

Lecture notes on PHY7500

## **Statistical Mechanics**

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# Chapter 1

## IDEAL SYSTEMS

### 1.1 Basics of statistical mechanics. Entropy and Temperature.

Consider a system of  $N$  particles with total energy  $E$ . A system with a given energy can be found in different quantum states. The statistical mechanics is build upon one and only one postulate:

*Main postulate of Statistical Mechanics: at any given time the system is equally likely to be found in any of possible quantum states.*

If we denote by  $\Omega(N, E)$  the total number of possible different quantum states (which is called the *degeneracy factor* in quantum mechanics) the probability to find the system in a given quantum state  $n$ , equal for all states, is

$$p_n = \frac{1}{\Omega(N, E)} \quad (1.1.1)$$

The *entropy* of the system is defined as the logarithm of the degeneracy factor:

$$\boxed{\sigma \equiv \ln \Omega}; S = k\sigma \text{ --(dimensionless and dimensionfull) entropy} \quad (1.1.2)$$

where  $k = 1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$  is the Boltzmann constant.

If two isolated systems are brought into thermal contact (are allowed to exchange energy, such that  $E_1 + E_2 = E = \text{const}$ ) the probability to find them with energies  $E_1$  and  $E_2 = E - E_1$  is proportional to the total number of quantum states the combined system has for this configuration:

$$\Omega(E) = \Omega_1(E_1)\Omega_2(E_2 = E - E_1) \quad (1.1.3)$$

One defines the *equilibrium* state and the corresponding equilibrium energies as such that the probability has a maximum. Differentiating  $\sigma(E_1, E_2 = E - E_1) = \sigma_1(E_1) + \sigma_2(E_2)$  with respect to  $E_1$  and equating to zero, one finds that in equilibrium

$$d\sigma_1/dE_1|_{\bar{E}_1} = d\sigma_2/dE_2|_{\bar{E}_2=E-\bar{E}_1} \quad (1.1.4)$$

Introducing temperature as inverse of  $d\sigma/dE$ :

$$\boxed{\left(\frac{\partial \sigma}{\partial E}\right)_{V,N} \equiv \frac{1}{T}} \quad (1.1.5)$$

we find that in equilibrium  $T_1 = T_2$ . The temperature has a dimension of energy. Boltzmann constant is used to convert it in Kelvins ( $T_E = T_K k$ , or  $\left(\frac{\partial S}{\partial E}\right)_{V,N} \equiv \frac{1}{T_K}$ , where the subscript is used to identify temperature values expressed in energy units or in Kelvins).

Similarly, if the subsystem volumes are allowed to change such that the total volume is a constant,  $V_1 + V_2 = V = \text{const}$ , one finds that in equilibrium  $P_1 = P_2$ , where the pressure  $P$  is defined as:

$$\boxed{\left(\frac{\partial\sigma}{\partial V}\right)_{E,N} \equiv \frac{P}{T}} \quad (1.1.6)$$

Finally, if the systems allowed to exchange particles, the equilibrium will be reached when  $\partial\sigma_1/dN_1 = \partial\sigma_2/dN_2$ . Introducing *chemical potential*

$$\boxed{\left(\frac{\partial\sigma}{\partial N}\right)_E \equiv -\frac{\mu}{T}} \quad (1.1.7)$$

the equilibrium condition can be written as  $\mu_1 = \mu_2$ .

The set of definitions via partial derivatives introduced above can be written via corresponding differentials:

$$\boxed{dE = Td\sigma - PdV + \mu dN.} \quad (1.1.8)$$

Note *extensive*,  $E$ ,  $V$ ,  $N$ ,  $\sigma$ , and *intensive*,  $P$ ,  $T$ ,  $\mu$ , quantities. From the extensivity of entropy it follows (see Homework problem) that

$$E = T\sigma - PV + \mu N. \quad (1.1.9)$$

For further reference we note here that partial derivatives can be written via Jacobians with the latter being conveniently worked with as with ratios. An example of such a transformations is given below:

$$P = \frac{\left(\frac{\partial S}{\partial V}\right)_{N,E}}{\left(\frac{\partial S}{\partial E}\right)_{N,V}} = \frac{\partial(S,E)\partial(E,V)}{\partial(V,E)\partial(S,V)} = -\left(\frac{\partial E}{\partial V}\right)_S. \quad (1.1.10)$$

To calculate the *fluctuations in energy*, which are quantified by  $\langle(E - \langle E \rangle)^2\rangle = \langle(\Delta E)^2\rangle$ , we expand entropy as a function of energy to the second order in deviation from the equilibrium:

$$\sigma(E_1) = \sigma(\bar{E}_1) + \left.\frac{d\sigma}{dE_1}\right|_{E_1=\bar{E}_1} (E_1 - \bar{E}_1) + \frac{1}{2} \left.\frac{d^2\sigma}{dE_1^2}\right|_{E_1=\bar{E}_1} (E_1 - \bar{E}_1)^2 + \dots \quad (1.1.11)$$

From that one gets

$$\overline{(\Delta E_1)^2} = \frac{1}{\frac{1}{T^2 C_V^{(1)}} + \frac{1}{T^2 C_V^{(2)}}} \quad (1.1.12)$$

For the case  $C_V^{(1)} \gg C_V^{(2)}$

$$\boxed{\overline{(\Delta E_1)^2} = C_V T^2} \quad (1.1.13)$$

## 1.2 Ideal gas

*Ideal gas is a system/gas of particles for which the potential energy of interaction can be neglected*

### 1.2.1 First look

Consider  $N$  particles in a volume  $V = L^3$ . Recall the energy levels of a particle in the infinitely deep potential well:

$$E_n = \frac{\pi^2 \hbar^2 n^2}{2mL^2}. \quad (1.2.1)$$

Based on that, the number of quantum states of the gas (degeneracy) is equal to the number of different sets  $\{n_i\}$ , such that

$$\sum_i^{3N} n_i^2 = \frac{2mV^{2/3}E}{\pi^2 \hbar^2}. \quad (1.2.2)$$

The calculation of the number is given in the next subsection, here we only note that such a number does not depend on the volume and energy independently but in combination  $V^{2/3}E$ . This immediately leads to a relation

$$PV = \frac{2}{3}E. \quad (1.2.3)$$

It is naturally to assume that the number of states for one particle is proportional to the volume, and that for  $N$  particles,  $\Omega \propto V^N$  (this assumption is not that obvious, but correct, see the exact calculation below). From here one obtains:

$$PV = NT \quad (1.2.4)$$

### 1.2.2 Calculation of the number of states

To calculate the number of states given by condition 1.2.2 we first calculate *the volume and the surface area of  $n$ -dimensional sphere*:

$$V_n = \int_{\sum_{i=1}^n x_i^2 < R^2} dx_1 dx_2 \dots dx_n = C_n R^n; \quad dV_n = S_n dR; \quad S_n = C_n n R^{n-1}. \quad (1.2.5)$$

Coefficient  $C_n$  can be determined by evaluating an auxiliary integral

$$\int dx_1 dx_2 \dots dx_n e^{-\sum_{i=1}^n x_i^2} = \int_0^\infty C_n R^{n-1} n dR = \pi^{n/2}. \quad (1.2.6)$$

The final expression for the volume of  $n$ -dimensional sphere:

$$\boxed{V_n = \frac{\pi^{(n/2)}}{(n/2)!} R^n}. \quad (1.2.7)$$

We will continue with approximation of very large number of particles,  $\ln N \gg 1$ , and keep only two leading terms in the expansion of  $\ln(N!)$ . For the latter we use Stirling approximation:

$$N! \approx \sqrt{2\pi N} e^{-N} N^N \quad (1.2.8)$$

Then,

$$\ln N \approx \ln \sqrt{2\pi N} + N \ln N - N \approx N \ln N - N. \quad (1.2.9)$$

Within this approximation,  $\ln V_n \approx \ln S_n$  and the problem of finding the number of micro-states of the ideal gas reduces to a calculation of the volume of  $3N$  dimensional where:

$$\Omega = \frac{1}{2^{3N}} \frac{\pi^{3N/2}}{(3N/2)!} \left( \frac{2mE}{\pi^2 \hbar^2} \right)^{3N/2} V^3 \quad (1.2.10)$$

It yields for entropy:

$$\sigma = N \ln \left[ \left( V \frac{mE}{3\pi \hbar^2 N} \right)^{3/2} \right] + \frac{3N}{2}, \quad (1.2.11)$$

the expression that is obviously non-extensive (“twice” the system does not have twice the entropy). This observation is called *the Gibbs paradox*.

The solution to the paradox is in the correct accounting for the indistinguishability of particles:  $\Omega_{correct} = \Omega_{old}/N!$ . Correct expression for the entropy of an ideal gas

$$\sigma = N \ln \left[ \left( \frac{mE}{3\pi \hbar^2 N} \right)^{3/2} \right] + \frac{5N}{2} \quad (1.2.12)$$

Using this expression one easily finds the relations  $E = 3/2 NT$ ,  $PV = NT$ , and the *chemical potential of an ideal gas at constant volume*:

$$\mu = kT \ln \left[ \frac{N}{V} \left( \frac{3\pi \hbar^2 N}{mE} \right)^{3/2} \right] \quad (1.2.13)$$

Note: all quantities (temperature, pressure, chemical potential) in the above expressions are functions of  $E$ ,  $V$ , and  $N$ .

Finally note that the number of micro-states for an ideal gas can be calculated directly based on Bohr quantization rule  $\oint dpdx \approx 2\pi\hbar(n+1/2)$ , which is equivalent to the statement that the number of quantum states corresponding to the phase-space volume  $\Delta p \Delta x$  is equal  $\Delta n = \Delta p \Delta x / (2\pi\hbar)$ . Then for an ideal gas consisting of  $N$  particles:

$$\Omega = \frac{\int_{\sum p_i^2/2m < E} d^{3N}p d^{3N}x}{2\pi\hbar N!} = \frac{V^N}{(2\pi\hbar)^{3N} N!} \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{3N/2}, \quad (1.2.14)$$

an expression, which coincides with our previous result.

### 1.3 Ensemble theory. Canonical and microcanonical distributions.

By *ensemble* one calls a collection of “mental copies” of a given system. It is assumed that these copies represent the system taken at random instants of time. The latter means that for any physical quantity the time average and the average over ensemble are equivalent. A system at a given state is represented by a point in the *phase space*  $\equiv$  configuration space  $\otimes$  momentum space.

Ensemble average of quantity  $f$  can be written:

$$\langle f \rangle = \frac{\int f(p, q) \rho(p, q) d^{3N}q d^{3N}p}{\int f(p, q) d^{3N}q d^{3N}p}, \quad (1.3.1)$$

where  $\rho(p, q)$  is the *phase space density*.

Phase point trajectory (on a hyper-surface  $H(p, q) = E$ ) is determined by Hamilton's equations:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}; \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (1.3.2)$$

Continuity equation  $\partial\rho/\partial t + \text{div}(\rho\vec{v}) = 0$  applied to the phase space density leads to:

$$\frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial\rho}{\partial q_i} \dot{q}_i + \frac{\partial\rho}{\partial p_i} \dot{p}_i \right) + \rho \sum_{i=1}^{3N} \left( \frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i} \right) = 0, \quad (1.3.3)$$

where the last sum equals zero according to Hamilton's equations. The remaining part can be rewritten as full derivative of phase space density, meaning that the phase space density must be an integral of motion (*Liouville's theorem*):

$$\boxed{\frac{d\rho(p, q; t)}{dt} = 0} \quad (1.3.4)$$

Considering two non interacting subsystems (two parts of a bigger system) one has to conclude that  $\rho(q_1, p_1, q_2, p_2) = \rho_1(q_1, p_1)\rho_2(q_2, p_2)$ , which means that the logarithm of the phase space density must be an additive integral of motion. Further, taking into account that there exist only seven additive integrals of motion one finds:

$$\boxed{\ln \rho = \alpha + \beta E + \vec{\gamma}\vec{P} + \vec{\delta}\vec{M}} \quad (1.3.5)$$

Considering system at rest (and not rotating),  $\vec{P} = 0$  and  $\vec{M} = 0$ , one is left with only dependence on the total energy. It defines two major cases:

*Microcanonical* ensemble which describes systems at constant energy:  $\rho \propto \delta(E - E_0)$ , and *Canonical* distribution,  $\rho \propto \exp(-\beta E)$ , which describes systems at constant temperature.

