

# Statistical physics.

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## I. LIMITATIONS OF MICROSCOPIC APPROACHES.

- We deal with very large amounts of atoms in everyday scale  $\sim 10^{20} - 10^{30}$ . It is impossible to solve these many equations of motion, it is even harder to define the initial conditions.

- Most of dynamical phenomena we are dealing with are chaotic in nature. Chance plays a very important role everywhere around us. This means that the outcome of a certain process is very susceptible to slightest changes in the initial conditions in external perturbations etc. Physically one can define a chaotic process as such where information which is not significant at present is crucial for predicting future. Usually chaos is opposite to dissipation associated with the loss of information: information important now is not important in future. Chaos and dissipation come together. Consider a drop of ink which fell into a glass of water. Solving the problem microscopically is almost impossible, solving diffusion equation and getting probability distribution of ink is easy. Microscopic solution: have to deal with chaotic system. Probabilistic solution: microscopic details do not matter (only very little information is really important: size of the drop, initial shape, diffusion coefficient).
- Statistical physics is closely connected to information. In chaotic systems most of information about microscopic degrees of freedom is lost due to chaotic dynamics. Only very limited macroscopic information about energy, volume, pressure, magnetization, which are called macroscopic constraints, is accessible. Statistical physics is based on maximum ignorance principle, i.e. we usually assume a maximally random state consistent with macroscopic constraints.
- The relation between statistical physics and quantum mechanics is even more complex. (i) Quantum mechanics is intrinsically probabilistic. It is often not very easy to separate intrinsic quantum probability coming from uncertainty principle from the statistical probability coming from incomplete knowledge about the system. (ii) The Hilbert space is exponentially large. This implies that for the full description of a quantum system we need to know the exponentially large number of coefficients describing the wave function in an arbitrary basis. Let us take as an example 100 particles leaving in a discrete space of 200 lattice sites (this is approximately equal to the crystal of the size  $6 \times 6 \times 6$ ). The size of the Hilbert space for (spinless) fermions is  $200!/(100!)^2 \sim 10^{50}$  and for bosons it is  $300!/(200!100!) \sim 10^{80}$ . The amount of particles in the Universe is  $\sim 10^{50}$ . It is fundamentally impossible to simulate dynamics microscopically even for such a small system. Also the typical level spacing is exponentially small: it is impossible to resolve levels during life time of universe. Any tiny perturbation will can mix these levels. (iii) The Schrödinger equation describing time evolution of a quantum system is linear. Thus there is no chaos associated with the unstable dynamics, unlike in the classical case. Quantum chaos is contained in the structure of the

eigenstates of the Hamiltonian. Yet in many cases the quantum and classical descriptions are just two different languages describing the same phenomenon. The precise relation between these two descriptions is currently a subject of active research.

- There is a compelling evidence that often phenomenological macroscopic approaches work very well: fluid and gas dynamics accurately describes the motion of airplanes. Newton's equations are work very well large composite objects. Phenomenological friction forces well describe dissipation, i.e. energy loss of macroscopic degrees of freedom due to their interaction with the chaotic environment. One can think about many more examples of accurate quantitative descriptions of static and dynamic properties of macroscopic objects. The reason for such success is that many phenomena are universal (insensitive to precise microscopic details characterizing the system). For example for sound waves we can generically write the dispersion  $\omega(k) = ck$  - microscopic details only affect the precise value of the sound velocity (which is usually very hard to compute from the first principles) but not the details of the spectrum itself. Contemporary understanding of universality comes from the renormalization group.

The main purpose of statistical physics is to establish the link between microscopic description of many-particle systems and their macroscopic properties. Despite statistical physics is a very old subject and despite tremendous progress in this subject there are still many open questions especially in non-equilibrium systems. Therefore statistical physics remains a very active field of research.

## II. QUICK INTRODUCTION INTO PROBABILITY AND STATISTICS.

Statistical physics gives us intrinsically probabilistic description of various phenomena. Thus its laws are largely based on the probability theory and mathematical statistics. In this chapter we will give a very brief and superficial introduction into the basic concepts of the probability theory which will be crucial in the following chapters. We will not attempt to be mathematically rigorous and often give sketchy proofs. A good textbook for additional reading is a book by W. Feller: "An Introduction to Probability Theory and Its Applications, Vol. 1".

Suppose we have a set  $\mathcal{S}$  which can be either discrete or continuous. Probability  $p(s \in \mathcal{S})$  is a map to real axis, which satisfies the following properties:

- $p(s) \geq 0$ : probability can not be negative.

- $p(\mathcal{S}) = 1$ : probability that the outcome belongs to the whole set  $\mathcal{S}$  is unity
- If  $s_1 \cap s_2 = 0$  then  $p(s_1 \cup s_2) = p(s_1) + p(s_2)$ .

Starting from these simple and intuitive postulates one builds the whole machinery of the probability theory.

It is important to differentiate between probability and statistics. The latter is the analysis of events which already happened. Let us consider an example where we are tossing a coin. Before the process the probability of "head" or "tail" is 50%. However, after the coin is tossed we have a definite outcome. In physical terms probability assigns chances to certain outcomes of physical experiments, statistics deals with the results of such outcomes.

Let us also mention the intuitive definition of the probability. Assume that we repeat the same experiment many ( $N$ )times. Suppose that the outcome  $s$  happened  $N_s$  times. Then probability of  $N_s$  is

$$p(s) = \lim_{N \rightarrow \infty} \frac{N_s}{N}. \quad (\text{II.1})$$

#### A. Discrete Sets.

Assume now that our set  $\mathcal{S}$  is a discrete set of numbers. Then the normalization requires that

$$\sum_s p(s) = 1. \quad (\text{II.2})$$

Next we introduce some important concepts. Expectation value of  $s$  or mean or average is

$$\bar{s} = \sum_s s p_s. \quad (\text{II.3})$$

This average satisfies simple equalities:

$$\overline{s_1 + s_2} = \bar{s}_1 + \bar{s}_2, \quad (\text{II.4})$$

If  $a$  is some constant then

$$\overline{a s} = a \bar{s}. \quad (\text{II.5})$$

The variance is defined as

$$\delta s^2 = \overline{(s - \bar{s})^2} = \overline{s^2} - (\bar{s})^2. \quad (\text{II.6})$$

This is a very important result to remember. Variance tells us about the width of distribution. Note that variance is in general not additive:

$$\overline{(s_1 + s_2)^2} - (\overline{s_1 + s_2})^2 = \delta s_1^2 + \delta s_2^2 + 2\overline{s_1 s_2} - 2\bar{s}_1 \bar{s}_2. \quad (\text{II.7})$$

The two events are called independent if

$$p(s_1 \cap s_2) = p(s_1)p(s_2). \quad (\text{II.8})$$

In this case it is easy to see that  $\overline{s_1 s_2} = \bar{s}_1 \bar{s}_2$ . Then from Eq. (II.7) it immediately follows that the variance is additive:

$$\overline{(s_1 + s_2)^2} - (\overline{s_1 + s_2})^2 = \delta s_1^2 + \delta s_2^2 \quad (\text{II.9})$$

In general one can write

$$p(s_1 \cap s_2) = p(s_1)p(s_2|s_1), \quad (\text{II.10})$$

where  $p(s_2|s_1)$  is the conditional probability. It tells us the probability that the event  $s_2$  happens given that the event  $s_1$  already happened. For independent events clearly  $p(s_2|s_1) = p(s_2)$  since the information about the outcome  $s_1$  does not affect the chances of the outcome  $s_2$ .

Let us consider the following illustrative example. The true coin is tossed two times. We ask the question: what is the probability that we get first head and the second tail. The answer is clearly  $1/4$  since this combination is one of the four equally possible arrangements:  $hh, ht, th, tt$ . This answer can also be obtained by multiplying the probabilities of first head  $1/2$  and the second tail  $1/2$ . Indeed  $1/4 = 1/2 \times 1/2$ . Next let us consider a second example: the true coin is tossed three times. We now ask what is the probability that (i) we get two out of three heads and (ii) the last toss is head. There are now eight possibilities:

$$hhh, hht, hth, htt, thh, tht, tth, ttt \quad (\text{II.11})$$

Out of these eight only two configurations  $hth$  and  $thh$  satisfy both conditions (i) and (ii) so the probability of both (i) and (ii) happening is  $1/4$ . At the same time the probability of (i) is  $p_1 = 3/8$  and of (ii) is  $1/2$ . Clearly  $1/4 \neq 3/8 \times 1/2$ . So these events are not independent or as is often said in physics are correlated. The correlation is intuitively clear since having the event (i): two out of three increases chances of event (ii): the last toss is tail. Indeed the three configurations satisfying the constraint (i) are  $thh, hth, hht$ . Out of these three configurations the first two satisfy the constraint (ii) so we can write  $p(ii|i) = 2/3$ . We can thus recover the answer

for joint the probability of (i) and (ii) using Eq. (II.10):  $p(i \cap ii) = 3/8 \times 2/3 = 1/4$ , which is the correct result. This trivial example illustrates a very important point, which will become a subject of detailed discussions when we analyze interacting systems. As we will see there nontrivial conditional probabilities are equivalent to correlations in the system which are often induced by interactions.

Higher moments of  $s$  are less used but sometimes they play an important role. The moments themselves are not very representative because they contain information already included in the lower moments. For example,  $\overline{s^2}$  includes both the information about the average  $\bar{s}$  and the width  $\delta s^2$ . The same situation happens with other moments. The  $n^{\text{th}}$  moment of  $s$  with “subtracted” information contained in the lower moments of  $s$  is called  $n$ -th cumulant of  $s$ . We will formally introduce cumulants and give explicit expressions for the cumulants up to the fourth order later in this section after we discuss continuous distributions.

Let us point an important difference between probability and statistics. In probability theory we assume some probability distribution  $P(s)$  which describes chances for different outcomes of the experiment or measurement of  $s$ . In statistics we have a data and we are trying to reconstruct the probability distribution which best describes the data. It is intuitively clear that in order to better reconstruct the probability distribution or in particular the expectation value, variance and other moments of some variable  $s$  we need to collect more data. Indeed a single measurement gives us a particular value of  $s$  another experiment gives another value and so on. If we accumulate enough values we can reconstruct the probability distribution. To make this intuition more formal we denote a random variable describing possible outcomes of a particular experiment  $s_i, i = 1, 2 \dots N$ . We assume that all experiments are identical meaning that all  $s_i$  have the same distribution and independent from each other meaning that there is no propagating error where outcome of the  $i$ -th experiment may affect outcomes of future experiments. From this  $N$  variables let us construct another variable  $\tilde{s}_N$  which describes their mean:

$$\tilde{s}_N = \frac{s_1 + s_2 + \dots + s_N}{N}. \quad (\text{II.12})$$

This is still a random variable which has its own probability distribution. It is clear that the expectation value of  $\tilde{s}$  is the same as  $\bar{s}$ . This follows from Eqs. (II.4) and (II.5) generalized to  $N$  variables and the fact that all variables  $s_j$  have the same expectation value. Next using statistical independence of  $s_j$ , which physically corresponds to the assumptions that there is no systematic error propagating from one experiment to another, from Eq. (II.9) we obtain that

$$\delta \tilde{s}_N^2 = \frac{1}{N} \delta s^2 \quad (\text{II.13})$$

We see that as the number of experiments  $N$  grows the statistical uncertainty in  $\tilde{s}_N$  decreases while the average remains the same. So when  $N$  becomes sufficiently large  $\tilde{s}_N$  with almost certainty predicts the value of  $\bar{s}$ . This is exactly what our intuition tells us that if  $N$  is large then any measurement of  $\tilde{s}_N$  with a good accuracy predicts the value of  $\bar{s}$ .

