momentum are not conserved (a typical situation in a laboratory) the energy is the only parameter which defines the distribution function of a subsystem

$$\log \varrho_a = \alpha_a + \beta E_a(\mathbf{p}, \mathbf{q}), \qquad \text{or} \qquad \varrho_a(\mathbf{q}_a, \mathbf{p}_a) = A_a e^{\beta E_a(\mathbf{q}_a, \mathbf{p}_a)}$$

- It is clear that mathematically A_a is just a normalization constant, as we must have $\int \varrho_a(\mathbf{q}_a, \mathbf{p}_a) d\mathbf{q}_a d\mathbf{p}_a = 1$, and β is just a parameter.
- We still need to figure out the physical meaning of A_a and β.
- All of the above arguments work for a subsystem of a large system. Or in other words for a system coupled to a thermal bath.

LECTURE 19
Microcanonical distribution. Quantum.

19.1. Significance of energy

In last lecture we showed that

$$\log \varrho_a = \alpha_a + \beta E_a(\mathbf{p}, \mathbf{q}),$$

Notice that if there are two subsystems that are completely disconnected from each other and there is no energy exchange between them, then their energies E_1 and E_2 are conserved separately, and then any linear combination of the form $\beta_1 E_1 + \beta_2 E_2$ is also a conserved quantity. Hence βs can be different for different systems. However, if there is a vary slow exchange of energy between the subsystems, then only the combination $\beta E_1 + \beta E_2$ is conserved. So for the subsystems in thermal contact βs must be the same.

19.2. Microcanonical distribution. LL 4

- Consider a closed system.
- Simplest solution of the Liouville's equation $\varrho =$const. The "gas of systems" spreads out over all allowed phase volume uniformly.
- We have $2N$ dimensional phase space.
- However, there are 7 conservation laws

$$E(\mathbf{p}, \mathbf{q}) = E_0, \quad \mathbf{P}(\mathbf{p}, \mathbf{q}) = \mathbf{P}_0, \quad \mathbf{M}(\mathbf{p}, \mathbf{q}) = \mathbf{M}_0.$$

- So the distribution function is constant on the $2N - 7$ dimensional manifold defined above, and zero everywhere else.
- The integral of the distribution function over all phase space should be 1. So the distribution function is

$$\varrho = \text{const.} \times \delta(E - E_0)\delta(\mathbf{P} - \mathbf{P}_0)\delta(\mathbf{M} - \mathbf{M}_0).$$

Every micro state has the same probability (probability density). The question: How come we do not see that all air in the room is just in a left side of the room? What our intuition tells us?

Consider a simple example: We have a machine which randomly selects five digits. Which result is more likely 00000 or 19462? The correct answer is, of course, that the probability is the same. A less formal, but intuitively clear question is which result is more likely: the

one that "looks like" the first number or the one which "looks like" the second number? In order to answer it we need to understand what the words "looks like" mean. Again it is clear, that the first number has an evident structure, while the second one is structureless. Then we know, that there are a lot more structureless numbers then structured ones. So the probability of to get some structureless number is higher. In other words we say that the space of structureless numbers is larger.

This is the same with the air in the room. There are a lot more micro states that "look like" the air fills up all the room uniformly, than the number of states that "look like" all the air is in the left half of the room.

19.3. Quantum statistical mechanics.

In quantum mechanical approach we have a problem from the very beginning: we cannot define the phase space, as the operators $\hat{\mathbf{p}}$ and $\hat{\mathbf{r}}$ do not commute. We need to start form redefining the main object of study – the probability density. Before we do that let's see what the huge number of particles mean for the quantum mechanics.

- Consider a particle $(1D)$ in a box. It's energy $\epsilon_n = \frac{\hbar^2\pi^2}{2L^2 m} n^2$.
- Two non-interacting particles in the same box $E = \epsilon_{n_1} + \epsilon_{n_2} = \frac{\hbar^2\pi^2}{2L^2 m} \left(n_1^2 + n_2^2\right)$.
- Consider two axes n_1 and n_2. Different states are just points on the plane. The total energy is the square of the distance from the origin to the state (with a factor $\varepsilon = \frac{\hbar^2\pi^2}{2L^2 m}$).
- All states with energy less then E are withing a circle of the radius $\sqrt{E/\varepsilon}$.
- The number of states $d\Gamma$ with energies between E and $E + dE$ is the number of points between the circles with radii $R = \sqrt{E/\varepsilon}$ and $R + dR = \sqrt{E + dE}$. So we find that $dR \propto dE/\sqrt{E}$ and the number of states $d\Gamma \propto R dR = dE$.
- For N particles instead of a circles we will have two N dimensional spheres of radii $\sqrt{E/\varepsilon}$ and $\sqrt{E + dE}$.
- The distance between the spheres $dR \propto E^{-1/2} dE$
- The volume in between these two spheres is $\propto R^{N-1} dR \propto E^{N/2-1} dE$, so the number of states at energies between E and $E + dE$ is $d\Gamma \propto E^{N/2-1} dE$.
- In other words the distance between two energy levels $\Delta E = dE/d\Gamma \propto E^{1-N/2}$.

The energy is additive, so when the number of particles grows the energy also grows $E = \epsilon_0 N$, where ϵ_0 is an average energy per particle. The energy gaps between the levels is $\Delta E \propto (\epsilon_0 N)^{1-N/2} \to 0$ as $N \to \infty$.

The last result shows that the energy gaps between the multiparticle states decreases exponentially with the number of particles. For a macroscopic number of particles $N \sim 10^{23}$ the levels are very close to each other, so no perturbation is small (including the perturbations which are introduced by measurement). This is the reason why

- a macroscopic body cannot be in a stationary state.

An important concept useful in the future is the density of states (DOS) $\nu(E)$, which gives the number of states in the energy interval dE, so $d\Gamma = \nu(E)dE$.

Figure 1. Energy levels and density of states.

LECTURE 20
Statistical matrix. Quantum Liouville's theorem

From the last lecture:"A macroscopic body cannot be in a stationary state."

20.1. The statistical matrix. LL 5

- Consider a subsystem of a large system. If we ignore the interaction of the subsystem with the rest we can introduce normalized wave functions $\psi_n(q)$, where q are all coordinates and n are all quantum numbers. The energies of these states are E_n.
- Functions $\psi_n(q)$ are a complete set and any quantum mechanical state can be written as $\Psi = \sum c_n \psi_n$.

Wave function Ψ is not gauge invariant it can always be multiplied by an arbitrary phase factor $e^{i\phi}$, so any measurable/observable is quadratic in Ψ (or bilinear in Ψ, Ψ^*).

- Mean value of an operator $\hat{f}$ in a state $\Psi = \sum_n c_n \psi_n$ is written as

$$\bar{f} = \langle \Psi | \hat{f} | \Psi \rangle = \sum_{n,m} c_n^* c_m f_{nm}, \qquad f_{nm} = \int \psi_n^* \hat{f} \psi_m dq.$$

- Due to the interaction with the rest the subsystem is not in a fixed state Ψ. It fluctuates. Or we can say, that the coefficients c_m fluctuate.
- Thus to calculate the average $\bar{f}$ we also need to calculate the statistical average of the product $c_n^* c_m$.
- The average of the product does not equal to the product of averages!
- The average of the product $c_n^* c_m$ is some Hermitian matrix

$$c_n^* c_m \to w_{mn}, \qquad \text{Notice the order of indexes!}$$

The mean value of the operator $\hat{f}$ is now

$$\bar{f} = \sum_{n,m} w_{mn} f_{nm}.$$

- Matrix w_{mn} is called *statistical matrix*. It can be written in a different bases. For example in a coordinate bases (it is called density matrix then) it is $\varrho(q, q') = \sum_{m,n} w_{mn} \psi_n^*(q') \psi_m(q)$.
- If we regard w_{mn} as matrix elements of some statistical operator $\hat{w}$, then

$$\bar{f} = \sum_{n,m} w_{mn} f_{nm} = \sum_n \left(\hat{w} \hat{f} \right)_{nn} = \text{tr} \left(\hat{w} \hat{f} \right)$$

- In any state $c_n^* c_n > 0$, and $\sum_n c_n^* c_n = 1$, for the statistical matrix it means

$$w_n \equiv w_{nn} > 0, \qquad \mathrm{tr}\hat{w} = \sum_n w_n = 1$$

- Distinction between *pure* (Ψ) and *mixed* states.

20.2. Statistical distribution. Quantum Liouville's theorem. LL 6

- In a pure state the coefficients c_n depend on time. From the Schrödinger equation $\dot{\Psi} = -\frac{i}{\hbar}\hat{H}\Psi$, using $\hat{H}\psi_n = E_n\psi_n$, $\Psi = \sum_m c_m\psi_m$, and the fact that ψ_m are orthogonal for different m: $\langle \psi_n | \psi_m \rangle = \delta_{mn}$ we get

$$\frac{\partial}{\partial t}c_m = -\frac{i}{\hbar}E_m c_m$$

$$\frac{\partial}{\partial t}c_n^* = \frac{i}{\hbar}E_n c_n^*$$

- These equations give

$$\frac{\partial}{\partial t}c_n^* c_m = \frac{i}{\hbar}\left(E_n - E_m\right)c_n^* c_m$$

- after substitution $c_n^* c_m \to w_{mn}$ it becomes

$$\dot{w}_{mn} = \frac{i}{\hbar}\left(E_n - E_m\right)w_{mn}.$$

- Noticing $\left(E_n - E_m\right)w_{mn} = \sum_l \left(w_{ml}H_{ln} - H_{ml}w_{ln}\right) = \left[\hat{w}, \hat{H}\right]_{mn}$ we write

$$\dot{\hat{w}} = \frac{i}{\hbar}\left[\hat{w}, \hat{H}\right]$$

This is quantum mechanical analogue of the Liouville's theorem
- It differs by the sign from usual Heisenberg equation.

LECTURE 21
Role of energy. Quantum microcanonical distribution.

21.1. Example.

Here I consider just a simple Hamiltonian of a two level system.

$$\hat{H} = -\Delta\hat{\sigma}_z, \qquad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

The eigen states of the Hamiltonian are

$$\chi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad E_\uparrow = -\Delta, \qquad \text{and} \qquad \chi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad E_\downarrow = \Delta$$

A wave function can be written as $\chi = c_\uparrow\chi_\uparrow + c_\downarrow\chi_\downarrow$, where $|c_\uparrow|^2 + |c_\downarrow|^2 = 1$. The statistical matrix then is

$$(21.1) \qquad \hat{w} = \begin{pmatrix} c_\uparrow^* c_\uparrow & c_\downarrow^* c_\uparrow \\ c_\uparrow^* c_\downarrow & c_\downarrow^* c_\downarrow \end{pmatrix}, \qquad \text{and} \qquad \begin{aligned} s_x &= \tfrac{1}{2}\langle\sigma_x\rangle = \tfrac{1}{2}\mathrm{tr}\,(\hat{w}\hat{\sigma}_x) = \tfrac{1}{2}(c_\uparrow^* c_\downarrow + c_\downarrow^* c_\uparrow), \\ s_y &= \tfrac{1}{2}\langle\sigma_y\rangle = \tfrac{1}{2}\mathrm{tr}\,(\hat{w}\hat{\sigma}_y) = \tfrac{i}{2}(c_\uparrow^* c_\downarrow - c_\downarrow^* c_\uparrow), \\ s_z &= \tfrac{1}{2}\langle\sigma_z\rangle = \tfrac{1}{2}\mathrm{tr}\,(\hat{w}\hat{\sigma}_z) = \tfrac{1}{2}(c_\uparrow^* c_\uparrow - c_\downarrow^* c_\downarrow) \end{aligned}$$

For time evolution we can use

$$\dot{w}_{\alpha,\beta} = \frac{i}{\hbar}(E_\beta - E_\alpha)w_{\alpha,\beta} \qquad \begin{aligned} &\dot{w}_{\uparrow,\uparrow} = \dot{w}_{\downarrow,\downarrow} = 0, & w_{\uparrow,\uparrow}(t) &= w_{\uparrow,\uparrow}^0, & w_{\downarrow,\downarrow}(t) &= w_{\downarrow,\downarrow}^0 \\ &\dot{w}_{\uparrow,\downarrow} = \tfrac{i}{\hbar}(E_\downarrow - E_\uparrow)w_{\uparrow,\downarrow}, & w_{\uparrow,\downarrow}(t) &= e^{2\Delta t/\hbar}w_{\uparrow,\downarrow}^0 \\ &w_{\downarrow,\uparrow} = w_{\uparrow,\downarrow}^* \end{aligned}$$

and find

$$s_x(t) = \tfrac{1}{2}\mathrm{tr}(\hat{w}(t)\hat{\sigma}_x) = s_x^0\cos(\Delta t/\hbar) + s_y^0\sin(\Delta t/\hbar)$$
$$s_y(t) = \tfrac{1}{2}\mathrm{tr}(\hat{w}(t)\hat{\sigma}_y) = -s_x^0\sin(\Delta t/\hbar) + s_y^0\cos(\Delta t/\hbar)$$
$$s_z(t) = \tfrac{1}{2}\mathrm{tr}(\hat{w}(t)\hat{\sigma}_z) = s_z^0$$

This is a standard quantum mechanical result which can be obtained by using $c_\uparrow = c_\uparrow^0 e^{i\Delta t/\hbar}$, and $c_\downarrow = c_\downarrow^0 e^{-i\Delta t/\hbar}$. The spin rotates around the magnetic field.

If we, however, are not restricted by the quantum mechanical form (21.1) of the statistical matrix we can have a very different result. For example, if we take the statistical matrix to

be of the form

$$(21.2) \qquad \hat{w} = \begin{pmatrix} 1/2 + a & 0 \\ 0 & 1/2 - a \end{pmatrix}, \qquad -1/2 < a < 1/2, \qquad \text{tr}\,\hat{w} = 1, \quad w_{ii} > 0$$

This same calculation as before now gives

$$\begin{aligned} s_x &= \tfrac{1}{2}\langle \sigma_x \rangle = \tfrac{1}{2}\text{tr}\,(\hat{w}\hat{\sigma}_x) = 0, \\ s_y &= \tfrac{1}{2}\langle \sigma_y \rangle = \tfrac{1}{2}\text{tr}\,(\hat{w}\hat{\sigma}_y) = 0, \\ s_z &= \tfrac{1}{2}\langle \sigma_z \rangle = \tfrac{1}{2}\text{tr}\,(\hat{w}\hat{\sigma}_z) = a, \end{aligned}$$

Notice, that in this case $d\hat{w}/dt = i\left[\hat{w}, \hat{H}\right] = 0$, as both operators are diagonal. So the components are constant in time.

21.2. Role of energy.

- In equilibrium we expect the statistical matrix to be static (averages of the time in-dependent operators do not depend on time), so $\hat{w}$ commutes with $\hat{H}$. In other words they are diagonal in the same bases. So in the representation of the energy states the off diagonal matrix elements of the statistical matrix are zero. The statistical matrix is diagonal in this bases.
- $w_n \equiv w_{nn}$ are positive numbers and their sum is 1. The set w_n is the analogue of the distribution function in quantum statistics.
- The mean value of an operator $\hat{f}$ then is

$$\bar{f} = \sum_n w_n f_{nn}$$

  contains only diagonal matrix elements of $\hat{f}$.
- As w is an integral of motion and the subsystems are statistically independent we find

$$\log w_n^a = \alpha^a - \beta E_n^a$$

  where a labels different subsystems.
- Important. The index n labels states! not energy levels. A single energy level can correspond to many states!

21.3. Example of two level system.

Our statistical matrix (21.2) gives

$$\begin{aligned} w_\uparrow &= w_{\uparrow,\uparrow} = 1/2 + a = Ae^{\beta\Delta} \\ w_\downarrow &= w_{\downarrow,\downarrow} = 1/2 - a = Ae^{-\beta\Delta} \end{aligned}, \qquad A = \frac{1}{2\cosh(\beta\Delta)}, \quad a = A\sinh(\beta\Delta) = \frac{1}{2}\tanh(\beta\Delta)$$

Or

$$w_\uparrow = \frac{e^{\beta\Delta}}{2\cosh(\beta\Delta)}, \qquad \text{and} \qquad w_\downarrow = \frac{e^{-\beta\Delta}}{2\cosh(\beta\Delta)}.$$

The coefficient β will be later identified with $1/T$.

LECTURE **22**
Entropy.

22.1. Entropy. LL 7

- Consider a macroscopic subsystem of a large system.
- The distribution function of the subsystem is w_n – the probability of the subsystem to be in the **state** n.
- This distribution function depends only on the energy E_n of the state n, $w_n = w(E_n)$.
- Let's consider probability $W(E)dE$ to find the subsystem's energy to be in the interval between E and $E + dE$.
- Consider a function $\Gamma(E)$ which is the number of states with energies below E.
- The number of states with energy between E and $E + dE$ is then $d\Gamma = \frac{d\Gamma(E)}{dE}dE$.
- The probability to find the system in one of the these states is $wd\Gamma$, or $W(E)dE = w(E)\frac{d\Gamma(E)}{dE}dE$, or

$$(22.1) \qquad\qquad W(E) = w(E)\frac{d\Gamma(E)}{dE}.$$

- Notice, that we know $w(E) = Ae^{-\beta E}$, where A is a normalization constant.

Now we want to understand how this distribution function $W(E)$ looks.

- First, the distribution $W(E)$ is normalized $\int W(E)dE = 1$.
- Second, it is sharply peaked around the average value of energy $\bar{E}$.
- Let's denote the width of this sharp peak as ΔE. It can be defined from the normalization condition

$$(22.2) \qquad\qquad W(\bar{E})\Delta E = 1.$$

This ΔE is of the order of the mean fluctuation of subsystem's energy.
- Using (22.1) and the fact that the energy distribution is very sharply peaked at $\bar{E}$ we have

$$1 = \int W(E)dE = \int w(E)\frac{d\Gamma(E)}{dE}dE \approx w(\bar{E})\int_{\bar{E}-\Delta E/2}^{\bar{E}+\Delta E/2}\frac{d\Gamma(E)}{dE}dE = w(\bar{E})\Delta\Gamma$$

where $\Delta\Gamma$ is the number of micro states in the peak.

$$(22.3) \qquad w(\bar{E})\Delta\Gamma = 1, \qquad \Delta\Gamma = \left.\frac{d\Gamma}{dE}\right|_{E=\bar{E}} \Delta E.$$

This $\Delta\Gamma$ is the degree of broadening of the macroscopic state of the subsystem with respect to the microscopic states. Or how many microscopic states the macroscopic state is spread over.

22.2. Statistical weight of a macroscopic state.

In yet other words the value $\Delta\Gamma$ is the statistical weight of the macroscopic state of the subsystem. If we consider the "gas of subsystems" in the phase space, then it is clear, that the most "random" situation is when the gas spreads over all allowed subspace in the phase space, or one can conclude that this "gas" tends to take as large volume in the phase space as possible. The value $\Delta\Gamma$ is the measure of volume of the available phase space. So in equilibrium a subsystem is in the macrostate which has the largest possible $\Delta\Gamma$. Here is the point number one

#1 A macroscopic state is the equilibrium state if it's statistical weight is maximal of all possible.

Next, consider two subsystems of the same system. If the first one can be in one of $\Delta\Gamma_1$ states, and the second subsystem can be in one of $\Delta\Gamma_2$ states, then the two of them together can be in one of $\Delta\Gamma_1\Delta\Gamma_2$ states. So the statistical weight of the of the two subsystems together is $\Delta\Gamma = \Delta\Gamma_1\Delta\Gamma_2$. In other words

$$\log\Delta\Gamma = \log\Delta\Gamma_1 + \log\Delta\Gamma_2$$

(notice, that $\Delta\Gamma$ is just a number of states — dimensionless) So here is the point number two:

#2 Quantity $\log\Delta\Gamma$ is additive.

The two points together mean that $\log\Delta\Gamma$ is additive and is at maximum in equilibrium! So it is entropy.

$$(22.4) \qquad\qquad S = k\log\Delta\Gamma$$

(k is Boltzmann constant needed for correct units.)

22.3. Entropy and Quantum mechanics.

According to (22.3) we can write the entropy in a different form

$$(22.5) \qquad\qquad S = -\log w(\bar{E})$$

We, however, know that for the distribution function $\log w(E_n) = \alpha + \beta E_n$, so we find

$$\log w(\bar{E}) = \alpha - \beta\bar{E} = \overline{\alpha - \beta E_n} = \overline{\log w(E_n)} = \overline{\log w_n}$$

Or

$$S = -\langle\log w_n\rangle = -\sum_n w_n \log w_n$$

If we now use the definition of the statistical matrix $\hat{w}$, we find

$$S = -\mathrm{tr}\left(\hat{w}\log\hat{w}\right).$$

22.4. Physical meaning of β and α

According to (22.5) we now write

$$-S = \alpha - \beta \bar{E}$$

$\bar{E}$ is the averaged energy of the macroscopic state of the subsystem, so it is exactly the energy as defined in thermodynamics. Previously we defined temperature as $1/T = \partial S/\partial E$, so using above equation we find that $\beta = 1/T$ and our equation now reads

$$-S = \alpha - \bar{E}/T, \qquad \text{or} \qquad T\alpha = \bar{E} - TS,$$

but $\bar{E} - TS$ is just free energy. So $\alpha = F/T$. Now using this for the distribution function we find

$$w_n = e^{F/T} e^{-E_n/T}$$

This distribution function must satisfy the normalization condition

$$\sum_n w_n = 1, \qquad \text{or} \qquad e^{-F/T} = \sum_n e^{-E_n/T} = \text{tr}\left(e^{-\hat{H}/T}\right)$$

(I want to emphasize that the summation is the summation over **states**, not over energy levels)

The sum $Z = \sum_n e^{-E_n/T} = \text{tr}\left(e^{-\hat{H}/T}\right)$ is called *partition function*.

$$Z = \sum_n e^{-E_n/T}, \qquad F = -T \log Z$$

The summation goes over all states. If we want instead to sum over energy levels, then we need to know the degeneracy of each level, say energy level E_k has degeneracy ν_k, then $Z = \sum_k \nu_k e^{-E_k/T}$. Now k in this sum runs over energy levels. Notice, that we do not need to know the wave functions.

LECTURE 23
WKB. Level spacing. Quantum microcanonical distribution.

23.1. Messages of the previous lecture

Here I will try to distill the messages of the previous lecture.

Message# 1. The equilibrium state is the state that we observe. It is then the macro state which has the largest probability. As all micro states have almost the same probability we observe the state with the largest statistical weight — number of micro states involved.

Message# 2. The quantity $\Delta\Gamma = 1/w(\bar{E})$ is a good measure of the statistical weight. and thus must be at maximum in equilibrium.

Message# 3. The quantity $\log\Delta\Gamma$ is additive. It also is at maximum in equilibrium, so it is the entropy.

So

$$S = -k\log w(\bar{E})$$

23.2. Quasi classical, WKB.

Now let's take the classical limit of this formulas. According to WKB a quantum state takes a "cell" of volume $(2\pi\hbar)^s$ (s is the number of degrees of freedom) in the phase space. So we define a volume $\Delta\mathbf{p}\Delta\mathbf{q}$ of the phase space in the classical statistics as

$$\varrho(\bar{E})\Delta\mathbf{p}\Delta\mathbf{q} = 1.$$

Then the statistical weight = number of states is

$$\Delta\Gamma = \frac{\Delta\mathbf{p}\Delta\mathbf{q}}{(2\pi\hbar)^s}$$

So in the classical limit

$$S = \log\frac{\Delta\mathbf{p}\Delta\mathbf{q}}{(2\pi\hbar)^s}, \qquad S = -\langle\log\left[\varrho(2\pi\hbar)^s\right]\rangle = -\int\varrho\log\left[\varrho(2\pi\hbar)^s\right]d\mathbf{p}d\mathbf{q}$$

Notice the appearance of $\hbar$ even in the classical limit. Without it the $\log\Delta\mathbf{p}\Delta\mathbf{q}$ is not well defined, as it is not a dimensionless number under the log. So if one changes units this

number will be multiplied by the conversion factor. The log then will acquire an addition. So the entropy without $\hbar$ is not a well defined quantity, but the change of entropy is!