*Canonical* distribution in its turn have different types: canonical distribution at constant volume or at constant pressure, constant number of particles or constant chemical potential. The latter is very important and has a special name of *Grand canonical* distribution.

## 1.4 Most important examples of ideal systems. Microcanonical distribution.

Statistical mechanics (of ideal systems) in examples:

1. Ideal gas.  $N$  particles in a volume  $V$ .
2. System of  $N$  oscillators. Classical and quantum cases.
3. Two level system:  $E_i = \pm\varepsilon$ ,  $N$  particles.

### 1.4.1 Ideal gas

Ideal gas at fixed energy (microcanonical distribution) has been already discussed in detail in section 1.2.

### 1.4.2 System of N classical oscillators

Hamiltonian describing one classical oscillator

$$H = \frac{m\omega^2}{2}x^2 + \frac{p^2}{2m} \quad (1.4.1)$$

It leads to

$$\int \frac{dp dx}{2\pi\hbar} = \sqrt{mE} \sqrt{\frac{2E}{m\omega^2}} \frac{\pi}{2\pi\hbar} = n \quad (1.4.2)$$

For a system of  $N$  particles:

$$\frac{1}{(2\pi\hbar)^N} \int_{\sum(p_i^2/2m+m\omega^2 x_i^2/2) \leq E} d^N p d^N x = (2m)^{N/2} \left(\frac{2}{m\omega^2}\right)^{N/2} \frac{\pi^N}{N!} e^N \frac{1}{(2\pi\hbar)^N} = E^N/\omega^N \quad (1.4.3)$$

Differentiating entropy with respect to the energy yields

$$\boxed{E/N = T.} \quad (1.4.4)$$

### 1.4.3 $N$ quantum oscillators

Recall that  $E_i = \hbar\omega(n_i + 1/2)$ . Introducing

$$R = (E - N\hbar\omega/2)/(\hbar\omega) = E/(\hbar\omega) - N/2 \quad (1.4.5)$$

Combinatorial problem:  $R$  balls in  $N$  boxes.

$$\Omega = \frac{(R + N - 1)!}{R!(N - 1)!} \quad (1.4.6)$$

The entropy:

$$\sigma = (R + N) \ln(R + N) - R \ln R - N \ln N \quad (1.4.7)$$

Differentiating with respect to the energy

$$\frac{\partial\sigma}{\partial E} = \frac{1}{kT} = \frac{\partial\sigma}{\partial R} \frac{\partial R}{\partial E} = \frac{\partial\sigma}{\partial R} \frac{1}{\hbar\omega} = \frac{1}{\hbar\omega} \ln \frac{R + N}{R} \quad (1.4.8)$$

$$\frac{\hbar\omega}{T} = \ln \frac{E + N\hbar\omega/2}{E - N\hbar\omega/2} \quad (1.4.9)$$

$$\boxed{E = \frac{N\hbar\omega}{2} \frac{1 + e^{-\hbar\omega/T}}{1 - e^{-\hbar\omega/T}} = N \left( \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/T} - 1} \right)} \quad (1.4.10)$$

Consider two limiting cases:  $\hbar\omega \ll T$  and  $\hbar\omega \gg T$ .

### 1.4.4 Two level system

$N$  particles,  $E_i = \pm\varepsilon$ ,  $R = E/\varepsilon$ . The number of particles at the upper level  $M$  and at the lower level  $L$ . The entropy

$$\sigma = \ln \frac{N!}{M!L!}. \quad (1.4.11)$$

$$\frac{\partial\sigma}{\partial E} = \frac{1}{\varepsilon} \frac{\partial\sigma}{\partial R} = \frac{1}{T} = \frac{1}{2\varepsilon} \ln \frac{N - R}{N + R}. \quad (1.4.12)$$

$$\boxed{E = -\varepsilon N \tanh(\varepsilon/T)} \quad (1.4.13)$$

Note that a two level system with positive energy corresponds to the negative temperature. From this observation and/or plot of temperature as function of energy one finds that negative temperature corresponds to a “hotter” state, such that  $T = -\infty$  coincides with  $T = +\infty$ .

Among examples of the two level systems are: spin 1/2 particles (electrons) in the magnetic field, gas of excited atoms with two close energy levels.

An interesting example is the model of rubber (polymer): A linear chain of  $N$  links of length  $A$ . Each link can take only one of two positions, parallel or anti-parallel to the  $x$  axis. The total length is  $L$ . Note the similarity of this problem to the two level system problem (though it is not clear how to calculate energy in this case). Nevertheless, in analogy to  $p/T = \partial\sigma/\partial V$  one can introduce a generalized force:  $f/T = \partial\sigma/\partial L$ . Also note that generalized force can be considered as external or internal:  $f^{ext} = -f^{int}$ . Then

$$L = aN \tanh \frac{f^{ext} a}{kT} \quad (1.4.14)$$

## 1.5 Canonical distribution. General properties.

Consider two systems in thermal contact, such the second system is much larger than the first. The probability to find the system “1” with energy  $E_1$  can be written as

$$p(E_1) \propto e^{\sigma_1(E_1) + \sigma_2(E_2 = E - E_1)}, \quad (1.5.1)$$

where  $E$  is the total energy. Assuming  $E_1 \ll E_2$  and expanding  $\sigma_2$  in series, one has

$$p(E_1) \propto e^{\sigma_1(E_1) - E_1/T}, \quad (1.5.2)$$

where  $T$  is the temperature of the bigger system, the “thermal bath”. This expression can be rewritten as

$$p(E_1) \propto e^{-(E_1 - \sigma_1 T)/T} \propto e^{-\Delta A/T} \quad (1.5.3)$$

where we have introduced quantity  $A = E - T\sigma$ , which is called *free energy*. Note that the equilibrium corresponds to the *minimum* of free energy and the probability for deviation from an equilibrium (fluctuations) is proportional to  $\exp(-\Delta A/T)$ ; the latter expression we will use later in discussion of the fluctuations during phase transitions.

Noting that  $e^{\sigma(E_1)}$  gives the degeneracy of the state with given energy  $E_1$ , one can write that the probability to find a system in each given micro-state  $i$  is given by:

$$p_i = e^{-E_i/T}/Q, \quad (1.5.4)$$

where the normalization is satisfied with a factor

$$\boxed{Q = \sum_i e^{-E_i/T}}, \quad (1.5.5)$$

which is called the *partition function* or the *statistical sum*.

Note that an introduction of free energy can be done formally with the help of the so-called *Lagrange transformation*. An expression  $dE = Td\sigma - PdV + \mu dN$  can be considered as a differential of potential  $E$  with respect to the entropy, volume, and number of particles:  $E(\sigma, V, N)$ . One can introduce a potential with respect to other combination of variables, e.g.  $(T, V, N)$ . Let us consider:

$$d(E - \sigma T) = dE - \sigma dT - T d\sigma = -T d\sigma - PdV + \mu dN \quad (1.5.6)$$

One can see that the obtained potential is the free energy  $A(T, V, N)$ . In a similar way one can introduce other thermodynamic potentials. Most often used are  $H = E + PV$  - *enthalpy*,  $G =$

$A + PV = E - T\sigma + PV = \mu N$  - *Gibbs free energy* (potential  $A$  is often called *Helmholtz free energy*). The corresponding differentials are:

$$dH = Td\sigma + VdP + \mu dN \quad (1.5.7)$$

$$dG = -\sigma dT + VdP + \mu dN \quad (1.5.8)$$

Also, for a later use we give the definitions of heat capacity at constant volume and at constant pressure

$$C_V = T \left( \frac{\partial \sigma}{\partial T} \right)_V = \left( \frac{\partial E}{\partial T} \right)_V; \quad C_P = T \left( \frac{\partial \sigma}{\partial T} \right)_P = \left( \frac{\partial H}{\partial T} \right)_P. \quad (1.5.9)$$

### 1.5.1 Free energy and entropy

When not talking about fluctuations we would always assume the quantities taken at equilibrium.

$$\bar{E} = A + T\sigma = A - T \left( \frac{\partial A}{\partial T} \right)_{N,V} = -T^2 \frac{\partial(A/T)}{\partial(1/T)} \quad (1.5.10)$$

Comparing this to  $\bar{E} = -\frac{\partial \ln Q}{\partial(1/T)}$  we conclude that

$$\boxed{A = -T \ln \left( \sum_i e^{-E_i/T} \right)} \quad (1.5.11)$$

Note that as energy fluctuates, so the entropy. For an equilibrium value one finds

$$\sigma = -\frac{\partial A}{\partial T} = \ln \left( \sum_i e^{E_i/T} \right) + \frac{1}{T} \frac{\sum_i E_i e^{E_i/T}}{\sum_i e^{E_i/T}} = E/T - A/T \quad (1.5.12)$$

Taking a closer look at the intermediate stage one finds

$$\boxed{\sigma = -\overline{\ln p_i}} \quad (1.5.13)$$

### 1.5.2 Energy fluctuations

$$\frac{\partial \bar{E}}{\partial(1/T)} = \frac{\sum_i (-E_i^2) e^{-E_i/T}}{\sum_i e^{-E_i/T}} - \frac{\sum_i E_i e^{-E_i/T} \sum_i E_i e^{-E_i/T}}{(\sum_i e^{-E_i/T})^2} = -\overline{(\Delta E)^2} \quad (1.5.14)$$

Recalling the definition of heat capacity

$$\boxed{\frac{\partial \bar{E}}{\partial(1/T)} = -T^2 \frac{\partial \bar{E}}{\partial T} = -T^2 C_V} \quad (1.5.15)$$

## 1.6 Canonical distribution. Examples.

### 1.6.1 Ideal gas

For an ideal gas of  $N$  particles:

$$Q_N(V, T) = \frac{1}{N!} \int e^{-H(p,x)/T} \frac{d^{3N}p d^{3N}x}{(2\pi\hbar)^{3N}} = \frac{Q_1^N}{N!} \quad (1.6.1)$$

$$Q_1 = \int e^{p^2/2mT} \frac{d^3p d^3x}{(2\pi\hbar)^3} = \frac{V}{(2\pi\hbar)^3} (2\pi mT)^{3/2} \quad (1.6.2)$$

The free energy is given by

$$A = -T \ln Q_N = NT \left( \ln \left[ \frac{N}{V} \left( \frac{(2\pi\hbar)^2}{2\pi mT} \right)^{3/2} \right] - 1 \right) \quad (1.6.3)$$

Calculation of (mean) energy and entropy is strait-forward:

$$E = \frac{\partial(A/T)}{\partial(1/T)} = \frac{3}{2} NT \quad (1.6.4)$$

$$\sigma = -\frac{\partial A}{\partial T} = N \left( \ln \frac{N}{V} \left[ \frac{(2\pi\hbar)^2}{2\pi mT} \right]^{3/2} - \frac{5}{2} \right), \quad (1.6.5)$$

which coincides with the expression for the entropy for a gas with fixed energy (micro-canonical ensemble) if  $E = 3NT/2$  is put in.

Chemical potential,  $\mu = \left( \frac{\partial A}{\partial N} \right)_{T,V}$  is given by:

$$\frac{\mu}{T} = \frac{\partial}{\partial N} (N \ln Q_1 - N \ln N + N) = \ln \frac{Q_1}{N} = \frac{\mu}{T}. \quad (1.6.6)$$

### 1.6.2 System of $N$ classical oscillators

$$Q_1 = \int \frac{dp dx}{2\pi\hbar} e^{-\left( \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} \right) / T} = \frac{T}{\hbar\omega}, \quad (1.6.7)$$

$Q_N = Q_1^N$ , and

$$A = -T \ln \frac{\hbar\omega}{T} \quad (1.6.8)$$

As expected

$$E = NT. \quad (1.6.9)$$

### 1.6.3 $N$ quantum oscillators

Energy levels of a quantum oscillator is given by  $E_n = \hbar\omega(n + 1/2)$ . Then

$$Q_1 = \sum_i^{\infty} e^{-\frac{\hbar\omega(n+1/2)}{T}} = \frac{e^{-\frac{\hbar\omega}{2T}}}{1 - e^{-\frac{\hbar\omega}{T}}}; \quad Q_N = Q_1^N \quad (1.6.10)$$

It translates into

$$A = -NT \left[ -\frac{\hbar\omega}{2T} - \ln \left( 1 - e^{-\frac{\hbar\omega}{T}} \right) \right] \quad (1.6.11)$$

The mean energy is given by

$$\boxed{\bar{E} = \frac{\partial(A/T)}{\partial(1/T)} = \frac{N\hbar\omega}{2} + \frac{N\hbar\omega}{e^{\hbar\omega/T} - 1}} \quad (1.6.12)$$

Plot  $E(T)$ !