Similarly it is useful to define a fluctuating variable which estimates the variance of  $s$ :  $\delta s^2$ . The most convenient choice is

$$\tilde{\sigma}_N^2 = \frac{1}{N-1} \sum_{i=1}^N \left( s_i - \frac{1}{N} \sum_j s_j \right)^2. \quad (\text{II.14})$$

Note that there is somewhat nonintuitive prefactor in this expression  $1/(N-1)$  instead of  $1/N$ . It is related to the fact that instead of expectation value of  $s$  we are subtracting its estimate, which is determined from the same set of measurements. It is straightforward to verify that with this prefactor the expectation value of  $\tilde{\sigma}_N^2$  coincides with  $\delta s^2$ :

$$\overline{\tilde{\sigma}_N^2} = \frac{1}{N-1} \sum_i \overline{s_i^2} - \frac{1}{N(N-1)} \sum_{i,j} \overline{s_i s_j} = \overline{s^2} - (\bar{s})^2. \quad (\text{II.15})$$

It is also straightforward to check that as  $N$  increases the fluctuations of  $\tilde{\sigma}_N^2$  decay as  $1/N$  but with a prefactor larger than that in  $\tilde{s}$ . This trend is true in general: in order to estimate higher order cumulants one needs to perform more measurements. Experimentally it is rare when one can accurately estimate cumulants beyond the third or the fourth order.

### Examples of discrete distributions.

*Binomial distribution.* Imagine that we have a process (like a coin toss) with the two possible outcomes which we will term as the “success” and the “failure”. The probability of success is  $p$  and the probability of failure is  $q = 1 - p$ . If we have a true coin then  $p = q = 1/2$ , but in general these two probabilities can be nonequal. Suppose we perform this process  $N$  times and assume that each time the result is independent of previous outcomes. Let us now find the probability of having  $n$  successes and  $N - n$  failures. We will solve this problem in steps. First we find the probability of having first  $n$  successes and next  $N - n$  failures. Because all the processes are statistically independent this probability is  $p^n q^{N-n}$ . Now let us find the number of independent configurations of  $n$  successes and  $N - n$  failures (note that each configuration has the same probability). This problem is equivalent of finding number of different configurations for placing  $n$  blue balls and  $N - n$  red balls into  $N$  baskets. For the first blue ball there are obviously  $N$  available baskets, for the second -  $N - 1$  and so on. So there are  $N(N-1) \dots (N-n+1)$  ways to distribute them in this way. But there is over-counting involved. Because all configurations obtained by permuting

blue balls between each other are equivalent. Thus we need to divide this answer by  $n!$ . The net result for the probability of  $n$ -successes is

$$P(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}. \quad (\text{II.16})$$

Note that  $\sum P(n) = (p+q)^N = 1$  is the binomial, hence the name - ‘‘binomial distribution’’. Let us now compute the expectation value of number of successes and its the variance:

$$\bar{n} = \sum_n n \frac{N!}{n!(N-n)!} p^n q^{N-n} = Np \sum_n \frac{(N-1)!}{(n-1)!(N-1-(n-1))!} p^{n-1} q^{(N-1)-(n-1)} = pN \quad (\text{II.17})$$

as it should be.

$$\bar{n}^2 = \sum_n n^2 \frac{N!}{n!(N-n)!} p^n q^{N-n} = \sum_n (n-1+1) \frac{N!}{(n-1)!(N-n)!} p^n q^{N-n} = N(N-1)p^2 + Np \quad (\text{II.18})$$

Therefore

$$\delta n^2 = Np(1-p) \quad (\text{II.19})$$

Note that

$$\delta(n/N) = \frac{1}{\sqrt{N}} \sqrt{(1-p)p}. \quad (\text{II.20})$$

in agreement with the general expectation that intensive variables should not fluctuate at large  $N$  (II.13). The results (II.17) and (II.19) can be also obtained directly from noting that

$$n = \sum_{\alpha} n_{\alpha}, \quad (\text{II.21})$$

where  $n_{\alpha}$  are independent fluctuating variables which have two possible outcomes 1 with probability  $p$  and 0 with probability  $q$ . It is straightforward to check that each variable  $n_{\alpha}$  has the expectation value  $p$  and the variance  $p(1-p)$ . Using the additivity of the expectation value and the variance for the sum of independent random variables we arrive to (II.17) and (II.19).

*Poisson distribution.* Poisson distribution is another very important distribution in statistics. It describes variety of phenomena from radioactivity to statistics of defective items. It can be obtained from the binomial distribution when  $p \rightarrow 0$ ,  $N \rightarrow \infty$  such that  $pN = \text{const}$ . In this case

$$P(n) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n} \approx \frac{(pN)^n}{n!} \exp[-pN] = \frac{\lambda^n}{n!} \exp[-\lambda], \quad (\text{II.22})$$

where  $\lambda = pN$ . It is easy to check that this distribution is correctly normalized. In derivation we used the fact that  $n \sim \lambda \ll N$  so that  $(1-p)^{N-n} \approx (1-p)^N \approx \exp[-\lambda]$ . Likewise  $N!/(N-n)! \approx N^n$ .

Let us illustrate how Poisson distribution emerges for the problem of radioactive decay. Let us assume that the probability of decay of a nucleus per unit time is  $\gamma$  and we are interested in times such that only a small fraction of nuclei decays. We will solve this problem in two different ways.

(i) In the first way we treat decay of each nuclei during time  $t$ , which we call a success, as an independent event. The probability of this event is obviously  $p = \gamma t$ . Since we have  $N$  nuclei the average number of successes is  $\lambda = Np = N\gamma t$ . Because  $p \ll 1$  and  $N \gg 1$  we can use the Poisson distribution:

$$p(n) \approx \frac{(N\gamma t)^n}{n!} \exp[-N\gamma t]. \quad (\text{II.23})$$

(ii) In the second way of deriving the Poisson distribution we split the time interval  $t$  into infinitesimally short subintervals  $\delta t$  and let  $M = t/\delta t$  to be the number of such intervals. Since  $\delta t$  is vanishingly small with probability close to unity there will be no decay detected during this subinterval. The probability of detecting a single decay is  $\tilde{p} = N\gamma\delta t$ . The probability of two or more decays is negligibly small because it is proportional to higher powers of  $\delta t$ . Now we have  $M$  independent events with probability of success  $\tilde{p} \rightarrow 0$  as  $\delta t \rightarrow 0$  but  $\lambda = M\tilde{p} = N\gamma t$  being constant. Thus we can again use the Poisson distribution coming to Eq. (II.23).

This example illustrates that there are more than one ways for defining the elementary event, which we call the success. One or another choice can be dictated by a particular experimental setting, physical intuition, or other factors. Other instructive examples of how Poisson distribution works in practice can be found in the book by Feller (pages 160-161). These examples include radioactive decay from the famous Rutherford paper of 1920, flying bomb hits London (statistics of bomb hits during world war II of various London districts), statistics of permutations in chromosomes after X-ray radiation and many more.

## B. Continuous distributions.

Now assume that the set  $\mathcal{S}$  represents a continuous set of numbers  $x$  which can be real or complex. Then one defines a non-negative real-valued function, probability density  $p(x)$ , which satisfies the normalization condition:

$$\int_{\mathcal{S}} dx p(x) = 1. \quad (\text{II.24})$$

Most commonly for us  $\mathcal{S}$  will be a set of real numbers:  $\mathcal{S} = (-\infty, \infty)$ . In what follows we will skip limits of integration implying that unless otherwise specified the integration is taken over the set  $\mathcal{S}$ .

The expectation value of any function which depends on  $x$  is defined similarly to the discrete case:

$$\langle F(x) \rangle = \int dx p(x) F(x). \quad (\text{II.25})$$

Note that if  $y$  is a monotonic function of  $x$  we can change variables from  $y$  to  $x$ . The conservation of probability requires that  $p(x)dx = p(y)dy$ . Therefore

$$p(y) = p(x) \left| \frac{dx}{dy} \right|. \quad (\text{II.26})$$

In general (for arbitrary nonmonotonic function) one can define  $p(y)$  as

$$p(y) = \int dx p(x) \delta(y(x) - y). \quad (\text{II.27})$$

*Example.* Let us take a Gaussian distribution

$$p(x) = \frac{1}{\sqrt{2\pi}} e^{-x^2/2} \quad (\text{II.28})$$

and change the variables from  $x$  to  $y = x^2$ . If  $x$  represents the velocity of the particle then  $x^2$  represents the kinetic energy. So such change of variables is equivalent to going from the velocity to the energy distribution. Then according to Eq. (II.27) we have

$$\begin{aligned} p(y) &= 0 \text{ for } y \leq 0 \\ p(y) &= \frac{2}{\sqrt{2\pi y}} \exp[-y/2] \text{ for } y > 0. \end{aligned} \quad (\text{II.29})$$

Physically the factor  $1/\sqrt{y}$  represents the effect of the density of states. From  $y = x^2$  it is obvious that the same interval of length  $dy$  corresponds to a larger interval of  $x$  for smaller  $y$ .

*Examples of continuous distributions.* Here we will consider two most common examples of continuous distributions

- Exponential distribution:

$$p(x) = \gamma \exp[-\gamma x], \quad (\text{II.30})$$

This distribution describes e.g. the probability density of a nuclei to decay at moment  $x$  (if  $x$  is interpreted as a time). The parameter  $\gamma$  plays the role of the decay rate. Straightforward calculation shows that the expectation value and the variance of  $x$  are both given by  $1/\gamma$ .

- Normal distribution:

$$p(x) = \frac{1}{\sqrt{2\pi\sigma}} \exp \left[ -\frac{(x - x_0)^2}{2\sigma^2} \right]. \quad (\text{II.31})$$

This is probably the most important distribution in statistics. The parameters  $x_0$  and  $\sigma^2$  represent the mean and the variance of  $x$  respectively.

One can also define joint probability distribution of multiple variables:  $p(x_1, x_2, \dots)$ . The probability density factorizes if and only if the random variables are independent.

*Characteristic function.* A very useful concept for both continuous and discrete distributions is the characteristic function. It is defined as a Fourier transform of the probability distribution or, alternatively, as the expectation value of  $\exp[-ikx]$ :

$$\tilde{p}(k) = \langle \exp[-ikx] \rangle = \int dx \exp[-ikx] p(x). \quad (\text{II.32})$$

Clearly the probability density is the inverse Fourier transform of the characteristic function. Sometimes it can be useful to define other transforms of the probability distribution using Bessel functions or other complete set of functions. The characteristic function is the generator of the moments of the distribution:

$$\tilde{p}(k) = \sum_n \frac{(-ik)^n}{n!} \langle x^n \rangle. \quad (\text{II.33})$$

Similarly

$$\exp[ikx_0] \tilde{p}(k) = \sum_n \frac{(-ik)^n}{n!} \langle (x - x_0)^n \rangle. \quad (\text{II.34})$$

The logarithm of the characteristic function generates cumulant expansion of the distribution:

$$\ln \tilde{p}(k) = \sum_n \frac{(-ik)^n}{n!} \langle x^n \rangle_c \quad (\text{II.35})$$

The first four cumulants have special names since they are quite frequently used. Their explicit expressions immediately follow from Eq. (II.33):

$$\langle x \rangle_c = \langle x \rangle, \quad (\text{II.36})$$

$$\langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2 \equiv \sigma^2, \quad (\text{II.37})$$

$$\langle x^3 \rangle_c = \langle x^3 \rangle - 3\langle x^2 \rangle \langle x \rangle + 2\langle x \rangle^3, \quad (\text{II.38})$$

$$\langle x^4 \rangle_c = \langle x^4 \rangle - 4\langle x^3 \rangle \langle x \rangle + 3\langle x^2 \rangle^2 + 12\langle x^2 \rangle \langle x \rangle^2 - 6\langle x \rangle^4. \quad (\text{II.39})$$

$$(\text{II.40})$$

As we already discussed the first and the second cumulants are simply the mean and the variance.

The normalized third cumulant is called skewness:

$$\gamma_1 = \frac{\langle x^3 \rangle_c}{\sigma^3}. \quad (\text{II.41})$$

It is a good measure of the asymmetry of the distribution. And finally one defines kurtosis as the normalized fourth cumulant:

$$\gamma_2 = \frac{\langle x^4 \rangle_c}{\sigma^4}. \quad (\text{II.42})$$

Kurtosis also characterizes the shape of the distribution. Higher kurtosis corresponds to sharper distributions with longer tails.