23.3. Density of states. Level spacing.

In equilibrium entropy is a function of energy. By the definition of entropy we have $\Delta\Gamma = e^{S(E)}$ is a number of state in the interval ΔE, which describes the width of the energy distribution. The ration $\Delta E/\Delta\Gamma$ is the separation between the adjoining levels near energy E. So typical separation is

$$D(E) = e^{-S(E)}\Delta E$$

Since the entropy is additive the function $e^{-S(E)}$ decreases very fast (exponentially) with the increase of the system size.

23.4. Quantum microcanonical distribution. LL 6

For the "classical" microcanonical distribution we found $\varrho = \text{const.}\times\delta(E-E_0)\delta(\mathbf{P}-\mathbf{P}_0)\delta(\mathbf{M}-\mathbf{M}_0)$. The question is what do we integrate it over?

- Consider a closed system.
- Let's $d\Gamma$ be a number of states corresponding to an energy interval dE of the energy of the whole system.
- If we split the whole system into a bunch of subsystems we can introduce $d\Gamma_a$ for each subsystem. Then

$$d\Gamma = \prod_a d\Gamma_a.$$

- If the total energy of the system is E_0 — a conserved quantity, then the distribution of the whole system is

$$dw = \text{const} \times \delta(E - E_0) \prod_a d\Gamma_a, \qquad E = \sum_a E_a.$$

- Notice, that it is quantum mechanics that allowed us to set the measure $\prod_a d\Gamma_a$ unambiguously, as in classical mechanics the quantity "number of states" does not exist. We then expect that if we take the limit of very small $\hbar$ — which corresponds to classical limit — we will still have quantum mechanical origin in the measure of integration.

Instead of integration/summation over states we would like to integrate over the energies of the subsystems instead, so we have

$$dw = \text{const} \times \delta(E - E_0) \prod_a \frac{d\Gamma_a}{dE_a} dE_a,$$

Consider both the statistical weight $\Delta\Gamma_a$ and the energy spread ΔE_a as a functions of energy of the subsystem E, then the derivative $d\Gamma_a/dE_a$ can be replaced by $\Delta\Gamma_a/\Delta E_a$. On the other hand $\Delta\Gamma_a = e^{S_a}$, so using the fact that the total entropy $S = \sum_a S_a$ we find

$$dw = \text{const} \times \delta(E - E_0)\frac{e^S}{\prod_a \Delta E_a} \prod_a dE_a$$

Again e^S is a very steep function. In comparison to it the function $\prod_a \Delta E_a$ can be regarded to be constant as a function of energy. It then can be absorbed into the normalization constant. Finally we get:

$$dw = \text{const} \times \delta(E - E_0)e^S \prod_a dE_a, \qquad E = \sum_a E_a.$$

Again I remind that S is the entropy of the whole system.

LECTURE 24
Gaussian Integrals.

24.1. Gaussian integrals. LL 110,111

24.1.1. Why Gaussian integrals?

- A typical integral we need to calculate to find an average of some function $f(x)$ is $A \int f(x) e^{S(x)} dx$, where $e^{S(x)}$ is the statistical weight (S is entropy).
- We know that the function S has a maximum at some value of $x = x_0$ which corresponds to equilibrium. We then can write $S(x) = S(x_0) - \frac{1}{2}\beta(x - x_0)^2$.
- The maximum of the function $S(x)$ may be shallow, but the exponent is a steep function and the maximum of $e^{S(x)}$ at $x = x_0$ is sharp.
- In this case the major contribution to the integral $A \int f(x) e^{S(x)} dx$ comes from the vicinity of the point x_0, so with a good accuracy we can write our distribution function as $w dx = A e^{S_0} e^{-\frac{1}{2}\beta(x - x_0)^2} dx$.
- In this case we can calculate the normalization constant as $\int w dx = 1$ and obtain

$$w dx = \sqrt{\frac{\beta}{2\pi}} e^{-\frac{1}{2}\beta(x - x_0)^2} dx$$

- Now we calculate the average value of x

$$\langle x \rangle = \int_{-\infty}^{\infty} x w(x) dx = x_0$$

- We can calculate the standard deviation $\sigma^2 = \langle (x - \langle x \rangle)^2 \rangle$

$$\sigma^2 = \int_{-\infty}^{\infty} (x - x_0)^2 w dx = -\sqrt{\frac{\beta}{2\pi}} 2 \frac{\partial}{\partial \beta} \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta(x - x_0)^2} dx = -\sqrt{\frac{\beta}{2\pi}} 2 \frac{\partial}{\partial \beta} \sqrt{\frac{2\pi}{\beta}} = \beta^{-1}$$

- So we can write the same distribution function as

$$w dx = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x - \langle x \rangle)^2}{2\sigma^2}} dx$$

It also means that if we have a Gaussian distribution of some variable we can read the average value and the standard deviation for this variable right from the distribution, without taking the integrals.

- For any function $f(x)$ which is smooth around x_0 on the scale β we use $f(x) \approx f(x_0) + f'(x_0)(x - x_0) + \frac{1}{2}f''(x_0)(x - x_0)^2$ and write

$$\langle f \rangle = f(x_0) + \frac{1}{2}f''(x_0)\langle (x - x_0)^2 \rangle = f(x_0) + \frac{1}{2}f''(x_0)\beta^{-1} = f(x_0) + \frac{1}{2}f''(x_0)\sigma^2$$

- To find the standard deviation of the function f in the first order in β^{-1} we write $\Delta f = f - \langle f \rangle = f'(x_0)(x - x_0) + \frac{1}{2}f''(x_0)(x - x_0)^2 - \frac{1}{2}f''(x_0)\beta^{-1}$. Now we need to square it and keep only the terms which will give β^{-1} after averaging. It is clear that there is only one such term and it comes from $[f'(x_0)(x - x_0)]^2$, which after averaging gives:

$$\langle (\Delta f)^2 \rangle \approx (f_0')^2 \beta^{-1}$$

24.1.2. Many Variables.

Let's now consider a function $S(\{x\})$ of many variables x_i, $i = 1 \ldots N$. We want to calculate an integral of the form $A \int f(\{x\})e^{S(\{x\})} \prod_{i=1}^{N} dx_i$, where A is normalization constant such that $A \int e^{S(\{x\})} \prod_{i=1}^{N} dx_i = 1$. Again the function $S(\{x\})$ must have a maximum. Let's denote the position of this maximum as x_{0i}, and $S(\{x_0\}) = S_0$. Then in the vicinity of x_{0i} we have

$$S(\{x\}) = S_0 - \frac{1}{2}\beta_{i,j}(x_i - x_{0i})(x_j - x_{0j}),$$

where β_{ij} is a symmetric positive-definite matrix and summation over the repeated indexes is assumed. Let's first calculate the normalization constant $1 = Ae^{S_0} \int e^{-\frac{1}{2}\beta_{i,j}(x_i-x_{0i})(x_j-x_{0j})} \prod_{i=1}^{N} dx_i$. To calculate this integral we can first shift the variables $x_i - x_{0i} \to x_i$, then we have $1 = Ae^{S_0} \int e^{-\frac{1}{2}\beta_{i,j}x_i x_j} \prod_{i=1}^{N} dx_i$. As $\hat{\beta}$ is a symmetric matrix there exists an orthogonal transformation $x_i = o_{i,k}\tilde{x}_k$ which diagonalizes $\hat{\beta}$, namely $o_{k',i}\beta_{i,j}o_{j,k} = \lambda_k \delta_{k,k'}$, where λ_k are the eigen values of $\hat{\beta}$. The Jacobian of this transformation

$$J = \frac{\partial(x_1 \cdots x_N)}{\partial(\tilde{x}_1 \cdots \tilde{x}_N)} = \det\left(\frac{\partial x_i}{\partial \tilde{x}_j}\right) = \det(o_{i,j}) = 1$$

So upon change of variables we get

$$Ae^{S_0} \int e^{-\frac{1}{2}\beta_{i,j}x_i x_j} \prod_{i=1}^{N} dx_i = Ae^{S_0} \int e^{-\frac{1}{2}\sum_{i=1}^{N} \lambda_i \tilde{x}_i \tilde{x}_i} \prod_{i=1}^{N} d\tilde{x}_i = Ae^{S_0} \prod_{i=1}^{N} \int e^{-\frac{1}{2}\lambda_i(\tilde{x}_i)^2} d\tilde{x}_i = Ae^{S_0} \frac{(2\pi)^{N/2}}{\sqrt{\prod \lambda_i}}.$$

But the product of all eigen values is just the determinant: $\prod \lambda_i = \det \hat{\beta}$, and we have

$$Ae^{S_0} = (2\pi)^{-N/2}\sqrt{\det \hat{\beta}}.$$

Let's now calculate the average value of x_k and "correlators" $\langle x_k x_{k'} \rangle$.

24.1.2.1. _First method._ We have

$$\langle x_k \rangle = Ae^{S_0} \int (x_k - x_{0k} + x_{0k})e^{-\frac{1}{2}\beta_{i,j}(x_i-x_{0i})(x_j-x_{0j})} \prod_{i=1}^{N} dx_i = x_{0k}.$$

From here we find

$$\delta_{k,k'} = \frac{\partial x_{0k}}{\partial x_{0k'}} = \frac{\partial}{\partial x_{0k'}}\langle x_k \rangle = Ae^{S_0} \int x_k \beta_{k',l}(x_l - x_{0l})e^{-\frac{1}{2}\beta_{i,j}(x_i-x_{0i})(x_j-x_{0j})} \prod_{i=1}^{N} dx_i =$$

$$\langle x_k \beta_{k',l}(x_l - x_{0l}) \rangle = \beta_{k',l}\langle (x_k - x_{0k})(x_l - x_{0l}) \rangle$$

So we have

$$\langle x_k - x_{0k} \rangle = 0, \qquad \langle (x_k - x_{0k})(x_l - x_{0l}) \rangle = (\hat{\beta}^{-1})_{k,l}$$

If S is entropy the term "*thermodynamically conjugated variables*" is often used for the quantities

$$X_i = -\partial S/\partial x_i, \qquad dS = -\sum_i X_i dx_i.$$

Close to the equilibrium (maximum of S) we have

$$X_i = \sum_j \beta_{i,j}(x_j - x_{0j}), \qquad dS = -\sum_i X_i dx_i = -\sum_{i,j} \beta_{i,j}(x_j - x_{0j})d(x_i - x_{0i}) = -\sum_j (x_j - x_{0j})dX_j$$

So the conjugation is reciprocal. We also see that

$$\langle X_i x_j \rangle = \delta_{i,j}, \qquad \langle X_i X_j \rangle = \beta_{i,j}$$

For any function $f(\{x\})$ we then find (up to the first order in $1/\beta$)

$$\langle (\Delta f)^2 \rangle = \left.\frac{\partial f}{\partial x_i}\right|_{x=x_0} \left.\frac{\partial f}{\partial x_j}\right|_{x=x_0} (\hat{\beta}^{-1})_{i,j}.$$

24.1.2.2. *Alternative method.*. First lets shift our variables x_k by x_{0k}, so that our distribution function is

$$w(\{x\}) = (2\pi)^{-N/2}\sqrt{\det \hat{\beta}} e^{-\frac{1}{2}\beta_{i,j}x_i x_j}$$

Let's now find the average of a function $e^{X_k x_k}$ for some variables X_k

$$F(\{X\}) = \langle e^{X_k x_k} \rangle = (2\pi)^{-N/2}\sqrt{\det \hat{\beta}} \int e^{-\frac{1}{2}\beta_{i,j}x_i x_j + X_k x_k} \prod_{i=1}^N dx_i$$

In order to do that we need to find such values of $\{x\}$ (I call them $\{\tilde{x}\}$) at which the quantity $-\frac{1}{2}\beta_{i,j}x_i x_j + X_k x_k$ is at maximum. In order to do that we differentiate this quantity with respect to x_i and find where this derivative is zero:

$$-\beta_{i,j}\tilde{x}_j + X_i = 0, \qquad X_i = \beta_{i,j}\tilde{x}_j, \qquad \tilde{x}_i = (\beta^{-1})_{i,j}X_j$$

(Notice, that X_i are exactly the "thermodynamically conjugated variables", as using the definition of the matrix $\hat{\beta}$ we see that they can be written as $X_i = -\partial S/\partial x_i$.)

We now change the variables $x_i \to \delta x_i$, by the following $x_i = \tilde{x}_i + \delta x_i$ and get

$$F(\{X\}) = e^{\frac{1}{2}(\beta^{-1})_{i,j}X_i X_j}(2\pi)^{-N/2}\sqrt{\det \hat{\beta}} \int e^{-\frac{1}{2}\beta_{i,j}\delta x_i \delta x_j} \prod_{i=1}^N d\delta x_i = e^{\frac{1}{2}(\beta^{-1})_{i,j}X_i X_j}$$

Now we can calculate all averages.

$$\langle x_k \rangle = \left.\frac{\partial F}{\partial X_k}\right|_{X=0} = 0, \qquad \langle x_k x_{k'} \rangle = \left.\frac{\partial^2 F}{\partial X_{k'}\partial X_k}\right|_{X=0} = (\beta^{-1})_{k,k'}.$$

We can also calculate higher correlators

$$\langle x_k x_{k'} x_{k''} \rangle = \left.\frac{\partial^3 F}{\partial X_{k''}\partial X_{k'}\partial X_k}\right|_{X=0} = 0,$$

$$\langle x_{k_1} x_{k_2} x_{k_3} x_{k_4} \rangle = \left.\frac{\partial^4 F}{\partial X_{k_1}\cdots\partial X_{k_4}}\right|_{X=0} = (\beta^{-1})_{k_4,k_3}(\beta^{-1})_{k_1,k_2} + (\beta^{-1})_{k_4,k_1}(\beta^{-1})_{k_3,k_2} + (\beta^{-1})_{k_4,k_2}(\beta^{-1})_{k_1,k_3}$$

It is a simple exercise to prove, that $\langle x_{k_1}\cdots x_{k_n} \rangle = 0$ for odd n while for even n we have the result which is sum of products of β^{-1} over all possible pairings – Wick's theorem.

LECTURE 25
Fluctuations of fundamental thermodynamical quantities.

25.1. Fluctuations of fundamental thermodynamical quantities. LL 112

Consider a small, but macroscopic subsystem of a large macroscopic system (heat bath). The thermodynamical variables describing the subsystem will fluctuate around their average values. We want to understand these fluctuations.

Consider the whole system. From this point of view the fluctuation of the subsystem brings the whole system out of equilibrium. This means that the entropy of the whole system decreases.

The microcanonical distribution for the whole system is proportional to $e^{\Delta S_w}$. So the probability of the fluctuation of the subsystem is proportional to the $e^{\Delta S_w}$, where ΔS_w is the change of entropy of the whole system.

Let's calculate this change of entropy of the whole system when the subsystem changes its macroscopic state. This change of the entropy has been calculated before (see section 8.1) and is equal to

$$\Delta S_w = -\frac{R_{min}}{T_0},$$

where R_{min} is the minimal work required to bring the subsystem into the changed state, and T_0 is the bath temperature.

$$R_{min} = \Delta E - T_0 \Delta S + P_0 \Delta V,$$

where E, S, and V are the energy, entropy, and volume of the subsystem. Consider the change of the subsystem. Its energy $E(S, V)$ changes and if the fluctuations are small we can write

$$\Delta E = \frac{\partial E}{\partial S}\Delta S + \frac{\partial E}{\partial V}\Delta V + \frac{1}{2}\frac{\partial^2 E}{\partial S^2}(\Delta S)^2 + \frac{\partial^2 E}{\partial S \partial V}\Delta S \Delta V + \frac{1}{2}\frac{\partial^2 E}{\partial V^2}(\Delta V)^2$$

But $\partial E/\partial S = T_0$, and $\partial E/\partial V = -P_0$. So for the minimal work we find

$$R_{min} = \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\Delta S)^2 + 2\frac{\partial^2 E}{\partial S \partial V}\Delta S \Delta V + \frac{\partial^2 E}{\partial V^2}(\Delta V)^2\right].$$

It can be rewritten using

$$\frac{\partial^2 E}{\partial S^2}(\Delta S)^2 + 2\frac{\partial^2 E}{\partial S \partial V}\Delta S \Delta V + \frac{\partial^2 E}{\partial V^2}(\Delta V)^2 =$$

$$\Delta S \left(\Delta S \frac{\partial}{\partial S}\frac{\partial E}{\partial S} + \Delta V \frac{\partial}{\partial V}\frac{\partial E}{\partial S} \right) + \Delta V \left(\Delta S \frac{\partial}{\partial S}\frac{\partial E}{\partial V} + \Delta V \frac{\partial}{\partial V}\frac{\partial E}{\partial V} \right) =$$

$$\Delta S \left(\Delta S \frac{\partial}{\partial S} + \Delta V \frac{\partial}{\partial V} \right)\frac{\partial E}{\partial S} + \Delta V \left(\Delta S \frac{\partial}{\partial S} + \Delta V \frac{\partial}{\partial V} \right)\frac{\partial E}{\partial V} =$$

$$\Delta S \Delta \left(\frac{\partial E}{\partial S} \right) + \Delta V \Delta \left(\frac{\partial E}{\partial V} \right) = \Delta S \Delta T - \Delta V \Delta P$$

so

$$\Delta S_w = -\frac{\Delta S \Delta T - \Delta V \Delta P}{2 T_0}$$

The probability of subsystem fluctuation with given ΔS, ΔT, ΔV, and ΔP is thus

$$w \propto \exp\left(\frac{\Delta V \Delta P - \Delta S \Delta T}{2 T_0} \right)$$

However, S, T, V, and P are not all independent variables. Only two of them are independent, the other two must be expresses through the independent ones.

25.1.1. T and V

Consider first temperature and volume as independent variables. Then we have

$$\Delta S = \left(\frac{\partial S}{\partial T} \right)_V \Delta T + \left(\frac{\partial S}{\partial V} \right)_T \Delta V = \frac{C_V}{T}\Delta T + \left(\frac{\partial P}{\partial T} \right)_V \Delta V$$

$$\Delta P = \left(\frac{\partial P}{\partial T} \right)_V \Delta T + \left(\frac{\partial P}{\partial V} \right)_T \Delta V$$

Thus

$$\Delta V \Delta P - \Delta S \Delta T = -\frac{C_V}{T}(\Delta T)^2 + \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2$$

According to the thermodynamic inequality the derivative $(\partial P / \partial V)_T$ is negative and C_V is positive. Notice, that without this inequalities we would not be sure that the fluctuations do not diverge. Or in the other way, one can say that the requirement that the equilibrium state is stable against small fluctuations is the origin of the thermodynamic inequalities.

From our understanding of the Gaussian integrals we read off right away

$$\langle (\Delta T)^2 \rangle = T^2/C_V, \quad \langle (\Delta V)^2 \rangle = -T\left(\frac{\partial V}{\partial T} \right)_T = TV\beta_T, \quad \langle \Delta T \Delta V \rangle = 0$$

25.1.2. P and S

If we consider P and S as independent variables, then we find

$$\Delta V = \left(\frac{\partial V}{\partial P} \right)_S \Delta P + \left(\frac{\partial V}{\partial S} \right)_P \Delta S = \left(\frac{\partial V}{\partial P} \right)_S \Delta P + \left(\frac{\partial T}{\partial P} \right)_S \Delta S$$

$$\Delta T = \left(\frac{\partial T}{\partial P} \right)_S \Delta P + \left(\frac{\partial T}{\partial S} \right)_P \Delta S = \left(\frac{\partial T}{\partial P} \right)_S \Delta P + \frac{T}{C_P}\Delta S$$

So for the fluctuation probability we get

$$w \propto \exp\left(\frac{1}{2T}\left(\frac{\partial V}{\partial P}\right)_S (\Delta P)^2 - \frac{1}{2C_P}(\Delta S)^2\right)$$

and then

$$\langle(\Delta S)^2\rangle = C_p, \quad \langle(\Delta P)^2\rangle = -T(\partial P/\partial V)_S = T/V\beta_S, \quad \langle\Delta S\Delta P\rangle = 0$$

25.1.3. Fluctuation of Energy.

Knowing these standard deviations for T, S, V, and P allows us to find the other averages. Lets calculate the energy fluctuation $\langle(\Delta E)^2\rangle$. We consider E as function of V and T and write:

$$\Delta E = \left(\frac{\partial E}{\partial V}\right)_T \Delta V + \left(\frac{\partial E}{\partial T}\right)_V \Delta T = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]\Delta V + C_V\Delta T = [T\alpha/\beta_T - P]\Delta V + C_V\Delta T$$

Taking the square and averaging we find

$$\langle(\Delta E)^2\rangle = [T\alpha - P\beta_T]^2 TV + C_V T^2$$

Notice, that $\langle(\Delta E)^2\rangle \propto V$, as it should. Also for ideal gas energy does not depend on volume, and we get $\langle(\Delta E)^2\rangle = C_V T^2$.

25.1.4. Fluctuation of the number of particles.

Let's take the formula for the fluctuation of the volume. It was calculated assuming fixed number of particles. Lets then divide it by the number of particles squared. We get

$$\left\langle(\Delta(V/N))^2\right\rangle = \frac{TV\beta_T}{N^2}$$

Now we can consider this fluctuation as a fluctuation of volume at fixed N, or fluctuations of N at fixed V – it is the same process. But in the later case we write $\Delta(V/N) = -(V/N^2)\Delta N$, so we have

$$\langle(\Delta N)^2\rangle = TV\beta_T(N/V)^2$$

Again this is proportional to the volume. For the ideal gas it gives $\langle(\Delta N)^2\rangle = PN/k$.

Notice, that the fluctuations of extensive variables S, V, N, E are proportional to the size of the system, while fluctuations of the intensive variables T and P are proportional to the inverse of the system size.

LECTURE 26
Canonical distribution.

26.1. Canonical (Gibbs) distribution.

Canonical (unlike Grand Canonical) Gibbs distribution is the distribution over states for fixed number of particles.

$$w_n = Ae^{-E_n/T}\text{— Quantum.} \qquad dw(\mathbf{p},\mathbf{q}) = Ae^{-E(\mathbf{p},\mathbf{q})/T}d\mathbf{p}d\mathbf{q} \text{ — Classical.}$$

There are cases when some of the microscopic degrees of freedom can be considered classically (such as translation motion), while the others are quantum (such as internal degrees of freedom of molecules/atoms). In this case we can use

$$dw_n = Ae^{-E_n(\mathbf{p}_{cl},\mathbf{q}_{cl})/T}d\mathbf{p}_{cl}d\mathbf{q}_{cl}$$

26.2. Virial theorem

Let's consider a Hamiltonian $E(\mathbf{p},\mathbf{r}) = K(\mathbf{p}) + U(\mathbf{r})$, where the potential energy of the interaction of the particles is a homogeneous function of degree n of the coordinates of all particles, meaning

$$U(\lambda\mathbf{r}) = \lambda^n U(\mathbf{r}), \quad \forall \lambda > 0$$

For example a Coulomb interaction is a homogeneous potential of degree -1. The requirement of homogeneity seems to be a serious restriction on a potential, however, almost any potential at asymptotically large distances will have this property or it will decay exponentially.