The heat capacity is given by

$$C_{V,osc} = N \left( \frac{\hbar\omega}{T} \right)^2 \frac{e^{\hbar\omega/T}}{(e^{\hbar\omega/T} - 1)^2} \quad (1.6.13)$$

### 1.6.4 Two-level system

The calculations are strait-forward:

$$Q_1 = e^{\varepsilon/T} + e^{-\varepsilon/T} = 2 \cosh(\varepsilon/T) \quad (1.6.14)$$

$$A = -NT \ln [2 \cosh(\varepsilon/T)] \quad (1.6.15)$$

$$\boxed{E = -N\varepsilon \tanh(\varepsilon/T)} \quad (1.6.16)$$

### 1.6.5 Spin 1/2 particles in the magnetic field

Potential energy of a particle with magnetic moment in the magnetic field  $E = -\vec{\mu}\vec{H}$ . Recalling from the quantum mechanics that the magnetic moment of a particle  $\mu = g\mu_B m$ , where  $g$  is Lande's factor (for the electron  $g = 2$ ),  $\mu_B = \frac{e\hbar}{2m_e}$  is Bohr's magneton, and  $m$  is the magnetic quantum number (for the electron  $m = \pm 1/2$ ,  $g = 2$ , and  $\mu_e = \mu_B$ ):

$$E = \pm\varepsilon = \pm\mu_B H \quad (1.6.17)$$

Magnetization of the system,  $M = \langle \mu \rangle N$ :

$$M = N \frac{\sum_i \mu_i e^{-E_i/T}}{\sum_i e^{-E_i/T}} = NT \frac{\partial \ln Q_1}{\partial H} \quad (1.6.18)$$

Note that in general

$$\boxed{M = -\frac{\partial A}{\partial H}} \quad (1.6.19)$$

In our case

$$M = N\mu_B \tanh(\mu_B \hbar/T); \quad E = -MH = -N\varepsilon \tanh(\varepsilon/T) \quad (1.6.20)$$

*Magnetic susceptibility* (classical electron gas):

$$\chi \equiv \frac{1}{V} \left. \frac{\partial M}{\partial H} \right|_{H=0} = \frac{n\mu_e^2}{T} \quad (1.6.21)$$

so called *Curie law*  $M \propto 1/T$ .

Also note *Schottky specific heat*

$$C_V = n\varepsilon \frac{1}{\cosh^2(\varepsilon/T)} \frac{\varepsilon}{T^2} \quad (1.6.22)$$

Draw a plot!

### 1.6.6 Generalized forces

Previously established relation,  $M = -\partial A/\partial H$ , can be rewritten in a generalized differential of free energy:

$$dA = -\sigma dT - PdV + \mu dN - MdH \quad (1.6.23)$$

The last term, very analogous to  $-PdV$  can be also considered as the pair of conjugate generalized force and coordinate. One could consider “external” force and “internal”, such that  $f^{ext} = -f^{int}$ . For example, for a one dimensional system,

$$dA = -\sigma dT + f^{ext} dL, \quad (1.6.24)$$

where  $L$  is the length of the system.

### 1.6.7 Model of rubber (polymer)

Consider a chain of  $N$  elements, each of length  $a$ . Each link can take only one of two positions, parallel or anti-parallel to the  $x$  axis. The chain is kept at temperature  $T$  under external force  $f_{ext}$ . What is the length of the polymer under such conditions?

This is a typical two level system problem, as each element of the chain, depending on position has energy  $\varepsilon = \pm f_{ext}a$ . The free energy of the system is given by

$$A = -NT \ln[2 \cosh(f_{ext}a/T)]. \quad (1.6.25)$$

The (average) length of the polymer is

$$L = -\frac{\partial A}{\partial f_{ext}} = Na \tanh(f_{ext}a/T). \quad (1.6.26)$$

Note Hook’s law!

### 1.6.8 Ideal gas of diatomic molecules

Recall that for a monoatomic ideal gas  $C_V = 3/2 NT$ .

For diatomic molecules along with (translational) kinetic energy one has to consider vibrations (oscillations) and rotation. The Hamiltonian:

$$H = \frac{p^2}{2m} + \hbar\omega\left(n + \frac{1}{2}\right) + l(l+1)\frac{\hbar^2}{2I}. \quad (1.6.27)$$

The partition function can be written as

$$Q_N = \frac{(Q_{1;transl}Q_{1;rot}Q_{1;osc})^N}{N!} = (Q_{1;monoatomic}Q_{1;rot}Q_{1;osc})^N. \quad (1.6.28)$$

and the free energy  $A = A_{mono} + A_{rot} + A_{osc}$ .

For  $N$  quantum oscillators  $E_{osc} = N\hbar\omega(1/2 + (\exp(\hbar\omega/T) - 1)^{-1})$ . It gives the contribution to the specific heat:

$$C_{V,osc} = N \left( \frac{\hbar\omega}{T} \right)^2 \frac{e^{\hbar\omega/T}}{(e^{\hbar\omega/T} - 1)^2} \quad (1.6.29)$$

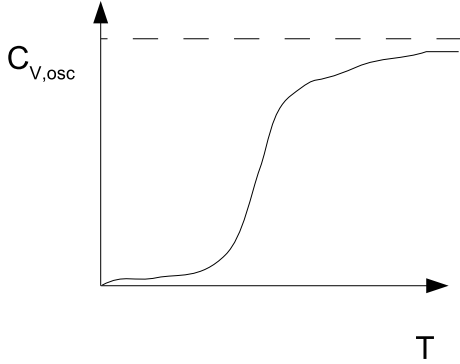


Figure 1.1: Heat capacity, oscillatory part.

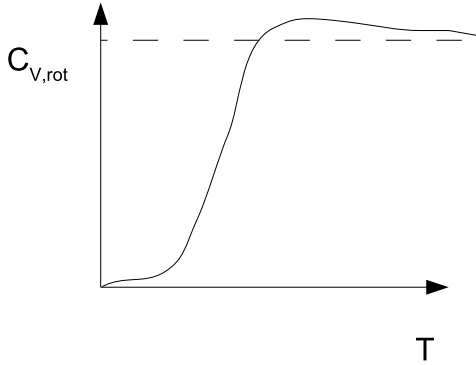


Figure 1.2: Heat capacity, rotational part.

Let us proceed with rotational part of heat capacity. Rotational energy of one particle is  $\epsilon_{rot} = l(l+1)\hbar^2/(2I)$ .

$$Q_{rot} = \sum_{L=0}^{\infty} (2l+1) e^{-\frac{l(l+1)\hbar^2}{2IT}} \approx \int_0^{\infty} dl 2l e^{-\frac{l(l+1)\hbar^2}{2IT}} \approx \frac{2IT}{\hbar^2} \quad (1.6.30)$$

Then

$$A = -T \ln \frac{2IT}{\hbar^2} = T \ln \frac{\hbar^2}{2IT} \quad (1.6.31)$$

and  $E = T$ . For  $N$  particles  $C_{V,rot} = N$ . Exact calculations show that the heat capacity approaches its asymptotic values from above as shown in Fig. 1.2.

## 1.7 Grand-Canonical distribution.

Consider two systems in thermal and chemical contact (chemical contact  $\equiv$  possibility to exchange particles), such that the second system is much larger than the first. The probability to find the system "1" in a state with energy  $E_1$  and number of particles  $N_1$  can be written as

$$p(E_1) \propto e^{\sigma_1(E_1, N_1) + \sigma_2(E_2 = E - E_1, N_2 = N - N_1)}, \quad (1.7.1)$$

where  $E$  and  $N$  are the total energy and the total number of particles. Assuming  $E_1 \ll E$  and  $N_1 \ll N$ , and expanding  $\sigma_2$  in series, one finds

$$p(E_1) \propto e^{\sigma_1(E_1) - E_1/T + N_1\mu/T} \quad (1.7.2)$$

where  $T$  is the temperature of the bigger system ("thermal bath"), and  $\mu$  is its chemical potential. This expression can be rewritten as

$$p(E_1) \propto e^{-\Phi_G/T} \quad (1.7.3)$$

where we have introduced quantity  $\Phi_G = E - T\sigma - \mu N$ , which is called *grand potential* or *Landau free energy*. Note that equilibrium corresponds to the *minimum* of the grand potential.

Noting that  $e^{\sigma(E_1, N_1)}$  gives the degeneracy of the state with given energy  $E_1$ , the probability to find a system in each given micro-state  $i$  is given by

$$p_{i,N} = \frac{1}{Z} e^{-(E_i - \mu N)/T}, \quad (1.7.4)$$

where  $Z$  is the *grand-canonical partition function* or *grand statistical sum*. It is defined as

$$Z = \sum_N \sum_i e^{-(E_i - \mu N)/T} = \sum_N \sum_i z^N e^{-E_i/T}, \quad (1.7.5)$$

with  $i$  running over all quantum states at given  $N$ . We have also introduced *fugacity*

$$z \equiv e^{\mu/T}. \quad (1.7.6)$$

Recalling that the mean entropy can be written as

$$\sigma = -\overline{\ln p_{i,N}} = \ln Z + \frac{E}{T} - \frac{\mu N}{T} \quad (1.7.7)$$

and that  $E = \sigma T - PV + \mu N$  one arrives to

$$\Phi_G = -T \ln Z = -PV. \quad (1.7.8)$$

Treating fugacity as an independent (of temperature) variable one also finds useful relations:

$$\bar{N} = T \left( \frac{\partial \ln Z}{\partial \mu} \right)_T; \quad \bar{E} = T^2 \left( \frac{\partial \ln Z}{\partial T} \right)_z \quad (1.7.9)$$

### 1.7.1 Ideal gas

In the case of an ideal gas the grand-partition function can be written as

$$Z = \sum_N z^N Q_1^N / N! = \exp(zQ_1). \quad (1.7.10)$$

After substitution into this equation of an expression for  $Q_1$  calculated earlier, and recalling that  $\ln Z = PV/T$ , one finds an expression for the chemical potential as function of pressure and temperature,  $\mu(P, T)$ .

$$PV = T e^{\mu/T} \frac{V}{(2\pi\hbar)^3} (2\pi mT)^{3/2}, \quad (1.7.11)$$

$$\boxed{e^{\mu/T} = (2\pi\hbar^2/m)^{3/2} P T^{-5/2}} \quad (1.7.12)$$

Similarly, an expression for mean number of particles

$$\langle N \rangle = zQ_1 = e^{\mu/T} \frac{V}{(2\pi\hbar)^3} (2\pi mT)^{3/2} \quad (1.7.13)$$

can be used to find  $\mu(N, V, T)$ . Note that the above equation is equivalent to the relation Eq.1.6.6 between the number of particles and the chemical potential obtained for the canonical distribution.

*Multiplicity distribution* is easily calculated by summing up the probability  $p_{i,N}$  over all quantum states with fixed number of particles. For an ideal gas it yields:

$$w_N = \frac{z^N Q_1^N}{N!} \frac{1}{Z} = \frac{\langle N \rangle^N}{N!} e^{-\langle N \rangle}, \quad (1.7.14)$$

which is a Poisson distribution with mean number of particles:

$$\boxed{\langle N \rangle = zQ_1}. \quad (1.7.15)$$

Recall from homework that Poisson distribution is exactly what one would expect for a distribution in number of uncorrelated particles in a subvolume of a very large reservoir.

### 1.7.2 Problem: mean occupancy of an absorbing site in contact with ideal gas.

The energy of absorption is given as  $-\varepsilon$ . The partition function of one site is

$$Z = 1 + z e^{\varepsilon/T} \quad (1.7.16)$$

Mean occupancy

$$\langle n \rangle = \frac{1}{1 + e^{-(\varepsilon+\mu)/T}} = \frac{1}{1 + e^{-\varepsilon/T} (2\pi\hbar^2/m)^{-3/2} T^{5/2}/P}. \quad (1.7.17)$$

As expected the mean occupancy is increasing with  $\varepsilon$  and pressure, and decreases with temperatures.