Let us observe that the Gaussian distribution is also special because all its cumulants higher than the second are equal to zero. This immediately follows from finding its characteristic function:

$$\tilde{p}(k) = \exp \left[ -ikx_0 - \frac{k^2 x^2}{2} \right] \quad (\text{II.43})$$

so that indeed  $\ln \tilde{p}(k) = -ikx_0 - k^2 x^2/2$ . This is a very important property of the Gaussian distribution which shows that the moments higher than second are not independent. This property is central for many perturbative expansions in statistical physics, high energy physics, condensed matter physics. It also underlies the Feynman's diagrammatic techniques.

*Central limit theorem.* What really makes Gaussian distribution stand alone among all other distributions is the central limits theorem. Suppose that we are dealing with  $N$  independent random variables  $x_i$  which have finite mean and variance. It is not required that the mean and the variance are identical for all  $x_i$  but it is important that they are bounded with a bound being independent of  $N$ . Then in the limit when number of these variables is large the distribution of their sum  $X = \sum_{i=1}^N x_i$  approaches gaussian distribution with mean  $\langle X \rangle = \sum_{j=1}^N \langle x_j \rangle$  and the variance  $\sigma_X^2 = \sum_{j=1}^N \sigma_j^2$ , i.e.

$$p(X) \rightarrow \frac{1}{\sqrt{2\pi}\sigma_X} \exp \left[ -\frac{(X - \langle X \rangle)^2}{2\sigma_X^2} \right]. \quad (\text{II.44})$$

Very often we will deal with the sums of identically distributed variables. In this case  $\langle X \rangle = N\langle x_1 \rangle$  and  $\sigma_X^2 = N\sigma_1^2$ . The theorem also holds for weakly dependent variables, where covariances (correlations) between different variables,  $\langle x_i x_j \rangle - \langle x_i \rangle \langle x_j \rangle$ , decay sufficiently fast with  $|i - j|$ , i.e. the variables, which are far from each other are almost independent. In this case, the mean of  $X$  is still given by the sum of  $\langle x_j \rangle$ , however, the variance  $\sigma_X^2$  is no longer given by the sum of the variances.

Let us now present a sketch of the proof of the central limit theorem. We showed that the mean and the variance are additive for independent variables. In order to show that the distribution approaches the Gaussian form it is sufficient to prove that all higher order cumulants of  $X$  vanish.

For simplicity we assume that all variables  $x_j$  are identically distributed. Let us define a new variable

$$y = \frac{X - Nx_0}{\sigma\sqrt{N}}. \quad (\text{II.45})$$

Then clearly  $\langle y \rangle_c = 0$ ,  $\langle y^2 \rangle_c = 1$ . It is straightforward to verify that higher order cumulants satisfy:

$$\langle y^n \rangle_c = \langle x^n \rangle_c \frac{N}{\sigma^N N^{n/2}} \quad (\text{II.46})$$

They vanish in the limit  $N \rightarrow \infty$  for all  $n > 2$ . The reason for such dependence on  $N$  is the following: in denominator  $N^{n/2}$  comes from the definition of  $y$ . The factor of  $N$  in numerator comes from the summation over independent variables. We already saw that for independent variables the second cumulant (variance) of the sum is additive. This property is actually true for all cumulants (see problems to this section).

Example: Let us take the Poisson distribution

$$p(n) = \frac{\lambda^n}{n!} \exp[-\lambda] \quad (\text{II.47})$$

Recall that this distribution is obtained from the binomial distribution with  $\lambda = pN$ . We are interested in the limit  $\lambda \rightarrow \infty$ . Using the Stirling's formula we find

$$p(n) \approx \frac{1}{\sqrt{2\pi n}} \exp[n \log \lambda - n \log n + n - \lambda]. \quad (\text{II.48})$$

Let us treat  $n$  approximately as a continuous variable (which is justified if  $\lambda \gg 1$ ) and expand the probability near the maximum up to the second order in  $n$  (this is equivalent to using the saddle-point approximation in evaluating any sums of smooth functions weighted by  $p(n)$ ). It is easy to check that the maximum of the probability corresponds to  $n \approx \lambda$ . Expanding to the second order in  $(n - \lambda)$  the exponent in Eq. (II.48) we find

$$p(n) \approx \frac{1}{\sqrt{2\pi\lambda}} \exp \left[ -\frac{(n - \lambda)^2}{2\lambda} \right]. \quad (\text{II.49})$$

QED. Note that the next, cubic term in the expansion gives the correction in the exponent

$$\exp \left[ \frac{1}{6\lambda^2} (n - \lambda)^3 \right]. \quad (\text{II.50})$$

This correction becomes significant only at  $|n - \lambda| \gtrsim |\lambda|^{2/3}$ . But at this values of  $n$  the probability is already exponentially small  $p(|n - \lambda| \gtrsim |\lambda|^{2/3}) \lesssim 1/\sqrt{2\pi\lambda} \exp[-1/2|\lambda|^{1/3}]$ . So the correction is significant only for very improbable events. From this analysis we can get a very important lesson: normal distribution can accurately describe typical (probable) events but does not describe tails (so called extreme values), e.g. does not describe accurately extreme value statistics.

*Application: a random walk.* Assume that we have a random walker who randomly makes a step to the left or to the right. Find the probability distribution of a position of a random walker after large number of steps. Solution: Each step changes the position of a walker either by  $\Delta x = +1$  or by  $\Delta x = -1$  so the mean displacement per step is  $x_0 = 0$  and the variance is  $\sigma^2 = 1/2 + 1/2 = 1$ . By the central limit theorem after  $N = t$  (interpret  $N$  as time) steps the distribution is Gaussian with the probability

$$p(x) \approx \frac{1}{\sqrt{2\pi t}} \exp\left[-\frac{x^2}{2t}\right]. \quad (\text{II.51})$$

This is the famous formula for diffusion. It generalizes to arbitrary number of dimensions.

*Remarks.* The central limit theorem is valid only if all variables have finite moments. If this is not the case the sum can still converge but to a non-gaussian Levi distribution. The central limit theorem is useless when we are interested by rare events, i.e. by the tails of the distribution (like maxima). Instead we get completely different extreme value statistics distributions.

*When the central limit theorem does not work. Extreme value statistics.* The central limit theorem tells us about the probability of typical events close to the maximum. We can be interested in a different question of distribution of very untypical (extreme) events. E.g. suppose we are dealing with size distribution of bacteria. If there is abundance of food and there is no natural selection we expect Gaussian distribution of sizes of bacteria according to the central limit theorem. What if, however, food is scarce and bacteria has to fight for it. We expect that stronger bacteria, e.g. bigger in size, will dominate and weaker bacteria will die. So it is not the typical bacteria which are important but extreme, largest, bacteria. To be specific let us solve the following problem: assume that we have  $N$ -independent experiments where the outcome  $x$  has a particular distribution  $p(x)$  and ask what is the probability distribution of  $x_{max}$  in this series of experiments. It is clear that the probability that  $x_{max} = r$  is equivalent that one of the experiments yielded  $x = r$  and all  $N - 1$  other experiments gave  $x < r$ . So

$$P_{max}(r) = Np(r) \left( \int_{-\infty}^r p(x) dx \right)^{N-1}. \quad (\text{II.52})$$

The first factor reflects the fact that there are  $N$  places where the maximum can occur, the second factor is the probability (density) that one of the experiments gave  $x = r$  and the last term tells us that all other  $N - 1$  experiments gave  $x < r$ . Let us consider exponential distribution to be specific:

$$p(x) = \lambda \exp(-\lambda x). \quad (\text{II.53})$$

Then

$$P_{max}(r) = N\lambda \exp[-\lambda r](1 - \exp[-\lambda r])^{N-1}. \quad (\text{II.54})$$

Note that when  $N$  is large we expect that  $r \gg 1/\lambda$  - reflecting the fact that maximum is much bigger than typical. In this case the last term can be exponentiated and we get

$$P_{max}(r) \approx N\lambda \exp[-\lambda r - N \exp[-\lambda r]]. \quad (\text{II.55})$$

This is so called Gumbel distribution. We can find the mean approximately using the saddle point approximation  $\lambda \approx N \exp[-\lambda \bar{r}]$ , so that  $\bar{r} \approx 1/\lambda \log[N/\lambda]$ . It is straightforward to see that the Gumbel distribution is highly asymmetric. The probability to find  $r > \bar{r}$  falls off exponentially. However, the probability to find  $r < \bar{r}$  falls off doubly exponentially. It means that there is a very small chance to find maximum significantly smaller than  $\bar{r}$ . Note that the width of the distribution does not change with  $N$  (unlike for the average  $x$ , where it decreases according to the central limit theorem) and remains of the order of  $1/\lambda$ . In Fig. 1 we show a plot of the Gumbel

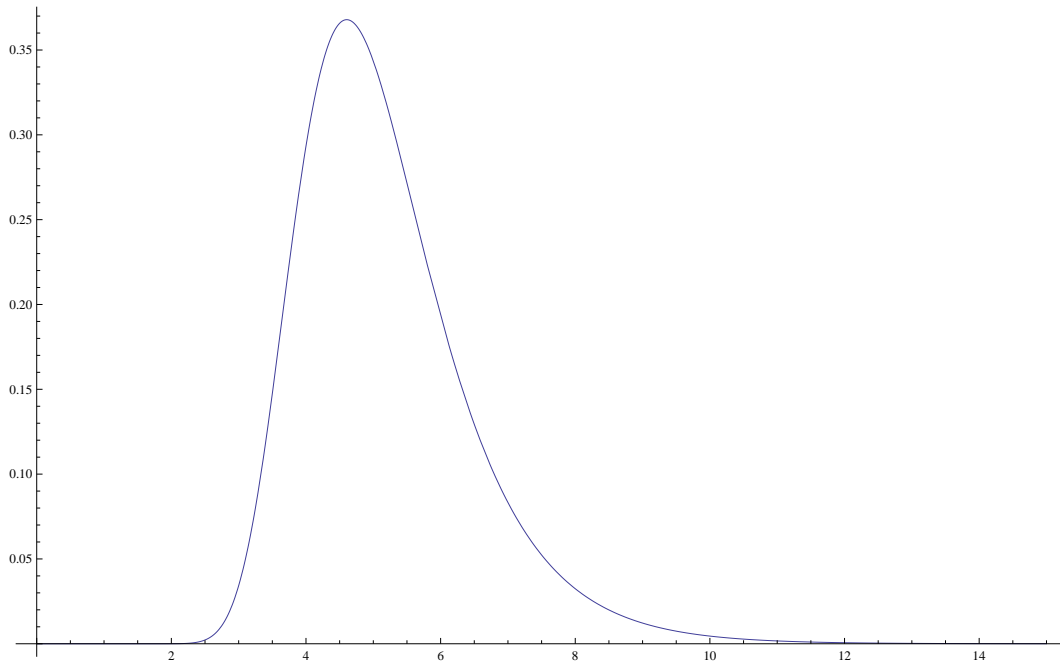


FIG. 1 Example of the Gumbel distribution (II.55) with  $\lambda = 1$  and  $N = 100$ .

distribution (II.55) for  $\lambda = 1$  and  $N = 100$ .

### C. Problems for Sec. II

1. How many random digits one needs to get in order that the probability to have at least one "7" there is 90%? (From Feller).
2. What is the probability that six random people have birthdays within the same two months and the other 10 months are birthday free? (Hint start from two people, then consider three, four etc.)
3. A book of 500 pages contains 100 missprints. Estimate the probability that at least one page contains 5 missprints. (Hint use Poisson distribution).
4. Prove that the Poisson distribution (II.22) is normalized. Find the mean and the variance of  $n$  as a function of  $\lambda$ . Discuss how the Poisson distribution looks like for large and small values of  $\lambda$ .
5. Find  $\xi = \langle x^3 \rangle_c / \langle x^2 \rangle_c^{3/2}$  for the binomial distribution as a function of  $N$ . Analyze what happens to  $\xi$  for large  $N$ , give interpretation for your result. Repeat this exercise for the Poisson distribution, look carefully at the limit  $\lambda \gg 1$ . Find the first three cumulants for the exponential distribution:  $p(x) = \lambda \exp[-\lambda x]$ ,  $x \geq 0$  and  $p(x) = 0$  otherwise.
6. Check that Eq. (II.46) holds for  $n = 3$ .
7. Prove the central limit theorem for the binomial distribution. I.e. consider the distribution (II.16) in the limit when  $N$  is large. Using Stirling's formula and treating  $n$  as a continuous variable derive the approximate form of the distribution  $P(n)$ . Show it is gaussian with the mean  $pN$  and the variance  $Npq$ .