Notice, that normally kinetic energy $K(\mathbf{p})$ is a a homogeneous function of all momenta of degree 2. We will consider a more general case, when the kinetic energy is a homogeneous function of momenta of degree m. Also notice, that differentiating a a homogeneous function of degree n with respect to λ and then using $\lambda = 1$ we find

$$\sum_i \mathbf{r}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} U(\mathbf{r}) = nU(\mathbf{r})$$

Lets take a sum $\sum_i \mathbf{r}_i \cdot \mathbf{p}_i$ over all particles and find its time derivative.

$$\frac{d}{dt}\sum_i \mathbf{r}_i \cdot \mathbf{p}_i = \sum_i \frac{d}{dt}\mathbf{r}_i \cdot \mathbf{p}_i + \sum_i \mathbf{r}_i \cdot \frac{d}{dt}\mathbf{p}_i = \sum_i \frac{\partial K(\mathbf{p})}{\partial \mathbf{p}_i} \cdot \mathbf{p}_i + \sum_i \mathbf{r}_i \cdot \frac{d}{dt}\mathbf{p}_i = mK(\mathbf{p}) + \sum_i \mathbf{r}_i \cdot \frac{d}{dt}\mathbf{p}_i$$

Let's take an average of this equation. As $\sum_i \mathbf{r}_i \cdot \mathbf{p}_i$ is a bounded function the average of its time derivative is zero, so we have

$$mK + \left\langle \sum_i \mathbf{r}_i \cdot \dot{\mathbf{p}}_i \right\rangle = 0,$$

where K is averaged total kinetic energy.

$\dot{p}_i$ is all the forces that act on a particle. These are forces of interatomic interactions $-\frac{\partial U(\mathbf{r})}{\partial \mathbf{r}_i}$ plus the forces on the boundary $P d\mathbf{f}$, where P is pressure and $d\mathbf{f}$ is the element of area. So we have

$$\left\langle \sum_i \mathbf{r}_i \cdot \dot{\mathbf{p}}_i \right\rangle = - \left\langle \sum_i \mathbf{r}_i \cdot \frac{\partial U(\mathbf{r})}{\partial \mathbf{r}_i} \right\rangle - P \oint \mathbf{r} \cdot d\mathbf{f} = -nV - P \int \nabla \cdot \mathbf{r} dV = -nU - DPV,$$

where D is the space dimensionality, normally $D = 3$.

Finally we have

$$mK - nU - DPV = 0$$

For ideal gas $U = 0$ then

$$E = K = \frac{D}{m} PV.$$

In general case $U = E - K$ and we have

$$K = \frac{n}{m+n} E + \frac{D}{m+n} PV, \quad \text{for } n \neq -m \text{ and } E = \frac{D}{m} PV, \quad \text{for } n = -m.$$

For classical gas $(m = 2)$ with Coulomb's interaction $n = -1$ in $3D$:

$$K = -E + 3PV$$

LECTURE 27
Maxwell distribution.

27.1. Maxwell distribution. LL 29

The separation of energy in the kinetic and potential energies is standard in classical mechanics, so

$$E(\mathbf{p}, \mathbf{r}) = K(\mathbf{p}) + U(\mathbf{r}),$$

and then

$$dw(\mathbf{p}, \mathbf{r}) = A_1 e^{-K(\mathbf{p})/T} d\mathbf{p} A_2 e^{-U(\mathbf{q})/T} d\mathbf{q} = dw(\mathbf{p}) dw(\mathbf{r})$$

The kinetic energy of a body is the sum of the kinetic energies of all particles, so

$$dw(\mathbf{p}) = \prod_i w(\mathbf{p}_i) dp_{x_i} dp_{y_i} dp_{z_i},$$

where now $w(\mathbf{p}_i) dp_{x_i} dp_{y_i} dp_{z_i}$ is the probability for a single particle to have a momentum $\mathbf{p}_i$. As the probability to find a particle at some momentum state is always 1 we can use $\int dw(\mathbf{p}_i) = 1$ and find that

$$dw_p = \frac{1}{(2\pi m T)^{3/2}} e^{-(p_x^2 + p_y^2 + p_z^2)/2mT} dp_x dp_y dp_z$$

This is Maxwell distribution. Notice, that it does not depend on the way particle interact with each other or with outside world. It can be written as a distribution of velocities

$$dw_v = \left(\frac{m}{2\pi T}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2T} dv_x dv_y dv_z.$$

Factorizing even further we have

$$dw_{v_x} = \left(\frac{m}{2\pi T}\right)^{1/2} e^{-mv_x^2/2T} dv_x$$

In particular we see, that

$$\overline{v_x} = 0, \qquad \overline{v_x^2} = T/m.$$

and then

$$\langle \vec{v} \rangle = 0, \qquad \langle \vec{v}^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\langle v_x^2 \rangle = \frac{3T}{m}, \qquad \sqrt{\langle \vec{v}^2 \rangle} = \sqrt{3T/m}.$$

We now can calculate the average kinetic energy of a particle

$$K = m\overline{v^2}/2 = 3T/2.$$

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Together with virial theorem $2K - nU - 3PV = 0$ it gives

$$NT - PV = \frac{n}{3}U$$

27.2. Solid angle

We can ask what is the probability for particle in a gas to have the magnitude of the velocity between v and $v + dv$ and the direction of the velocity within a solid angle $d\Omega$. Using $dv_x dv_y dv_z = v^2 dv d\Omega = v^2 \sin\theta d\theta d\phi dv$ we see that

$$dw = \left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T} v^2 dv d\Omega = \left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T} v^2 \sin\theta d\theta d\phi dv$$

For example we can calculate the average magnitude of the velocity

$$\langle v \rangle = \left(\frac{m}{2\pi T}\right)^{3/2} \int_0^\infty e^{-mv^2/2T} v^3 dv d\Omega = \left(\frac{8T}{\pi m}\right)^{1/2}, \qquad \langle v \rangle = \sqrt{\frac{8}{3\pi}} \sqrt{\langle \vec{v}^2 \rangle}.$$

Or we can calculate how many particles hit an area $d\mathcal{A}$ per unit time. Consider a cylinder with the base $d\mathcal{A}$ at the angle θ, ϕ to the normal to the $d\mathcal{A}$ with the length vdt. The volume of this cylinder is $dV = d\mathcal{A}\cos\theta vdt$ the number of particles in this cylinder with velocity v moving in the right direction is $ndV \left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T} v^2 \cos\theta$, so the total number of particles hitting the wall is

$$dz = \int_0^\infty \int_0^{2\pi} \int_0^{\pi/2} nd\mathcal{A}\cos\theta vdt \left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T} v^2 \sin\theta dv d\theta d\phi =$$

$$2\pi nd\mathcal{A}dt \left(\frac{m}{2\pi T}\right)^{3/2} \int_0^\infty \int_0^{\pi/2} e^{-mv^2/2T} v^3 \cos\theta \sin\theta dv d\theta = d\mathcal{A}dt\frac{1}{4}\left(\frac{8T}{\pi m}\right)^{1/2} = \frac{1}{4}n\langle v\rangle d\mathcal{A}dt$$

More useful is a differential form of this equation. Namely we want to know how many particles hit the wall with velocity between v and $v + dv$ coming at the angles between ϕ and $\phi + d\phi$ and θ and $\theta + d\theta$ per unit area per unit time. Looking at the integrand above we see

$$z(v, \phi, \theta) = n\left(\frac{m}{2\pi T}\right)^{3/2} e^{-mv^2/2T} v^3 \cos\theta \sin\theta$$

In particular if we want to calculate the normal force acting on the wall we notice, that the particle with velocity v and angles ϕ, θ changes its momentum after an elastic collision by $2mv\cos\theta$. The total change of momentum then is

$$dp = d\mathcal{A}dt \int z(v, \phi, \theta) 2mv \cos\theta dv d\theta d\phi = nTd\mathcal{A}dt$$

Then we can calculate the force $f = dp/dt = nTd\mathcal{A}$. Finally we can calculate the pressure $P = f/d\mathcal{A}$,

$$P = nT,$$

where n is the density of particles close to the wall.

LECTURE 28
Ising model.

28.1. Ising model. Mean field.

The problem of N independent spins $1/2$ was considered in Homework 6. What was found is that

$$\chi(T, h) = \frac{N(\mu/2)^2}{T} \frac{1}{\cosh^2(\mu h/2T)}, \qquad \chi(T, h = 0) = \frac{N(\mu/2)^2}{T}$$

The magnetic susceptibility at zero field is inversely proportional to the temperature and diverges at $T = 0$. This is called Curie law.

Let's see how interactions change this picture. For this we will consider a simpler problem/model, which is called Ising model. Here is how it is formulated.

On every site of a D-dimensional square lattice there is a classical variable σ which can be equal either $+1$ or -1 (They are classical as they are not operators). Such variables sometimes are called Ising spins. Two neighboring Ising spins interact with each other, the spins also interact with the magnetic field h. So the Hamiltonian is

$$\mathcal{H} = -\frac{1}{2}J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i,$$

where $\sum_{\langle i,j \rangle}$ means summation over all nearest neighbors (summation over bonds. As each bond counts twice, we put $1/2$ in front). The total number of sites N of the lattice is large. We are mostly interested in thermodynamic limit $N \to \infty$.

Let's consider this model for $h = 0$. It is clear that if $J > 0$, then all spins tend to have the same direction — ferromagnetic. If $J < 0$, then the directions of the spins alternate — antiferromagnetic. In a bipartite lattice such as square lattice we can substitute $\sigma \to -\sigma$ in every other site. This substitution will change $J \to -J$. So in a bipartite lattice the two cases are equivalent. They are not, however, equivalent for, say, triangle lattice.

One needs to find a partition function of this model

$$Z = \sum_n e^{-E_n/T}$$

where n enumerates different states. Each state is a list of N numbers, each number is either $+1$, or -1. E_n is the energy of such state.

The partition function can be calculated exactly (in thermodynamic limit) for $D = 2$ (Onsager solution) and for $D = 1$ – this will be in the next homework. The exact solution for $D > 2$ is not known.

It is, however possible to calculate it approximately by what is called mean field approximation. The word of caution: this is an approximate solution, the validity of the approximation must be checked separately. It terns out that in the cases of $D = 1$ and $D = 2$ this approximation is not valid and gives a wrong answer.

Here how the mean field approximation works. At finite temperature on each site we will have a probability to find σ either at $+1$ or at -1. The average $\bar{\sigma}$ is some number from -1 to $+1$. As the system is translation invariant the average $\bar{\sigma}$ is independent of which site it is. If the fluctuations are "small" then the we can use averages instead of σ everywhere. Or we can substitute the mean value $\bar{\sigma}$ instead of σ_i.

Let's consider a single site i_0. The spin σ_{i_0} is interacting with $2D$ of its nearest neighbors. Each nearest neighbor site has a mean value of spin $\bar{\sigma}$. So the total energy of the spin on the sight i_0 is

$$\mathcal{H}_{i_0} = -(JD\bar{\sigma} + h)\sigma_{i_0} = -h_m \sigma_{i_0}$$

We see, that the spin σ_{i_0} fluctuates in a mean field $h_m = JD\bar{\sigma} + h$ which is a sum of the external field and the field from all nearest neighbors. It is also clear, that the larger the number of the nearest neighbors is the better it is to substitute the mean value for them.

The probability to find $\sigma_{i_0} = \pm 1$ is given by $Ae^{-h_m \sigma_{i_0}/T}$, where A is the normalization constant given by $A \sum_{\sigma_{i_0}=\pm 1} e^{h_m \sigma_{i_0}/T} = 1$. Now we want to calculate the mean value of σ_{i_0}:

$$\bar{\sigma}_{i_0} = \frac{\sum_{\sigma_{i_0}=\pm 1} \sigma_{i_0} e^{h_m \sigma_{i_0}/T}}{\sum_{\sigma_{i_0}=\pm 1} e^{h_m \sigma_{i_0}/T}} = \tanh(h_m/T)$$

But according to our notations $\bar{\sigma}_{i_0}$ is just $\bar{\sigma}$. So we have an equation

(28.1) $$\bar{\sigma} = \tanh(JD\bar{\sigma}/T + h/T)$$

Let's consider different cases

28.1.1. $J = 0$

The spins are independent from each other, The total magnetization and susceptibility are

$$M = N\bar{\sigma} = N\tanh(h/T), \qquad \chi(T,h) = \frac{\partial M}{\partial h} = \frac{N}{T} \frac{1}{\cosh^2(h/T)}, \qquad \chi(T, h = 0) = \frac{N}{T}$$

The result is very similar to the one for the independent spins. The susceptibility at zero field diverges as $1/T$ at small temperature.

28.1.2. $J \neq 0$, $h = 0$

Our equation is

$$\bar{\sigma} = \tanh\left(\frac{JD}{T}\bar{\sigma}\right)$$

Comparing two graphs $y = x$ and $y = \tanh(\alpha x)$ we see, that this equation has a single solution $\bar{\sigma} = 0$ for $T > JD$ and has three solutions for $T < JD$. It means that there is a phase transition at $T = T_c \equiv JD$.

Let's calculate a zero field susceptibility $\chi(T) = N\partial\bar{\sigma}/\partial h|_{h=0}$ close to the transition temperature. Close to the transition at very small fields we expect $\bar{\sigma}^2 \ll 1$. Let's solve (28.1) for small $\bar{\sigma}$, h, at T close, but larger than T_c. We have

$$\bar{\sigma} \approx \frac{T_c}{T}\bar{\sigma} + \frac{h}{T}, \qquad \bar{\sigma} \approx \frac{h}{T - T_c},$$

so that

$$\chi = \frac{N}{T - T_c}$$

We see that although at $T > T_c$ the net magnetization is zero, the susceptibility diverges when $T \to T_c$. The system responds to the external field more and more enthusiastically.

In order to find a differential susceptibility at arbitrary temperature we need to differentiate (28.1) with respect to h at fixed temperature. We then find

$$\chi = N\frac{1 - \bar{\sigma}^2}{T - T_c(1 - \bar{\sigma}^2)}. \qquad \chi(T \approx T_c) = \frac{N}{T - T_c}, \qquad \chi(T \to 0) \approx \frac{4N}{T}e^{-2T_c/T} \to 0.$$

28.2. Effective Mean field theory.

I want to construct an effective mean field theory. What it means is that I wan to write energy not as a function of local fluctuating parameters σ_i, but as a function of some parameter which has the meaning of the average sigma $\bar{\sigma}$ at equilibrium. I'll do that for the case $h = 0$. I need to calculate the partition function.

$$Z = \sum_{\{\sigma_i\}} e^{\frac{J}{2T}\sum_{\langle i,j\rangle}\sigma_i\sigma_j}$$

where the summation is over all possible sets of σ's. I want to express this partition function as an integral over some variable ϕ which at equilibrium has a meaning of average sigma. Using the fact that $\int_{-\infty}^{\infty} d\phi\delta(\phi - \frac{1}{N}\sum_i \sigma_i) = 1$, I write

$$Z = \int_{-\infty}^{\infty} d\phi \sum_{\{\sigma_i\}} \delta(\phi - \frac{1}{N}\sum_i \sigma_i)e^{\frac{J}{2T}\sum_{\langle i,j\rangle}\sigma_i\sigma_j} = \int_{-\infty}^{\infty} d\phi \sum_{\{\sigma_i\}} \delta(\phi - \frac{1}{N}\sum_i \sigma_i)e^{\frac{JD}{T}\sum_i \sigma_i\frac{1}{2D}\sum'_j \sigma_j} \approx$$

$$\int_{-\infty}^{\infty} d\phi \sum_{\{\sigma_i\}} \delta(\phi - \frac{1}{N}\sum_i \sigma_i)e^{\frac{JD}{T}\sum_i \sigma_i\phi}.$$

The sum with prime in $\frac{1}{2D}\sum'_j \sigma_j$ is the sum over all neighbors of the site i. I approximated this sum by the average $\frac{1}{N}\sum_j \sigma_j$, where summation is over ALL sites. Then I substituted ϕ instead of this sum since δ-function ensures that it can be done.

In the next step I will use $\delta(x) = \int d\lambda e^{ix\lambda}$ to represent the δ-function.

$$Z = \int_{-\infty}^{\infty} d\phi \sum_{\{\sigma_i\}} \int_{-\infty}^{\infty} d\lambda e^{i\lambda\phi}e^{-i\lambda\frac{1}{N}\sum_i \sigma_i}e^{\frac{JD}{T}\sum_i \sigma_i\phi} = \int_{-\infty}^{\infty} d\phi \int_{-\infty}^{\infty} d\lambda e^{i\lambda\phi} \sum_{\{\sigma_i\}} e^{\sum_{i=1}^{N}\sigma_i\left(-i\frac{\lambda}{N} + \frac{JD}{T}\phi\right)}$$

$$= \int_{-\infty}^{\infty} d\phi \int_{-\infty}^{\infty} d\lambda e^{i\lambda\phi} \sum_{\{\sigma_i\}} \prod_{i=1}^{N} e^{\sigma_i\left(-i\frac{\lambda}{N} + \frac{JD}{T}\phi\right)}.$$

We see that all sites are now independent. So instead to first take a product for a given state $\{\sigma_i\}$ and then sum over all possible states of N sites. I can first sum over all possible states

of one site an then take a product over all sites.

$$Z = \int_{-\infty}^{\infty} d\phi \int_{-\infty}^{\infty} d\lambda e^{i\lambda\phi} \prod_{i=1}^{N} \sum_{\sigma=\pm1} e^{\sigma\left(-i\frac{\lambda}{N} + \frac{JD}{T}\phi\right)} = \int_{-\infty}^{\infty} d\phi \int_{-\infty}^{\infty} d\lambda e^{i\lambda\phi} \left(2\cosh\left(-i\frac{\lambda}{N} + \frac{JD}{T}\phi\right)\right)^N$$

$$= 2^N \int_{-\infty}^{\infty} d\phi \int_{-\infty}^{\infty} d\lambda e^{i\lambda\phi + N\log\left(\cosh\left(-i\frac{\lambda}{N} + \frac{JD}{T}\phi\right)\right)}$$

the argument of cosh is small, so me can write $\log\left(\cosh\left(-i\frac{\lambda}{N} + \frac{JD}{T}\bar\sigma\right)\right) \approx \frac{1}{2}\left(JD\bar\sigma/T - i\lambda/N\right)^2 + \frac{5}{24}\left(JD\bar\sigma/T\right)^4$. We will also see, that typical λ/N in integration are of the order of $(T - T_c)\phi$ and even later we will see, that typical ϕ close to transition are of the order of $\sqrt{T - T_c}$, so close to the transition λ/N is of the order of $\lambda/N \sim (T - T_c)^{3/2} \sim \phi\phi^3$. It means that in the fourth order term we can neglect λ/N.

$$Z = 2^N \int_{-\infty}^{\infty} d\phi \int_{-\infty}^{\infty} d\lambda e^{i\lambda\phi + N\frac{1}{2}(\lambda/N + iJD\phi/T)^2} e^{N\frac{5}{24}(JD\phi/T)^4}$$

So we got the Gaussian integral over λ. Taking it we find

$$Z \propto \int_{-\infty}^{\infty} d\phi e^{-N\left((T-JD)\phi^2 + \frac{5(JD)^4}{24T^3}\phi^4\right)/T}$$

We see that the effective energy has a form

(28.2) $\qquad\qquad NF(\phi, T) \qquad$ where $\qquad F(\phi) = (T - JD)\phi^2 + b\phi^4,$

where ϕ is a continuous variable. Notice, that because of the factor N in the exponent the integrand has a very sharp maximum at the value of ϕ at which (28.2) has a minimum. The fluctuations of the variable ϕ are very small. We then can treat (28.2) as a free energy of our system which depends on a parameter ϕ, where the equilibrium value of ϕ is given by the minimum of $F(\phi, T)$ at fixed T. The value of ϕ has a meaning of the average $\langle\sigma_i\rangle$. We saw such free energy before. It has a phase transition at $T = T_c \equiv JD$.

LECTURE 29
Thermodynamic perturbation theory.

29.1. $\int' d\Gamma = \frac{1}{N!} \int d\Gamma$

In the Gibbs distribution we have the sum over all different quantum mechanical states $\sum_n$ of the system. As we know in the WKB approximation we change:

$$\sum_n \rightarrow \int' \frac{d^{3N}\mathbf{p}\, d^{3N}\mathbf{q}}{(2\pi\hbar)^{3N}}.$$

One, however, should remember that the integral over phase space stands for the summation of the *different* states. The prime in the integration sign is to remind about it. In particular if the particles are identical, then the exchange of the particles does not change the state. So we need to integrate over the part of the phase space which does not include the particles exchange. This can be done simpler by noting that there is $N!$ ways to exchange N particles, so the one concludes that $\int' = \frac{1}{N!} \int$, where the last integration is done over the full $6N$ dimensional space.

29.2. Classical and Quantum oscillator. LL 30

It was considered in the problems in Homework 6 and 7.

29.3. Thermodynamic perturbation theory. LL 32

Let's consider the following situation. We know how to calculate the free energy F_0 for a Hamiltonian H_0, but the real Hamiltonian of our system differs from H_0 by a small perturbation V. We want to calculate the correction to the free energy F_0. We will do that both classically and using quantum mechanics.

29.4. Classical.

In classical mechanics we write

$$E(\mathbf{p}, \mathbf{q}) = E_0(\mathbf{p}, \mathbf{q}) + V(\mathbf{p}, \mathbf{q}),$$

where V is small.

To calculate the free energy we write

$$e^{-F/T} = \int' e^{-E_0(\mathbf{p},\mathbf{q})/T} e^{-V(\mathbf{p},\mathbf{q})/T} d\Gamma \approx \int' e^{-E_0(\mathbf{p},\mathbf{q})/T} \left(1 - \frac{V(\mathbf{p},\mathbf{q})}{T} + \frac{V^2(\mathbf{p},\mathbf{q})}{2T^2}\right) d\Gamma =$$

$$e^{-F_0/T} \int' e^{F_0 - E_0(\mathbf{p},\mathbf{q})/T} \left(1 - \frac{V(\mathbf{p},\mathbf{q})}{T} + \frac{V^2(\mathbf{p},\mathbf{q})}{2T^2}\right) d\Gamma = e^{-F_0/T} \left(1 - \frac{\langle V\rangle_0}{T} + \frac{\langle V^2\rangle_0}{2T^2}\right),$$

where $\langle\rangle_0$ is averaging with respect to the unperturbed Hamiltonian.

Taking the logarithm of the above we find

$$F = F_0 + \langle V\rangle_0 - \frac{1}{2T}\langle(V - \langle V\rangle_0)^2\rangle_0$$

Notice:the first order correction is just the mean value of the perturbation; the second order correction is always negative, so if $\bar{V} = 0$ the perturbation decreases the free energy.

The validity of this expansion can be deduced from the requirement that the second order correction is much smaller then the first order. As both correction are roughly proportional to the number of particles it means that the perturbation energy per particle must be smaller than temperature.

29.5. Quantum.

Now we do the same for the quantum case. We have

$$\hat{H} = \hat{H}_0 + \hat{V}.$$

Where we know all the energy levels $E_n^{(0)}$ (I assume they are not degenerate) and wave functions $\psi_n^{(0)}$ of the "zeroth order" Hamiltonian $\hat{H}_0$. We then know the "zeroth order" free energy $F_0 = \mathrm{tr}e^{-\hat{H}_0/T}$. We want to calculate the correction to the free energy due to the perturbation $\hat{V}$.