### 1.7.3 Multiplicity fluctuations

Multiplicity fluctuations can be found similarly to a derivation of energy fluctuations in the canonical ensemble. Let us differentiate the expression for  $\langle N \rangle$  with respect to the chemical potential

$$\bar{N} = T \frac{\partial \ln Z}{\partial \mu} = \frac{\sum N e^{-(E_i - \mu N)/T}}{\sum e^{-(E_i - \mu N)/T}} \quad (1.7.18)$$

One finds

$$\overline{(\Delta N)^2} = T \frac{\partial \bar{N}}{\partial \mu} \quad (1.7.19)$$

From the above expression one can derive more practical formula:

$$\boxed{\frac{\overline{(\Delta N)^2}}{\bar{N}^2} = -\frac{T}{V^2} \left( \frac{\partial V}{\partial P} \right)_{T,V}} \quad (1.7.20)$$

In order to prove the latter we introduce a specific volume  $v = V/N$ . Then

$$\frac{\overline{(\Delta N)^2}}{\bar{N}^2} = \frac{T^2 v^2}{V^2} \left( \frac{\partial (V/v)}{\partial \mu} \right)_{T,V} = -\frac{T}{V} \left( \frac{\partial v}{\partial \mu} \right)_T \quad (1.7.21)$$

Recalling that  $Nd\mu = VdP - \sigma dT$  (easily obtained from relations  $E = T\sigma - PV + \mu N$  and  $dE = Td\sigma - PdV + \mu dN$ ) one finds that at  $T = \text{const}$ ,  $d\mu = vdP$ . It results to

$$\boxed{\frac{\overline{(\Delta N)^2}}{\bar{N}^2} = -\frac{T}{V} \frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T = -\frac{T}{V^2} \left( \frac{\partial V}{\partial P} \right)_{T,N}} \quad (1.7.22)$$

Note also that from this equation follows that  $\partial V/\partial P < 0$ .

For an ideal gas  $\overline{(\Delta N)^2}/\bar{N}^2 = 1/\bar{N}$ .

### 1.7.4 Energy fluctuations in grand-canonical ensemble

First note that the energy fluctuations can be written as

$$\overline{(\Delta E)^2} = T^2 \left( \frac{\partial \bar{E}}{\partial T} \right)_{z,V}, \quad (1.7.23)$$

where  $z$  is fugacity. (Note that fugacity should be treated as an independent variable – no differentiation with respect to  $T$  in the definition of  $z = \exp(\mu/T)$ ). The above equation can be rewritten in a more practical form:

$$\left( \frac{\partial E}{\partial T} \right)_{z,V} = \left( \frac{\partial E}{\partial T} \right)_{N,V} + \left( \frac{\partial E}{\partial N} \right)_{T,V} \left( \frac{\partial N}{\partial T} \right)_{z,V}, \quad (1.7.24)$$

which has a clear physical meaning: the first term describes fluctuations in energy at fixed number of particles, and the second term describes fluctuations in energy due to fluctuations in the number of particles. Taking into account that

$$T \left( \frac{\partial N}{\partial T} \right)_{\mu,V} = \frac{\partial^2 \ln Z}{d\mu dT} = \left( \frac{\partial E}{\partial \mu} \right)_{T,V}, \quad (1.7.25)$$

the second term can be also written in a more explicit form

$$\boxed{\overline{(\Delta E)^2} = T^2 C_V + \left( \frac{\partial E}{\partial N} \right)_{T,V}^2 \overline{(\Delta N)^2}} \quad (1.7.26)$$

Note that for an ideal gas the two terms are of the same order.

## Chapter 2

# IDEAL BOSE AND FERMI GASES

### 2.1 Fermi-Dirac and Bose-Einstein distributions

Let us apply grand-canonical distribution to the system represented by just one energy level  $\varepsilon$ . As known from quantum mechanics particles with half integer spin (fermions) can not occupy the same quantum state. The partition function in this case would be limited to the sum of only two terms:

$$Z_{\varepsilon;FD} = 1 + e^{(\mu-\varepsilon)/T}, \quad (2.1.1)$$

where the subscript  $FD$  stands for Fermi-Dirac statistics. Strait-forward calculations give the mean multiplicity (occupancy) of this energy level

$$n_{\varepsilon;FD} = T \frac{\partial \ln Z}{\partial \mu} = \frac{1}{e^{(\varepsilon-\mu)/T} + 1}. \quad (2.1.2)$$

In case of particles with integer spin (Bose-Einstein statistics)

$$Z_{\varepsilon;BE} = \sum_{N=0}^{\infty} e^{(\mu-\varepsilon)N/T} = \frac{1}{1 - e^{(\mu-\varepsilon)/T}}, \quad (2.1.3)$$

which leads to an expression for mean occupancy

$$n_{\varepsilon;BE} = T \frac{\partial \ln Z}{\partial \mu} = \frac{1}{e^{(\varepsilon-\mu)/T} - 1}. \quad (2.1.4)$$

Note that in Bose-Einstein statistics case, in order for  $n$  to be positive definite the chemical potential must be  $\mu \leq 0$ .

One can calculate the fluctuation in mean occupancy in a standard way

$$\overline{(\Delta n_{BE,FD})^2} = \frac{\partial n}{\partial \mu/T} = n(1 \pm n) \quad (2.1.5)$$

where plus sign stands for bosons and minus sign for fermions: the fluctuations are increased in the case of bosons and decreased for fermions.

#### 2.1.1 Hanbury-Brown and Twiss intensity interferometry

The observation about change in fluctuations lead to a very interesting phenomena, which is often called Hanbury-Brown and Twiss (HBT) effect. It was first used by these astronomers to measure the angular size of a star (Sirius). In this measurement they used a coincidence rate of detecting two photons in two separated photon detectors as function of the distance between the detectors. Note that for photons (which are bosons, spin one particles)  $\langle n(n-1) \rangle / \langle n \rangle^2$  equal 2 is photons occupy

the same quantum state and one otherwise (according to Poisson distribution). One quantum state correspond to the phase space volume  $\Delta p \Delta x \sim \hbar$ . Then having two photon detectors at the distance  $\Delta x$  and measuring photons coming from the star with angular size  $\Delta\theta$ , which corresponds to  $\Delta p = p \Delta\theta$ , one can study the coincidence rate ( $\langle n(n-1) \rangle$ ) relative to the expectations for random process ( $\langle n \rangle^2$ ) as function of the distance between detectors. Then the distance at which the coincidence rate change from Bose distribution to Poisson, can be directly related to the angular size of the star.

$$\Delta\theta = \frac{\hbar}{p \Delta x} = \frac{\lambda}{\Delta x}, \quad (2.1.6)$$

where  $\lambda$  is the wave length. In this way the angular size of Sirius was first measured in 1956 (with visible light,  $\lambda = 500$  nm, and the distance between detectors  $\Delta x = 10$  m) to be  $\sim 5 \cdot 10^{-8}$ , which later was confirmed by other measurements ( $3.1 \pm 0.2 \cdot 10^{-8}$ ).

Though intensity interferometry is not used in astronomy, it become a very common (and the only one available) technique to measure the size of the objects at the femtometer ( $10^{-15}$  m) scale in high energy hadronic reactions. In this case one study the correlation in particle (most often pions) production as function of the momentum difference, which provides information on the spatial extend of the region where these particles have been produced.

## 2.2 Thermodynamics of ideal Bose gas

To derive thermodynamic relations for ideal Bose gas we will start with equation  $PV = T \ln Z$ . As the partition function for a single energy level has been calculated, one can write

$$Z = \prod_{\varepsilon} Z_{\varepsilon}; \quad \ln Z = \sum_{\varepsilon} \ln Z_{\varepsilon} \quad (2.2.1)$$

Then

$$\begin{aligned} \ln Z &= - \int \frac{d^3 p d^3 x}{(2\pi\hbar)^3} \ln(1 - e^{(\mu-\varepsilon)/T}) \\ &= \frac{V}{(2\pi\hbar)^3} 2\pi(2m)^{3/2} \frac{2}{3T} \int_0^{\infty} \varepsilon^{3/2} d\varepsilon \frac{1}{e^{(\varepsilon-\mu)/T} - 1} \end{aligned} \quad (2.2.2)$$

Finally

$$\boxed{PV = T \frac{V}{\lambda^3} g_{5/3}(z)} \quad (2.2.3)$$

where,  $z$  is the fugacity,  $\lambda$  is the thermal wave length,

$$\lambda = \left( \int_{-\infty}^{\infty} \frac{dp}{2\pi\hbar} e^{-p^2/(2mT)} \right)^{-1} = \frac{2\pi\hbar}{\sqrt{2\pi mT}}, \quad (2.2.4)$$

and we have introduced function

$$g_{\nu}(z) = \frac{1}{\Gamma(\nu)} \int_0^{\infty} \frac{x^{\nu-1} dx}{z^{-1} e^x - 1} = z + \frac{z^2}{2^{\nu}} + \frac{z^3}{3^{\nu}} + \dots \quad (2.2.5)$$

The mean number of particles in the system is given by

$$N = \frac{\partial(\ln Z)}{\partial(\mu/T)} = \frac{V}{(2\pi\hbar)^3} (2m)^{3/2} \int_0^{\infty} \varepsilon^{1/2} d\varepsilon \frac{1}{e^{(\varepsilon-\mu)/T} - 1} \quad (2.2.6)$$

Note that the last expression has a clear physical meaning representing the sum of the mean occupancies over all energy levels. Using the above introduced notations:

$$N = \frac{V}{\lambda^3} g_{3/2}(z) \quad (2.2.7)$$

Similarly an expression for the energy of Bose gas can be found in two ways, differentiating the logarithm of the partition function with respect to  $1/T$  at constant fugacity, or summing up the energies of particles in each energy level. It yields:

$$E = \frac{3}{2} T \frac{V}{\lambda^3} g_{5/2}(z) = \frac{3}{2} PV \quad (2.2.8)$$

### 2.2.1 Equation of state, virial coefficients

The relation between  $V$ ,  $T$ ,  $P$ , and  $N$  is called *the equation of state*. For the ideal Bose gas it can be obtained in the following way. From Eq. 2.2.7 one can determine fugacity as a function of number of particles, volume, and temperature  $z(N, V, T)$  (Note that in reality the fugacity depends only on combination  $n\lambda^3$ , where  $n = N/V$ ) and substitute it in Eq. 2.2.3:

$$PV = \frac{TV}{\lambda^3} g_{5/2}(z(n, T)) = NT \sum_{l=1}^{\infty} a_l (n\lambda^3)^{l-1} \quad (2.2.9)$$

The coefficients  $a_l$  in this expansion are called *virial coefficients*. Note that the parameter  $n\lambda^3$  has a physical meaning of the fraction of the entire volume occupied by all particles if one assumes that the volume of a particle is  $\lambda^3$ . This parameter is small in the classical limit (as the fugacity itself, see Eq. 2.2.3). In the classical limit, from Eq. 2.2.7,  $n\lambda^3 = z$ . Substituting this into Eq. 2.2.3 and keeping only leading term in an expansion of  $g_{5/2}(z)$  leads to  $PV = TV/\lambda^3 \cdot n\lambda^3 = NT$ , which is the equation of state of the ideal classical gas. Comparison to Eq. 2.2.9 gives  $a_1 = 1$ . Keeping more terms in expansions lead to

$$a_1 = 1; \quad a_2 = -\frac{1}{4\sqrt{2}}; \quad a_3 = -\left(\frac{2}{9\sqrt{3}} - \frac{1}{8}\right). \quad (2.2.10)$$

Finally note how the heat capacity can be expressed via virial coefficients

$$\begin{aligned} C_V &= \left(\frac{\partial E}{\partial T}\right)_{N,V} = \frac{3}{2} \left(\frac{\partial(PV)}{\partial T}\right)_{N,V} \\ &= \frac{3}{2} N \left(1 + a_2 \left(\frac{2\pi\hbar^2}{m}\right)^{3/2} \left(-\frac{1}{2}\right) T^{-3/2} + \dots\right) \end{aligned} \quad (2.2.11)$$

Note that the first correction to the ideal gas expression is positive (recall that  $a_2 < 0$ ) and decaying as  $T^{-3/2}$  with temperature.