### III. MICROSCOPIC ENSEMBLES, ERGODICITY

As we discussed it is virtually impossible to describe large macroscopic systems deterministically. Due to many various factors we can use only probabilistic description, i.e. there is a function  $f(\mathbf{x}, \mathbf{p}, t)$  of all coordinates and momenta of all particles, which describes the probability of a system to occupy a certain microscopic state. Thus the average of any observable is:

$$\langle \Omega(t) \rangle = \int d\mathbf{x} d\mathbf{p} \Omega(\mathbf{x}, \mathbf{p}, t) f(\mathbf{x}, \mathbf{p}, t) d\mathbf{x} d\mathbf{p}. \quad (\text{III.1})$$

Note by  $\mathbf{x}$  and  $\mathbf{p}$  we understand all phase space coordinates, discrete (like e.g. magnetization) or continuous. In quantum statistical mechanics one has to distinguish between two averages (often a source of confusion!): quantum mechanical average and statistical (probabilistic) average. The first one is related to fundamental uncertainty of QM which states that even if we have a complete knowledge about the wave-function of the system - we have intrinsically probabilistic description about the system: e.g. we can not possibly measure coordinates and momenta of a particle. Statistical average is related to the fact that we do not know the wave function of the system (or this wave function might not exist at all due to mixing with the environment). Then we have statistical uncertainty about the wave-function itself. General description of mixed states (states not described by a single wave function) is given by a density matrix. There are many ways to introduce it. Let us use the one which emphasizes its statistical nature. Assume that the system is described by some wave function with statistically random coefficients

$$|\Psi\rangle = \sum_m a_m |\psi_m\rangle, \quad (\text{III.2})$$

where  $|m\rangle$  is some basis. Then expectation value of any observable is

$$\bar{\Omega} = \sum_{m,n} a_n^* a_m \Omega_{n,m}. \quad (\text{III.3})$$

Note that in order to measure the expectation value we have to perform many experiments. But for each experiment  $a_n$  and  $a_m$  are randomly chosen according to some statistical probability distribution. So in practice we have to do both quantum and statistical average and it is very hard to distinguish between them (though sometimes it is possible - HBT effect - examples later!). Then

$$\langle \bar{\Omega} \rangle \equiv \langle \Omega \rangle = \sum \rho_{m,n} \Omega_{n,m} = \text{Tr}(\rho\Omega), \quad (\text{III.4})$$

where  $\rho_{nm} = \langle c_n^* c_m \rangle$ . Note that for a pure state we have  $(\rho\rho)_{nm} = \sum_{n,p,m} c_n^* c_p c_p^* c_m = c_n^* c_m = \rho_{nm}$ . For non-pure states this does not hold.

Density matrix in quantum statistical physics plays the same role as the distribution function  $f(\mathbf{x}, \mathbf{p})$  in classical statistical physics. Instead of integral over phase space we are dealing with sum over Hilbert space. Diagonal elements of the density matrix play the role of probability of occupying certain microscopic state:  $\rho_{nn} = \langle c_n^* c_n \rangle$ .

**Unless it is explicitly mentioned that we are dealing *only* with classical or quantum systems averaging over classical statistical distribution immediately translates to averaging over density matrix in quantum statistical physics and vice versa.**

*Wigner function: connection between classical and quantum fluctuations.* An interesting connection between quantum density matrix and statistical probability distribution comes using the Wigner function. We will not go into the details of a very interesting subject of representing quantum mechanics through phase space. But let us mention a few things using a simple example of a harmonic oscillator described by the Hamiltonian

$$\hat{\mathcal{H}}_0 = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 \quad (\text{III.5})$$

The ground state wave-function of this oscillator is

$$\psi_0(x) = \frac{1}{(2\pi)^{1/4}\sqrt{x_0}} e^{-x^2/4a_0^2}, \quad (\text{III.6})$$

where  $a_0 = \sqrt{\hbar/2m\omega}$  is the oscillator length. The Wigner transform corresponding to this wave function is defined in the following way

$$W(x, p) = \int d\xi \psi^*(x + \xi/2)\psi(x - \xi/2)e^{ip\xi/\hbar} = 2 \exp\left[-\frac{x^2}{2a_0^2} - \frac{p^2}{2q_0^2}\right], \quad (\text{III.7})$$

where  $q_0 = \hbar/2a_0 = \sqrt{m\omega/2\hbar}$ . In this case  $W(x, p)$  is positive definite (in general it is not) and can be straightforwardly interpreted as the probability distribution for the initial coordinate and momentum. If we are interested in expectation values of certain observables, e.g.  $\langle x^2 \rangle$ , then it is easy to see that they are given by phase space average of the corresponding classical operator (Weyl symbol) over the phase space variables:

$$\langle x^2 \rangle = \int \frac{dx dp}{2\pi\hbar} x^2 W(x, p). \quad (\text{III.8})$$

In general Weyl symbol of the operator  $\hat{\Omega}$  is defined as

$$\Omega_W(x, p, t) = \int d\xi \left\langle x + \frac{\xi}{2} \left| \hat{\Omega}(\hat{x}, \hat{p}, t) \right| x - \frac{\xi}{2} \right\rangle \exp\left[-\frac{ip\xi}{\hbar}\right] \quad (\text{III.9})$$

it corresponds to quantum-classical correspondence of the symmetrized operator e.g.

$$\hat{x}\hat{p} = \frac{\hat{x}\hat{p} + \hat{p}\hat{x}}{2} + \frac{1}{2}[\hat{x}, \hat{p}] \rightarrow xp + i\frac{\hbar}{2} \quad (\text{III.10})$$

The equivalence with equilibrium statistical physics becomes more transparent if we consider a system of harmonic oscillators at finite temperatures. Then the Wigner function is defined as the Weyl symbol of the density matrix:

$$W(x, p) = \int d\xi \left\langle x - \frac{\xi}{2} \left| \rho \right| x + \frac{\xi}{2} \right\rangle e^{ip\xi/\hbar} \quad (\text{III.11})$$

For a system of harmonic oscillators at a finite temperature (Gibbs distribution) one can show that the Wigner function becomes:

$$W(x, p, T) = \frac{2}{\coth(\hbar\omega/2T)} \exp \left[ -\frac{x^2}{2a_0^2 \coth(\hbar\omega/2T)} - \frac{p^2}{2q_0^2 \coth(\hbar\omega/2T)} \right], \quad (\text{III.12})$$

At high temperatures  $T \gg \hbar\omega$  the Wigner function becomes the Boltzmann's function

$$W(x, p, T) \rightarrow \frac{\hbar\omega}{T} \exp \left[ -\frac{m\omega^2 x^2 + p^2/m}{2T} \right]. \quad (\text{III.13})$$

So there is a smooth crossover between quantum and classical distribution functions and no real point where statistical fluctuations become quantum. Of course, there are many issues and subtleties. The Wigner function is not-positive definite, which makes it only quasi-probability distribution. Time evolution is more complicated than time evolution of the statistical probability distribution (although again in the classical limit time dependence of the Wigner function is governed by classical Liouville equation). However, it is very hard to find a definite boundary separating classical and quantum effects whether we talk about equilibrium statistics or dynamics.

*Ergodic hypothesis:* in macroscopic systems average over equilibrium ensemble describing equilibrium is equivalent to time average, i.e.

$$\langle \Omega \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^t \Omega(t) dt \quad (\text{III.14})$$

The RHS of this equation is statistical average over many realizations of the experiment. The LHS is the time average of a single realization. Ergodic hypothesis is the conjecture. There is no microscopic proof (as far as I know). There is a subtlety in quantum case, because measurement itself has a back-action: it introduces additional statistical uncertainty into the system by randomly projecting the system in the one of the eigenstates of the observable. Usually measurements destroy pure states and make them mixed states.

*Fermi Pasta Ulam Problem.* Ergodic hypothesis is a very natural concept. We are implicitly dealing with it all the time. E.g., if we measure equilibrium fluctuations of voltage we do not care if we average over time or we start over voltmeter again and again. However, this hypothesis is very hard to prove. The first numerical attempt to do this was by Fermi, Pasta, and Ulam at Los Alamos National lab using one of the first computers. They considered a 1D system of coupled oscillators with a weak nonlinearity (see Fig. 2). They initially excited the lowest mode with  $k = 2\pi/L$  and expected that after some time because of nonlinearity the energy will be equipartitioned between different modes (as we will learn later in the course). However, what they found was quite opposite: after a sufficiently long time the energy almost completely returned to the first mode. This is like in

# STUDIES OF NON LINEAR PROBLEMS

E. FERMI, J. PASTA, and S. ULAM  
Document LA-1940 (May 1955).

A one-dimensional dynamical system of 64 particles with forces between neighbors containing nonlinear terms has been studied on the Los Alamos computer MANIAC I. The nonlinear terms considered are quadratic, cubic, and broken linear types. The results are analyzed into Fourier components and plotted as a function of time.

The results show very little, if any, tendency toward equipartition of energy among the degrees of freedom.

$$\ddot{x}_i = (x_{i+1} + x_{i-1} - 2x_i) + \alpha [(x_{i+1} - x_i)^2 - (x_i - x_{i-1})^2]$$

$$(i = 1, 2, \dots, 64),$$

FIG. 2 FPU report: the abstract and the main conclusion

movies you destroy some object and then magically it reorganizes back to the same shape. Typically you need some divine form like Fairy to do this. However, here it happened without such intrusion. People later understood why this happened: 1D nonlinear systems can be almost exactly described by nonlinear excitations (solitons), which in many respects behave as noninteracting objects. Thus they do not cause thermalization. This example was partially understood (although till now there is no unique consensus on what kind of nonlinearities are acceptable for non-ergodicity). Even now we know very little about which systems are ergodic and which are not. This is a subject of an active research.

*Statistical independence.* Imagine that we split a large system into two subsystems. Each subsystem is not independent. However, it knows about another subsystem only because of surface effects. Those effects should be small if the subsystems are small too. Therefore we expect that the

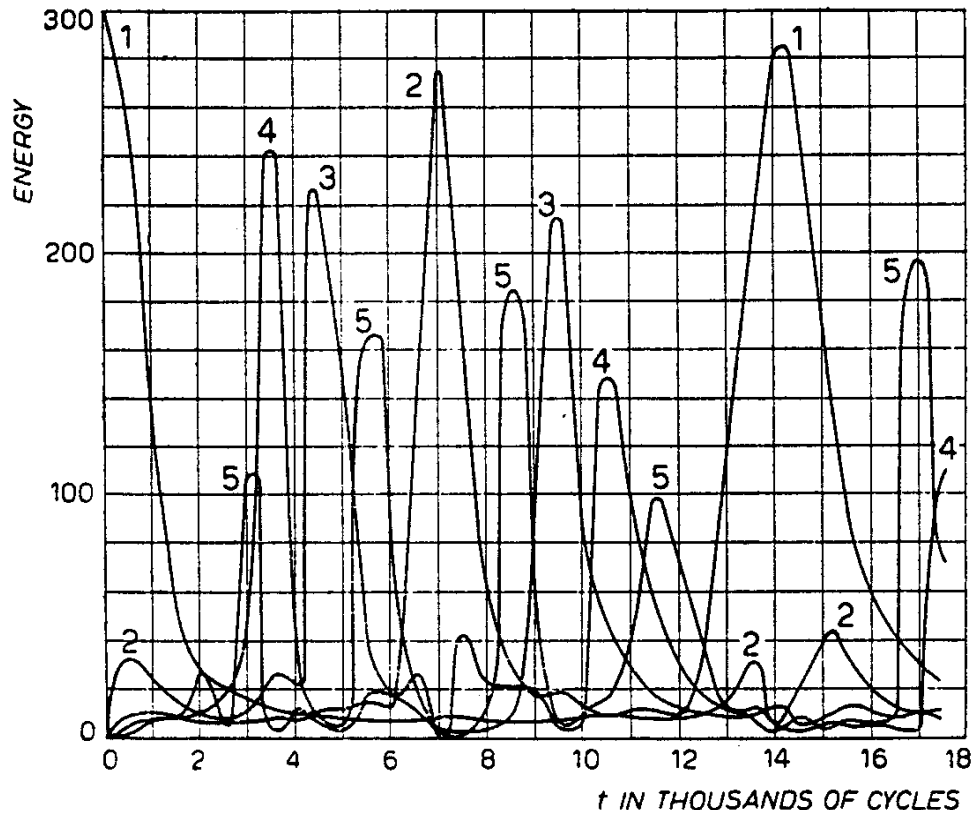


FIG. 3 FPU report: time dependence of the energy of first several modes.

two subsystems are approximately independent from each other. This means that the distribution function should approximately factorize:  $f(\mathbf{x}, \mathbf{p}) \approx f_1(\mathbf{x}_1, \mathbf{p}_1)f_2(\mathbf{x}_2, \mathbf{p}_2)$  (the same should be true about density matrix - the latter should be roughly block diagonal). This in turn implies that logarithm of the distribution function is roughly additive:  $\ln f(\mathbf{x}, \mathbf{p}) \approx \ln f_1(\mathbf{x}_1, \mathbf{p}_1) + \ln f_2(\mathbf{x}_2, \mathbf{p}_2)$ . So the log of the distribution function should know only about additive quantities. As we know from the previous chapter statistical independence means that fluctuations of all additive thermodynamic quantities (like energy) should become small in large systems.