We start from pure quantum mechanical problem to calculate the corrections to the energy levels. In order to calculate the correction to the energy levels due to the perturbation $\hat{V}$ we need to calculate all matrix elements of the perturbation $V_{nm} = \langle\psi_n^{(0)*}|\hat{V}|\psi_m^{(0)}\rangle$ ($\langle\rangle$ in this formula is just quantum mechanical averaging) and then calculate

$$E_n = E_n^{(0)} + V_{nn} + {\sum_m}' \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} = E_n^{(0)} + \delta E_n^{(1)} + \delta E_n^{(2)},$$

We can now calculate the correction to the partition function.

$$e^{-F/T} = \sum_n e^{-E_n/T} = e^{-F_0/T}\sum_n e^{(F_0 - E_n^{(0)})/T - \delta E_n^{(1)}/T - \delta E_n^{(2)}/T} = e^{-F_0/T}\sum_n e^{(F_0 - E_n^{(0)})/T}e^{-\delta E_n^{(1)}/T - \delta E_n^{(2)}/T} \approx$$

$$e^{-F_0/T}\sum_n e^{(F_0 - E_n^{(0)})/T}\left(1 - \delta E_n^{(1)}/T - \delta E_n^{(2)}/T + \frac{1}{2}\left(\frac{\delta E_n^{(1)}}{T}\right)^2\right) =$$

$$e^{-F_0/T}\left(1 - \frac{1}{T}\sum_n w_n \delta E_n^{(1)} - \frac{1}{T}\sum_n w_n \delta E_n^{(2)} + \frac{1}{2T^2}\sum_n w_n\left(\delta E_n^{(1)}\right)^2\right),$$

where $w_n = e^{(F_0 - E_n^{(0)})/T}$ – unperturbed Gibbs distribution. This is correct up to the second order in perturbation. Now we take the logarithm of the both sides and again expand it up

to the second order in perturbation.

$$F = F_0 + \sum_n w_n \delta E_n^{(1)} + \sum_n w_n \delta E_n^{(2)} - \frac{1}{2T} \sum_n w_n \left(\delta E_n^{(1)} \right)^2 + \frac{1}{2T} \left(\sum_n w_n \delta E_n^{(1)} \right)^2$$

This formula can be rewritten in the following way

$$F = F_0 + \sum_n w_n \delta E_n^{(1)} + \sum_n w_n \delta E_n^{(2)} - \frac{1}{2T} \sum_n w_n \left[\left(\delta E_n^{(1)} \right)^2 - \left(\sum_{n'} w_{n'} \delta E_{n'}^{(1)} \right)^2 \right]$$

Using expressions for $\delta E^{(1)}$ and $\delta E^{(2)}$ we find $\sum_n w_n \delta E^{(1)} = \sum_n w_n V_{nn} = \bar{V}$, $\sum_n w_n \left(\delta E^{(1)} \right)^2 = \overline{V_{nn}^2}$. Notice, that in the last formula it is not the average of the $\hat{V}^2$, as $\widehat{\bar{V}^2} = \sum_n w_n \sum_m V_{nm}^* V_{mn}$, while we have only $\sum_n w_n V_{nn} V_{nn}$!!! That is why I use the notation $\overline{V_{nn}^2}$. The second term can be written as

$$\sum_n w_n \delta E^{(2)} = \sum_n w_n {\sum_m}' \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} = \sum_{m \neq n} \frac{w_n |V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} = -\frac{1}{2} \sum_{m \neq n} \frac{(w_m - w_n)|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}$$

This term is always negative, as $\frac{w_m - w_n}{E_n^{(0)} - E_m^{(0)}}$ is always positive. Then

$$F = F_0 + \bar{V} - \frac{1}{2} \sum_{m \neq n} \frac{(w_m - w_n)|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} - \frac{1}{2T} \langle (V_{nn} - \bar{V})^2 \rangle$$

Again both second order correction terms are negative. And again the result is correct if the perturbation energy per particle is less then temperature.

If the differences between the energy levels are also small in comparison to the temperature, then the result can be simplified further. Using $w_m = e^{-E_m^{(0)}/T} = e^{-E_n^{(0)}/T} e^{(E_n^{(0)} - E_m^{(0)})/T} \approx w_n + \frac{1}{T} w_n (E_n^{(0)} - E_m^{(0)})$, we find that the second term becomes

$$-\frac{1}{2} \sum_{m \neq n} \frac{(w_m - w_n)|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} = -\frac{1}{2T} \sum_{m \neq n} w_n |V_{nm}|^2$$

Together with the third term it gives

$$-\frac{1}{2T} \sum_{m \neq n} w_n V_{nm}^* V_{mn} - \frac{1}{2T} \sum_n w_n (V_{nn})^2 + \frac{1}{2T} \bar{V}^2 = -\frac{1}{2T} \sum_{m,n} w_n V_{nm}^* V_{mn} + \frac{1}{2T} \bar{V}^2 =$$

$$-\frac{1}{2T} \left(\langle \hat{V}^2 \rangle - \bar{V}^2 \right) = -\frac{1}{2T} \langle (\hat{V} - \bar{V})^2 \rangle$$

We then have

$$F = F_0 + \bar{V} - \frac{1}{2T} \langle (\hat{V} - \bar{V})^2 \rangle$$

Formally this is the same result as classical. However, in this expression the average is both quantum mechanical and statistical.

LECTURE 30
Grand canonical ensemble.

30.1. Gibbs distribution for a variable number of particles. LL 35

The Gibbs distribution $w_n = e^{(F-E_n)/T}$ assumes that the number of particles is constant. It is not always so. Moreover, in calculation of the partition function the conserved number of particle is often a constraint which is difficult to keep. So in many cases it is beneficial or necessary to consider the number of particle as one of the variables.

To make this problem meaningful me need to fix the volume of the system and instead of the change of the volume think that particles go out or into the fixed volume.

In such a case as the particles may interact the energy levels E_{nN} of the system are labeled by the quantum numbers n and the number of particles N.

Let's now consider our system and the thermal bath it is coupled to together. The total number of particles in both systems together is N_0 and is conserved, the total energy is E_0 and is also conserved. If the system has energy E , number of particles N and we denote the element of it's phase space as $d\Gamma$, while the same for the bath we denote as E', N', and $d\Gamma'$, then microcanonical distribution is

$$dw = \text{const.} \times \delta(E + E' - E_0)d\Gamma d\Gamma'.$$

What we want is to find the probability for our system to be in a state which is characterized by the number of particles N and energy E_{nN}. The state of the thermal bath is of no interest for us, so we need to sum over all possible states of the bath, while keeping N and E_{nN} of our system. We thus want to find

$$w_{nN} = \text{const.} \times \delta(E_{nN} + E' - E_0)d\Gamma'$$

(We integrate out all degrees of freedom of the bath.)

Now in the same way as before we write $d\Gamma' = \frac{d\Gamma'}{dE'}dE'$. As before defining characteristic phase space volume over which the bath is "spread" as $\Delta\Gamma' = e^{S'(E',N')}$, and the corresponding energy spread $\Delta E'$ we write $\frac{d\Gamma'}{dE'} = \Delta\Gamma'/\Delta E' = e^{S'(E',N')}/\Delta E'$. Then using that $e^{S'(E',N')}$ is a very steep function, while $\Delta E'$ is almost independent of E' we can calculate

$$w_{nN} = \text{const.} \times \delta(E_{nN} + E' - E_0)\frac{e^{S'(E',N')}}{\Delta E'}dE' = \text{const.} \times e^{S'(E_0 - E_{nN}, N_0 - N)}$$

Remember, S' is the entropy of the bath! So the probability of the system is defined by the entropy of the bath.

The bath is huge, so $E_{nN} \ll E_0$ and $N \ll N_0$. We then can write $S'(E_0 - E_{nN}, N_0 - N) \approx S'(E_0, N_0) - \left(\frac{\partial S'}{\partial E'}\right)_{N,V} E_{nN} - \left(\frac{\partial S'}{\partial N'}\right)_{E',V} N = S'(E_0, N_0) - \frac{E_{nN}}{T} + \frac{\mu N}{T}$, where μ is the chemical potential. So we finally have

$$w_{nN} = Ae^{(\mu N - E_{nN})/T}$$

In the same way as before the entropy of the system (not bath!) is given by $-\langle \log w_{nN} \rangle$, so

$$S = -\langle \log w_{nN} \rangle = -\log A + \frac{\bar{E}}{T} - \frac{\mu \bar{N}}{T}, \qquad T \log A = \bar{E} - TS - \mu \bar{N} = \Omega$$

So finally the grand canonical Gibbs distribution is

$$w_{nN} = e^{(\Omega + \mu N - E_{nN})/T}$$

The normalization condition for the w_{nN} is $\sum_{N,n} w_{nN} = 1$, so we have

$$\Omega = -T \log \left(\sum_N e^{\mu N/T} \sum_n e^{-E_{nN}/T} \right)$$

For classical mechanics this formula is

$$\Omega = -T \log \left(\sum_N e^{\mu N/T} \int' e^{-E_N(p,q)/T} d\Gamma_N \right)$$

The prime in the integral is very important, remember that for identical particles $\int' d\Gamma = \frac{1}{N!} \int d\Gamma$. Without this factor $1/N!$ the last sum may not converge.

The average number of particles in the system is given by

$$\bar{N} = -\left(\partial \Omega / \partial \mu\right)_T.$$

Very often this relation is used as an equation to determine the chemical potential $\mu(T, \bar{N})$.

LECTURE 31
Occupation numbers.

31.1. Ideal Gas. Occupation numbers.

Let's consider an Ideal gas. Ideal means that there is no interaction between the particles. In this case there is a great simplification of the problem, because the quantum numbers of the system do not depend on the number of particles. We then can enumerate the quantum mechanical states of one particle in the system by say number k. Then the N particle state is constructed just by populating these one particle states with different numbers of particles. Then we distinguish the N particle quantum mechanical states by how many particles are in each state k. The number of particles in the state k is called the occupation number of the state k and is denoted as n_k. The set of these numbers fully specifies the many particle quantum mechanical state of the system.

In thermodynamics, when the system is at finite temperature, the state of the system is not a pure quantum mechanical state. It then does not make sense to talk about the numbers n_k, as they fluctuate. In this case we should talk about the average occupation number in a state k. I will denote them as $\overline{n_k}$.

We want to find $\overline{n_k}$ in a given thermodynamical, macro state.

I will consider this problem with the total number of particles not fixed. Then the thermodynamic potential Ω is given by

$$\Omega = -T \log \left(\sum_N e^{\mu N/T} \sum_n e^{-E_{nN}/T} \right)$$

The average number of particles is given by

$$\bar{N} = - \left(\partial \Omega / \partial \mu \right)_T$$

Consider a micro state of the system with given occupation numbers $\{n_k\}$. As particles do not interact the total energy is just the sum of all energies $E_{nN} = \sum_k \epsilon_k n_k$, where ϵ_k is the energy of the state k. The total number of particles is $N = \sum_k n_k$. So we have

$$\Omega = -T \log \left(\sum_{\{n_k\}} e^{\mu \sum_k n_k/T} e^{-\sum_k \epsilon_k n_k/T} \right) = -T \log \left(\sum_{\{n_k\}} \prod_k e^{(\mu-\epsilon_k)n_k/T} \right)$$

As different states do not "interact" we can interchange the product and summation and write

$$\Omega = -T \log \left(\sum_{\{n_k\}} \prod_k e^{(\mu - \epsilon_k)n_k/T} \right) = -T \log \left(\prod_k \sum_{n_k} e^{(\mu - \epsilon_k)n_k/T} \right)$$

Notice, that now the summation $\sum_{n_k}$ is done over all possible values of the occupation number n_k of a particular state k. Finally

$$\Omega = -T \sum_k \log \left(\sum_{n_k} e^{(\mu - \epsilon_k)n_k/T} \right) = \sum_k \Omega_k, \qquad \Omega_k \equiv -T \log \left(\sum_{n_k} e^{(\mu - \epsilon_k)n_k/T} \right).$$

Again the summation in Ω_k is over all possible values of occupation number n_k of a one particle state k.

Let's look at the meaning of the above result. It tells us that we can consider each state k as it's own thermodynamic system. Each state is in thermal equilibrium with all other states, so they all have the same T and μ. But then we can calculate the average number of particles in the state k,

$$\overline{n_k} = -(\partial \Omega_k/\partial \mu)_T.$$

31.2. The Fermi distribution. LL 53

Let's calculate the average occupation number of a state k of a system of identical fermions. we need to calculate the sum over all possible values of the occupation number of the state k. For fermions this occupation number can be either 1, or 0, as two fermions cannot occupy the same state. So we get

$$\Omega_k^F = -T \log \left(1 + e^{(\mu - \epsilon_k)/T} \right)$$

or

$$\overline{n_k}^F = \frac{1}{e^{(\epsilon_k - \mu)/T} + 1}.$$

This is called Fermi-Dirac distribution. Notice, that as exponent is always positive the average occupation numbers $\overline{n_k}^F < 1$. As it should be.

If we know the average number of particles, then $N = \sum_k \overline{n_k}$ where the summation is done over all STATES. This normalization gives

$$N = \sum_k \frac{1}{e^{(\epsilon_k - \mu)/T} + 1},$$

which is an equation to find $\mu(T, N)$.

31.3. The Bose distribution. LL 54

For bosons the occupation number can take any non-negative value, so

$$\Omega_k^B = -T \log \left(\sum_{n=0}^{\infty} \left(e^{(\mu - \epsilon_k)/T} \right)^n \right).$$

The sum is the geometrical series. It must converge for any state k. In order to do that μ must be less then the energy of the one particle ground state. If we measure our energy from the energy of the ground state, then the one particle ground state energy is zero. Then we have an important condition for the stability of the bose gas.

$$\mu \leq 0.$$

If this condition is satisfied we can calculate the sum under the log to get $\left(1 - e^{(\mu-\epsilon_k)/T}\right)^{-1}$, so

$$\Omega_k^B = T \log\left(1 - e^{(\mu-\epsilon_k)/T}\right)$$

and for the occupation numbers we get

$$\overline{n_k}^B = \frac{1}{e^{(\epsilon_k-\mu)/T} - 1}.$$

This is called Bose-Einstein distribution. For $\mu \leq 0$ the exponent is always larger then 1, however, the denominator can be smaller or larger then 1.

The function $\mu(N,T)$ can be found from the normalization condition

$$N = \sum_k \frac{1}{e^{(\epsilon_k-\mu)/T} - 1}.$$

31.4. The Boltzmann distribution. LL 37

Consider now a classical limit for both bose and fermi distributions. Let's write both of them in the form

$$\overline{n_k} = \frac{e^{(\mu-\epsilon_k)/T}}{1 \pm e^{(\mu-\epsilon_k)/T}}.$$

In the classical limit the occupation numbers are small, as the number of states increases exponentially with the volume, while the number of particles is linear with the volume at constant density. It means that classical limit is the limit when the exponent $e^{(\mu-\epsilon_k)/T}$ is small. In this limit both Bose and Fermi statistics give

$$\overline{n_k} = e^{(\mu-\epsilon_k)/T}$$

This is called Boltzmann distribution. The chemical potential $\mu(N,T)$ is defined by the equation

$$N = \sum_k e^{(\mu-\epsilon_k)/T},$$

where again the summation is over the one particle states.

LECTURE 32
Classical Ideal gas.

32.1. Classical Ideal gas.

Here we consider the classical ideal gas. Classical will mean that we disregard the Fermi/Bose statistics and use Boltzmann distribution for the particles. Ideal means that the particles do not interact with each other.

32.2. The free energy. LL 41

In order to calculate the free energy we need to calculate the partition function.

$$Z = \sum_n e^{-E_n/T}$$

For the noninteracting gas the total energy is just the sum of energies of individual particles $E_n = \sum_i \epsilon_{k_i}$, where the summation is over the particles, and ith particle is in k_i one particle state. Each many particle state n is specified by the one particle state k_i for each particle. In addition as particles are indistinguishable we need a factor $1/N!$. So me have

$$Z = \frac{1}{N!} \sum_{\{k_i\}} \prod_i e^{-\epsilon_{k_i}/T} = \frac{1}{N!} \prod_i \sum_{k_i} e^{-\epsilon_{k_i}/T} = \frac{1}{N!} \left(\sum_k e^{-\epsilon_k/T} \right)^N.$$

The ϵ_k are one particle energy levels and the sum $\sum_k e^{-\epsilon_k/T}$ is a one particle partition function.

In the absence of external field one particle energy levels are given by a sum of the kinetic energy $\epsilon(p)$ of a particle and the internal energy level ε_k of the particle. So we have

$$Z_D = \frac{1}{N!} \left(\int \frac{d^D p\, d^D q}{(2\pi\hbar)^D} e^{-\epsilon(p)/T} \right)^N \left(\sum_k e^{-\varepsilon_k/T} \right)^N = \frac{1}{N!} \left(\frac{V}{(2\pi\hbar)^D} \int d^D p\, e^{-\epsilon(p)/T} \right)^N \left(\sum_k e^{-\varepsilon_k/T} \right)^N$$

In the case of isotropic kinetic energy we can write $\frac{d^D p}{(2\pi\hbar)^D} = \nu_D(\epsilon)d\epsilon$, where $\nu_D(\epsilon) = \frac{S_D p^{D-1}(\epsilon)}{(2\pi\hbar)^D} \frac{dp(\epsilon)}{d\epsilon}$ is called the density of states, or one particle density of states, and $S_D = 2\frac{\pi^{D/2}}{\Gamma(D/2)}$. As velocity is $v = d\epsilon/dp$ we have for the density of states $\nu_D(\epsilon) = \frac{S_D p^{D-1}(\epsilon)}{(2\pi\hbar)^D v(\epsilon)}$ Then the kinetic energy contribution is $\frac{V}{(2\pi\hbar)^D} \int d^D p\, e^{-\epsilon(p)/T} = V \int \nu_D(\epsilon) e^{-\epsilon/T} d\epsilon$.

For the standard kinetic energy $\epsilon(p) = p^2/2m$ the velocity is $v = p/m$, and the density of states is $\nu_D(\epsilon) = \frac{S_D m p^{D-2}(\epsilon)}{(2\pi\hbar)^D}$, and

$$\nu_D(\epsilon) = \frac{S_D}{2} \frac{(2m)^{D/2}}{(2\pi\hbar)^D} \epsilon^{\frac{D}{2}-1}$$

In particular

$$\nu_1(\epsilon) = \frac{\sqrt{2m}}{2\pi\hbar} \frac{1}{\sqrt{\epsilon}}, \qquad \nu_2(\epsilon) = \pi \frac{2m}{(2\pi\hbar)^2}, \qquad \nu_2(\epsilon) = 2\pi \frac{(2m)^{3/2}}{(2\pi\hbar)^3} \sqrt{\epsilon}$$

The kinetic energy term is then

$$\frac{V}{(2\pi\hbar)^D} \int d^D p\, e^{-\epsilon(p)/T} = V \frac{S_D}{2} \frac{(2m)^{D/2}}{(2\pi\hbar)^D} \int_0^\infty \epsilon^{\frac{D}{2}-1} e^{-\epsilon/T} d\epsilon = V \frac{S_D}{2} \frac{(2mT)^{D/2}}{(2\pi\hbar)^D} \Gamma(D/2) = V \frac{(2\pi mT)^{D/2}}{(2\pi\hbar)^D}.$$

So the partition function

$$Z_D = \frac{1}{N!} \left(V T^{D/2} \left(\frac{m}{2\pi\hbar^2}\right)^{D/2} \right)^N \left(\sum_k e^{-\varepsilon_k/T} \right)^N.$$

The free energy then is $(N! \approx (N/e)^N)$

$$F_D = -T \log Z_D = -TN \log \left(\frac{eVT^{D/2}}{N} \left(\frac{m}{2\pi\hbar^2}\right)^{D/2} \sum_k e^{-\varepsilon_k/T} \right).$$

32.3. The equation of state. LL 42

In order to find the equation of state we use $P = -(\partial F/\partial V)_{N,T}$ and get

$$P = \frac{TN}{V}.$$

Notice, that this equation is correct in any dimension and for any internal energy level structure.

We can easily find the thermodynamic potential $\Phi_D = F_D + PV$:

$$\Phi_D(P,T) = -TN \log \left(\frac{T^{D/2+1}}{P} \left(\frac{m}{2\pi\hbar^2}\right)^{D/2} \sum_k e^{-\varepsilon_k/T} \right)$$

and chemical potential $\mu = \Phi/N$

$$\mu_D(P,T) = -T \log \left(\frac{T^{D/2+1}}{P} \left(\frac{m}{2\pi\hbar^2}\right)^{D/2} \sum_k e^{-\varepsilon_k/T} \right).$$

For the entropy $S(V,T,N) = -(\partial F/\partial T)_{N,V}$ we find

$$S_D(V,T,N) = N \log \left(\frac{eVT^{D/2}}{N} \left(\frac{m}{2\pi\hbar^2}\right)^{D/2} \sum_k e^{-\varepsilon_k/T} \right) + \frac{1}{2} ND + \frac{N}{T} \frac{\sum_k \varepsilon_k e^{-\varepsilon_k/T}}{\sum_k e^{-\varepsilon_k/T}}$$

Or writing it shorter

$$S_D(V,T,N) = -\frac{F_D}{T} + \frac{1}{2} ND + N \frac{\langle \varepsilon \rangle (T)}{T},$$

where $\langle \varepsilon \rangle (T)$ is the average internal energy. It depends only on temperature.

The energy is given by $E = F + TS$ and enthalpy $W = E + PV = E + NT$ are:

$$E_D(T, V, N) = \frac{D}{2}TN + N\langle\varepsilon\rangle(T), \qquad W_D(T, P, N) = (1 + D/2)\,TN + N\langle\varepsilon\rangle(T).$$

The heat capacity is $C_V = (\partial E/\partial T)_{V,N}$, $C_P = (\partial W/\partial T)_{P,N}$, so we have

$$C_V = \frac{D}{2}N + N\frac{\partial\langle\varepsilon\rangle}{\partial T}, \qquad C_P = (1 + D/2)N + N\frac{\partial\langle\varepsilon\rangle}{\partial T}, \qquad C_P - C_V = N.$$

We can start from a different form of the kinetic energy $\epsilon(p) = p^\alpha/(\alpha m)$, then $v = p^{\alpha-1}/m = (\alpha m\epsilon)^{1/\alpha}/m$, so $\nu_D(\epsilon) = \frac{S_D}{\alpha}\frac{(\alpha m)^{D/\alpha}}{(2\pi\hbar)^D}\epsilon^{D/\alpha-1}$. We see that this does not change the equation of state, but it does change the heat capacities

$$C_V = \frac{D}{\alpha}N + N\frac{\partial\langle\varepsilon\rangle}{\partial T}, \qquad C_P = (1 + D/\alpha)N + N\frac{\partial\langle\varepsilon\rangle}{\partial T}, \qquad C_P - C_V = N.$$

Now we see that in the case of usual kinetic energy in the expression for the heat capacity

$$c_V = C_V/N = 3/2 + \frac{\partial\langle\varepsilon\rangle}{\partial T}$$

the number 3 is the space dimensionality, and the number 2 is the power of the momentum in the kinetic energy. Notice, however, that equation of state as well as $c_P - c_V$ are independent of these details. They come only from the fact the in free energy the volume dependent term is $-TN\log(V/eN)$, which appears because the integration over the coordinates of each particle is independent of the other particles, which is the consequence of the assumption of non interacting particles.