## 2.3 Bose-Einstein Condensation

The relation  $n\lambda^3 = g_{3/2}(z)$  defines the chemical potential at given particle density and temperature. The higher the density the smaller (in magnitude, remember that  $\mu \leq 0$ ) the chemical potential. But the smallest possible value for chemical potential is zero, which gives  $g_{3/2}(1) = \zeta(3/2) \approx 2.61$  ( $\zeta(x)$  is the Riemann zeta-function). What happens at higher particle density? The answer to this question is in a more accurate treatment of the energy level  $\varepsilon = 0$  (it was neglected earlier, as it

is only one single level). One can divide the total number of particles into two categories, those which occupy excited states ( $\varepsilon > 0$ ) and those with zero energy:

$$N_e = \frac{V}{\lambda^3} \zeta(3/2) = N \left( \frac{T}{T_c} \right)^{3/2}; \quad N_0 = N - N_e. \quad (2.3.1)$$

where  $T_c$  is the *critical* temperature, at which *Bose-Einstein condensation*, the phenomenon of accumulation of macroscopic number of particles in a single quantum state, starts.

The exact value of fugacity can be calculated directly from

$$N_0 = \frac{1}{1/z - 1}; \quad \rightarrow \quad z = \frac{N_0}{N_0 + 1} \quad (2.3.2)$$

When  $N_0$  become a large (macroscopic) number the fugacity is very close to unity.

The energy and the heat capacity at  $T < T_c$  are given

$$E = \frac{3VT}{2\lambda^3} g_{5/2}(1) \propto T^{5/2}; \quad C_V \propto T^{3/2} \quad (2.3.3)$$

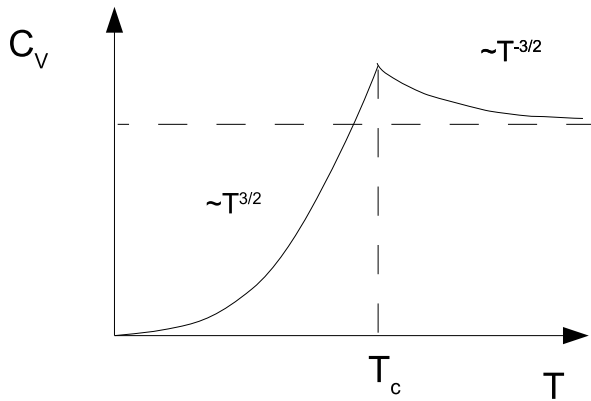


Figure 2.1: Heat capacity

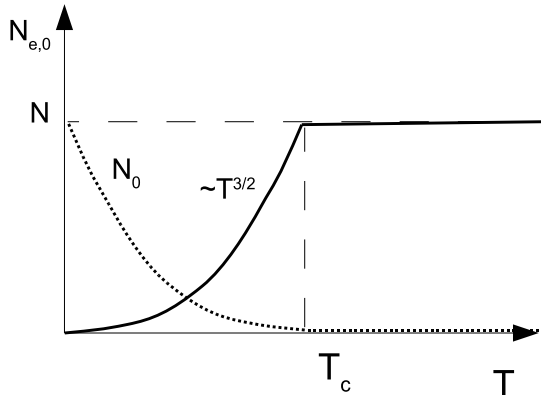


Figure 2.2: Number of particles in the excited states and at the ground level

## 2.4 Photon Gas

Consider a volume filled with electro-magnetic radiation at temperature  $T$ . The number of photons is not conserved and should be determined from equilibrium condition. It results into  $\partial A/\partial N = 0$ , which means that this system is described by chemical potential  $\mu = 0$ . Taking into account that for photon  $\varepsilon = pc = \hbar\omega$ , the density of states can be written as:

$${}^{\prime\prime}2^{\prime\prime} \frac{d^3p d^3x}{(2\pi\hbar)^3} \rightarrow \frac{2V4\pi\omega^2 d\omega}{(2\pi)^3 c^3} = \frac{V\omega^2 d\omega}{\pi^2 c^3}, \quad (2.4.1)$$

where the factor “2” accounts for two polarization states of the photon (spin 1 massless particle). Then the mean number of photons and mean energy is given by:

$$dN = \frac{V\omega^2 d\omega}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/T} - 1} \quad (2.4.2)$$

and

$$dE_\omega = \hbar\omega \frac{V\omega^2 d\omega}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/T} - 1}. \quad (2.4.3)$$

The energy density as function of frequency has a maximum at  $\hbar\omega_{max}/T = 2.822$ , which corresponds to  $\lambda_{max} = 0.51 \cdot 10^{-2}/T$  m, where  $T$  is taken in Kelvin. Note the similarity of the expression for the mean number of photons with frequency  $\omega$  with the corresponding equation for probability of excitation of quantum oscillator of corresponding frequency at temperature  $T$  (see equation 1.6.12).

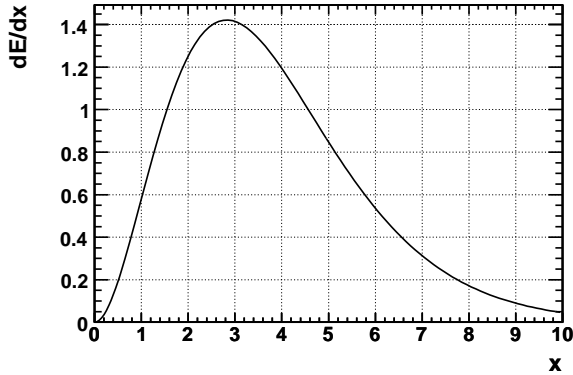


Figure 2.3: Spectral form for photon gas as function of  $x = \hbar\omega/T$

Classical (high temperature, or high wave length) limit of the latter is called *Rayleigh-Jeans* formula:

$$dE = V \frac{T}{\pi^2 c^3} \omega^2 d\omega \quad (2.4.4)$$

(note that in this limit  $\hbar$  does not enter!). In high frequency limit

$$dE = V \frac{\hbar}{\pi^2 c^3} e^{-\hbar\omega/T} \omega^3 d\omega \quad (2.4.5)$$

so called *Wien* law. Integration over photon energies lead to the energy density

$$E/V = \frac{T^4}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^2 T^4}{15 \hbar^3 c^3} = \frac{4\sigma}{c} T^4 \quad (2.4.6)$$

where we used that the integral equals  $\pi^4/15$  and introduced Stefan-Boltzmann constant

$$\sigma = \frac{\pi^2 k^4}{60 \hbar^3 c^2} = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \quad (2.4.7)$$

(where in the latter equation we used Boltzmann constant  $k$ ). Pressure is give by

$$PV = T \ln Z = - \int_0^\infty V \frac{\omega^2 d\omega}{\pi^2 c^3} \ln \left( 1 - e^{-\hbar\omega/T} \right) = \frac{VT^4}{3\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^2 T^4 V}{45 \hbar^3 c^3} = \frac{EV}{3} \quad (2.4.8)$$

Note that pressure does not depend on volume (!) and that the relation between pressure and energy coincides with the one for any ultra-relativistic gas. As chemical potential is zero  $A = E - TS = -PV = -E/3$ . Then

$$S = \frac{E - A}{T} = \frac{4E}{3T} \propto VT^3. \quad (2.4.9)$$

One can find from here an expression for adiabats:

$$S = \text{const} \Rightarrow VT^3 \propto VP^{3/4} = \text{const} \Rightarrow PV^{4/3} = \text{const}. \quad (2.4.10)$$

### 2.4.1 Black Body Radiation

Let us calculate the intensity of black body radiation - the energy emitted from a unit area in a unit time. We start from a problem of a gas of density  $\rho$  and velocity distribution  $f(v)$  (normalized to unity) hitting the area  $dS$  in time  $dt$ :

$$dN = \int_0^{\pi/2} \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^\infty v^2 dv \rho f(v) \cos \theta dS v dt \quad (2.4.11)$$

Simple integration yields for the rate

$$R = \frac{dN}{dS dt} = \frac{\rho \langle v \rangle}{4} \quad (2.4.12)$$

Applying the above equation to the case of thermal radiation one finds

$$I = \frac{dE_{\text{emitted}}}{dS dt} = \frac{c E}{4 V} = \sigma T^4 \quad (2.4.13)$$

### 2.4.2 Example: Estimate of the temperature of (the surface of) the Sun

A simple way to obtain an estimate of the temperature of the Sun “with a ruler” is based on observation that the temperature of the Earth is about 300 K, and that the Earth must emit as much energy as it gets from the Sun. The energy balance can be written as

$$\left( 4\pi R_S^2 \sigma T_S^4 \right) \left( \frac{\pi R_E^2}{4\pi L_{ES}^2} \right) = 4\pi R_E^2 \sigma T_E^4, \quad (2.4.14)$$

where  $L_{ES}$  is the average distance between the Earth and the Sun. On the left hand side, the first expression in parenthesis equals to the energy emitted by the Sun in unit time, the second expression gives the fraction of this energy “intercepted” by the Earth, the right hand side is the energy emitted by the Earth. From that one finds

$$T_S = 2T_E \sqrt{\frac{L_{ES}}{2R_S}}. \quad (2.4.15)$$

The angular size of the diameter of the Sun can be easily measured with “a ruler”,  $2R_S/L_{ES} \approx 1/100$ , and one obtains that the temperature of the Sun is  $T_S \approx 6000$  K.

## 2.5 Phonons

Oscillations of atoms in the solid can be decomposed as a sum of normal modes. Each normal mode can be considered as a quantum oscillator. Consider acoustic standing waves. The normal modes are given by  $2L/\lambda = n$ . It can be rewritten in terms of frequencies

$$dn = 2Ld\omega/(2\pi c_s) = Ld\omega/(\pi v_s), \quad (2.5.1)$$

where  $c_s$  is the speed of sound. Compare that with analogous expression for the photon gas

$$dn = dpdx/(2\pi\hbar) \rightarrow Ldp/(2\pi\hbar) = L2d\varepsilon/(2\pi\hbar c) = Ld\omega/(\pi c), \quad (2.5.2)$$

where the factor “2” in  $dp = 2d\varepsilon/c$  takes into account that integration over  $p$  is taken over  $(-\infty, \infty)$ , but  $\varepsilon \geq 0$ .

Noticing that the “occupancy number” of  $n$ -th energy level for a quantum oscillator in the canonical ensemble

$$\bar{n} = \frac{\bar{E} - E_0}{\hbar\omega} = \frac{1}{e^{\hbar\omega/T} - 1} \quad (2.5.3)$$

is exactly the same as the occupancy for Bose gas with chemical potential  $\mu = 0$  (the same as for photon gas), and taking into account two transverse polarization and one longitudinal,

$$\frac{\omega^2 d\omega}{2\pi^2 c_L^3} + \frac{\omega^2 d\omega}{\pi^2 c_T^3} \equiv \frac{3\omega^2 d\omega}{2\pi^2 \bar{c}^3}, \quad (2.5.4)$$

one arrives to the expression for the energy of oscillations (acoustic waves)

$$dE = \frac{\hbar\omega}{(e^{\hbar\omega/T} - 1)} \frac{3\omega^2 d\omega}{2\pi^2 \bar{c}^3}. \quad (2.5.5)$$

Comparing this expression with the corresponding one for the photon gas leads to the interpretation of the system as an ideal gas of *phonons* – quasi-particles with energy  $\hbar\omega = pc_s$ , and momentum  $\mathbf{p} = \hbar\mathbf{k}$ . In a general case, e.g., when crystal cell contains several atoms, the dispersion relation,  $\varepsilon(p)$  can have more complicated form, but for *acoustic* waves  $\varepsilon(0) = 0$ , for *optical* waves,  $\varepsilon(0) \geq 0$ . Note that phonons are *collective* excitations.

In analogy with photon gas one finds that the energy of the system is proportional to  $T^4$  and the heat capacity  $\propto T^3$ , which is in good agreement with experiment at low temperatures. At high temperature this dependence must obviously break, as the atoms should be treated as independent oscillators with heat capacity equals  $3N$ .