*Liouville's theorem.* In a closed system the distribution function is conserved along the trajectories. Let us consider an element of the phase space  $d\mathbf{x}d\mathbf{p}$ . Let us now consider an infinitesimal time step  $dt$ . Then this volume becomes  $d\mathbf{x}'d\mathbf{p}'$ . Note that  $x'_a = x_a + \dot{x}_a dt$  and similarly  $p'_a = p_a + \dot{p}_a dt$ .

This means that  $dx'_a = dx_a + \frac{\partial \dot{x}_a}{\partial x_a} dx_a dt$ . From this we find that

$$dx'_a dp'_a = dx_a dp_a \left[ 1 + \left( \frac{\partial \dot{x}_a}{\partial x_a} + \frac{\partial \dot{p}_a}{\partial p_a} \right) dt \right] = dx_a dp_a \quad (\text{III.15})$$

by Hamilton equations of motion:  $\dot{x}_a = \partial H / \partial p_a$  and  $\dot{p}_a = -\partial H / \partial x_a$ . The Liouville's theorem implies that all the pure states are transformed from the point  $(\mathbf{x}, \mathbf{p})$  to the point  $(\mathbf{x}', \mathbf{p}')$  and the phase volume does not change. In practice this phase space volume of course impossible to measure, but one can draw several formal consequences from this theorem. In particular, because  $f d\Gamma = f' d\Gamma'$  (conservation of probability) we find that  $df/dt = 0$ . Note that this is a full derivative:  $df/dt = \partial f / \partial t + \sum_a \frac{\partial f}{\partial x_a} \dot{x}_a + \frac{\partial f}{\partial p_a} \dot{p}_a$ .

Consequences.

- Consider a statistical average of some observable  $\Omega$ , which explicitly does not depend on time. Then

$$\begin{aligned} \frac{d\langle \Omega \rangle}{dt} &= \int d\Gamma \frac{\partial f(\mathbf{x}, \mathbf{p}, t)}{\partial t} \Omega(\mathbf{x}, \mathbf{p}) = - \sum_a \int d\Gamma \Omega(\mathbf{x}, \mathbf{p}) \left( \frac{\partial f}{\partial x_a} \dot{x}_a + \frac{\partial f}{\partial p_a} \dot{p}_a \right) \\ &= \sum_a \int d\Gamma f \left( \frac{\partial \Omega}{\partial x_a} \frac{\partial H}{\partial p_a} - \frac{\partial \Omega}{\partial p_a} \frac{\partial H}{\partial x_a} \right) = \langle \{ \Omega, H \} \rangle. \end{aligned} \quad (\text{III.16})$$

If the Poisson brackets of the observable  $\Omega$  with the Hamiltonian vanish (recall this is true for all conserved quantities) then the corresponding average is a constant of motion. This is a statement, which is intuitively clear in any case.

- The equilibrium distribution function should satisfy  $\{f_{\text{eq}}, H\} = 0$ . Clearly any function which depends only on  $H$  satisfies this requirement:  $\{f(H), H\} = 0$ . If we use this choice then we imply that within the energy shell all states are equally probable. Note if there are additional conserved quantities than the stationary distribution function can depend on all these quantities and still be stationary. This implies equipartition between all possible phase space points satisfying the constraints.

Quantum Liouville's theorem. Recall that  $\rho_{nm}(t) = \langle c_n^*(t) c_m(t) \rangle$ . Let us compute time derivative of  $\rho$ :

$$\dot{\rho}_{nm}(t) = \langle \dot{c}_n^* c_m + c_n^* \dot{c}_m \rangle = i(E_n - E_m) \rho_{nm}(t) = iH_{np} \rho_{pm} - i\rho_{np} H_{pm} = i[H, \rho]. \quad (\text{III.17})$$

So

$$i \frac{d\rho}{dt} = [\rho, H]. \quad (\text{III.18})$$

Let us check the observables corresponding to stationary operators commuting with the Hamiltonian are conserved in time.

$$d\langle\Omega\rangle/dt = \text{Tr}[\dot{\rho}\Omega] = -i\text{Tr}[\rho H\Omega - H\rho\Omega] = -i\langle[H, \Omega]\rangle = 0. \quad (\text{III.19})$$

The consequences of the quantum Liouville's theorem are basically identical to those of the classical Liouville's theorem: (i) Stationary density matrix should commute with the Hamiltonian. In turn this implies that it should be diagonalizable simultaneously with the Hamiltonian. (ii) The density matrix, which is some functional of the Hamiltonian and other conserved quantities automatically satisfies (i) and thus is conserved in time.

### A. Problems for Sec. III

1. Consider a system of two spins. Find its density matrix in two situations: (i) both spins are in the state  $(|\uparrow\rangle + |\downarrow\rangle)/\sqrt{2}$  and (ii) each spin is in either  $|\uparrow\rangle$  or  $|\downarrow\rangle$  state with equal probability. Find  $\rho^2$  in both situations. What do you get for pure state (i), for mixed state (ii)?
2. Consider the same problem as above but now two spins are in a pure states  $|\psi_{1,2}\rangle = (|\uparrow\rangle_{1,2} + \exp[i\phi_{1,2}]|\downarrow\rangle_{1,2})/\sqrt{2}$ , where indices 1, 2 refer to two different spins and  $\phi_{1,2}$  are some phases. Find density matrix for the two spins assuming (i)  $\phi_1 = \phi_2 = \phi$ , where  $\phi$  is random and (ii)  $\phi_1$  and  $\phi_2$  are two independent random phases. Compare your answers with the problem above.
3. Prove Eq. (III.7).
4. Prove Eq. (III.12). For this note that the Gibbs distribution requires that the probability to be in  $nb$ -th excited state of the oscillator is proportional to  $p_n \propto \exp[-\hbar\omega n/T]$ . The prefactor can be obtained from normalization. Now the density matrix can be written as  $\sum_n p_n |n\rangle\langle n|$ . It should be straightforward to take the Wigner transform of the density matrix now using properties of Hermite polynomials and check the result.

## IV. ENTROPY, TEMPERATURE, LAWS OF THERMODYNAMICS.

The main postulate of the statistical physics is that the system tends to equally populate all available states within the constraints of total available energy, volume and other macroscopic constraints.

## A. Statistical Entropy

One of the key quantities in statistical physics (and thermodynamics) is the entropy which is the measure of available phase space  $\Gamma$ . Formally  $S = -\ln \Gamma$ . (We will later give a more general definition in the case when the probabilities to occupy different states are not equal).

Example: consider a system of spin  $1/2$  systems with total magnetization  $M_z = \gamma \sum_i s_i^z$ . In isolated systems with no external magnetic field in the  $xy$ -plane then  $M_z$  is a conserved quantity. Next let us assume that the system is in the external magnetic field so the energy of the system is

$$U = -hM_z = -h\gamma \sum_i s_i^z. \quad (\text{IV.1})$$

Let us first find how the entropy is connected with magnetization (and thus) energy. We need to find the phase space available for a given magnetization. We know the answer: it comes from the binomial distribution:

$$\Gamma = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{(N/2 + L/2)!(N/2 - L/2)!}, \quad (\text{IV.2})$$

where  $L = N_\uparrow - N_\downarrow = M_z/\gamma$ . This expression is quite cumbersome. Let us study its logarithm, i.e. entropy. For simplicity we assume that  $L$  is small

$$S(L) = \ln \Gamma(L) \approx N \ln N - \frac{N+L}{2} \ln \left( \frac{N+L}{2} \right) - \frac{N-L}{2} \ln \left( \frac{N-L}{2} \right) + \mathcal{O}(\ln N) \quad (\text{IV.3})$$

Expanding the expression into the Taylor series in  $L$  we find

$$S(L) \approx N \ln 2 - \frac{N+L}{2} \frac{L}{N} + \frac{N-L}{2} \frac{L}{N} = N \ln 2 - \frac{L^2}{2N} = N \ln 2 - \frac{1}{N} \left( \frac{U}{\gamma h} \right)^2. \quad (\text{IV.4})$$

This function is of course strongly peaked around  $U = 0$ . So if we have no constraints at all we expect that the probability is highly peaked around  $L = 0$ , i.e. zero magnetization. This state corresponds to maximum entropy in the system.

Now let us imagine that  $U$  is fixed (i.e. we fix the total energy). Because  $U = -hM_z$  it means that the average magnetization is fixed. Now imagine that we split the system into two subsystems and ask in how many ways we can distribute magnetization (energy) in a particular way  $U = U_1 + U_2$  or  $M^z = M_1^z + M_2^z$ . Because systems are noninteracting clearly we have

$$\tilde{\Omega}(U_1, U_2) = \Omega_1(U_1)\Omega_2(U_2) \quad (\text{IV.5})$$

and

$$\Omega(U) = \sum_{U_1} \tilde{\Omega}(U_1, U - U_1). \quad (\text{IV.6})$$

Assume that the first block contains  $N_1$  spins and the second block contains  $N_2$  spins. Then

$$S(U_1, U - U_1) \approx N \ln 2 - \frac{1}{N_1} \left( \frac{U_1}{\gamma h} \right)^2 - \frac{1}{N_2} \left( \frac{U - U_1}{\gamma h} \right)^2. \quad (\text{IV.7})$$

Since  $S$  is extensive (proportional to  $N$ ) and total number of configurations (=probability) is exponential in  $S$  the distribution is highly peaked near the maximum of the entropy (maximum number of available configurations). To find the maximum of the entropy we need to differentiate  $S(U_1, U - U_1)$  with respect to  $U_1$ :

$$\frac{\bar{U}_1}{N_1} = \frac{\bar{U}_2}{N_2} \quad (\text{IV.8})$$

thus  $\bar{U}_1 = U N_1 / N$  or equivalently  $\bar{M}_1^z = M N_1 / N$ . Thus we find that with the highest probability the magnetization is uniformly distributed in the system. Note that the entropy is additive. Within the saddle point approximation

$$S(U) = N \ln 2 - \frac{1}{N} \left( \frac{U}{\gamma h} \right)^2 = \tilde{S}(\bar{U}_1, U - \bar{U}_1). \quad (\text{IV.9})$$

The result of uniform magnetization is of course what we can anticipate intuitively. However, let us stress here that it comes as a consequence of the main postulate which tells us that all microscopic configurations are equally probable. The entropy counts (logarithm) of the number of microscopic configurations corresponding to a given macro-state. So the entropy gives (logarithm of) the probability to occupy a given macroscopic configuration. Using the fact that there are many degrees of freedom we anticipate that the probability is highly peaked around the maximum (central limit theorem) so the maximum of the entropy gives most likely macroscopic configuration.