LECTURE 33
Internal degrees of freedom.

33.1. Internal degrees of freedom. Classical. LL 44

We showed in the previous lecture, that the internal degrees of freedom of molecules of ideal gas do not contribute to the equation of state: $PV = NT$. They do, however, contribute to the energy, entropy, heat capacity, etc. In this lecture we want to calculate the effect of the internal degrees of freedom on the gas's thermodynamics.

$$Z = \sum_k e^{-E_k/T}.$$

Where E_k is the total one particle energy. The translational degrees of freedom can always be treated classically. We start from calculating the contribution from internal degrees of freedom also classically.

Let's first consider the contribution from the vibration modes of the molecule. Each of the n atoms of a molecule is vibrating around its stable position which corresponds to the minimum of the potential energy When we shift the atoms from their stable positions the change of the potential energy will be quadratic in the change of coordinates q_i.

$$u = \sum_{i,j}^{r} a_{i,j} q_i q_j,$$

where r is the number of the vibrational degrees of freedom. The number of such degrees is the total number of degrees of freedom $3n$ minus the translational 3 and rotational 3 degrees, $r = 3n - 6$. If the molecule is linear, then there is only 2 rotation degrees of freedom and $r = 3n - 5$, while for monoatomic gas $r = 0$.

The kinetic energy is always quadratic in all momenta, so

$$k = \sum_{i,j}^{3n} b_{i,j} p_i p_j.$$

The total energy is the sum of both potential and kinetic (vibrational, rotational, and translational) energies. In the calculation of the partition function we then have to integrate $e^{-(k+u)/T}$ over r vibrational coordinates, and $3n$ momenta, 3 center of mass coordinates, and 3 (or 2, or 0) rotational coordinates. The integration over center of mass coordinates gives us volume V, the integration over rotation coordinates gives us just a number. Now to integrate over vibrational coordinates and all momenta we will make the following transformation

$p = p'\sqrt{T}$ and $q = q'\sqrt{T}$. Under this transformation $e^{-(k(p)+u(q))/T} = e^{-(k(p')+u(q'))}$, while $d^{3n}p\,d^r q = T^{(3n+r)/2}d^{3n}p'\,d^r q'$. Then we see that

$$Z \sim VT^{(3n+r)/2} \int e^{-(k(p')+u(q'))} d^{3n}p'\,d^r q' \sim VT^{(3n+r)/2}$$

(constant factors in Z are not important in classical treatment as they just shift the entropy by a constant value.)

This form of the partition function immediately gives

$$PV = NT, \qquad c_V = \frac{3n+r}{2}$$

In particular, for monoatomic, diatomic, and polyatomic molecules we have $r = 0$, $r = 1$, and $r = 3n - 6$ and correspondingly $c_V = 3/2$, $c_v = 7/2$, and $c_V = 3n - 3$.

The above result can be interpreted as the law of equipartition: each letter (p or q) the energy of the gas's molecule depends upon gives the equal contribution $1/2$ the specific heat capacity.

Notice, that in classical treatment of an ideal gas the heat capacity does not depend on temperature.

33.2. Monoatomic. LL 45, 46

It is clear, that at the sufficiently large temperature the atoms of a gas will ionize (loose electrons). Our picture of an ideal, noninteracting gas works only if the number of ionized molecules is small. This requirement means the $T \ll E_{ion}$, where E_{ion} is the ionization energy.

The electronic states of atoms in a monoatomic gas have different quantum numbers. One of them is the principal quantum number. The energy difference for the states of different principal numbers is comparable to E_{ion}. Thus for our discussion we should assume that the temperature is low enough, so only states with the first principle quantum number is important.

Electrons of an atom have a definite angular momentum L and spin S. In the presence of the spin-orbit interaction $\vec{S}\cdot\vec{L}$ the energy levels with different total momentum J are split and the energy can be written as $\epsilon_J = \frac{A}{2}J(J+1)$. Each of these levels has a degeneracy $2J+1$. In this case the "internal" partition function $z = \sum_J (2J+1)e^{-\epsilon_J/T}$, where $|L-S| \leq J \leq L+S$ and either integer, or half integer, depending on S.

For very small temperature only the ground state matters. If we measure energy from the ground state, then exponent is 1 and the sum has only one term and is equal to $2J_0+1$, where J_0 is the angular momentum in the ground state. The sum is then temperature independent and $c_V = 3/2$.

For very large temperature all states contribute equally and the sum gives the total number of states $z \propto e^{\epsilon/T}(2L + 1)(2S + 1)$. Again this contribution is just equivalent to the shift of the zero of energy and gives no contribution to the specific heat capacity, so $c_V = 3/2$.

We see, that c_V is the same constant at very low and very high temperatures. In between it has a maximum.

33.3. Diatomic, rotation. LL 47

For diatomic molecules we can write

$$\epsilon_{\nu k} = \hbar\omega(\nu + 1/2) + \hbar^2 K(K+1)/2I,$$

then

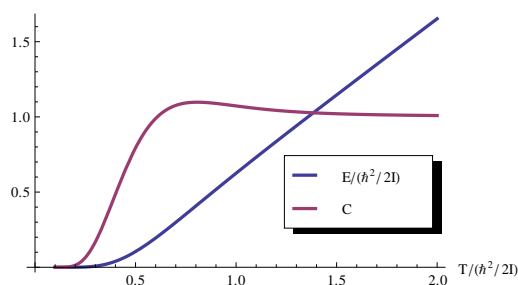$$Z = Z_{tr}Z_{rot}Z_{vib}, \qquad c_V = 3/2 + c_{rot} + c_{vib}$$

For unlike atoms the rotational energy is given by $\epsilon_K = \hbar^2 K(K+1)/2I$, the degeneracy of each level is $2K+1$. The partition function corresponding to this energy levels is $z = \sum_{K=0}^{\infty}(2K+1)e^{-\epsilon_k/T}$.

For small temperature $T \ll \hbar^2/2I$ we can keep only first two terms in the sum and write $z \approx 1 + 3e^{-\hbar^2/IT}$, which gives $c_{rot} = 3(\hbar^2/TI)e^{-\hbar^2/TI} \to 0$, for $T \to 0$.

For large $T \gg \hbar^2/2I$ the classical result (equipartition) is correct and $c_{rot} = 1$.

Heat capacity then depends on temperature, with characteristic temperature scale $T \approx \hbar^2/2I$.

Figure 1. Energy and heat capacity for the rotation degree of freedom.

For like atoms the situation is more complicated as one has to consider fermionic and bosonic (helium and deuterium, for example) atoms and odd or even total nuclear spin. It is described in LL 48.

33.4. Diatomic, vibration. LL 49

In the approximation we use the contribution of the vibrational degree of freedom is exactly the same as that of a quantum oscillator, which was considered before. Correspondingly

$$Z_{vib} = \sum_{\nu=0}^{\infty} e^{-\hbar\omega\nu/T} = \frac{1}{1 - e^{-\hbar\omega/T}}$$

The contribution of the vibrations to the heat capacity is

$$c_{vib} = \left(\frac{\hbar\omega}{T}\right)^2 \frac{e^{\hbar\omega/T}}{(e^{\hbar\omega/T} - 1)^2}$$

Because of the gap in the energy of the first excited state at low temperature $T \ll \hbar\omega$ the heat capacity contribution c_{vib} is exponentially small

$$c_{vib} \approx (\hbar\omega/T)^2 e^{-\hbar\omega/T}, \qquad T \ll \hbar\omega.$$

At large temperature we use $e^{\hbar\omega/T} \approx 1 + \hbar\omega/T + \frac{1}{2}(\hbar\omega/T)^2$ and get

$$c_{vib} \approx 1 - \frac{1}{12}\left(\frac{\hbar\omega}{T}\right)^2, \qquad T \gg \hbar\omega.$$

LECTURE 34
Magnetism of gases. LL 52

34.1. Magnetism.

I will consider only a uniform magnetic field here. It is clear that when magnetic field is zero the magnetic moment of the gas is also zero (even if each atom has a magnetic moment, the directions of the moment will be randomized and the net magnetic field will be zero.) So at weak magnetic fields we should get the magnetic moment proportional to the magnetic field $\mathbf{M} = N\chi\mathbf{H}$, where N is a number of particles and χ is the magnetic susceptibility of the gas per particle. The magnetic susceptibility can be either

positive = paramagnetic or
negative = diamagnetic.

In order to calculate the susceptibility of a gas at given temperature we need to calculate the free energy of the gas in the magnetic field, $F(T, V, N, \mathbf{H})$, then find the magnetic moment

$$\mathbf{M} = - \left(\partial F / \partial \mathbf{H} \right)_{T,N,V}$$

and then $N\chi = (\partial \mathbf{M}/\partial \mathbf{H})_{T,N,V}$. We see that we need to calculate F at least up to the second order in H.

I will consider the monoatomic gas.

The atoms are neutral, so the translation motion of the atoms does not contribute to the magnetization in contrast to, say, a gas of electrons in a metal.

34.2. Classical.

In classical mechanics in order to calculate the partition function we would need to integrate $e^{-H(\mathbf{p}-\frac{e}{c}\mathbf{A})/T}$ over momentum $\mathbf{p}$. A simple change of variables $\mathbf{p}' = \mathbf{p} - \frac{e}{c}\mathbf{A}$ then shows that the partition function does not depend on $\mathbf{A}$ and thus on magnetic field. The nonzero susceptibility is purely quantum effect.

34.3. Quantum

An atom in a magnetic field $\mathbf{H}$ is described by a Hamiltonian

$$\hat{H} = \frac{1}{2m} \sum_a \left[\hat{\mathbf{p}}_a + \frac{|e|}{c} \mathbf{A}(\mathbf{r}_a) \right]^2 + U + \frac{|e|\hbar}{mc} \mathbf{H} \cdot \hat{\mathbf{S}},$$

where $\mathbf{r}_a$ are the coordinates of electrons and $\mathbf{A}$ is vector potential. For a uniform magnetic field the vector potential can be chosen to be $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{H} \times \mathbf{r}$, then the Hamiltonian is

$$\hat{H} = \hat{H}_0 - \hat{\mathbf{m}} \cdot \mathbf{H} + \frac{e^2}{8mc^2}\sum_a (\mathbf{H} \times \mathbf{r}_a)^2,$$

where $\hat{H}_0$ is the Hamiltonian without the magnetic field, $\hat{\mathbf{m}} = -\mu_B(2\hat{\mathbf{S}} + \hat{\mathbf{L}})$ is the operator of the "intrinsic magnetic moment" of the atom, and $\mu_B = |e|\hbar/2mc$ is the Bohr magneton.

Let's take the $\hat{z}$ direction along the magnetic field, then the Hamiltonian takes the form

$$\hat{H} = \hat{H}_0 - H\hat{m}_z + H^2 \frac{e^2}{8mc^2}\sum_a \left(x_a^2 + y_a^2\right),$$

We want to consider a weak magnetic field, so we regard the magnetic field dependent terms as perturbation.

We can use the results of the thermodynamic perturbation theory, but here the perturbation mixes terms linear and quadratic in H, so it is easier (and more physically interesting) to do the calculation again.

Up to the second order in the magnetic field H, the correction to the energy levels of the unperturbed Hamiltonian is

$$\epsilon_k = \epsilon_k^{(0)} - A_k H - \frac{1}{2}B_k H^2, \qquad \text{where} \qquad \begin{array}{l} A_k = (m_z)_{kk} \\[6pt] B_k = 2\sum'_{k'} \frac{|(m_z)_{kk'}|^2}{\epsilon_{k'}^{(0)} - \epsilon_k^{(0)}} - \frac{e^2}{4mc^2}\sum_a \left(x_a^2 + y_a^2\right)_{kk}, \end{array}$$

where k numbers the unperturbed atomic states and all matrix elements are taken between the unperturbed states.

If temperature is larger then $\Delta\epsilon_k$ (which is as small as H is small), then in calculating the "internal partition function" we can expand the exponent

$$z = \sum_k e^{-\epsilon_k/T} = \sum_k e^{-\epsilon_k^{(0)}/T}e^{-\Delta\epsilon_k/T} = \sum_k e^{-\epsilon_k^{(0)}/T}\left[1 + \frac{A_k H}{T} + \frac{A_k^2 H^2}{2T^2} + \frac{B_k H^2}{2T}\right]$$

$$= \left[1 + \frac{H}{T}\frac{\sum_k A_k e^{-\epsilon_k^{(0)}/T}}{z^{(0)}} + \frac{H^2}{2T^2}\frac{\sum_k A_k^2 e^{-\epsilon_k^{(0)}/T}}{z^{(0)}} + \frac{H^2}{2T}\frac{\sum_k B_k e^{-\epsilon_k^{(0)}/T}}{z^{(0)}}\right] z^{(0)}$$

$$= \left[1 + \frac{H}{T}\overline{A} + \frac{H^2}{2T}\left(\frac{1}{T}\overline{A^2} + \overline{B}\right)\right] z^{(0)},$$

where bar means both statistical and quantum mechanical averaging over unperturbed (zero magnetic field) atomic states. At zero magnetic field $\overline{A} = \overline{(m_z)_{kk}} = 0$ (it is clear for there is no $\hat{z}$ direction at zero magnetic field). So we have

$$z = \left[1 + \frac{H^2}{2T}\left(\frac{1}{T}\overline{A^2} + \overline{B}\right)\right] z^{(0)}, \qquad F = F_0 - \frac{1}{2}NH^2\left(\frac{1}{T}\overline{A^2} + \overline{B}\right),$$

and for the susceptibility

$$\chi = \frac{1}{T}\overline{A^2} + \overline{B}$$

Let's now consider temperatures which are smaller then the the atom's energy levels splitting $T \ll \epsilon_1 - \epsilon_0$, then only the atom's ground state plays role. The contribution from all other states is suppressed by $e^{-(\epsilon_{k\neq0} - \epsilon_0)/T}$.

34.3.1. $L = 0$, $S = 0$

Now let us suppose that our atoms have no spin and no orbital moment: $\hat{\mathbf{m}} = 0$. Then $A = 0$ and we find

$$B_0 = -\frac{e^2}{4mc^2} \sum_a \left(x_a^2 + y_a^2\right)_{00} = -\frac{e^2}{6mc^2} \sum_a \left(\mathbf{r}_a^2\right)_{00}, \qquad \chi = -\frac{e^2}{6mc^2} \sum_a \left(\mathbf{r}_a^2\right)_{00}.$$

The susceptibility is negative (diamagnetic), very small $1/mc^2$, and temperature independent. This is just diamagnetic susceptibility of the atom.

34.3.2. Total moment is not zero.

Now suppose that the total angular momentum $\hat{J} = \hat{L} + \hat{S}$ is not zero. Then the intrinsic magnetic moment in the ground state of our atom is not zero $A_0 \neq 0$. As $T \ll \epsilon_1^{(0)} - \epsilon_0^{(0)}$ the first term in susceptibility ($\sim \mathbf{m}^2/T$) is larger then the second term (it is proportional to $\mathbf{m}^2/(\epsilon_1^{(0)} - \epsilon_0^{(0)})$ as the second term in B_k is divided by mc^2 and is even smaller) So $\chi = A_0^2/T$.

From quantum mechanics we know that in a state with total angular momentum J and with a given M_J projection of the total angular momentum on the $\hat{z}$ axis

$$A_0 = -\mu_B\langle 0|2\hat{S}_z + \hat{L}_z|0\rangle = -\mu_B g M_J, \qquad g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

(g is called the Landé factor.)

So $A_0^2 = \mu_B^2 g^2 M_J^2$, the states with different M_J are equally probable[1], as they are degenerate, so we have $\overline{M_J^2} = \frac{1}{2J+1}\sum_{M_J=-J}^{J} M_J^2 = \frac{1}{3}J(J+1)$.[2] Finally we have

$$\chi = \frac{\mu_B^2 g^2}{3T} J(J+1).$$

This is paramagnetic (positive) susceptibility. Its temperature dependence follows Curie's law. The Curie's law is not surprising as we have non interacting magnetic moments at finite temperature.

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[1] Remember, we are averaging over unperturbed (zero magnetic field) ground state.

[2] This calculation can be done differently. We want to calculate $\overline{M_J^2}$ where the averaging is done over the unperturbed ground state $\overline{M_J^2} = \langle 0|\hat{J}_z^2|0\rangle$. The unperturbed ground state is symmetric, so we write $\overline{M_J^2} = \langle 0|\hat{J}_z^2|0\rangle = \frac{1}{3}\langle 0|\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2|0\rangle = \frac{1}{3}\langle 0|\hat{J}^2|0\rangle = \frac{1}{3}J(J+1)$.

LECTURE 35
Fermi and Bose gases.

35.1. Fermi and Bose gases.

Let's consider gases of Fermi or Bose particles. We want to know how quantum statistics effects the properties of gases.

We will take the gas to be D-dimensional and have a dispersion relation $\epsilon(p) = \vec{p}^2/2m$.

The Fermi and Bose distributions are given by $1/(e^{(\epsilon-\mu)/T} \pm 1)$, where upper sign is for Fermions and lower sign is for bosons. The number of particles in the phase volume $d^D p d^D q$ is given by

$$dN = \frac{1}{e^{(\epsilon-\mu)/T} \pm 1} \frac{g d^D p d^D q}{(2\pi\hbar)^D},$$

where g is a spin factor $g = 2s + 1$. Again introducing the density of states, $\nu_D(\epsilon)$ and integrating over $d^D q$ we have

$$dN_\epsilon = \frac{g S_D V}{(2\pi\hbar)^D} \frac{1}{e^{(\epsilon-\mu)/T} \pm 1} p^{D-1} dp = V \frac{\nu_D(\epsilon) d\epsilon}{e^{(\epsilon-\mu)/T} \pm 1}, \qquad \nu_D(\epsilon) = g \frac{S_D}{2} \left(\frac{m}{2\pi^2\hbar^2}\right)^{D/2} \epsilon^{D/2-1}$$

This expression tells us how many particles in volume V have energy in between ϵ and $\epsilon + d\epsilon$, if we fix the chemical potential μ. These formulas take place of the classical Boltzmann distribution.

Integrating the distribution over ϵ we find the total number of particles, or particle density $n \equiv \frac{N}{V}$.

$$n = \int_0^\infty \frac{\nu_D(\epsilon) d\epsilon}{e^{(\epsilon-\mu)/T} \pm 1} = \frac{g S_D}{2} \left(\frac{m}{2\pi^2\hbar^2}\right)^{D/2} \int_0^\infty \frac{\epsilon^{D/2-1} d\epsilon}{e^{(\epsilon-\mu)/T} \pm 1} = T^{D/2} \frac{g S_D}{2} \left(\frac{m}{2\pi^2\hbar^2}\right)^{D/2} \int_0^\infty \frac{z^{D/2-1} dz}{e^{z-\mu/T} \pm 1}$$

This shows that for both Fermi and Bose gases $n = T^{D/2} f_1(\mu/T)$

We can calculate the energy of the system by

$$E = \int_0^\infty \epsilon dN_\epsilon = V \frac{g S_D}{2} \left(\frac{m}{2\pi^2\hbar^2}\right)^{D/2} \int_0^\infty \frac{\epsilon^{D/2} d\epsilon}{e^{(\epsilon-\mu)/T} \pm 1}.$$

Again $E = V T^{1+D/2} f_2(\mu/T)$.

and the thermodynamic potential $\Omega = \mp T \sum_k \log(1 \pm e^{(\mu - \epsilon)/T})$

$$\Omega = \mp TV \frac{gS_D}{2} \left(\frac{m}{2\pi^2 \hbar^2} \right)^{D/2} \int_0^\infty \epsilon^{D/2-1} d\epsilon \log(1 \pm e^{(\mu-\epsilon)/T}) =$$

$$-\frac{2}{D} V \frac{gS_D}{2} \left(\frac{m}{2\pi^2 \hbar^2} \right)^{D/2} \int_0^\infty \frac{\epsilon^{D/2} d\epsilon}{e^{(\epsilon-\mu)/T} \pm 1} = -\frac{2}{D} E$$

In particular we can write $\Omega = -\frac{2}{D} V T^{1+D/2} f_2(\mu/T) = -\frac{2}{D} V \mu^{1+D/2} f_3(T/\mu)$. Differentiating with respect to temperature we find that $S = V \mu^{D/2} \tilde{f}(\mu/T)$. On the other hand $N = Vn = V \mu^{D/2} \left[(\mu/T)^{-D/2} f_1(\mu/T) \right]$. Hence, $S/N = \phi(\mu/T)$, where $\tilde{f}(x)$ and $\phi(x) = x^{D/2} \tilde{f}(x)/f_1(x)$ are some functions.

In adiabatic process the entropy per particle is fixed, so in adiabatic process $\mu/T =$const., so $N/VT^{D/2} = f_1(\mu/T) =$const. So in adiabatic process we find that (I use $\Omega = -PV$)

$$VT^{D/2} = \text{const.}, \qquad P/T^{1+D/2} = \text{const.}, \qquad PV^{1+2/D} = \text{const.}$$

for both Fermi and Bose gases

We also know from thermodynamics, that $\Omega = -PV$, so we get

$$PV = \frac{2}{D} E$$

which is also correct for both Bose and Fermi gases.

Also we see, that

$$P = T^{D/2+1} \frac{gS_D}{D} \left(\frac{m}{2\pi^2 \hbar^2} \right)^{D/2} \int_0^\infty \frac{z^{D/2} dz}{e^{z - \mu/T} \pm 1}.$$

Together with expression for n this gives the equation of state.

In particular we can calculate the first quantum correction to the equations of state of classical ideal gas. If the gas is close to classical the exponent $e^{\mu/T-z}$ is small, so expanding the integrands in both expressions for P and for n we find

$$P \approx T^{D/2+1} \frac{2}{D} \frac{gS_D}{2} \left(\frac{m}{2\pi^2 \hbar^2} \right)^{D/2} \int_0^\infty z^{D/2} dz e^{\mu/T-z} \left(1 \mp e^{\mu/T-z} \right) =$$

$$T^{D/2+1} \frac{gS_D}{2} \left(\frac{m}{2\pi^2 \hbar^2} \right)^{D/2} \frac{2}{D} \Gamma(D/2+1) e^{\mu/T} \left(1 \mp \frac{1}{2^{D/2+1}} e^{\mu/T} \right)$$

$$n \approx T^{D/2} \frac{gS_D}{2} \left(\frac{m}{2\pi^2 \hbar^2} \right)^{D/2} \int_0^\infty z^{D/2-1} dz e^{\mu/T-z} \left(1 \mp e^{\mu/T-z} \right) =$$

$$T^{D/2} \frac{gS_D}{2} \left(\frac{m}{2\pi^2 \hbar^2} \right)^{D/2} \Gamma(D/2) e^{\mu/T} \left(1 \mp \frac{1}{2^{D/2}} e^{\mu/T} \right)$$

As $\frac{2}{D} \Gamma(D/2+1) = \Gamma(D/2)$ and $S_D \Gamma(D/2) = 2\pi^{D/2}$ we find, that

$$n = A e^{\mu/T} \left(1 \mp \frac{e^{\mu/T}}{2^{D/2}} \right), \qquad P = T A e^{\mu/T} \left(1 \mp \frac{1}{2} \frac{e^{\mu/T}}{2^{D/2}} \right), \qquad A = g \left(\frac{mT}{2\pi \hbar^2} \right)^{D/2}.$$

In the same order in $e^{\mu/T}$ we can write

$$\frac{P}{nT} = 1 \pm \frac{1}{2} \frac{e^{\mu/T}}{2^{D/2}}, \qquad e^{\mu/T} = n/A$$

and finally

$$\frac{P}{nT} = 1 \pm \frac{1}{2}\frac{n}{2^{D/2}A} = 1 \pm \frac{n}{2g}\left(\frac{\pi\hbar^2}{mT}\right)^{D/2}$$

The first term is just our standard classical ideal gas equation of state. The second term is the first quantum correction. From the second term we see:

(a) The correction to pressure is positive for Fermi gas and negative for Bose gas.