### 2.5.1 Debye interpolation model

To solve the problem, Debye proposed to introduce high frequency cutoff,  $\omega_{max} = \omega_D$ , given by equation

$$\int_0^{\omega_D} \frac{3\omega^2 d\omega}{2\hbar^2 c_s^3} = 3N \quad (2.5.6)$$

which gives

$$\boxed{\omega_D = 6\pi^2 c_s^3 N/V} \quad (2.5.7)$$

Using this frequency as a cutoff, heat capacity can be written as

$$C_V = 3ND(x_0); \quad x_0 \equiv \frac{\hbar\omega_D}{T} \equiv \frac{\theta_D}{T}, \quad (2.5.8)$$

where  $\theta_D$  is the so-called Debye temperature, and

$$D(x_0) = \frac{3}{x_0^3} \int_0^{x_0} \frac{x^4 e^x dx}{(e^x - 1)^2}. \quad (2.5.9)$$

The above formula for  $C_V$  describes (interpolates between) two limiting cases of low and high temperatures.

## 2.6 Superfluidity

Consider a liquid moving in a narrow tube (capillary). We show below, that under certain conditions, the viscosity, the energy dissipation due to interaction of the liquid with the walls of the tube, can be identically zero. This effect is called *superfluidity*.

We start with the simplest case of  $T = 0$  and considering the motion in the system, where the liquid is at rest and walls are moving. Suppose one phonon excitation occurs, with energy  $E_0 = \varepsilon$  and momentum  $\mathbf{p}$ . Using Galilean transformation one finds that in the system, where tube is at rest, the energy of the liquid is

$$E = \varepsilon + \mathbf{p}\mathbf{v} + \frac{Mv^2}{2} \quad (2.6.1)$$

As the last term is easily identified as the kinetic energy of the system, and the the change in energy due to dissipation must be negative, one has to conclude that

$$\varepsilon + \mathbf{p}\mathbf{v} < 0 \Rightarrow \varepsilon - pv < 0 \quad (2.6.2)$$

In the case of (oversimplified) linear dispersion relation  $\varepsilon = pc_s$ , it means that dissipation can occur only if the liquid is moving with the speed larger than the speed of sound.

What happens at higher temperature? Interestingly, one can see that the condition of  $T = 0$  is not really required for the line of arguments presented above. The appearance of (new) phonons still will be described by the same condition. (Note that we neglect interaction of phonons, the importance of which is increasing with temperature).

At finite temperature one can describe the system as being partially in superfluid phase and partially in the normal phase. (Semi)quantitative measure of the fraction of the fluid being in the normal phase can be obtained by computing the fraction of the total momentum of the liquid carried by phonons:

$$P_z = \int p_z n(\varepsilon - \mathbf{p}\mathbf{v}) \frac{d^3p d^3x}{(2\pi\hbar)^3} \quad (2.6.3)$$

$$= \frac{-V}{(2\pi\hbar)^3} \int p_z(\mathbf{p}\mathbf{v}) \frac{\partial n}{\partial \varepsilon} d^3p = \frac{-4\pi v_z V}{3(2\pi\hbar)^3} \int p^4 \frac{\partial n}{\partial \varepsilon} dp \quad (2.6.4)$$

$$= \frac{4\pi v_z V}{3(2\pi\hbar)^3 c_s} \int \varepsilon n(p) 4p^3 dp = v_z \frac{4E}{3c_s^2} = v_z M_{eff} \quad (2.6.5)$$

## 2.7 Ideal Fermi Gas

### 2.7.1 Fermi energy

Consider Fermi gas at temperature  $T = 0$ . In this case particles occupy all the lowest energy possible (*completely degenerate Fermi Gas*). In this limit

$$n_F(\varepsilon) = \begin{cases} 1 & \varepsilon < \varepsilon_{max} \equiv \varepsilon_F \\ 0 & \varepsilon > \varepsilon_F \end{cases} \quad (2.7.1)$$

One finds  $\varepsilon_F$  from the expression for the number of particles:

$$N = V \frac{g_s 4\pi}{(2\pi\hbar)^3} \int_0^{p_F} p^2 dp = V \frac{g_s 4\pi p_F^3}{3(2\pi\hbar)^3}; \quad p_F = \sqrt{2m\varepsilon_F}, \quad (2.7.2)$$

where  $g_s = (2s + 1)$  reflects spin degeneracy factor.

Using above definitions one easily finds the energy per particle

$$\frac{E}{N} = \frac{3}{5} \varepsilon_F \quad (2.7.3)$$

and, from  $PV = 2/3 E$ , pressure:

$$P = \frac{2}{5} \varepsilon_F \frac{N}{V} \propto n^{5/3} \quad (2.7.4)$$

If the temperature is not exactly zero, but small,  $T \ll \varepsilon_F$  one can be interested in corrections to the above equations. Such case we will call *degenerate Fermi Gas*.

### 2.7.2 Thermodynamics of Fermi Gas

Note almost complete analogy with Bose Gas, with one important difference, namely that chemical potential is not restricted to take only negative values. One obtains all the necessary relations with substitution of  $g_\nu(z) \rightarrow -g_\nu(-z) \equiv f_\nu(z)$ :

$$f_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1} dx}{z^{-1} e^x + 1} = z - \frac{z^2}{2^\nu} + \frac{x^3}{3^\nu} - \dots \quad (2.7.5)$$

$$\frac{P}{T} = \frac{(2s+1)}{\lambda^3} f_{3/2}(z) \quad (2.7.6)$$

$$E = \frac{3(2s+1)TV}{\lambda^3} f_{5/2}(z) \quad (2.7.7)$$

The equation of state is given simply by

$$PV = NT \sum_1^\infty a_j (n\lambda^3)^{j-1} (-1)^{j-1} \quad (2.7.8)$$

with the virial coefficients  $a_l$  exactly the same as for the Bose Gas.

For degenerate Fermi gas, one would find the following expressions useful (expansion in terms of  $T/\mu$ ):

$$f_{3/2} = \frac{4}{3\pi^{1/2}} (\ln z)^{3/2} \left[ 1 + \frac{\pi^2}{8} (\ln z)^{-2} + \dots \right] \quad (2.7.9)$$

$$f_{5/2} = \frac{8}{15\pi^{1/2}} (\ln z)^{5/2} \left[ 1 + \frac{5\pi^2}{8} (\ln z)^{-2} + \dots \right] \quad (2.7.10)$$

Also, one can find very useful an approximation

$$\begin{aligned} \int_0^\infty \frac{f(\varepsilon) d\varepsilon}{e^{(\varepsilon-\mu)/T} + 1} &= \int_0^\mu f(\varepsilon) d\varepsilon - T \int_0^{\mu/T} \frac{f(\mu - Tx) dx}{e^x + 1} + T \int_0^\infty \frac{f(\mu + Tx) dx}{e^x + 1} \\ &\approx \int_0^\mu f(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (T)^2 f'(\mu) + \frac{7\pi^4}{360} (T)^4 f'''(\mu) + \dots \end{aligned} \quad (2.7.11)$$

The heat capacity dependence on temperature can be considered similar to that of Bose-Gas. At large temperatures the correction to the ideal classical gas is negative which smoothly connects to the low temperature limit given by

$$\frac{E}{N} = \frac{3}{5} \varepsilon_F \left[ 1 + \frac{5\pi^2}{12} \left( \frac{T}{\varepsilon_F} \right)^2 + \dots \right], \quad (2.7.12)$$

which yields  $C_V \propto T$ .

## 2.8 Magnetic properties of ideal Fermi gas

### 2.8.1 Pauli paramagnetism

For the case of completely degenerate Fermi Gas:

$$M = \mu(N_+ - N_-) = \frac{4\pi\mu(2m)^{3/2}}{3(2\pi\hbar)^3} \left\{ (\varepsilon_F + \mu B)^{3/2} - (\varepsilon_F - \mu B)^{3/2} \right\} \quad (2.8.1)$$

which yields:

$$\chi_{Pauli} = \frac{3}{2} \frac{n\mu^2}{\varepsilon_F} \quad (2.8.2)$$

This expression is to be compared to Eq. 1.6.21:

$$\xi_{classical} = \frac{n\mu^2}{T} \quad (2.8.3)$$

Temperature dependence is given by (see homework):

$$\chi(T) = \xi_0 \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{\varepsilon_f} \right)^2 \right] \quad (2.8.4)$$

### 2.8.2 Landau diamagnetism

This effect is due to induced (therefore, negative) magnetic moment of the circular motion of a charged particle in the magnetic field. In quantum mechanics such a motion is quantized, with the (*Landau*) energy levels given by

$$\varepsilon_n = \hbar\omega(n + 1/2) = \hbar \frac{eB}{mc} (n + 1/2) \quad (2.8.5)$$

The degeneracy of such states can be found by calculating the total number of states in the case of  $B = 0$  that correspond to the energy interval between two energy levels:

$$g = L_x L_y \frac{eB}{2\pi\hbar c} \quad (2.8.6)$$

Grand partition function is given by

$$\ln Z = \int_{-\infty}^{\infty} \frac{L_z dp_z}{2\pi\hbar} \sum_{j=0}^{\infty} \frac{L_x L_y eB}{2\pi\hbar c} \ln \left[ 1 + z e^{-2\mu_e B(j+1/2)/(mcT) - p_z^2/(2mT)} \right] \quad (2.8.7)$$

$$\approx \frac{V e B}{(2\pi\hbar)^2 c} \left\{ \int_0^{\infty} dx \int_{-\infty}^{\infty} dp_z \ln \left[ 1 + z e^{-(2\mu_e B x + p_z^2/(2m))/T} \right] - \frac{\mu_e B}{12T} \int_{-\infty}^{\infty} \frac{dp_z}{(x^{-1} e^{p_z^2/2mT} + 1)} \right\} \quad (2.8.8)$$

where we have used Euler summation formula

$$\sum_{j=0}^{\infty} f(j + 1/2) \approx \int_0^{\infty} f(x) dx + \frac{1}{24} f'(0). \quad (2.8.9)$$

Noticing that the first integral does not depend on  $B$ , finally one obtains:

$$\chi_{Pauli} = \frac{3}{2} \frac{n\mu_{eff}^2}{\varepsilon_F}, \quad (2.8.10)$$

where we used notation  $\mu_{eff} = e\hbar/(2m_{eff}c)$ . Note that in general  $m_{eff} \neq m_e$  due to electron interactions with phonons (atoms).

## 2.9 Thermionic emission and photoeffect

Electron current from the surface of a metal characterized by potential well depth  $W$  is given by

$$R = \int_{-\infty}^{\infty} \frac{dp_z}{\sqrt{2mW}} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \frac{2''}{(e^{(\varepsilon+\hbar\omega-\mu)/T} + 1)} \frac{v_z}{2\pi\hbar} \quad (2.9.1)$$

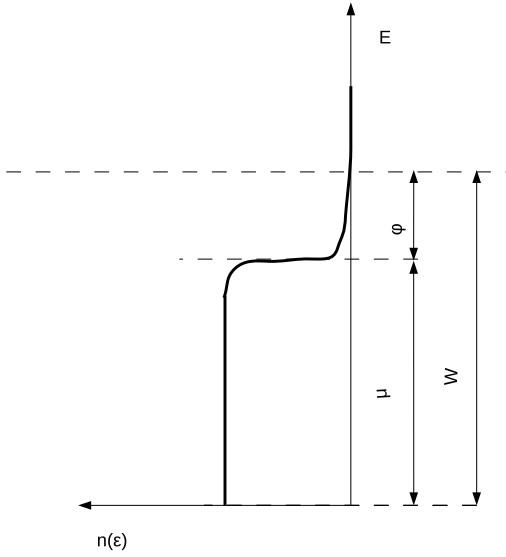
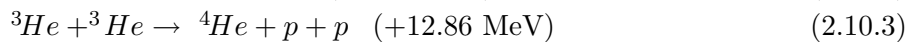
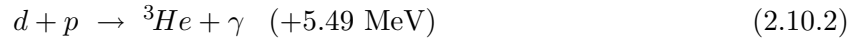


Figure 2.4: Electron distribution in energy inside metal

## 2.10 White dwarf and neutron stars. Strange matter.

thermonuclear reactions:



White dwarf star - star consisting mostly of helium nuclei and electrons. Local neutrality. Kinetic energy is carried mostly by electrons

$$K \approx N \frac{3}{2} \frac{p_F^2}{2m_e} \propto \frac{N^{5/3}}{R^2}, \quad (2.10.4)$$

taking into account that  $p_F \propto N^{1/3}/R$ . Potential (gravitational) energy is determined by mostly interactions of nuclei

$$U_G \propto G \frac{MM}{R} \quad (2.10.5)$$

It follows that

$$\boxed{R \propto M^{-1/3}} \quad (2.10.6)$$

At larger mass the system become ultra relativistic and kinetic energy become inversely proportional to the first power of radius which eventually leads to collapse of the system.