## B. Temperature

Now assume that we have two arbitrary systems in a contact with each other. Then quite generally we can write

$$\Omega(E) = \sum_{E_1} \Omega_1(E_1) \Omega_2(E - E_1) \quad (\text{IV.10})$$

In equilibrium we require that sum is dominated by the maximum so

$$\Omega(E) \approx \Omega_1(\bar{E}_1) \Omega_2(E - \bar{E}_1) \quad (\text{IV.11})$$

where

$$\frac{\partial \Omega_1}{\partial \bar{E}_1} \Omega_2(\bar{E}_2) = \Omega_1(\bar{E}_1) \frac{\partial \Omega_2(\bar{E}_2)}{\partial \bar{E}_2} \Leftrightarrow \frac{\partial S_1}{\partial \bar{E}_1} = \frac{\partial S_2}{\partial \bar{E}_2}. \quad (\text{IV.12})$$

From now on we will drop over-line over average energy since in thermodynamics we are interested mostly in average quantity, so unless otherwise specified we will imply  $E \equiv \bar{E}$ . The derivative in the equation above we call inverse temperature:  $\partial S(E)/\partial E = 1/T$ . Thus the equilibrium between the two subsystems immediately results in the requirement of constant temperature:  $T_1 = T_2$ .

Let us return to our example. From Eq. (IV.3) we find

$$\frac{1}{T} = \frac{1}{2\gamma h} \ln \left[ \frac{N\gamma h - U}{N\gamma h + U} \right]. \quad (\text{IV.13})$$

Note that the minimum of the energy occurs at  $U = -N\gamma h$  when all the spins are polarized along the magnetic field. In this case we clearly have  $T = 0$  (as well as  $S = 0$ ) - there is only one configuration corresponding to the minimal energy (well known statement from quantum mechanics). Correspondingly this configuration corresponds to zero temperature. Now assume that  $U = -N\gamma h + \delta U$ . Then we have

$$T \approx 2\gamma h \frac{1}{\ln \left[ \frac{2N\gamma h}{\delta U} \right]} \quad (\text{IV.14})$$

or in a more familiar form

$$\delta U \approx N2\gamma h \exp \left[ -\frac{2\gamma h}{T} \right]. \quad (\text{IV.15})$$

This is of course the familiar Boltzmann's distribution. We can interpret Eq. (IV.15) in the following way. The energy required to excite a particular spin is  $2\gamma h$ . The probability of this excitation is  $\exp[-2\gamma h/T]$  (later we will return to a more general justification of this postulate). The average energy (above the ground state) is then the probability of exciting a particular state times the energy of each excitation times the total number of magnets.

One can invert Eq. (IV.3) without the assumption about small temperature. Then

$$\delta U \equiv N\gamma h + U = 2N\gamma h \frac{1}{\exp \left[ \frac{2\gamma h}{T} \right] + 1}. \quad (\text{IV.16})$$

As the energy further increases both entropy and temperature increase until we reach maximally probable unconstrained configuration where  $S = N \ln 2$  and  $T = \infty$ . After that the entropy starts to decrease and the temperature becomes negative. This is actually the artifact of our model with bounded spectrum. Usually the energy spectrum is unbounded from above and thus infinite temperature state corresponds to the infinite energy, so it can not be reached. However, this example shows an important distinction between temperature, showing how entropy changes with energy, and the energy itself.

### C. First law of thermodynamics.

Let us assume that the state of the system depends on some external parameter  $x$ , which can be volume, magnetic field etc. If we do reversible (adiabatic) transformation on the system the energy change is characterized by the work  $\delta W = -J\delta x$ . For the reversible process the entropy can not change. One can justify this statement in two ways. The first is relying on quantum mechanics (or more precisely to the fact the we are dealing with discrete states). Adiabatic perturbations imply that probabilities of the system to occupy particular microstates does not change. Therefore the number of occupied microstates does not change and thus the entropy. Let us illustrate this using the classical spin chain analyzed above. The energy of this system is given by  $U = -\gamma h \sum_i s_i^z$ . If we change magnetic field without flipping spins then clearly the number of configurations and the entropy does not change. A more complicated example will involve quantum spin chain with the Hamiltonian

$$H = -\gamma h_z \sum_i \sigma_z^i - \gamma h_x \sum_i \sigma_x^i, \quad (\text{IV.17})$$

where  $\sigma^z$  and  $\sigma^x$  are the Pauli matrices:

$$\sigma_z^i = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \sigma_x^i = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (\text{IV.18})$$

Now suppose that we change  $h_z$  in time from a large positive to a large negative value. If we do it slowly then according to quantum mechanics spins adiabatically follow the eigenstates: i.e. spins initially pointing up will be pointing down (spins in the ground state will remain in the ground state) and the spins initially pointing down will point up (excited spins will remain excited). Thus the entropy of the system will not change. On the other hand if  $h_z$  changes in time not infinitesimally slowly then the dynamics will cause transitions between levels and the entropy will not be constant (one can prove that it actually will increase).

The second argument for why the entropy in the reversible processes stays constant is based on the idea that the equilibrium corresponds to the maximum probable configuration, i.e. to the maximum entropy. If the entropy of the system during some process increases it means that it found more probable configuration during the time evolution, in turn this implies that the process can not be reversible. Postulating that the entropy for an adiabatic process does not change we can write

$$\Delta S = 0 = S(E - J\delta x, x + \delta x) \approx -\frac{\partial S}{\partial E} \Big|_x J\delta x + \frac{\partial S}{\partial x} \Big|_E \delta x. \quad (\text{IV.19})$$

Therefore

$$\left. \frac{\partial S}{\partial x} \right|_E = \frac{J}{T}. \quad (\text{IV.20})$$

Now for arbitrary process, where entropy can increase we have

$$dS = \left. \frac{\partial S}{\partial E} \right|_x dE + \left. \frac{\partial S}{\partial x} \right|_E dx = \frac{dE}{T} + \frac{Jdx}{T}. \quad (\text{IV.21})$$

Therefore

$$dE = TdS - Jdx. \quad (\text{IV.22})$$

We thus can identify  $TdS$  with the heat (irreversible part of the energy change). Note that  $J$  is the generalized force. Returning to the spin problem we can identify energy change coming from two sources (i) due to changing external parameter (magnetic field) without changing transition probabilities - second term (note that  $J$  is magnetization in this case) and (ii) changing probabilities of occupying different microstates at a fixed external field (first term). The first contribution is clearly reversible while the second is clearly not.

*Quasi-static vs. non-equilibrium processes.* The relation Eq. (IV.22), which is also known as fundamental thermodynamic relation, reflects the statement of the entropy being a unique function of energy and external parameters. So it is always valid as long as the system is in equilibrium. The dynamical processes where the system is always in the equilibrium state are called quasi-static. In thermodynamics one usually differentiates between two ways of changing energy in the system (i) thermal contact with another system where external parameters stay fixed and (ii) macroscopic work associated with the change of external parameters. The first way of changing energy is usually called heat. The first law of thermodynamics is thus a trivial statement of energy conservation

$$dE = dQ + dW, \quad (\text{IV.23})$$

where  $dW$  is work done on the system and  $dQ$  is heat (energy exchange due to contact with another body). If no work is done then the heat does not correspond to change of any parameters and thus is translated to change of entropy (heat always leads to irreversibility). So we conclude that if no work is done then  $dQ = TdS$ . Work on the other hand can result in both reversible and irreversible changes in the system. Thus if external parameters change adiabatically then  $dW = -Jdx$  and then Eq. (IV.22) is equivalent to the first law. For non-equilibrium processes (e.g. work is done non-adiabatically) the entropy will increase according to the second law of thermodynamics (see below). So part of the work will go into reversible change of the external parameter and part will

go to heating the system (like in a microwave). So we conclude that in general, if the system is thermally insulated, we have

$$dW \geq -Jdx. \quad (\text{IV.24})$$

Combining these two observations we find that

$$TdS = dE - Jdx = dQ + dW - Jdx \geq dQ \quad (\text{IV.25})$$

So for non-equilibrium processes we must have

$$dS \geq \frac{dQ}{T}. \quad (\text{IV.26})$$

If in each moment of time temperature is well defined we can integrate the equation above and obtain that

$$\Delta S \geq \oint \frac{dQ}{T}. \quad (\text{IV.27})$$

#### D. Second law of thermodynamics

Now assume that we start from two systems. Each one is in equilibrium, but they are not necessarily in equilibrium with each other. Then after any process the entropy can either increase or stay the same. The proof of this statement follows from the fact that at equilibrium the system occupies the largest phase space volume available within the macroscopic constraints, i.e.

$$\Omega_1(E_1^*)\Omega_2(E_2^*) \geq \Omega_1(E_1)\Omega_2(E_2), \quad (\text{IV.28})$$

where  $E_1$  and  $E_2$  are the energies of the systems 1 and 2 before they are brought to the contact, while  $E_1^*$  and  $E_2^*$  are the equilibrium values of energy corresponding to the same total energy  $E = E_1 + E_2 = E_1^* + E_2^*$ .

Consequence: Second law in the Clausius form. Assume that we put the systems in contact for a short time so that the entropy change is small then

$$\delta S = \left( \frac{\partial S_1}{\partial E_1} \Big|_{x_1} \right) \delta E_1 - \frac{\partial S_2}{\partial E_2} \Big|_{x_2} \delta E_1 = \delta E_1 \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \geq 0. \quad (\text{IV.29})$$

So we see that the heat flows from hotter to colder body. Similarly the second law in the Kelvin's form immediately follows from the fact that the entropy does not change in the adiabatic (reversible) cyclic process thus it can only increase if the process is irreversible.

Stability condition:

$$\frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2} \leq 0 \quad (\text{IV.30})$$

which implies that  $\partial T / \partial E_x \geq 0$ . This means that the heat capacity must be positive.

Second law of thermodynamics has many implications which are familiar to us from daily experience. For example, such seemingly different phenomena as friction (vs. acceleration) spontaneous decay of excited atoms (vs. their spontaneous excitation) etc. all follow from the second law without need to refer to any microscopic details. All these process lead to entropy increase (or more precisely to the increase of sum of the entropies of the system + environment) or simply correspond to more probable configuration. E.g. in the case of friction the kinetic energy of one macroscopic degree of freedom is distributed (as this degree of freedom slows down) among many degrees of freedom of the environment like phonons. Obviously there are many ways we can split this energy among phonons (implying higher entropy of the environment) so the system wants to go to this state. Likewise if an atom decays to the ground state it emits photons (which can later rethermalize among themselves). Obviously there are lots of ways we can split this energy among different photons while there is only single way we can store it in atom. So the entropy will increase by spontaneous radiation.

### E. Third law of thermodynamics

Entropy is zero at zero temperature. We saw how the third law works at a particular example. The third law of thermodynamics is purely quantum mechanical. It is related to the fact that the lowest energy state is always non-degenerate.

### F. Problems for Sec. IV.A

1. Taking the interpretation of the probability of a spin flip from Eq. (IV.15) (in the limit  $T \ll \gamma h$ ) compute the total energy distribution in the system  $P(E)$ . What is the name of this distribution function? What are the fluctuation of the energy and magnetization? Discuss what happens as  $N$  increases?
2. Show that one can formally derive Eq. (IV.16) by assuming that the probabilities of spin pointing down and up satisfy Boltzmann's distribution:  $p_{\downarrow}/p_{\uparrow} = \exp[-2\gamma h/T]$  and of course  $p_{\downarrow} + p_{\uparrow} = 1$ . Repeat calculations for the previous problem with this distribution. Does it become narrower or wider if at given  $N$  we increase temperature? Explain.

## V. PARTITION FUNCTION, CANONICAL ENSEMBLE, VON-NEUMANN ENTROPY

In the previous lecture we derived the properties of a spin system assuming it is *isolated*, and therefore *conserved energy*. We considered the situations with fixed total energy, i.e. we worked in the *micro-canonical ensemble*. Our approach was to start from the energy and derive the entropy and temperature as its derivatives. However, this approach is not always convenient. The total energy is usually hard to measure because we are typically dealing with open systems with unclear boundaries. Temperature is definitely a much better defined quantity which is constant throughout the system in equilibrium and thus can be locally measured. Once we start from temperature we can compute the magnetization and compare it to what we measure. In this way it is actually also much easier to do calculations.