(b) The correction goes to zero when $\hbar \to 0$. This shows the quantum origin of the correction.

(c) In order for the classical result to be a good approximation, the second term must be much smaller than the first one. It means that for the densities of the order of $n_q(T) = 2g\left(mT/\pi\hbar^2\right)^{D/2}$ or larger the quantum effects on statistics cannot be neglected.

(d) For a given density n there is a temperature $T_F \approx \frac{\hbar^2}{m}n^{2/D}$ below which the quantum corrections become very important

(e) The expansion of the equation of state goes in the powers of density $n/n_q(T)$.

For the temperatures well below T_F the Fermi gas is called a degenerate Fermi gas.

Degenerate electron gas $T = 0$.

36.1. Ideal Fermi gas. Degenerate electron gas.

We consider a gas of electrons. We will neglect the Coulomb interaction and treat it as an ideal degenerate electron gas. The spin degeneracy is two fold, so $g = 2$. I will also consider here $3D$ only. This problem for other dimensions will be given as homework.

Let's first consider $T = 0$. The gas is in the ground state. As there is no interaction the energy of each state is $\epsilon(\mathbf{p}) = \mathbf{p}^2/2m$. Two electrons cannot be in the same state, so the N particle state has the smallest energy if all one particle states with the smallest momenta are filled. It means that all states with momenta of magnitude less then some threshold p_F are filled and all states with momenta larger then p_F are empty. This threshold momentum p_F is called Fermi momentum. The corresponding energy $\epsilon_F = p_F^2/2m$ is called Fermi energy.

In the momentum space the filled states are the ones inside the sphere of radius p_F. The surface of this sphere is called Fermi sphere.

In a more general situation the dispersion relation can be more complicated: for example $\epsilon(\mathbf{p})$ is not necessarily spherically symmetric. Then all momentum states below threshold energy ϵ_F are occupied and all momentum states above this energy are empty. The equation $\epsilon(\mathbf{p}) = \epsilon_F$ defines a $D - 1$ dimensional surface in D dimensional momentum space. This surface is called Fermi surface and ϵ_F is called Fermi energy.
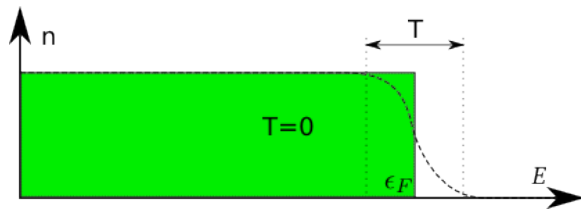
Figure 1. Fermi distribution at $T = 0$ and small $T \ll \epsilon_F$.

Now go back to the $3D$ space with dispersion $\epsilon(\mathbf{p}) = \mathbf{p}^2/2m$. The Fermi surface is a sphere of radius p_F in the momentum space. The volume of this sphere is $\frac{4}{3}\pi p_F^3$. The phase volume then is $V\frac{4}{3}\pi p_F^3$. The number of state in this volume is $\frac{2}{(2\pi\hbar)^3}V\frac{4}{3}\pi p_F^3$, where 2 is the spin degeneracy factor. Every one of these states is filled with an electron. If the total number of electrons is N, then we must have

$$N = \frac{2}{(2\pi\hbar)^3}V\frac{4}{3}\pi p_F^3, \qquad n = \frac{1}{3\pi^2\hbar^3}p_F^3$$

The last equation defines the Fermi momentum as a function of electron's density.

We can calculate the total energy of the gas. Each state has the energy $p^2/2m$. The number of states between p and $p+dp$ is given by $2V4\pi p^2/(2\pi\hbar)^3$ and all states up to p_F are filled, so

$$E = 2V\frac{4\pi}{2m(2\pi\hbar)^3}\int_0^{p_F}p^4dp = \frac{Vp_F^5}{10m\pi^2\hbar^3} = V\frac{(3\pi^2\hbar^3)^{5/3}}{10m\pi^2\hbar^3}n^{5/3} = \frac{3(3\pi^2)^{2/3}}{10}\frac{\hbar^2}{m}\frac{N^{5/3}}{V^{2/3}}$$

We then can calculate the pressure (at $T = 0$, Energy and Free energy are the same $E = F + TS = F$)

$$P = -(\partial E/\partial V)_{T=0,N} = \frac{(3\pi^2)^{2/3}}{5}\frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{5/3}$$

This is the pressure of the ground state of N fermions in volume V.

The chemical potential is

$$\mu = (\partial E/\partial N)_{T=0,V} = \frac{1}{2m}\left(3\pi^2\hbar\frac{N}{V}\right)^{2/3} = \frac{p_F^2}{2m}$$

This can be seen right from the distribution:

$$\overline{n} = \frac{1}{e^{(\epsilon-\mu)/T}+1}.$$

At $T = 0$ we have $\overline{n}_{\epsilon<\mu} = 1$ and $\overline{n}_{\epsilon>\mu} = 0$.

Let's consider interactions in the electron gas. The electron gas is charged and as such is unstable. In order to make it stable we need to consider a positively charged lattice. The interaction energy per electron is then of the order of $u \sim e^2/a$, where a is of the order of the distance between the electrons $a \sim n^{-1/3}$, so $u \sim n^{1/3}$. The average kinetic energy per electron is $\epsilon = E/N \sim n^{2/3}$. So we see that the $u/\epsilon \sim n^{-1/3}$, and the role of the potential energy decreases with the increase in concentration n.

LECTURE 37
Degenerate electron gas.

37.1. Specific heat of degenerate electron gas. LL 58

In order to calculate the specific heat we need to find how energy depends on temperature. Before we do the calculations we can find the dependence from a simple consideration. At temperature $T \ll \epsilon_F$, the number of excitations above the ground state is proportional to the temperature and the density of states at Fermi level $\sim \nu(\epsilon_F)T$, the energy of each excitation is also proportional to the temperature, so the total change of energy is proportional to $\sim \nu(\epsilon_F)T^2$. The specific heat then is $\sim \nu(\epsilon_F)T$.

Now we will do the calculations. Our variables are μ, T, and V. So it is more convenient to calculate the thermodynamic potential Ω. For the Fermi gas Ω is given by ($3D$ and $g = 2$)

$$\Omega = -\frac{2}{3}V4\pi \left(\frac{m}{2\pi^2\hbar^2}\right)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}d\epsilon}{e^{(\epsilon-\mu)/T}+1}$$

One then can proceed and calculate the small T expansion of the integral to find heat capacity. This model, however, is limited. The problem is that the chemical potential normally is not small. It means, that the energies ϵ which mostly contribute to the integral are not small. It is not very reasonable, then, to assume that the dispersion relation $\epsilon = p^2/2m$ is still valid at such large energies. It is certainly not true for the electron gas in metals. (If, however, μ is small, then the major contribution comes from the bottom of the dispersion relation, where energy can be approximated by $\epsilon = p^2/2m^*$. The "mass" m^*, although, will be different from the bare electron's mass.)

Instead of using the above formula I will do a more general calculation. I will assume that the density of states $\nu(\epsilon)$ is known, then

$$\Omega = -TV \int_0^\infty \nu(\epsilon)d\epsilon \log\left(1 + e^{(\mu-\epsilon)/T}\right) = -V \int_0^\infty \frac{\tilde{\nu}(\epsilon)d\epsilon}{e^{(\epsilon-\mu)/T}+1},$$

where $d\tilde{\nu}(\epsilon)/d\epsilon = \nu(\epsilon)$.

We need to calculate the integral for $T \ll \mu$. At $T = 0$ the distribution function is just a step function, so for any function $f(\epsilon)$ regular at $\epsilon = \mu$ we can write

$$\int_0^\infty \frac{f(\epsilon)d\epsilon}{e^{(\epsilon-\mu)/T}+1} = \int_0^\mu d\epsilon f(\epsilon) + \int_0^\mu d\epsilon f(\epsilon)\left(\frac{1}{e^{(\epsilon-\mu)/T}+1}-1\right) + \int_\mu^\infty \frac{f(\epsilon)d\epsilon}{e^{(\epsilon-\mu)/T}+1}$$

$$= \int_0^\mu d\epsilon f(\epsilon) - \int_0^\mu \frac{d\epsilon f(\epsilon)}{e^{(\mu-\epsilon)/T}+1} + \int_\mu^\infty \frac{f(\epsilon)d\epsilon}{e^{(\epsilon-\mu)/T}+1}$$

$$= \int_0^\mu d\epsilon f(\epsilon) - \int_0^\mu \frac{d\epsilon f(\mu-\epsilon)}{e^{\epsilon/T}+1} + \int_0^\infty \frac{f(\mu+\epsilon)d\epsilon}{e^{\epsilon/T}+1}$$

In the second integral the upper limit can be taken to be ∞, as $\mu \gg T$ and the integral converges on $\epsilon \sim T$. We then have

$$\int_0^\infty \frac{f(\epsilon)d\epsilon}{e^{(\epsilon-\mu)/T}+1} \approx \int_0^\mu d\epsilon f(\epsilon) + \int_0^\infty \frac{[f(\mu+\epsilon)-f(\mu-\epsilon)]\,d\epsilon}{e^{\epsilon/T}+1}$$

$$\approx \int_0^\mu d\epsilon f(\epsilon) + 2f'(\mu)\int_0^\infty \frac{\epsilon d\epsilon}{e^{\epsilon/T}+1} = \int_0^\mu d\epsilon f(\epsilon) + 2T^2 f'(\mu)\int_0^\infty \frac{z dz}{e^z+1}$$

The last integral is $\int_0^\infty \frac{z dz}{e^z+1} = \pi^2/12$. We see that the first term is independent of temperature at fixed μ and gives the $T = 0$ result, while the second term gives the $\sim T^2$ correction. Also notice, that the fact that the correction is proportional to T^2 is independent of $f(\epsilon)$.

In our case $f(\epsilon) = \tilde{\nu}(\epsilon)$ and we have

$$\Omega(\mu, T, V) = \Omega_0(\mu, V) - V\frac{\pi^2}{6}T^2\nu(\mu)$$

From here we can find the entropy as a function of μ, V, and T.

$$S(\mu, T, V) = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = V\frac{\pi^2}{3}T\nu(\mu)$$

For small temperatures $\mu \approx \epsilon_F - \ldots T^2$, so we can use $\nu(\mu) \approx \nu(\epsilon_F)$. As ϵ_F depends only on the number of particles N and volume V, we then have $S(N, T, V)$, and the heat capacity C

$$S(N, T, V) = V\frac{\pi^2}{3}T\nu(\epsilon_F), \qquad C = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = V\frac{\pi^2}{3}T\nu(\epsilon_F).$$

The heat capacity is linear in T and the coefficient gives the density of states at Fermi level!

For the case of $\epsilon(p) = \vec{p}^2/2m$ in three dimensions the final answer is ($g = 2$)

$$\nu(\epsilon) = 4\pi\left(\frac{m}{2\pi^2\hbar^2}\right)^{3/2}\epsilon^{1/2}, \qquad \mu = \frac{1}{2m}\left(3\pi^2\hbar n\right)^{2/3}, \qquad C = \left(\frac{\pi}{3}\right)^{2/3}\frac{m}{\hbar^2}TVn^{1/3}.$$

There is a subtle point in this calculation. We could have calculated E ($E = -\frac{3}{2}\Omega$ for $\epsilon(p) = \vec{p}^2/2m$) instead of Ω and then differentiate E with respect to temperature to obtain the heat capacity. This must be done with care. If we follow the same procedure as above to get E (simply multiplying Ω by $-3/2$ for $\epsilon(p) = \vec{p}^2/2m$) we would obtain energy as a function of chemical potential μ, temperature T, and volume V: $E(\mu, T, V)$. In order to get C, however, we need to differentiate E at constant V and N (not μ). To do that we need to know $\mu(T, N)$, as $C = (\partial E/\partial T)_{\mu,V} + (\partial E/\partial\mu)_{T,V}(\partial\mu/\partial T)_{N,V}$. So we also would need to know $\mu(T, N)$ which we have not calculated (this is in the homework).

LECTURE 38
Magnetism of degenerate electron gas.

This lecture is for self study.

38.1. Magnetism of the electron gas. Weak fields. LL59

A non interacting electron gas in magnetic field is described by the following Hamiltonian

$$\hat{H} = \frac{1}{2m} \sum_a \left[\hat{\mathbf{p}}_a + \frac{|e|}{c} \mathbf{A}(\mathbf{r}_a) \right]^2 + \frac{|e|\hbar}{mc} \mathbf{H} \cdot \hat{\mathbf{S}},$$

The magnetization of the electron gas consists of two independent parts:

- a paramagnetic response due to electron spin (The Pauli paramagnetism)
- diamagnetic response due to quantization of the orbital motion (the Landau diamagnetism)

I will consider the two contributions separately. I will also assume that the electron gas is degenerate $T \ll \epsilon_F$ and magnetic field H is weak $\mu_B H \ll T$, where

$$\mu_B = \frac{|e|\hbar}{2mc}$$

I will do calculations in grand canonical ensemble, so the chemical potential μ is fixed. For this ensemble the magnetization is given by

$$\mathbf{M} = - \left(\frac{\partial \Omega}{\partial \mathbf{H}} \right)_{T,V,\mu}$$

38.2. Paramagnetic response. LL59

Here I consider the paramagnetic response of the electron gas to the magnetic field. This response comes from the intrinsic electron's magnetic moment associated with the electron's spin. This magnetic moment couples to the magnetic field by $\sigma \mu_B H$, where $\sigma = \pm 1$ the plus or minus sign corresponds to the $\pm \frac{1}{2}$ spin component along the field. The one particle energy then is $\epsilon(p, \sigma) = \epsilon(p) + \sigma \mu_B H$.

We can consider up and down spin electrons as separate species with the condition that the chemical potentials of the two species are equal. At zero temperature the occupation numbers are given by $n(p, \sigma) = \left(e^{\epsilon_p/T - (\mu \pm \mu_B H)/T} + 1 \right)^{-1}$. So instead of a single Fermi surface

we will have two Fermi surfaces. In this picture the number of electrons with uncompensated spin is given by $2\mu_B H \nu(\mu) V$. The corresponding magnetic moment per volume is $M = 2\mu_B H \nu(\mu) \frac{1}{2}\mu_B = \mu_B^2 \nu(\mu) H$. The susceptibility is $\chi_{para} = \mu_B^2 \nu(\mu)$.

Here is more formal derivation.

The thermodynamic potential in magnetic field $\Omega_H(\mu)$ is

$$\Omega_H(\mu) = -T\sum_{p,\sigma} \log(1+e^{(\mu-\epsilon(p,\sigma))/T}) = -T\sum_p \log(1+e^{(\mu-\mu_B H-\epsilon(p))/T}) - T\sum_p \log(1+e^{(\mu+\mu_B H-\epsilon(p))/T})$$

The thermodynamic potential at zero magnetic field is

$$\Omega_0(\mu) = -2T\sum_p \log(1 + e^{(\mu-\epsilon(p))/T})$$

(the factor of 2 is due to spin degeneracy.) Comparing the two expressions we find

$$\Omega_H(\mu) = \frac{1}{2}\Omega_0(\mu - \mu_B H) + \frac{1}{2}\Omega_0(\mu + \mu_B H)$$

(One can think that there are two Fermi spheres: spin up and spin down with slightly different radii)

Expanding in powers of $\mu_B H$ we have

$$\Omega_H(\mu) = \Omega_0(\mu) + \frac{1}{2}\mu_B^2 H^2 \left(\frac{\partial^2 \Omega_0(\mu)}{\partial \mu^2}\right)_{T,V}$$

We can use $-(\partial \Omega_0/\partial \mu)_{T,V} = N$ to write

$$\Omega_H(\mu) = \Omega_0(\mu) + \frac{1}{2}\mu_B^2 H^2 \left(\frac{\partial N}{\partial \mu}\right)_{T,V}$$

Let's now consider the derivative $\partial N/\partial \mu$ for zero temperature. At zero temperature all states below μ are occupied. If we increase μ by $d\mu$ we increase the number of available states by $V\nu(\mu)d\mu$, where $\nu(\mu)$ is the density of states at Fermi level. All these newly available states must be occupied, so we need additional number of particles $dN = V\nu(\mu)d\mu$. We then see, that $dN/d\mu = V\nu(\mu)$, so

$$\Omega_H(\mu) = \Omega_0(\mu) + \frac{1}{2}\mu_B^2 H^2 V\nu(\mu)$$

Or magnetic susceptibility per volume

$$\chi_{\text{para}} = \mu_B^2 \nu(\mu), \qquad \chi_{\text{para}} = \frac{\mu_B^2 p_F m}{\pi^2 \hbar^3}$$

The first formula is very general, the second is correct only for $D = 3$, $\epsilon(p) = \vec{p}^2/2m$. We can compare this result with the result for the heat capacity per volume $c = \frac{\pi^2}{3}T\nu(\mu)$ and find that very generally at low temperatures for the electron gas

$$\frac{c}{T\chi_{\text{para}}} = \frac{\pi^2}{3}.$$

So heat capacity and magnetic susceptibility are not independent from each other.

38.3. Diamagnetic response. LL59

Here I consider the diamagnetic response only. I then will think that there is no Zeeman interaction of the magnetic field with the electron's spin.

This response is specific for the $3D$ it is also much easier to calculate for the dispersion $\epsilon(p) = \vec{p}^2/2m$. In this situation in the presence of the magnetic field we have Landau energy levels

$$\epsilon(p_z, n) = \frac{p_z^2}{2m} + 2\mu_B H(n + 1/2)$$

Each landau level is degenerate, the degeneracy equals to the number of magnetic fluxes $\Phi_0 = \frac{2\pi\hbar c}{|e|}$ penetrating the sample, so for each p_z each Landau level has a number of states equal to $\frac{H\mathcal{A}}{\Phi_0} = \frac{H\mathcal{A}|e|}{2\pi\hbar c}$, where $\mathcal{A}$ is the area of the sample perpendicular to the magnetic field. The motion in the $\hat{z}$ direction is not quantized and the phase space element is $\frac{L dp_z}{2\pi\hbar}$, where L is the length of the sample in $\hat{z}$ direction. So the number of states in the given interval dp_z on the Landau level n is

$$2\frac{HV|e|}{(2\pi\hbar)^2 c} dp_z,$$

where 2 accounts for the spin and $V = L\mathcal{A}$ is the volume of the sample. For Ω we then have

$$\Omega = 2\mu_B H \sum_{n=0}^{\infty} f[\mu - 2\mu_B H(n+1/2)], \qquad f(\mu) = -\frac{TmV}{2\pi^2\hbar^3} \int_{-\infty}^{\infty} \log\left[1 + \exp\left(\frac{\mu}{T} - \frac{p_z^2}{2mT}\right)\right] dp_z$$

The magnetic field is very small, so it is tempting to approximate the sum by the integral. However, if we try to do that we see, that the result will not depend on magnetic field at all. It means, that we need to find a correction to the approximation of a sum by an integral. Such correction is given by Euler-Maclaurin formula (check Wikipedia) which in our case can be written as

$$\sum_{n=0}^{\infty} F(n + 1/2) \approx \int F(x)dx + \frac{1}{24}F'(0)$$

In our case $F(x) = f[\mu - 2\mu_B Hx]$, $F'(0) = -2\mu_B H \partial f/\partial\mu$. We then have

$$\Omega \approx 2\mu_B H \int_0^{\infty} f[\mu - 2\mu_B Hx]dx - \frac{1}{24}(2\mu_B H)^2 \frac{\partial f(\mu)}{\partial\mu} = \int_{-\infty}^{\mu} f(x)dx - \frac{1}{6}\mu_B^2 H^2 \frac{\partial f(\mu)}{\partial\mu}$$

The first term does not depend on H, so it must be equal to Ω_0

$$\Omega_0 = \int_{-\infty}^{\mu} f(x)dx, \qquad \frac{\partial\Omega_0}{\partial\mu} = f(x)$$

Using this we find

$$\Omega \approx \Omega_0 - \frac{1}{6}\mu_B^2 H^2 \frac{\partial^2\Omega_0}{\partial\mu^2}$$

Or

$$\chi_{\text{dia}} = -\frac{1}{3}\mu_B^2 \frac{1}{V}\left(\frac{\partial N}{\partial\mu}\right)_{T,V}$$

For a free electron gas we then write

$$\chi_{\text{dia}} = -\frac{1}{3}\chi_{\text{para}}$$

And the total susceptibility is $\chi = \frac{2}{3}\chi_{\text{para}}$.

For electrons in solids the values of μ_B for paramagnetic response and for orbital response can be very different.

38.4. Magnetism of the electron gas. Strong fields. LL60

Please read LL60.

LECTURE 39
Degenerate Bose gas.

39.1. Ideal Bose gas. Degenerate Bose gas. LL 62

We consider a non interacting Bose gas. Degenerate Bose gas is very different from the degenerate Fermi gas.

Let's start by considering $T = 0$. The gas is in its ground state. As all particles are bosons they all occupy the same state – the ground state of the one particle Hamiltonian. So we have one quantum state which has a macroscopic occupation.

Let's measure energy from the energy of the lowest one particle state. Then the energy of the gas at $T = 0$ is zero. If we add one more particle to the gas the energy will still be zero. As at $T = 0$ energy and free energy are the same, then we find that the free energy is independent of the number of particles. So the chemical potential of the Bose gas at $T = 0$ is zero $\mu(T = 0) = 0$.

Now let's raise the temperature a little. Some of the particles will spread out from the ground state to the excited states in the energy interval $\Delta \epsilon \sim T$. There are two possibilities

- The number of states in this interval is not enough to accommodate all the particles. In that case the number of particles in the ground state remains macroscopic. It will remain so up to some finite temperature.
- There is plenty of states in the interval $\Delta \epsilon$ even for infinitesimally small $\Delta \epsilon$ then the number of particles in the ground state will become microscopic at the smallest temperature.

Let's see how it works: let's keep $\mu = 0$ even for nonzero, but small temperature. Then for $\epsilon \ll T$ we have $n(\epsilon) \approx T/\epsilon$. So we have $N = \int_0 \nu(\epsilon)n(\epsilon)d\epsilon \approx T \int_0 \epsilon^{-1}\nu(\epsilon)d\epsilon$. We see, that if $\nu(\epsilon) \not\to 0$, as $\epsilon \to 0$, then the integral diverges at the lower limit. So in this case we can accommodate as many particles as we want in as small energy interval as we want — this is the second possibility mentioned above.

On the other hand, if the integral converges on the lower limit, then we can accommodate only a finite number of particles in the excited states. This number of particles is small for small temperatures, so if the actual number of particles is larger, then we have to keep a macroscopic number of particles in the ground state.

Let's now look at the system closely.

As all the states we are interested in are close to the minimum of $\epsilon(\mathbf{p})$ we can use $\epsilon(p) = p^2/2m$ for the dispersion. Let's consider the Bose distribution at finite temperature

$$n(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/T} - 1}.$$

In D dimensions the density of states (for $\epsilon(p) = p^2/2m$) is $\nu_D = \frac{gS_D}{2} \left(\frac{m}{2\pi^2\hbar^2}\right)^{D/2} \epsilon^{D/2-1}$ ($g = 2S + 1$).