Collapse to neutron star

$$p + e^- \rightarrow n + \nu_e \quad (2.10.7)$$

Strange matter

$$d + \bar{d} \rightarrow s + \bar{s}; \quad u + \bar{u} \rightarrow s + \bar{s}; \quad (2.10.8)$$

## Chapter 3

# NONIDEAL SYSTEMS AND PHASE TRANSITIONS

### 3.1 Cluster expansion

Non-ideal system is the one when the interaction between particles (potential energy) can not be neglected. The non-ideal system is usually treated with a set of corrections in the form of expansion over some small parameter. Most often the parameter is taken as the ratio of the “particle volume” over the specific volume (“available” volume per particle).

As the interaction between particles is expected to be short-ranged, it is useful to introduce an auxiliary function

$$f_{ij} \equiv e^{-u_{ij}/T} - 1, \quad (3.1.1)$$

which deviates from zero only when two particles are close to each other in space. The partition function can be written as

$$Q_N = \frac{1}{N!\lambda^{3N}} \int d^{3N}x \exp\left(-\frac{\sum_{i<j} u_{ij}}{T}\right) = \frac{1}{N!\lambda^{3N}} I_N(V, T), \quad (3.1.2)$$

where the *configuration integral*

$$I_N = \int \prod_{i<j} e^{-U_{ij}/T} d^{3N}x = \int [1 + \sum_{i<j} f_{ij} + \sum_{i<j} f_{ij}f_{kl} + \dots] d^3x_1 d^3x_2 \dots d^3x_N. \quad (3.1.3)$$

One can easily identify in the configuration integral the contribution from interaction in pairs, triplets, quadruplets, etc., though the exact algebraic equations can be quite cumbersome. Without proof (for that see Pathria book) we provide equations

$$\ln Z = \ln \sum_N z^N Q_N = \boxed{\frac{PV}{T} = \frac{V}{\lambda^3} \sum_{k=1}^{\infty} b_k z^k} \quad (3.1.4)$$

where we have introduced the cluster coefficients:

$$b_k \equiv \frac{1}{k!\lambda^{3(k-1)}V} [\text{the sum of all } k - \text{clusters}]; \quad (3.1.5)$$

e.g.

$$b_2 = \frac{1}{2\lambda^3V} \int f_{12}(\mathbf{r}_{12}) d^3x_1 d^3x_2 = \frac{2\pi}{\lambda^3} \int f_{12}(r) r^2 dr. \quad (3.1.6)$$

From the grand partition function one also finds

$$\boxed{\frac{N}{V} = \frac{1}{\lambda^3} \sum_{k=1}^{\infty} k b_k z^k}, \quad (3.1.7)$$

Eliminating  $z$  from equations for pressure and number of particles one obtains the equation of state:

$$\boxed{PV = NT \sum_{k=1}^{\infty} a_k \left(\frac{\lambda^3}{v}\right)^{k-1}} \quad (3.1.8)$$

where  $a_k$  are the *virial* coefficients:

$$a_1 = b_1 = 1; \quad a_2 = -b_2; \quad a_3 = 4b_2^2 - 2b_3 = -2b_3^{irr}; \dots \quad (3.1.9)$$

## 3.2 Van der Waals gas

Neutral atoms interact via so-called van der Waals forces. Potential energy of interaction of two dipole moments can be written as

$$U_{12} = \frac{\mathbf{d}_1 \mathbf{d}_2 - 3(\mathbf{n} \mathbf{d}_1)(\mathbf{n} \mathbf{d}_2)}{r^3} \quad (3.2.1)$$

We will discuss atoms with zero dipole moment, which means that considering the interaction in the first order perturbation theory yields zero result as  $(U_{12})_{nm} = 0$ . The second order perturbation theory result is not zero. Recall that the second order correction is always negative, which means attractive effective potential. Also, as it is quadratic in  $U_{12}$ , it scales as  $1/r^6$ .

At short distances the potential should very fast become repulsive. Then the potential can be approximated as

$$U(r) = \begin{cases} \infty, & r < d_0 \\ -U_0(d_0/r)^6 & r > d_0 \end{cases} \quad (3.2.2)$$

which result in the second virial coefficient to be

$$a_2 = \frac{2\pi d_0^3}{3\lambda^3} \left(1 - \frac{U_0}{T}\right) = a - \frac{b}{T} \quad (3.2.3)$$

Expanding the equation of state of the van der Waals gas, which is usually written as

$$\left(P + \frac{a}{v^2}\right)(v - b) = T \quad (3.2.4)$$

and keeping only the leading terms one finds direct correspondence to the second virial coefficient calculated above.

## 3.3 Condensation of a van der Waals gas

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (3.3.1)$$

At critical point

$$\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0 \quad (3.3.2)$$

From the above one finds that at critical point  $v = 3b$  and

$$T_c = \frac{8a}{27bR}; \quad P_c = \frac{a}{27b^2} \quad (3.3.3)$$

It appears that the combination

$$K = \frac{RT_c}{P_c v_c} = \frac{8}{3} \quad (3.3.4)$$

does not depend on the parameters  $a$  and  $b$  and is an *universal* constant. Introducing further  $\tilde{p} = P/P_c$ ,  $\tilde{v} = v/v_c$  and  $\tilde{T} = T/T_c$  the van der Waals equation can be written in the universal form:

$$(\tilde{p} + 3/\tilde{v}^2)(3\tilde{v} - 1) = 8\tilde{T} \quad (3.3.5)$$

We will concentrate further on the vicinity of the critical point. For that we introduce  $\tilde{p} = 1 + \pi$ ,  $\tilde{v} = 1 + \psi$ ,  $\tilde{T} = 1 + \tau$ . Then the equation can be written as

$$\pi(2 + 7\psi + 8\psi^2 + 3\psi^3) + 3\psi^3 = 8\tau(1 + 2\psi + \psi^2) \quad (3.3.6)$$

For critical isotherm one finds:

$$\psi \approx \left(\frac{3}{2}\pi\right)^{1/3} \quad (3.3.7)$$

From Eq. 3.3.6 one finds for the isothermal compressibility:

$$-\frac{\partial\psi}{\partial\pi} = \frac{2}{7\pi + 9\psi^2 - 16\tau} \quad (3.3.8)$$

which we will use below. Also, at the critical point (and long the line)  $\psi = 0$  one finds that  $\pi \approx 4\tau$ . Taking into account that Maxwell construction line intersects isotherms Eq. 3.3.6 at a point very close to  $\psi = 0$ , one concludes that the relation  $\pi \approx 4\tau$  holds as well along the coexistence curve. Using the above one finds an equation for the coexistence curve itself:

$$\psi^2 + 8\tau\psi + 4\tau = 0 \quad (3.3.9)$$

which yields the solutions

$$\psi_{1,3} \approx \pm|\tau|^{1/2} \quad (3.3.10)$$

Finally for the isothermal compressibility we have

$$\left(\frac{\partial\psi}{\partial\pi}\right)_{\tau \rightarrow 0+} \approx -\frac{1}{6\tau} \quad (3.3.11)$$

$$\left(\frac{\partial\psi}{\partial\pi}\right)_{\tau \rightarrow 0-} \approx \frac{1}{12\tau} \quad (3.3.12)$$

Without proof we also present the expressions for the heat capacity

$$C_V = \begin{cases} C_{V,ideal} + \frac{9}{2}N(1 + \frac{28}{25}\tau) & \tau > 0 \\ C_{V,ideal} & \tau < 0 \end{cases} \quad (3.3.13)$$

### 3.4 Model systems with phase transition

Most models are formulated a lattice of different dimension. The lattice itself can have different structure (square, honeycomb, etc.) with the most important characteristic to be the number of nearest neighbors, *coordination number*  $q$ . For 2d honeycomb lattice  $q = 3$ , for 2d square lattice  $q = 4$ . etc.

*Lattice gas* is a system of  $N_a$  atoms on  $N$  sites with interaction between atoms occupying neighboring sites. The energy of the system can be written as  $E = \varepsilon_0 N_{aa}$ , where  $N_{aa}$  is the total number of *pairs* occupying neighboring sites. Then the partition function:

$$Q_N(N_a, T) = \sum_{N_{aa}} g_N(N_a, N_{aa}) e^{-\varepsilon N_{aa}/T} \quad (3.4.1)$$

where  $g$  is the total number of different combinations resulting to the same number of neighboring pairs.

*Binary alloy* system is a system consisting of two types of atoms occupying all sites of the lattice. There are three types of pairs, and each combination could have its own interaction. The energy can be written as

$$E = \varepsilon_{11} N_{11} + \varepsilon_{12} N_{12} + \varepsilon_{22} N_{22} \quad (3.4.2)$$

*Spin system* is a system of particles with spin  $s$  occupying all sites of the lattice. Considering only interaction of closest neighbors one obtains *Heisenberg model* with energy

$$E = \text{const} - 2J \sum \vec{s}_1 \vec{s}_2 \quad (3.4.3)$$

The simplest (and most important) case corresponds to spin 1/2 particles, the so-called *Ising model*.

It can be shown that all three models mentioned above have very much in common, and in fact become identical under certain transformations.

### 3.5 Ising Model

Model: spin 1/2, magnetic moment  $\mu$  particles on the lattice interacting with external magnetic field. Interaction of only nearest neighbors is included.

The Hamiltonian of the system is:

$$H = -J \sum_{\text{nearest neighbors}} \sigma_i \sigma_j - h \sum_i \sigma_i, \quad (3.5.1)$$

where  $\sigma_i = \pm 1$  represent the spin of  $i$ -th particle,  $J$  is the interaction constant (chosen to be positive for *attractive* interaction of two parallel spins),  $h = \mu B$  represents the external magnetic field. The partition function:

$$Q_N = \sum_{\sigma_1} \sum_{\sigma_2} \dots \sum_{\sigma_N} \exp(-H/T) \quad (3.5.2)$$

#### 3.5.1 Mean Field approximation

In this approximation, one of the spin in the interaction term is substituted by the overall average value, the *mean field*:

$$H = -J \sum_{\text{n.n.}} \sigma_i \sigma_j - h \sum_i \sigma_i \approx -J \sum_i \sigma_i \frac{q}{2} \langle \sigma \rangle - h \sum_i \sigma_i \quad (3.5.3)$$

where  $q$  is the coordination number and the factor (1/2) takes into account that the pair  $(i, j)$  and pair  $(j, i)$  is the same pair.

It is easier (and more instructive) to consider only one  $i$ -th particle:

$$H_i = -Jq\langle\sigma\rangle\sigma_i - h\sigma_i \quad (3.5.4)$$

In order for the picture to be self consistent we have to require that

$$\langle\sigma_i\rangle = \langle\sigma\rangle, \quad (3.5.5)$$

which is called *self-consistency* equation. We first consider the case  $h = 0$ . Then

$$\langle\sigma\rangle = \langle\sigma_i\rangle = \tanh \frac{qJ\langle\sigma\rangle}{T}. \quad (3.5.6)$$

The above equation has either only zero solution, if  $qJ/T \leq 1$ , or three (including two non zero) solutions for the case  $qJ/T > 1$ . Note that in the case of three solutions, one zero and two non-zero, the non-zero solution corresponds to the minimum of free energy (see later). Nonzero solution means non-zero magnetic moment of the system even when external magnetic field is zero (spontaneous magnetization, ferromagnetism). Expanding the hyperbolic tangent to the third order one find that

$$\langle\sigma\rangle \approx \sqrt{3(1 - T/T_c)} \propto (T_c - T)^{1/2} \quad (3.5.7)$$

Where the critical temperature is  $T_c = qJ$ .