If we are dealing with energies it is convenient to work with micro-canonical ensembles where the energy is well defined and conserved. Conversely if we use temperature as an independent variable it is convenient to assume that there is energy exchange with the environment, i.e. assume that our system is a part of much bigger system. Then the energy of the subsystem is not conserved and can fluctuate. The corresponding ensemble is called *canonical*.

Return to our spin system. Consider a subsystem of the system with  $N_1$  spins as a new system and correspondingly treat  $N - N_2$  spins as the environment. Now we assume that  $N_1 \ll N$ . Let us start from the extreme situation where  $N_1 = 1$ . Let us compute the phase space volumes corresponding to each of these situations:

$$\Omega_{\downarrow} = \Omega_1(E_1 = \gamma h) \Omega_2(E - E_1) \approx \exp \left[ S_2 + \frac{\partial S_2}{\partial E_2}(-\gamma h) \right] = C \exp[-\gamma h/T] \quad (\text{V.1})$$

similarly

$$\Omega_{\uparrow} = \Omega_1(E_1 = -\gamma h) = C \exp[\gamma h/T] \quad (\text{V.2})$$

If we are interested only in the state of a particular spin we worry only about these numbers, which give the probabilities to occupy “down” or “up” states. So we can write

$$p_{\uparrow} = \frac{1}{Z} \exp[\gamma h/T], \quad p_{\downarrow} = \frac{1}{Z} \exp[-\gamma h/T], \quad (\text{V.3})$$

where

$$Z = \exp[\gamma h/T] + \exp[-\gamma h/T] = \sum_n \exp[-\mathcal{E}_n/T] \quad (\text{V.4})$$

is called the partition function. It is customary to introduce the notation  $\beta = 1/T$ .

With this partition function we can calculate various quantities. For example average energy will be

$$\langle \mathcal{E} \rangle = \sum_n p_n \mathcal{E}_n = \frac{1}{Z} \sum_n \mathcal{E}_n \exp[-\beta \mathcal{E}_n] = -\frac{\partial \ln Z}{\partial \beta}. \quad (\text{V.5})$$

Let us play with our specific example a bit more

$$Z = 2 \cosh[\beta \gamma h]. \quad (\text{V.6})$$

Then the mean energy of a single spin is

$$\langle \mathcal{E} \rangle = -\gamma h \frac{\sinh(\beta \gamma h)}{\cosh(\beta \gamma h)} = -\gamma h + \frac{2\gamma h}{\exp[2\beta \gamma h] + 1}. \quad (\text{V.7})$$

Exactly what we had before. At small magnetic fields (high temperatures) we get  $\langle \mathcal{E} \rangle \approx -\frac{\gamma^2 h^2}{T}$ .

The average magnetization is

$$\langle S_z \rangle = -\frac{\langle \mathcal{E} \rangle}{\gamma h} = \tanh \beta \gamma h \quad (\text{V.8})$$

The other important quantity is the magnetic susceptibility

$$\chi = \frac{\partial M}{\partial h} = \beta \gamma^2 \frac{1}{\cosh^2(\beta \gamma h)}. \quad (\text{V.9})$$

At large temperatures (small magnetic fields) we have  $\chi \approx \gamma^2/T$ , which is the famous Curie law.

We can also define and find specific heat:

$$C = \frac{\partial E}{\partial T} = \frac{(\beta \gamma h)^2}{\cosh^2(\beta \gamma h)} \quad (\text{V.10})$$

Note that at small temperatures  $\beta \gg 1$  the heat capacity is exponentially small: this is a general property of gapped systems. In the opposite limit  $\beta \ll 1$  ( $T \gg 1$ ) the specific heat is small again. This is related to the maximum in the density of states: we can not add more energy to the system by increasing the temperature.

This single spin partition function is good for describing properties of a single spin. But what if we are interested in two-spin observables or even observables which include many spins. Then we have to consider larger subsystems. But the reasoning stays the same. The probability of each microscopic configuration is given by the Boltzmann factor  $C \exp[-\beta \mathcal{E}]$ . Indeed the corresponding contribution to the partition function is  $\Omega_1(\mathcal{E}) \exp[-\beta \mathcal{E}]$ . But  $\Omega_1(\mathcal{E})$  is precisely the number of microscopic configurations of the subsystem 1 having the energy  $\mathcal{E}$ . So quite generally we can write

$$p(\mathcal{E}) = \frac{1}{Z} \exp[-\beta \mathcal{E}] \quad (\text{V.11})$$

Note that there is nothing special about energy except this is a conserved quantity (for the total system). If there are other additive conserved quantities we should have similar ‘‘Boltzmann’s’’ weights to them (everything follows from the expansion of entropy around the maximum). For example if the total number of particles is allowed to fluctuate between the subsystem and environment then

$$p(\mathcal{E}, \mathcal{N}) = \frac{1}{Z} \exp[-\beta(\mathcal{E} - \mu\mathcal{N})], \quad (\text{V.12})$$

where

$$Z = \sum_{\mathcal{N}} \sum_{\mathcal{E}(\mathcal{N})} \exp[-\beta(\mathcal{E} - \mu\mathcal{N})], \quad (\text{V.13})$$

$\mu\beta = -\partial S/\partial\mathcal{N}|_{\mathcal{E}}$  or  $\mu = -T\partial S/\partial\mathcal{N}|_{\mathcal{E}}$ . So one can write

$$d\mathcal{E} = TdS + \mu d\mathcal{N}. \quad (\text{V.14})$$

One can write similar expressions if there are other additive conserved quantities (integrals of motion). The corresponding distributions are called generalized Gibbs ensembles. The ensemble where only energy and number of particles are allowed to fluctuate (Eq. (V.12)) is called grand canonical.

## A. Entropy

Starting from temperature we managed to derive energy and reproduce our earlier results. Next we need to find entropy. First let us make a formal derivation. We know that

$$TdS = dE \Leftrightarrow dS = \beta dE = d(\beta E) - E d\beta. \quad (\text{V.15})$$

Using that  $E = -d \ln Z / d\beta$  we find that  $S = \beta E + \ln Z$ . The arbitrary integration constant is fixed by the third law of thermodynamics  $S = 0$  at  $T = 0$ . Let us introduce the notation  $F = -T \ln Z$ , free energy. Then we find that

$$S = \frac{E - F}{T} \Leftrightarrow F = E - TS. \quad (\text{V.16})$$

From thermodynamics recall that  $F$  is defined as the free energy. Now we have its expression through the partition function (note that both  $F$  and  $E$  are expressed through  $Z$ , which in turn is the function of temperature. If we change temperature (keeping other external parameters fixed) then

$$dF = dE - TdS - SdT = -SdT \quad (\text{V.17})$$

so we also find that

$$S = -\frac{\partial F}{\partial T} = \frac{\partial(T \ln Z)}{\partial T}, \quad (\text{V.18})$$

which of course agrees with our previous formula.

How about the probabilistic interpretation of the entropy? Let us again return to our example and then generalize. Recall that for noninteracting spins

$$Z = \prod_j \sum_{n_j} \exp[-\beta E_j^{(n)}] = \left( \sum_n \exp[-\beta \mathcal{E}_n] \right)^N \quad (\text{V.19})$$

So the free energy is

$$F = -TN \ln \left[ \sum_n \exp[-\beta \mathcal{E}_n] \right] \quad (\text{V.20})$$

and thus the entropy

$$\begin{aligned} S = -dF/dT &= N \ln(z) + \frac{N}{zT} \sum_n \mathcal{E}_n \exp[-\beta \mathcal{E}_n] = \\ &= -\frac{N}{z} \sum_n \ln \left[ \frac{\exp[-\beta \mathcal{E}_n]}{z} \right] \exp[-\beta \mathcal{E}_n] = -N \sum_n p_n \ln p_n, \end{aligned} \quad (\text{V.21})$$

where  $z$  is the partition function corresponding to the single spin and  $p_n = \exp[-\beta \mathcal{E}_n]/z$  is the probability to occupy this state. Note that we actually did not have to assume that our subsystem contains a single spin. Generally we would have

$$S = - \sum_n p_n \ln p_n, \quad (\text{V.22})$$

where  $p_n = \exp[-\beta \mathcal{E}_n]/Z$ . This is the von Neumann entropy for the system in thermal equilibrium. One can also check this equality directly using

$$Z = \sum_n \exp[-\beta \mathcal{E}_n]. \quad (\text{V.23})$$

Then

$$S = \ln Z - \frac{\beta}{Z} \frac{\partial Z}{\partial \beta} = \sum_n \left[ \frac{\mathcal{E}_n}{T} - \ln Z \right] p_n = - \sum_n p_n \ln p_n. \quad (\text{V.24})$$

Let us try to get this answer purely probabilistically. Suppose we split the system into many subsystems and will start filling it with particles. The probability of the particle to go to the subsystem 1 is  $p_1$  and so on. Of course the most probable configuration is that we have  $Np_1$

particles in the first subsystem,  $Np_2$  particles in the second subsystem etc. Let us find the number of ways  $\Omega$  we can achieve the most probable configuration:

$$\Omega = \frac{N!}{(Np_1)!(Np_2)! \dots (Np_m)!} \quad (\text{V.25})$$

This is pure combinatorics: first we choose the first particle for the first subsystem:  $N$ -ways then the second particle for the first subsystem:  $N - 1$  ways and so on. Then we will need to divide by number of equivalent permutations within each subsystem because this permutations lead to equivalent configurations. Now let us use Stirling's formula and take the logarithm of the expression above:

$$\begin{aligned} S = \ln \Omega &\approx N \ln N - N - \sum_n (p_n N \ln(p_n N) - p_n N) \\ &= N(\ln N - \sum_n p_n \ln(Np_n)) = -N \sum_n p_n \ln p_n. \end{aligned} \quad (\text{V.26})$$

So indeed the von Neumann entropy has a purely probabilistic nature.

Let us recall the whole story again. We started from the microcanonical ensemble and the basic assumption that all states with the same energy are equally probable. We termed entropy the logarithm of number of available microstates. Then by splitting the system into a subsystem and environment we showed that microcanonical distribution naturally leads to the canonical distribution for the subsystem where the probability to occupy a certain microstate with energy  $\mathcal{E}$  is proportional to  $\exp[-\beta\mathcal{E}]$ . Then we computed the number of ways one can distribute particles over these microstates took the logarithm and derived von Neumann entropy. Note that for equal probabilities within a small energy window  $p_n = 1/\Omega_E$  the von Neumann's entropy reduces to the microcanonical entropy  $S = \ln \Omega(E)$ .

## B. Information and entropy.

Information theory was invented by Claude Shannon at AT&T Bell Labs beginning in the 1940s. Information theory attempts to quantify the information content of messages and studies the reliability of transmission of that information over noisy channels of finite frequency bandwidth.

What is information? Suppose you have a deck of cards. I randomly take on card the question is how much information I can transmit by revealing what the card is. Think the deck of cards being the next hot thing in Wall street. For how much can you sell this information? If there is only one card in the deck then there is no information content - by saying you took ace you do not say much if there is only one ace in the deck (by saying it is oil you do not say much if

you trade only with oil). Clearly the more cards in the deck (the more trading areas you see) the more information you reveal by opening your card (the better price you can get for revealing this information). So information should be monotonic function of  $N$  - the number of cards in a deck.

$$I(N + 1) \geq I(N) \quad (\text{V.27})$$

If you have another deck of  $M$  cards then if you reveal two cards one from first deck and one from the second deck your information is additive. Your earnings will add up. So we should have

$$I(NM) = I(N) + I(M) \quad (\text{V.28})$$

The sensitive definition of  $I$  satisfying this is

$$I(N) = \log_2(N) \quad (\text{V.29})$$

The base 2 is just the tradition. So far we assumed that all outcomes are equally probable. But suppose that one outcome has very large probability. Then by picking this outcome you do not reveal much information. This outcome is almost expected. If the outcome is not very probable you are revealing much more information but the probability of this outcome is small. What is the sensible definition of the information in this case?