The number of particles then is given by

$$N = V\frac{gS_D}{2}\left(\frac{m}{2\pi^2\hbar^2}\right)^{D/2}\int_0^\infty \frac{\epsilon^{D/2-1}d\epsilon}{e^{(\epsilon-\mu)/T} - 1}$$

Or rescaling $\epsilon/T = \epsilon'$ we find that

$$N = VT^{D/2}B_D\int_0^\infty \frac{\epsilon^{D/2-1}d\epsilon}{e^{\epsilon-\frac{\mu}{T}} - 1}. \qquad B_D = \frac{gS_D}{2}\left(\frac{m}{2\pi^2\hbar^2}\right)^{D/2}$$

The chemical potential must be negative. We also see, that the R.H.S. of the above equation is the monotonically increasing function of μ. Let's look at how the integral behaves when $\mu \to -0$. A simple calculation (using mathematica, or working out analytically) gives

$$N \approx VT^{1/2}B_1\frac{\pi}{\sqrt{-\mu/T}}, \qquad \text{for } D = 1$$

$$N \approx -VTB_2\log(-\mu/T), \qquad \text{for } D = 2$$

$$N \approx VT^{3/2}B_3\left(\frac{\sqrt{\pi}}{2}\zeta(3/2) - \pi\sqrt{-\mu/T}\right), \qquad \text{for } D = 3$$

For any temperature the integral on the RHS cannot be larger then $\int_0^\infty \frac{\epsilon^{D/2-1}d\epsilon}{e^{\epsilon/T}-1} = T^{D/2}\int_0^\infty \frac{z^{D/2-1}dz}{e^z-1}$. The last integral is divergent for $D = 1$ and $D = 2$, but is convergent for $D > 2$. For $D = 3$ the integral is $\int_0^\infty \frac{z^{D/2-1}dz}{e^z-1} = \frac{\sqrt{\pi}}{2}\zeta(3/2)$. It means that in $3D$ at a given temperature the number of particles cannot be larger then

$$N_{max} = V2\pi g\left(\frac{mT}{2\pi^2\hbar^2}\right)^{3/2}\frac{\sqrt{\pi}}{2}\zeta(3/2)$$

This result for $3D$ is very strange, as we can always add more and more particles in the system. This may only mean that in $D = 3$ if we have more particles the N_{max}, then the excess of particles will go to a state with $\epsilon = 0$ – to the ground state. This is exactly what we discussed at the beginning: there is a condensate of a macroscopic number of particles in the ground state.

If the particle concentration n is given we can find the condensation temperature (the temperature at which the condensate first appears) in $3D$.

Figure 1. $n(\mu/T)$ for $D = 1, 2, 3$ given by Bose distribution.

$$T_c = \left(\frac{2n}{\sqrt{\pi} B_3 \zeta(3/2)} \right)^{2/3}$$

At temperatures below T_c the chemical potential is 0. We then can calculate the number of particles that are not in condensate $\mathcal{N}$ at given temperature $T < T_c$.

$$\mathcal{N} = VT^{3/2} B_3 \frac{\sqrt{\pi}}{2} \zeta(3/2).$$

The total number of particles is exactly the same as at T_c, so

$$N = VT_c^{3/2} B_3 \frac{\sqrt{\pi}}{2} \zeta(3/2) = \mathcal{N} \frac{T_c^{3/2}}{T^{3/2}}$$

Or, the total number of particles in condensate $N_{\epsilon=0} = N - \mathcal{N}$ is

$$N_{\epsilon=0} = N \left(1 - (T/T_c)^{3/2} \right)$$

We can also calculate the energy of the gas in $3D$ at $T < T_c$. The particles in the condensate are in the ground state and do not contribute to the energy. Only the particles out of condensate do contribute. These particle are distributed according to the Bose distribution with $\mu = 0$. So the total energy is given by

$$E = VT^{5/2} B_3 \int \frac{\epsilon^{D/2} d\epsilon}{e^\epsilon - 1} = VT^{5/2} B_3 \frac{\sqrt{\pi}}{2} \frac{3}{2} \zeta(5/2) = T(T/T_c)^{3/2} N \frac{3}{2} \frac{\zeta(5/2)}{\zeta(3/2)}$$

We also know, that $\Omega = -\frac{2}{3} E$, and the free energy $F = \Omega + \mu N = \Omega$ (as $\mu = 0$) So we find

$$P = -\frac{1}{V} \Omega = \frac{2}{3} \frac{E}{V} = T^{5/2} B_3 \frac{\sqrt{\pi}}{2} \zeta(5/2)$$

So the pressure is independent of volume at fixed number of particles (so when we change the volume the concentration of particles does change, but the pressure remains the same).

The entropy is given by

$$S = -\left(\frac{\partial \Omega}{\partial T} \right)_V = \frac{5}{3} VT^{3/2} B_3 \frac{\sqrt{\pi}}{2} \frac{3}{2} \zeta(5/2) = \frac{5E}{3T},$$

and

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = \frac{5}{2} VT^{3/2} B_3 \frac{\sqrt{\pi}}{2} \frac{3}{2} \zeta(5/2) = \frac{5E}{2T}$$

There is no discontinuity in the heat capacity of the Bose gas at $T = T_c$ for noninteracting particles. The derivative $\partial C_V / \partial T$ is discontinuous at T_c. However, even the smallest interaction changes this result and C_V becomes discontinuous.

It is also important to recognize, that the interactions effect the Bose condensation very considerably. Even if the interaction is infinitesimally small when condensate appears it appears as a coherent wave function with macroscopic number of particles. If we now calculate the matrix element of the interaction of this state with any other state. The matrix element will by proportional to the interaction strength times the square root of the number of particles in the condensate. Even for very small interaction this matrix element will be large.

LECTURE 40
Black-body radiation.

40.1. Gas of photons. LL 63

There are three important cases of Bose gas.

- Electromagnetic field — photon gas.
- Field of elastic deformation in solids — phonon gas.
- Gas of ultracold atoms.

I will talk about the first two of these examples here.

We start with the gas of photons. I will consider the light in vacuum only. The properties of photons are:

- A photon is a particle of electromagnetic radiation. This particle has no mass and travels with the speed of light. Light has two possible polarizations. The photons have momentum and energy. The energy depends on the momentum according to the ultra-relativistic dispersion relation

$$\epsilon_p = cp$$

  The energy of the photon and the frequency of the light are connected to the energy, and the wave number (and wavelength) of light is connected to the momentum according to

$$\epsilon = \hbar\omega, \qquad p = \hbar k, \qquad \lambda = 2\pi/k = 2\pi c/\omega.$$

- The angular momentum of a photon is integer, so the photon's are bosons.
- A photon has one of the two possible polarizations.
- Maxwell equations are linear, so the photons do not interact with each other.

We want to consider a gas of photons in thermal equilibrium. In order to get to the equilibrium photons must interact with each other. The direct interaction between them is negligible (it may happen through a creation of the virtual electron positron pair), so the main interaction happens through the interaction with the matter. The amount of matter can be assumed to be infinitesimally small – this effects the time needed for the photon gas to relax to the equilibrium, but will not effect the final state.

It is, however, important, that matter can absorb and emit photons. It means that the number of photons is not conserved and is itself one of the parameters. We know that if a

macro state depends on a macro parameter, say ϕ, then

$$\left(\frac{\partial S}{\partial \phi}\right)_E = -\frac{1}{T}\left(\frac{\partial F}{\partial \phi}\right)_T$$

so the equilibrium value of the parameter (maximum entropy at fixed energy) is found as a minimum of the free energy at fixed temperature. In the present case the average number of photons is such a macro parameter, so $(\partial F/\partial N)_{T,V} = 0$. But the derivative $(\partial F/\partial N)_{T,V}$ is just the chemical potential, so we find that the equilibrium condition for the phonon gas is

$$\mu = 0.$$

The distribution of photons among the quantum states of momenta $\hbar\mathbf{k}$ and definite polarization s is

$$\bar{n}_{k,s} = \frac{1}{e^{\hbar\omega/T} - 1}.$$

This is called Plank's distribution.

We also need to know the elementary phase volume. This means that we need to calculate how many electromagnetic oscillation modes are in the interval of wave numbers from k to $k + dk$ in a volume V. It is, however, clear that there is no difference between the electromagnetic oscillation modes and quasiclassical states in quantum mechanics. So this nomber of modes must be given by the same expression $V\frac{d^3p}{(2\pi\hbar)^3}$. Using $d^3p = 4\pi p^2 dp$ and the relation $\omega = ck$ we find that the phase volume is given by (I included the factor of 2 due to two polarizations):

$$V\frac{\omega^2 d\omega}{\pi^2 c^3}$$

The number of phonons with frequency between ω and $\omega + d\omega$ is given by

$$dN_\omega = \frac{V}{\pi^2 c^3}\frac{\omega^2 d\omega}{e^{\hbar\omega/T} - 1}$$

As each photon in this interval has energy $\hbar\omega$ the radiation energy in this interval of frequencies is

$$dE_\omega = \frac{V\hbar}{\pi^2 c^3}\frac{\omega^3 d\omega}{e^{\hbar\omega/T} - 1}$$

For small frequencies $\hbar\omega \ll T$ this formula gives

$$dE_{\omega \ll T/\hbar} = V\frac{\omega^2 d\omega}{\pi^2 c^3}T$$

This is a classical result (it does not contain $\hbar$) It was derived classically and is called Rayleigh-Jeans formula. The result just shows that there is energy T for each mode in the interval $d\omega$ of frequencies. This result is very problematic as it shows that the total energy of the photon gas diverges.

Classically, this conundrum is impossible to resolve, as one would have to come up with some universal energy cutoff. However, the Maxwell equations do not have any parameter of the units of energy. This contradiction lead Plank to introduce a completely new fundamental constant of at the time an unclear nature – $\hbar$. This was the beginning of quantum mechanics.

In the opposite limit $\hbar\omega \gg T$ of the high frequencies we find

$$dE_{\omega \gg T/\hbar} = \frac{V\hbar}{\pi^2 c^3}\omega^3 e^{-\hbar\omega/T} d\omega$$

This is Wien's formula. It shows that the energy spectral density decreases exponentially at $\omega \gg T/\hbar$.

The spectral energy density $dE_\omega/d\omega$ is zero at $\omega = 0$ and at $\omega = \infty$. It has the maximum at

$$\hbar\omega_m/T = 2.822.$$

So that the maximum frequency shifts linearly with the temperature. The slope of the linear function $\omega_m(T)$ allows one to measure $\hbar$.

The wave length distribution $dE_\lambda/d\lambda$ is given by substituting $\omega = 2\pi c/\lambda$ into dE_ω and is:

$$dE_\lambda = V\frac{16\pi^2 c\hbar}{\lambda^5}\frac{d\lambda}{e^{2\pi\hbar c/T\lambda} - 1}$$

It has maximum at

$$2\pi\hbar c/T\lambda_m = 4.965$$

(Notice, that λ_m does not correspond to ω_m).

We can calculate the thermodynamic potentials. First we notice, that $\Omega = F - \mu N = F$, so

$$\Omega = F = T\frac{V}{\pi^2 c^3}\int_0^\infty \omega^2 \log\left(1 - e^{-\hbar\omega/T}\right) d\omega$$

Integrating by parts we find

$$\Omega = F = -\frac{1}{3}\frac{V\hbar}{\pi^2 c^3}\int_0^\infty \frac{\omega^3 d\omega}{e^{\hbar\omega/T} - 1}$$

Comparing this with $E = \int dE_\omega$ we find that

$$\Omega = F = -\frac{1}{3}E = -V\frac{T^4}{3\pi^2\hbar^3 c^3}\int_0^\infty \frac{x^3 dx}{e^x - 1}$$

The last integral equals to $\pi^4/15$, so

$$\Omega = F = -\frac{1}{3}E = -V\frac{4}{3c}\sigma T^4, \qquad \sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}$$

(σ is called Stefan-Boltzmann constant)

The entropy is given by $S = -(\partial F/\partial T)_V$ and is

$$S = V\frac{16}{3c}\sigma T^3$$

(one can check that indeed $E = F + TS$.) In adiabatic process $T^3 V$ =const.

Now we can find C_V and P.

$$C_V = 16\sigma T^3 V/c, \qquad P = -\Omega/V = \frac{4}{3c}\sigma T^4, \qquad PV = \frac{1}{3}E$$

The total number of photons is

$$N = \int dN_\omega = \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\omega^2 d\omega}{e^{\hbar\omega/T} - 1} = V\frac{2\zeta(3)}{\pi^3}\left(\frac{T}{\hbar c}\right)^3$$

40.2. Black-body radiation. LL 63

Let's now consider a black body radiation. A body at temperature T in a vacuum will radiate electromagnetic waves. The waves will go to infinity caring energy with them. Assuming that we keep the temperature of the body T constant what is the distribution of the radiated energy over frequencies? Notice, that the process we want to consider is not equilibrium.

To solve this we first consider the body at equilibrium with the radiation (We just imaging that the body is inside a huge closed volume, so it equilibrates with the radiation) Then the body emits as much as it absorbs. Let's assume that the surface of the body absorbs $A(\omega, \theta)$ portion of the radiation coming at frequency ω at angle θ to the normal. Let's also assume that the non absorbed portion reflects with the same angle θ and the same frequency ω.

Let's calculate how much energy the body absorbs from the radiation in the solid angle do in the interval of frequencies $d\omega$. Consider a small volume of the space the energy density in this volume in the interval $d\omega$ is

$$e(\omega) = \frac{1}{V}\frac{dE_\omega}{d\omega} = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/T} - 1}$$

This energy travels in all directions with the speed of light c. So the energy flux in the solid angle element do and frequency interval $d\omega$ is given by

$$ce(\omega)d\omega\frac{do}{4\pi}$$

The radiation energy coming on the surface area $d\mathcal{A}$ of the body from the solid angle do in the freq. interval $d\omega$ is

$$ce(\omega)\cos\theta do d\omega d\mathcal{A}$$

The flux absorbed by the body is

$$ce(\omega)A(\omega, \theta)\cos\theta do d\omega d\mathcal{A}$$

But in equilibrium the energy in the freq. interval $d\omega$ in the solid angle do must not change! The body must emit exactly the same energy flux. So if we measure the emission flux $J(\omega, \theta)do d\omega d\mathcal{A}$ we must find that

$$J(\omega, \theta) = ce(\omega)A(\omega, \theta)\cos\theta$$

In particular it means that for a body which reflects without changing frequency and the angle the quantity

$$\frac{J(\omega, \theta)}{A(\omega, \theta)} = ce(\omega)\cos\theta$$

is universal and does not depend on the details of interaction between the light and the body. This is called Kirchhoff's law. Notice that:

- in the LHS we have the ration of two quantities: one describing the emission of light and the other describing the absorption.
- $A(\omega, \theta) \leq 1$. The larger the A the larger portion of light is absorbed, but the larger the emission.

A black body is a body which absorbs all light and reflects none. It does not mean that the black body does not emit light. On the contrary. The fact that the black body absorbs all light means that $A(\omega, \theta) = 1$. By Kirchhoff's law we see, that the emission is in fact the largest for this body, is universal, and is given by

$$J(\omega, \theta) = ce(\omega)\cos\theta$$

The total intensity of emission of a unit area of a surface of a black body is obtained by integrating the above flux over all frequencies and over full hemisphere. We then find

$$J_0 = \sigma T^4.$$

LECTURE 41
Phonons.

41.1. Phonons.

Let's consider a crystal. We will ignore the electronic degrees of freedom and consider only atomic degrees of freedom in the crystal.

The atoms in a crystal can oscillate around their fixed places. This the thermodynamics of the crystal will be determined by the thermodynamics of the vibrations of the atoms. If N is the number of unit cells in the crystal and ν is the number of atoms per unit cell, then the total number of atoms in the crystal is $N\nu$. The total number of degrees of freedom is $3N\nu$, so the total number of vibrational degrees of freedom is $3N\nu - 6$. We obviously can neglect 6 in comparison to the $3N\nu$.

If we neglect the anharmonicity of the oscillations we can consider the crystal as a collection of $3N\nu$ oscillators each with its own frequency ω_α, α enumerates the normal modes of the crystal's oscillations.

We have calculated the free energy for the oscillator before and found that $F = \frac{1}{2}\hbar\omega + T\log\left(1 - e^{-\hbar\omega/T}\right)$. For the crystal we then have

$$F = N\epsilon_0 + T\sum_\alpha \log\left(1 - e^{-\hbar\omega_\alpha/T}\right),$$

where $N\epsilon_0$ depends on the number of atoms, but does not depend on temperature, and represents the zero point vibration energy of the crystal. The summation goes over all $3N\nu$ vibrational modes.

41.2. Small temperatures. LL64

Consider first small temperatures. At small temperatures only vibrations with small frequencies $\hbar\omega \sim T$ contribute to the sum. Vibration of the solid at small frequencies are call sound waves. Their wavelength is related to the frequency $\lambda \sim u/\omega$, where u is the velocity of sound. For the sound waves the wavelength must be much larger then the lattice constant $\lambda \gg a$, so $\omega \ll u/a$ and small temperature means

$$T \ll \hbar u/a.$$

Let's consider an isotropic solid. A sound wave has three polarizations: two transverse polarizations with the sound velocity u_t; and the third is longitudinal with velocity u_l. The

frequencies for all three sound waves are related to the wave number $\omega = u_t k$ for the transfers waves and $\omega = u_l k$ for the longitudinal. For each of the polarization the number of vibrational modes is given by $V d^3 k/(2\pi)^3 = 4\pi V k^2 dk/(2\pi)^3$, where V is the volume of the body. Using $k = \omega/u$ for each polarization we find that the total number of modes is

$$V\frac{\omega^2 d\omega}{2\pi^2}\left(\frac{1}{u_l^3} + \frac{2}{u_t^3}\right) = V\frac{3\omega^2 d\omega}{2\pi^2\bar{u}^3}, \qquad \text{where} \qquad \frac{3}{\bar{u}^3} = \frac{1}{u_l^3} + \frac{2}{u_t^3}$$

If $\bar{u}$ is understood as a velocity averaged on some particular way, then the above formula is applicable also to non isotropic media.

Now we can change summation to the integration in the expression for F

$$F = N\epsilon_0 + TV\frac{3}{2\pi^2\bar{u}^3}\int_0^\infty \log\left(1 - e^{-\hbar\omega/T}\right)\omega^2 d\omega$$

The integral converges vary rapidly for $\hbar\omega > T$, so we can extend the integration to infinity. Notice, that by this we overestimate the total number of degrees of freedom.

This form of free energy is the same as what we had for the black body radiation. The difference is the factor $3/2$ which accounts for the difference in the number of polarizations: the photons have 2 possible polarizations, while phonons have 3.

We thus know all thermodynamical quantities from the black body lecture.

$$F = N\epsilon_0 - V\frac{\pi^2 T^4}{30(\hbar\bar{u})^3}, \quad S = V\frac{2\pi^2 T^3}{15(\hbar\bar{u})^3}, \quad E = N\epsilon_0 + V\frac{\pi^2 T^4}{10(\hbar\bar{u})^3}, \quad C = V\frac{2\pi^2 T^3}{5(\hbar\bar{u})^3}$$

Notice, that at low temperatures the specific heat of phonons is $\sim T^3$, while for electrons the specific heat $\sim T$. So if one measures the specific heat as a function of temperature in a metal one would find $C = aT + bT^3$. If one then plots C/T as a function of T^2 one finds a straight line with the intersection point related to the electronic heat capacity and the slope related to the phonon heat capacity.

41.3. High temperature. LL65

For the high temperature we cannot ignore the fact that we have a finite number of degrees of freedom. For large T we write $\log\left(1 - e^{-\hbar\omega_\alpha/T}\right) \approx \log(\hbar\omega_\alpha/T) - \hbar\omega_a/2T$. Then

$$F = \epsilon_0' N + T\sum_\alpha \log(\hbar\omega_\alpha/T), \qquad \text{where} N\epsilon_0' = N\epsilon_0 - \sum_\alpha \frac{\hbar\omega_\alpha}{2}.$$

Now we introduce the geometric mean frequency

$$\log\bar{\omega} = \frac{1}{3N\nu}\sum_\alpha \log\omega_\alpha$$

And write

$$F = N\epsilon_0' - 3N\nu T\log T + 3N\nu T\log\bar{\omega}$$

The mean frequency $\bar{\omega}$ as well as $\bar{u}$ depend on density. The energy of the body is

$$E = F - T\partial F/\partial T = N\epsilon_0' + 3N\nu T.$$

This is just the equipartition theorem: each vibrational degree of freedom has energy T.

The heat capacity is independent of temperature

$$C = 3N\nu$$

41.4. Debye's interpolation. LL66

We saw that we need to be careful not to overcount the degrees of freedom. The easiest way to do this is to introduce the upper frequency cutoff ω_D — the Debye frequency — in the expression for the free energy

$$F = N\epsilon_0 + TV\frac{3}{2\pi^2\bar{u}^3}\int_0^{\omega_D}\log\left(1 - e^{-\hbar\omega/T}\right)\omega^2 d\omega.$$

This cutoff must be such as to fix the total number of degrees of freedom

$$3N\nu = V\frac{3}{2\pi^2\bar{u}^3}\int_0^{\omega_D}\omega^2 d\omega = \frac{V\omega_D^3}{2\pi^2\bar{u}^3}, \qquad \omega_D = \bar{u}\left(6\pi^2 N\nu/V\right)^{1/3} \sim \bar{u}/a$$

Substituting ω_D instead of $\bar{u}$ everywhere and introducing the Debye temperature

$$\Theta = \hbar\omega_D$$

we find

$$F = N\epsilon_0 + 9N\nu T(T/\Theta)^3\int_0^{\Theta/T}z^2\log(1 - e^{-z})dz$$

Integrating by parts we find

$$F = N\epsilon_0 + N\nu T\left[3\log(1 - e^{-\Theta/T}) - D(\Theta/T)\right], \qquad \text{where} \qquad D(x) = \frac{3}{x^3}\int_0^x\frac{z^3 dz}{e^z - 1}.$$

The function $D(x)$ is called Debye function.

Using this free energy we find

$$E = N\epsilon_0 + 3N\nu TD(\Theta/T)$$
$$C = 3N\nu\left(D(\Theta/T) - (\Theta/T)D'(\Theta/T)\right)$$

One can check that

$$D(x \gg 1) \approx \frac{\pi^4}{5x^3}, \qquad \text{and} \qquad D(x \ll 1) \approx 1.$$

Figure 1. Debye heat capacity.

and recover both low and high temperature results from the Debye's formulas.

There are two more messages in the Debye's theory:

- Small temperature is the temperature much smaller the Θ. In fact for the temperatures smaller then $\Theta/4$ the small temperature results work very well, for temperature larger $\Theta/4$ the high temperature results are fine.
- The specific heat depends only on the ration T/Θ. So the curves $C(T)$ for different materials should collapse on one if we plot them as a function of T/Θ, with the correct Θ for each material.
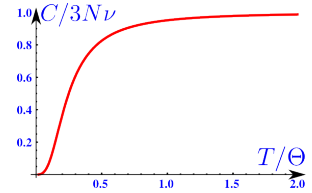
Non-Ideal gas. Van der Waal's equation.

This lecture is for self study.

42.1. Non-Ideal gas. LL74

I will consider the deviation of the actual gas from the ideal gas, which results from the interaction between atoms. I will consider a monoatomic gas. I assume that the gas is still so rarefied, that the triple and so on collisions can be neglected.