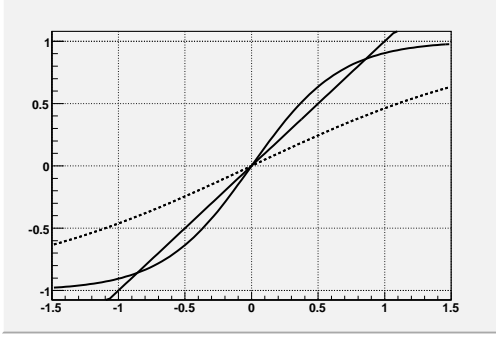


Figure 3.1: Graphical solution to the equation 3.5.6. The solid line show hyperbolic tangent function for  $qJ = 1.5$ .

The energy of the system is given by

$$E = -\frac{1}{2}qJN\langle\sigma\rangle^2 \quad (3.5.8)$$

for  $T < T_c$  and zero at higher temperature. Differentiating this with respect to temperature yields heat capacity increasing with temperature and abruptly dropping to zero.

$$C(T) = \begin{cases} 3qJT^2/T_c^3 & T < T_c \\ 0 & T > T_c \end{cases} \quad (3.5.9)$$

where only leading terms are shown (though it can be calculated exactly at all  $T$ ).

For non-zero magnetic field the self-consistency equation reads

$$\langle\sigma\rangle = \tanh \frac{(qJ\langle\sigma\rangle + h)}{T} \approx \frac{(T_c\langle\sigma\rangle + h)}{T} - \frac{1}{3} \frac{(T_c\langle\sigma\rangle + h)^3}{T^3} \quad (3.5.10)$$

From this equation one finds that at  $T = T_c$

$$\langle\sigma\rangle \propto h^{1/3} \quad (3.5.11)$$

Magnetic susceptibility can be found by differentiating equation with respect to  $h$ :

$$\chi = \left. \frac{\partial \langle \sigma \rangle}{\partial h} \right|_{h=0} = \frac{1}{T - T_c + T_c^3/T^2 \langle \sigma \rangle^2} \approx \begin{cases} -1/[2(T_c - T)] & T < T_c \\ (T - T_c)^{-1} & T > T_c \end{cases} \quad (3.5.12)$$

### 3.5.2 First order approximation. Zeroth order.

$$H = -J \sum_{j=1}^q (\sigma_i \sigma_j - (q-1) \sigma_j \langle \sigma \rangle) \quad (3.5.13)$$

$$Z = Z_+ + Z_- \quad (3.5.14)$$

$$Z_+ = \sum \sigma_j \exp \left[ \frac{J}{T} + \frac{J(q-1)\langle \sigma \rangle}{T} \sum_j \sigma_j \right] = \sum_{\sigma_j} \prod_j \dots = \left[ 2 \cosh \left( \frac{J}{T} + \frac{J(q-1)\langle \sigma \rangle}{T} \right) \right]^q \quad (3.5.15)$$

$$T_c = \frac{2J}{\ln[q/(q-2)]} \quad (3.5.16)$$

Note that phase transition occurs only for  $q > 2$ , which is related to possibility of the build-up of long range correlations.

### 3.5.3 Fluctuations and the correlation function

$$\chi = \frac{\partial M}{\partial B} = \frac{1}{T} (\langle M^2 \rangle - \langle M \rangle^2) = \frac{\mu^2}{T} \left[ \left\langle \left( \sum \sigma_i \right)^2 \right\rangle - \left( \left\langle \sum \sigma_i \right\rangle \right)^2 \right] = \frac{\mu^2}{T} \sum_{i,j} g(i,j), \quad (3.5.17)$$

where  $g(i,j)$  is the correlation function

$$g(i,j) \equiv \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle = g(|\mathbf{r}_i - \mathbf{r}_j|) \quad (3.5.18)$$

## 3.6 Critical exponents

In this section we give the definition of critical exponents:

$$C_V \sim \begin{cases} (T - T_c)^{-\alpha} & T > T_c \\ (T_c - T)^{-\alpha'} & T < T_c \end{cases} \quad (3.6.1)$$

$$m \sim (T_c - T)^\beta \quad (h = 0, T \leq T_c) \quad (3.6.2)$$

$$\chi \sim \begin{cases} (T - T_c)^{-\gamma} & T > T_c \\ (T_c - T)^{-\gamma'} & T < T_c \end{cases} \quad (3.6.3)$$

$$m \sim h^{1/\delta} \quad (T = T_c) \quad (3.6.4)$$

$$g(\mathbf{r}) = \frac{1}{(2\pi)^3} \int |\Delta \sigma(\mathbf{k})|^2 e^{i\mathbf{k}\mathbf{r}} d^3k \quad (3.6.5)$$

$$g(r) \sim e^{-r/\xi} / r^{d-2+\eta} \quad \xi \sim 1/t^\nu \quad (3.6.6)$$

$$d\nu = 2 - \alpha \quad (3.6.7)$$

### 3.7 Landau-Ginzburg phenomenological theory

Free energy has a minimum at equilibrium. Defining an order parameter as  $m$  one can expand free energy in the vicinity of the critical point

$$\frac{A}{T} \equiv \psi(t, m) = q(t) + a(t)m^2/2 + b(t)m^4/4 - ht \quad (3.7.1)$$

where  $t = (T - T_c)/T_c$ ;  $t \ll 1$ . The last term describes the interaction with external (“ordering”) field; to find the dependence of the magnetization in the vicinity of the critical point we first consider the case of  $h = 0$ . The minimum of the free energy is reached at  $m = 0$  for  $a(t) > 0$ , and at nonzero value for  $a(t) < 0$ . In order for the above form of the free energy to describe the phase transition we conclude that  $a(t) = a_1 t$  with  $a_1 > 0$ . In the vicinity of the critical point we also use  $b(t) \approx b_0 > 0$

To find the minimum of the free energy one has to solve

$$a_1 t m + b_0 m^3 = 0 \quad (3.7.2)$$

which yields

$$m = \begin{cases} 0 & t > 0 \\ \pm \sqrt{-a_1 t / b_0} & t < 0 \end{cases} \quad (3.7.3)$$

From the above we find the critical exponent  $\beta = 1/2$ .

Magnetic susceptibility can be calculated by differentiation with respect to  $h$  the corresponding equation for the minimum of free energy

$$-h + a m + b m^3 = 0 \quad (3.7.4)$$

which yields

$$\chi = \left. \frac{\partial m}{\partial h} \right|_{h=0} = \frac{1}{a_1 t + b_0 m^2} = \begin{cases} 1/(a_1 t) & t > 0 \\ 1/(4a_1 t) & t < 0 \end{cases} \quad (3.7.5)$$

and critical exponents  $\gamma = \gamma' = 1$ .

The dependence of the order parameter on the external field at the critical point,  $t = 0$ , can also readily found:

$$h = b_0 m^3 \quad (3.7.6)$$

which gives the critical exponent  $\delta = 3$ .

Finally note that the heat capacity  $C \propto \frac{\partial^2 \psi}{\partial t^2}$  is always finite,  $\alpha = \alpha' = 0$ , but experience a discontinuity at the critical point.

#### 3.7.1 Tricritical point

Let us consider free energy of the form

$$\psi(t, m) = \frac{1}{2}a(t)m^2 + \frac{1}{4}b(t)m^4 + \frac{1}{6}c(t)m^6 \quad (3.7.7)$$

The extrema are given by equation

$$a m + b m^3 + c m^5 = 0 \quad (3.7.8)$$

which yields solutions

$$m_{\pm}^2 = \frac{-b \pm \sqrt{b^2 - 4ac}}{2c} \quad (3.7.9)$$

with minima corresponding to plus sign. The first order phase transition line is defined by Eq. 3.7.8 and  $\psi = 0$ ,  $\Rightarrow m^2 = -2a/b \Rightarrow a = b^2/(4c)$ .

Find critical exponents in the tricritical point!

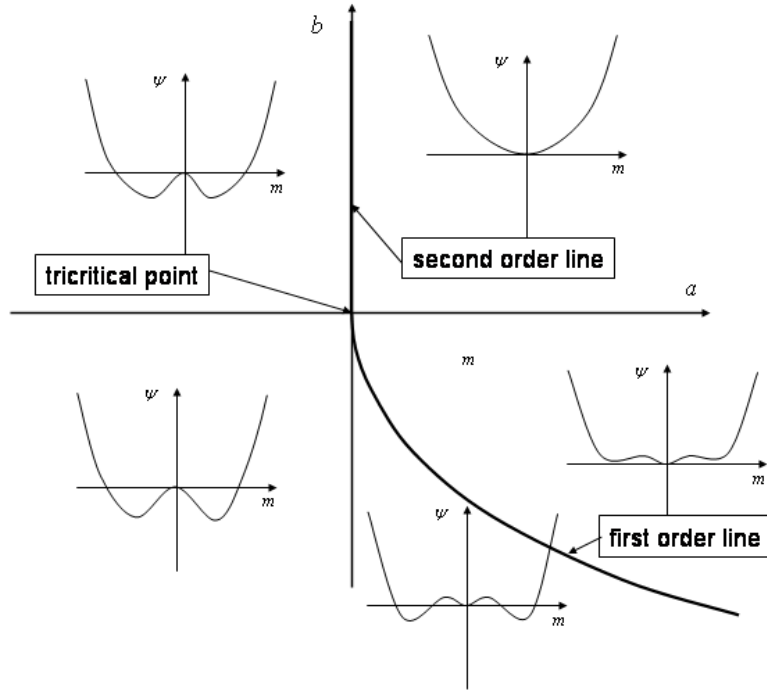


Figure 3.2: Phase diagram with typical dependences of free energy on the order parameter in each region.

### 3.8 Correlation function in the mean field approximation

The correlation function is given by expression

$$g(r) = \int \Delta m(\mathbf{r}_1) \Delta m(\mathbf{r}_2) \delta(\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{r}) d\mathbf{r}_1 d\mathbf{r}_2 \quad (3.8.1)$$

$$= \int \Delta m(\mathbf{r}_1) \Delta m(\mathbf{r}_2) \frac{1}{(2\pi)^3} \int d\mathbf{k} e^{-i\mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{r})} \quad (3.8.2)$$

Probability to find the system not in equilibrium state (the probability for a particular fluctuation) is given by

$$p_i \propto \exp(-\Delta A_i/T) \quad (3.8.3)$$

To take into account the spatial variation of the order parameter one can start from expression

$$\Delta A/T = \int dV \Delta \psi \quad (3.8.4)$$

where, in the first approximation (lowest order in gradient),

$$\Delta \psi = \frac{1}{2} a(t) m^2 + (\nabla m)^2 \quad (3.8.5)$$

$$\Delta A/T = (2\pi)^3 \int d^3 k (ck^2 + at) |m(\mathbf{k})|^2 \quad (3.8.6)$$

Recalling Eq. 3.8.3, one finds that the distribution in  $|m(\mathbf{k})|^2$  is Gaussian and

$$\langle |m(\mathbf{k})|^2 \rangle \sim \frac{1}{ck^2 + \alpha t} \quad (3.8.7)$$

Substitution into expression for the correlation function gives:

$$g(r) \sim \int |m(\mathbf{k})|^2 e^{i\mathbf{k}\mathbf{r}} \sim \frac{1}{r} e^{-r/\xi} \quad (3.8.8)$$

where  $\xi \sim \sqrt{c/(\alpha t)}$ . The critical exponents are  $\nu = 1/2$  and  $\eta = 0$ .

### 3.9 Importance of fluctuations. Ginzburg criterion

Why the mean field theory does not work? A: due to neglecting fluctuations. When one can neglect fluctuations:  $\langle (\Delta M)^2 \rangle \ll \langle M \rangle^2$ . Recalling

$$\chi = \frac{1}{V} \left. \frac{\partial M}{\partial B} \right|_{B=0} = \frac{\langle (\Delta M)^2 \rangle}{TV} \quad (3.9.1)$$

which leads to the *Ginzburg criterion*:

$$\boxed{\frac{T\chi V}{\langle (\Delta M)^2 \rangle} \ll 1} \quad (3.9.2)$$

In the vicinity of the critical point, in the volume with largest fluctuations ( $L \sim \xi$ ):

$$\frac{\chi^d (1/t^\gamma)}{(\chi^d t^\beta)^2} \sim t^{d\nu - \gamma - 2\beta} \ll 1 \quad (3.9.3)$$

Taking the critical exponents for the mean field one finds that inequality is satisfied only for  $d > 4$ . The value  $d = 4$  is called *upper critical dimension*.