Let's first treat the problem classically. The energy of the gas is given by

$$E(p,q) = \sum_{a=1}^{N} \frac{\mathbf{p}_a^2}{2m} + U,$$

where the first term is the kinetic energy of the N atoms of the gas. The second term is the potential energy, which depends only on the particles mutual interaction. We need to calculate the partition function

$$Z = \int e^{-E(p,q)/T} d\Gamma = \left[\frac{1}{N!} \int e^{-\sum_{a=1}^{N} \frac{\mathbf{p}_a^2}{2mT}} \frac{V^N d^{3N}p}{(2\pi\hbar)^{3N}} \right] \left[\frac{1}{V^N} \int e^{-U/T} dV_1 dV_2 \dots dV_N \right]$$

The first term in the product is just the partition function of the ideal gas. The free energy then is

$$F = F_{id} - T \log \left[\frac{1}{V^N} \int e^{-U/T} dV_1 dV_2 \dots dV_N \right],$$

where F_{id} is the free energy of the ideal gas. Adding and subtracting unity we find

$$F = F_{id} - T \log \left[1 + \frac{1}{V^N} \int \left(e^{-U/T} - 1 \right) dV_1 dV_2 \dots dV_N \right]$$

We are calculating the correction to the ideal gas. We then assume, that the particles in the gas are far away from each other on average, so their interaction is negligible, unless they fluctuate close to each other. Such an event is rear. If we neglect three and so on particle collisions then we can write

$$\frac{1}{V^N} \int \left(e^{-U/T} - 1 \right) dV_1 dV_2 \dots dV_N = \frac{N(N-1)}{2} \frac{1}{V^N} \int \left(e^{-U(\mathbf{r}_1 - \mathbf{r}_2)/T} - 1 \right) dV_1 dV_2 \int dV_3 \dots dV_N$$

$$\approx \frac{N^2}{2V^2} \int \left(e^{-U(\mathbf{r}_1 - \mathbf{r}_2)/T} - 1 \right) dV_1 dV_2 \approx \frac{N^2}{2V} \int \left(e^{-U(\mathbf{r})/T} - 1 \right) dV$$

Consider this as a small correction and using $\log(1+x) \approx x$ we get

$$F \approx F_{id} - \frac{TN^2}{2V} \int \left(e^{-U(\mathbf{r})/T} - 1 \right) dV$$

The coefficient

$$B(T) = \frac{1}{2} \int \left(1 - e^{-U(\mathbf{r})/T} \right) dV$$

is called the second virial coefficient.

Differentiating the free energy with respect to the volume we'll find the correction to the equation of state.

$$F \approx F_{id} + \frac{TN^2}{V} B(T), \qquad P \approx \frac{NT}{V} \left(1 + \frac{N}{V} B(T) \right)$$

This is the first correction to the equation of state in powers of density[1].

For the Joule-Thomson process we find

$$\left(\frac{\partial T}{\partial P} \right)_W = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] = \frac{N}{C_P} \left(T \frac{dB}{dT} - B \right)$$

We see, that the value and even the sign of the Joule-Thomson process depends on the interaction potential and it's structure.
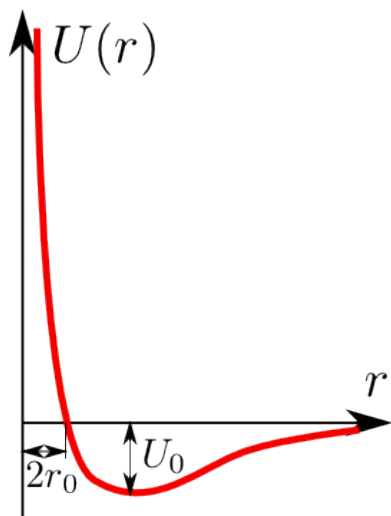
42.2. Van der Waal's equation. LL76, LL84

Figure 1. Interaction potential between atoms.

We want to include the interaction between the atoms and find the interpolation formula for equation of state which interpolates from ideal gas at very large volumes to liquid at very small volume (at fixed N and T). The exact equation of state will depend on the exact form of the interaction between molecule and as such is not very interesting. We want to find and approximate simple interpolation formula. So we have the following requirements

- The equation of state approaches that of ideal gas when volume increases at fixed N and T.
- It is impossible to compress the gas beyond some very small volume (for fixed N).

Let's consider a typical interaction between two atoms. The atoms weakly attract each other at large distances and strongly repel each other at distances smaller then some $2r_0$. A typical interaction is depicted on Fig. 1. I will assume, that the temperature is not small $T \gg U_0$. Using spherical coordinates and dividing the range of integration into two parts we find

$$B(T) = 2\pi \int_0^{r_0} \left(1 - e^{-U(r)/T} \right) r^2 dr + 2\pi \int_{r_0}^{\infty} \left(1 - e^{-U(r)/T} \right) r^2 dr$$

---

[1] One can expect that the full series will have the form $P = nT \left(1 + nB(T) + n^2 C(T) + \dots \right)$. It is indeed so. The coefficients $B(T)$, $C(T)$, etc. are called second, third, etc. virial coefficients. See LL75.

In the first integral $U \gg T$ and we can neglect the exponent. The integral then is just a constant $b = 16\pi r_0^3/3$, which is just 4 times the volume of the atom. In the second integral, the exponent is close two 1. The integral then becomes

$$-\frac{2\pi}{T} \int_{r_0}^{\infty} |U(r)| r^2 dr = -\frac{a}{T},$$

where a is a positive constant. So the result is

$$B(T) = b - a/T, \qquad F \approx F_{id} + N^2(Tb - a)/V.$$

Using the free energy for the ideal gas

$$F = -NT \log(eV/N) + Nf(T), \qquad f(T) = -NT \log\left[\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} \sum_k e^{-\epsilon'_k/T}\right]$$

(see Lecture 32.1. For the monoatomic gas $f(T) = -\frac{3}{2}NT \log T$.) We find

$$F \approx Nf(T) - NT \log(e/N) - NT \left(\log(V) - Nb/V\right) - N^2 a/V$$

This free energy does not diverge at any final volume, as it must at volume of the order of bN. However, with the same accuracy for $V \ll Nb$ we can rewrite $\log(V) - Nb/V \approx \log(V - Nb)$. Then

$$F \approx F_{id} - NT \log(1 - Nb/V) - N^2 a/V.$$

This free energy satisfies our conditions. It diverges at finite (but small) volume $V = Nb$ and it turns into an ideal gas free energy at large volume (at fixed N).
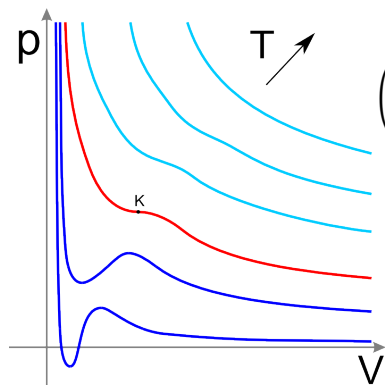
From here we can find the pressure

$$P = \frac{NT}{V - Nb} - \frac{N^2 a}{V^2}, \qquad \left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = NT$$

This is Van der Waal's equation of state.

Let's look at the isotherms of the Van der Waal's gas, see Fig. 2. Let's find where it has extrema.

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} = -\frac{NT}{(V - Nb)^2} + 2\frac{N^2 a}{V^3} = 0$$

The resulting third degree polynomial equation for V has one unphysical solution for $0 < V < Nb$ and two physical solutions at small enough temperatures. However, if the temperature is large there is no physical solutions, as the first term is always the largest. It means that there is one specific temperature where there is only one solution, see isotherm K on Fig. 2. At this temperature we must have

Figure 2. Isotherms of Van der Waal's equation of state.

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} = 0, \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T,N} = 0, \qquad P = \frac{NT}{V - Nb} - \frac{N^2 a}{V^2}$$

These are three equations for three unknowns P, T, and V (at fixed N). Solving these equations we find the critical point — point K on Fig. 2

$$T_c = \frac{8}{27}\frac{a}{b}, \qquad V_c = 3Nb, \qquad P_c = \frac{1}{27}\frac{a}{b^2}$$

If we now rescale the variables we find

$$T' = T/T_c, \quad P' = P/P_c, \quad V' = V/V_c, \qquad \left(P' + \frac{3}{V'^2}\right)(3V' - 1) = 8T'$$

Which shows that all results must be universal if we express everything in the variables rescaled by the critical point values.
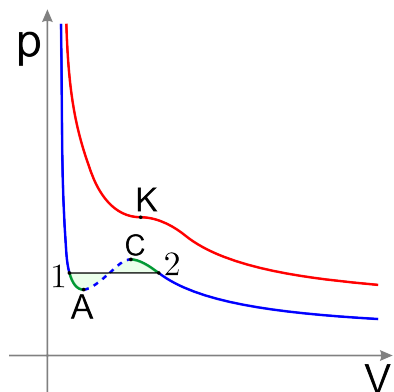

Below T_c the isotherms shows the instabilities and metastable states.

- The thermodynamic inequality requires the derivative $\left(\frac{\partial P}{\partial V}\right)_{T,N}$ to be negative (pressure increase when the volume is decreased).
- The part AC on the isotherm (see Fig. 3) is thermodynamically unstable. This is gas-liquid coexistence area.
- The parts $1A$ and $C2$ are metastable. The points 1 and 2 can be found from the condition of gas-liquid coexistence in equilibrium.

Figure 3.   A Van der Waal's isotherm.

For the coexistence $\mu_1(P,T) = \mu_2(P,T)$. Fixed P means horizontal line. Fixed T means that we are looking for two points on the same isotherm. So we need to find where a horizontal line which intersects an isotherm of $T < T_c$ in two points, such that the μ in the intersection points equal to each other. It means, that $\int_1^2 d\mu = 0$, where the integral is taken along the horizontal line. On the other hand if we take this integral along the isotherm we can write $0 = \int_1^2 (\partial\mu/\partial P)dP = \frac{1}{N}\int_1^2 (\partial\Phi/\partial P)_T dP = \frac{1}{N}\int_1^2 V dP$. Taking the last integral by parts we find $0 = P(V_2 - V_1) - \int_1^2 P dV$, or the area between the isotherms and the horizontal line is zero. This is called Maxwell rule.

LECTURE 43
Second order phase transitions.

This lecture is for self study.

43.1. Second order phase transitions. LL142

Second order phase transitions are characterized by the following

- The macroscopic state of a system changes continuously. There is no abrupt change of the state as in first order phase transitions.
- At second order transitions the symmetry of a state changes. It means that we always can tell one state from the other.
- In first order phase transition two states can be in equilibrium. At the second order transition the two states are the same at the transition point.
- For the second order transition above the transition temperature the symmetry of the macroscopic state is the same as the symmetry of the Hamiltonian.
- Below the transition temperature the symmetry of the macroscopic state is less (subgroup) than the symmetry of the Hamiltonian.

Let's consider the situation at fixed pressure. Above the transition temperature T_c the system is in the symmetric state. Below the transition temperature the system is in a broken symmetry state.

Let's start at temperature just above T_c. The system is in the symmetric state. Let's imagine, that we took a small volume of our system and put the system inside this volume in symmetry broken state. The work which we need to do will be proportional to the volume. For given volume this work becomes smaller and smaller as the temperature become close and closer to the transition temperature. It means that the fluctuation will lead to appearance of the finite volume regions of the symmetry broken state inside the symmetric state. These regions will become larger and larger as we lower the temperature towards T_c.

This picture suggest the following description. At the temperatures close to T_c there is a "slow" or macroscopic degree of freedom ϕ, which is called order parameter. All other degrees of freedom are fast and fluctuate at short-range, they average out on the time and range scales relevant for the order parameter ϕ. We thus can use adiabatic approximation considering all other degrees of freedom as living on the background of given ϕ. We then can take the integral in the partition function over the fast degrees of freedom at given configuration of the order parameter ϕ. After that only integration over ϕ will still be in the partition function.

We then are left with the free energy, or the thermodynamic potential which depends on the order parameter only. The value of the order parameter depends on the coordinate — it can have different values in the different parts of the system. Nevertheless, If we average ϕ over the whole sample, then above T_c, $\phi = 0$, and below T_c, $\phi \neq 0$. Thus close to T_c the value of the order parameter is small and we can use the Taylor expansion of, say, thermodynamic potential F, if we work at constant volume and temperature (or we can use Φ if the pressure and temperature are constant).

The order parameter may be real scalar, complex scalar, vector, or anything else, it depends on the transition we are considering. The order parameter is invariant of some subgroup of the total Hamiltonian symmetry group. The thermodynamic potential, however, must be invariant under the total symmetry group of the Hamiltonian. In Taylor expansion we then need to write all terms of the second, third, and fourth order in ϕ which are invariant under the full group.

For simplicity I will assume that the order parameter is just a scalar. And the thermodynamic potential must be invariant under $\phi \rightarrow -\phi$. We then have.

$$F = F_0 + V\alpha(T)\phi^2 + Vb\phi^4,$$

where F_0 is the ϕ independent part of the thermodynamic potential, $\alpha(T)$ and b are coefficients. Both F_0 and b also depend on temperature, but this dependence will not be critical and thus can be neglected in the vicinity of T_c.

The equilibrium value of the order parameter is given by the maximum of entropy at given energy, or $((\partial S/\partial\phi)_E = -T^{-1}(\partial F, \partial\phi)_{T,V})$ the minimum of the thermodynamic potential.

$$\frac{1}{V}\frac{\partial F}{\partial\phi} = 2\alpha(T)\phi + 4b\phi^3 = 0, \qquad \frac{1}{V}\frac{\partial^2 F}{\partial\phi^2} = 2\alpha(T) + 12b\phi^2 > 0.$$
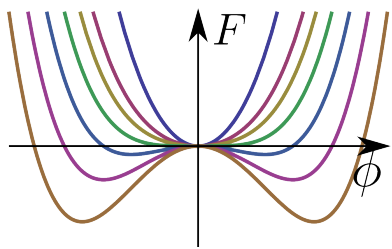

We see, that $\phi = 0$ is always a solution of the first equation. However, for $\alpha > 0$ it is the minimum, while for $\alpha < 0$ it is the maximum. So for the above F to describe the phase transition at T_c the coefficient α must be positive for $T > T_c$ and negative for $T < T_c$. The temperature dependence of the coefficients comes from the procedure of "integrating out" the fast degrees of freedom. Such procedure will produce only regular dependence of coefficients on temperature. So we can write $\alpha(T) = a(T - T_c)$. We then have

Figure 1.   A profile of $F(\phi)$ above and below transition temperature.

$$\phi = 0, \quad \text{for } T > T_c, \qquad \phi = \pm\sqrt{\frac{a(T_c - T)}{2b}}, \quad \text{for } T < T_c.$$

Plugging these values back into F we get (C is C_P)

$$\left.\begin{array}{l} F = F_0 \\ S = S_0 \\ C = C_0 \end{array}\right\}, \quad \text{for } T > T_c, \qquad \left.\begin{array}{l} F = F_0 - V\frac{a^2(T-T_c)^2}{4b} \\ S = S_0 + V\frac{a^2(T-T_c)}{2b} \\ C = C_0 + V\frac{a^2 T_c}{2b} \end{array}\right\}, \quad \text{for } T < T_c.$$

We see that thermodynamic potential and entropy are continuous functions of temperature, while the heat capacity has discontinuity (jump) at T_c.

43.2. Effect of the external field. LL144

Let's now introduce an external field to the system. We will consider the field is coupled linearly to the order parameter $-h\phi V$, where V is the volume. We then have:

$$F = F_0 + aV(T - T_c)\phi^2 + bV\phi^4 - h\phi V$$

The equilibrium value of ϕ is given by

$$2a(T - T_c)\phi + 4b\phi^3 = h$$

For $T > T_c$ LHS is a monotonic function of ϕ, so the equation has only one solution. For $T < T_c$ there are values of h for which there are three different solutions of the equation. The function $\phi(h)$ is not single valued. On the graph $\phi(h)$ there is a interval which has negative slope. This solution thermodynamically unstable as differentiating the above equation over h along this curve we find

$$\left(\frac{\partial\phi}{\partial h}\right)\left(\frac{\partial^2 F}{\partial\phi^2}\right) = V,$$

so if $\partial\phi/\partial h$ is negative, then F has a maximum.

All other parts of the graph $\phi(h)$ correspond to minimum of F, but some are metastable. We can calculate the differential susceptibility at zero field

$$\chi = \frac{\partial\phi}{\partial h} = \left.\frac{1}{2a(T - T_c) + 12b\phi^2}\right|_{h\to 0} = \begin{cases} \frac{1}{2a(T-T_c)}, & \text{for } T > T_c \\ \frac{1}{4a(T_c-T)}, & \text{for } T < T_c \end{cases}$$

It is also useful to note that

$$\left(\frac{\partial^2 F}{\partial\phi^2}\right)_{h=0} = \frac{V}{\chi}$$

43.3. Fluctuations of the order parameter. LL146

Let's now consider the fluctuations of the order parameter. We need to calculate the minimal work needed to change the order parameter from its equilibrium value $\bar\phi$ to some other value ϕ. At constant volume and temperature, the minimal work is given by the corresponding change of the thermodynamic potential F. Then we have

$$R_{min} = \Delta F = \left(\frac{\partial F}{\partial\phi}\right)_{\phi=\bar\phi}(\phi - \bar\phi) + \frac{1}{2}\left(\frac{\partial^2 F}{\partial\phi^2}\right)_{\phi=\bar\phi}(\phi - \bar\phi)^2, \qquad w \propto e^{-R_{min}/T}$$

The equilibrium value $\bar\phi$ was found from the condition $(\partial F/\partial\phi)_{\phi=\bar\phi} = 0$ and according to the previous section $(\partial^2 F/\partial\phi^2)_{\phi=\bar\phi} = V/\chi$. We are interested in temperatures close to T_c, so we have

$$R_{min} = \frac{V}{2\chi}(\phi - \bar\phi)^2, \qquad w \propto \exp\left[-\frac{V}{2T_c\chi}(\Delta\phi)^2\right]$$

This gives for the fluctuation of the order parameter

$$\langle(\Delta\phi)^2\rangle = T_c\chi/V$$

(It is not a coincidence that the fluctuation is proportional to the susceptibility. The more susceptible the system is the more it fluctuates. The above result can also be derived from the fluctuation-dissipation theorem.)

But this is not the end of the story. We have considered only the homogeneous fluctuations. The order parameter was considered uniform. This is obviously not the case in the

reality. In order to take into account the inhomogeneity of the order parameter we again will assume that we are close to the transition temperature. In this case, according to our picture, the range (the space extend of a typical fluctuation) of order parameter fluctuations is large. It then should be insensitive to the details of the short range physics. We then can split our sample on many subsamples. In each of them the order parameter is homogeneous. The total potential is then the sum of the potentials for the subsamples.

In this consideration it is easier if we fix volume and chemical potential instead of the number of particles. Then we should work with the potential $\Omega(\mu, T, \phi)$. For the homogeneous order parameter we then have

$$\Omega(\mu, T, \phi) = \Omega_0(\mu, T) + V\left[a(T - T_c)\phi^2 + b\phi^4 - h\phi\right]$$

If the order parameter is inhomogeneous, then we need to do three things

- Consider an order parameter **field** $\phi(\mathbf{r})$ instead just an order parameter ϕ.
- In the above formula instead just multiplication by V we need to integrate over d^3r.
- Add to the potential correction which arises from the inhomogeneity.

For very smooth fluctuations, when $\phi(\mathbf{r})$ is a very smooth function on the scale of interatomic distance the "inhomogeneity" term should depend only on derivatives of the order parameter $\partial\phi/\partial x_i$. We need only the term which is the lowest order in derivatives. Notice, that $\partial\phi/\partial x_i$ is a vector, while Ω is a scalar, so the lowest order term must be quadratic in $\partial\phi/\partial x_i$. We then can write:

$$\Omega(\mu, T, \phi) = \Omega_0(\mu, T) + \int \left[g(\partial\phi/\partial x_i)^2 + a(T - T_c)\phi^2 + b\phi^4 - h\phi\right] d^D r,$$

where g is a positive parameter.

Let's consider the fluctuations of the order parameter at $h = 0$ and $T > T_c$. We need to calculate the $\Delta\Omega$ up to the second order in $\Delta\phi(\mathbf{r}) = \phi(\mathbf{r}) - \bar\phi$. We obtain

$$\Delta\Omega = \int \left[g(\partial\Delta\phi/\partial x_i)^2 + a(T - T_c)(\Delta\phi)^2\right] d^D r, \qquad w \propto e^{-\Delta\Omega/T}.$$

In order to calculate the fluctuations I need to diagonalize the operator in the integrand. In order to do that I will expand the fluctuations in the Fourier series

$$\Delta\phi(\mathbf{r}) = \sum_{\mathbf{k}} \Delta\phi_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}, \qquad \Delta\phi_{-\mathbf{k}} = \Delta\phi_{\mathbf{k}}^*$$

and find

$$\Delta\Omega = V \sum_{\mathbf{k}} \left[gk^2 + a(T - T_c)\right] |\Delta\phi_{\mathbf{k}}|^2.$$

Now we see that the fluctuations of different modes are decoupled and[1]

$$\langle|\Delta\phi_{\mathbf{k}}|^2\rangle = \frac{T_c}{2V}\frac{1}{gk^2 + a(T - T_c)}.$$

Notice, that $k = 0$ result is exactly the result for the homogeneous fluctuation.

We now can calculate the correlator

$$G(\mathbf{r}) = \langle\Delta\phi(\mathbf{r}_1)\Delta\phi(\mathbf{r}_2)\rangle, \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_1$$

as it is given by

$$G(\mathbf{r}) = \sum_{\mathbf{k}}\langle|\Delta\phi_{\mathbf{k}}|^2\rangle e^{i\mathbf{k}\cdot\mathbf{r}} = V\int\langle|\Delta\phi_{\mathbf{k}}|^2\rangle e^{i\mathbf{k}\cdot\mathbf{r}}\frac{d^D k}{(2\pi)^D}$$

---

[1]For $T < T_c$ the result is the same except instead $a(T - T_c)$ we will get $2a(T_c - T)$

At $T = T_c$ the last integral diverges at $k \to 0$ for $D \leq 2$, but converges for $D > 2$. For $D = 3$ it can be calculated an gives

$$G(r) = \frac{T_c}{8\pi gr} e^{-r/r_c}, \qquad r_c = \sqrt{\frac{g}{a(T - T_c)}}$$

r_c is called correlation length. Notice, that it diverges at $T = T_c$.

Now lets figure out when the theory of phase transitions is applicable. In order for it to work the contribution to the thermodynamic potential Ω from fluctuations must be smaller then the one from the mean value of the order parameter. The typical fluctuation has a volume r_c^3, the fluctuation in this volume is $\langle (\Delta\phi)^2 \rangle \approx T_c \chi / V_c = T_c \chi / r_c^3$. The mean value of the fluctuation is $\bar{\phi}^2 \approx a|T - T_c|/b$ so we have

$$\langle (\Delta\phi)^2 \rangle \approx T_c \chi / r_c^3 \ll a|T - T_c|/b$$

In other words

$$|T - T_c| \gg \frac{T_c^2 b^2}{ag^3}.$$

This is called Ginzburg criterion.

So the Landau theory works only outside of the fluctuation region given by the above condition.

On the other hand the Landau theory is the expansion by powers of $|T - T_c|$ and works only when

$$|T - T_c| \ll T_c$$

We see that in order to have any region of applicability of the Landau theory we must have

$$\frac{T_c b^2}{ag^3} \ll 1.$$

43.4. Critical indices. LL148

Please read LL148

THE END!