Suppose now that we are using a transmission line sending a signal encoded in zeros and ones. Each zero occurs with the probability  $p$  and one with probability  $q$ . What is the amount of information we transmit in  $N$  bits. Assume  $N$  is large. Obviously if  $p = 1$  or  $p = 0$  our signal would consist of only zeros and one and we transmit no information. In general we will have total number of zeros  $pN$  and total number of ones  $qN$ . The total number of way we can arrange for having this many zeros and this many ones is

$$\Gamma = \frac{N!}{(Np)!(Nq)!} \quad (\text{V.30})$$

The information encoded in a particular sequence is defined as  $I = \log_2 \Gamma$  (note that  $\Gamma$  plays the role of number of cards in the deck) so

$$I = -N(p \log_2 p + q \log_2 q) \quad (\text{V.31})$$

So the information content per bit is  $I_1 = -p \log_2 p - q \log_2 q$ . This obviously generalizes to more outcomes:

$$I_1 = - \sum_i p_i \log_2 p_i \quad (\text{V.32})$$

So the Shannon information is directly related to the von Neumann entropy.

### C. Fluctuations of energy

Let us return to Boltzmann distribution and compute the energy fluctuations.

$$\delta E^2 = \langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Z} \sum_n E_n^2 \exp[-\beta E_n] - \left( \frac{\partial \ln Z}{\partial \beta} \right)^2 = \frac{\partial^2 \ln Z}{\partial^2 \beta} = -\frac{\partial E}{\partial \beta} = T^2 \frac{\partial E}{\partial T} = T^2 C_V. \quad (\text{V.33})$$

Note that  $C_V$  is the heat capacity. We put index  $V$  here to emphasize that this quantity is computed at fixed external parameters like volume. We already saw that  $C_V$  must be positive in order to have stable equilibrium: maximum entropy versus minimum or saddle point. Here we see that the same quantity  $C_V$  determines the energy fluctuations in the system. This is one of the examples of the fluctuation-dissipation theorem: fluctuations of some quantity is related to a certain susceptibility of this quantity. We will return to this issue in detail later.

Similarly in the grand canonical ensemble one can study fluctuations of the number of particles. We need to change  $\beta$  to  $-\beta\mu$  and repeat the analysis:

$$\langle N \rangle = T \frac{\partial \ln Z}{\partial \mu} \quad (\text{V.34})$$

and

$$\delta N^2 = T^2 \frac{\partial^2 \ln Z}{\partial \mu^2} = T \frac{\partial N}{\partial \mu} = TV \frac{\partial n}{\partial \mu} \quad (\text{V.35})$$

The latter quantity is called compressibility and we see that it must be positive in order to ensure the equilibrium in the system. Recall the chemical potential is a measure of how entropy of the system changes with the number of particles. We will see later that in ideal gases chemical potential is related to the pressure. High pressure means a high desire of the system to expand, i.e. the system can gain a lot of entropy expanding. So positive compressibility basically tells us that as we decrease volume of the system (increase  $n$ ) we necessarily increase pressure. We will derive this explicitly when we talk about ideal gases.

### D. Problems for Sec. V

1. Consider a system of noninteracting spins with arbitrary  $S$ :  $S_z = S, S-1, \dots, -S$  in a magnetic field with the Hamiltonian  $\mathcal{H} = -hS_z$ . Calculate the partition function for this system at finite temperature. Calculate average energy, magnetization, susceptibility and heat capacity. Discuss its behavior at large  $S$ . Now consider a classical spin in the magnetic field with the energy  $\mathcal{E} = -hS_z = -hS \cos \theta$ . Define the classical partition function

$Z_{cl} = \int \sin \theta d\theta d\phi \exp[-\beta \mathcal{E}(\theta, \phi)]$ . Calculate the same quantities as for the quantum problem. Compare your results with  $S = 1/2$  quantum case and large  $S$  quantum case. Discuss which of the computed quantities computed for large  $S$  are similar to the  $S = 1/2$  case and to the classical case and which quantities are qualitatively different in these three situations.

2. Derive the expression for the von Neumann entropy for the spin one half system in the magnetic field and compare it with Eq. (IV.3). Note that you will have to express either von Neumann entropy through energy or the entropy given by Eq. (IV.3) through temperature.

## VI. THE IDEAL GAS. THERMODYNAMIC POTENTIALS.

So far we dealt with the situations where the Hilbert space was finite and the partition function

$$Z = \sum_n \exp[-\beta \mathcal{E}_n] \quad (\text{VI.1})$$

was well defined. What shall we do if the spectrum is continuous. Let us consider the ideal one dimensional gas in the box of size  $L$ . Then from quantum mechanics we know that

$$\mathcal{E}_n = \frac{\hbar^2 k_n^2}{2m}, \quad (\text{VI.2})$$

where  $k_n = 2\pi n/L$ . If  $L$  is large then for all practical purposes we can change summation over  $n$  to integration over  $k$ . Note that

$$1 = \delta n = \frac{L}{2\pi} \delta k = \frac{L}{2\pi \hbar} \delta p \quad (\text{VI.3})$$

Therefore in this situations

$$Z = \sum_n \exp[-\beta \mathcal{E}_n] = \int \frac{dx dp}{2\pi \hbar} \exp[-\beta p^2/2m]. \quad (\text{VI.4})$$

We could have guessed this result from the beginning except for the factor  $2\pi \hbar$ . In classical physics it is arbitrary. But it is very convenient because it makes the partition function dimensionless and connects quantum and classical partition functions. This expression obviously generalizes to  $N$ -particles in  $d$ -dimensions

$$Z = \prod_i \int \frac{d\mathbf{x}_i d\mathbf{p}_i}{(2\pi \hbar)^d} \exp[-\beta \mathcal{E}(\mathbf{x}_i, \mathbf{p}_i)]. \quad (\text{VI.5})$$

Let us now compute the partition function for the ideal gas

$$\begin{aligned} Z &= \left( \int \frac{d\mathbf{x} d\mathbf{p}}{(2\pi \hbar)^d} \exp[-\beta \mathbf{p}^2/2m] \right)^N = \left( \frac{V}{(2\pi \hbar)^d} \left[ \int_{-\infty}^{\infty} \exp[-\beta p^2/2m] dp \right]^d \right)^N \\ &= \left( V \left[ \frac{mT}{2\pi \hbar} \right]^{d/2} \right)^N = \left( \frac{V}{\lambda_T^d} \right)^N, \end{aligned} \quad (\text{VI.6})$$

where  $\lambda_T = \sqrt{2\pi\hbar/mT}$  is the De-Broglie wave length. From this we can define free energy

$$F = -T \ln Z = -TN \ln \left( V \left[ \frac{mT}{2\pi\hbar} \right]^{d/2} \right), \quad (\text{VI.7})$$

similarly

$$E = -\frac{\partial \ln Z}{\partial \beta} = NT \frac{d}{2}. \quad (\text{VI.8})$$

So each particle has an average energy  $Td/2$  ( $3/2T$  in three dimensions). This result we could have obtained just using single particle Boltzmann's probability distribution. From standard thermodynamics we know that the pressure is defined as

$$P = -\frac{\partial E}{\partial V} \Big|_S = -\frac{\partial F}{\partial V} \Big|_T. \quad (\text{VI.9})$$

So for the ideal gas we find

$$P = NT/V. \quad (\text{VI.10})$$

This should sound familiar. Interestingly this is a very robust law: it does not depend on the dimensionality, mass of the particles their structure etc. It relies only on the fact that the particles are not interacting and the partition function is proportional to  $V^N$ .

We can actually also define the pressure in a usual way from the principle of maximum of the entropy. In the same way we defined temperature and chemical potential. Imagine that we have two gases separated by a membrane which can move. We will allow for the energy exchange to fix the temperature but will not allow for particle exchange. Then the total  $V = V_1 + V_2$  is fixed so we need to maximize the entropy with respect to  $V_1$ . Thus

$$\frac{\partial S_1}{\partial V_1} \Big|_{N_1, T} = \frac{\partial S_2}{\partial V_2} \Big|_{N_2, T} \quad (\text{VI.11})$$

Let us make the formal definition

$$P = T \frac{\partial S}{\partial V} \Big|_{T, N} \quad (\text{VI.12})$$

Now we can generally write (for the subsystem 1) that

$$dS_1 = \frac{\partial S_1}{\partial E_1} \Big|_{V_1} dE_1 + \frac{\partial S_1}{\partial V_1} \Big|_{E_1} dV_1 = \frac{1}{T_1} dE_1 + \frac{P_1}{T_1} dV_1 \quad (\text{VI.13})$$

From this we indeed recover that

$$dE = TdS - PdV, \quad dF = -SdT - PdV \quad (\text{VI.14})$$

So the two definitions of the pressure coincide.

### A. Gibbs paradox.

The expression for the free energy we obtained has a problem: it is not extensive. Suppose we increase the volume and the number of particles by a factor of two. Then  $N \rightarrow 2N$  and  $V \rightarrow 2V$  so that  $F \rightarrow 2F - TN \ln 2$ . Note that the energy itself is extensive:  $E \rightarrow 2E$ . So does the heat capacity. Pressure which is  $\partial F/\partial V$  is also not affected by this extra term. Yet it is annoying since we rather deal with extensive quantities. Note that

$$F = E - TS \quad (\text{VI.15})$$

since  $E$  is not affected by this extra term then the fact that  $F$  is not extensive means that entropy is not extensive. This is quite contrary to our previous discussion and the spin chain example.

To make the point even more transparent consider two subsystems containing identical ideal gases at the same temperature and pressure. Suppose one gas contains  $N_1$  particles and the other  $N_2$  particles. Then the initial entropy (while the gases are separated) is

$$S_1 + S_2 = -\frac{\partial F_1}{\partial T} - \frac{\partial F_2}{\partial T} = N_1 \ln \left( V_1 \left[ \frac{mT}{2\pi\hbar} \right]^{d/2} \right) + N_2 \ln \left( V_2 \left[ \frac{mT}{2\pi\hbar} \right]^{d/2} \right) + \frac{d}{2}(N_1 + N_2) \quad (\text{VI.16})$$

Suppose that  $N_1 = N_2 = N/2$  and  $V_1 = V_2 = V/2$ . Then

$$S_1 + S_2 = N \ln \left( \frac{V}{2} \sigma \right) + \frac{Nd}{2}, \quad (\text{VI.17})$$

$\sigma = \sqrt{(mT/2\pi\hbar)^d}$ . Let us pretend for a second and assume that gases in two parts are different. Then when we mix them (remove the barrier) the entropy will definitely increase. Clearly the final entropy is

$$S = N \ln (V\sigma) + \frac{Nd}{2} \quad (\text{VI.18})$$

so the difference between the two is

$$\Delta S_{mix} = S - S_1 - S_2 = N \ln 2 \quad (\text{VI.19})$$

This difference is called the mixing entropy. The fact that it is positive illustrates a well known point that once we remove the barrier the particles will mix with each other and never return to the original part of the container.

But what if the particles are identical? By removing the barrier we really did not do anything so the entropy increase is not real. The problem with our definition of  $Z$  is that we are over-counting states. We count the state where the particle 1 was in the phase space point  $\mathbf{x}_1, \mathbf{p}_1$  and the particle

2 was in the phase space point  $\mathbf{x}_2, \mathbf{p}_2$  and vice versa as two different states. But if the particles are indistinguishable this is one state. In quantum mechanics this issue is naturally resolved because the wave function of identical particles is always the superposition of say  $|1\rangle|2\rangle$  and  $|2\rangle|1\rangle$ . So this state in quantum mechanics would be counted once. So better definition of  $Z$  for identical particles is

$$Z = \frac{1}{N!} \prod_i \int \frac{d\mathbf{x}_i d\mathbf{p}_i}{(2\pi\hbar)^d} \exp[-\beta\mathcal{E}(\mathbf{x}_i, \mathbf{p}_i)]. \quad (\text{VI.20})$$

This gives additional contribution to the free energy which makes it extensive (without affecting energy, heat capacity, pressure, etc.) After all this prefactor is just a constant. So we get

$$F = -T \ln Z = -TN \ln \left( \frac{V}{N} \left[ \frac{mT}{2\pi\hbar} \right]^{d/2} \right) - TN, \quad (\text{VI.21})$$

Now the free energy is explicitly extensive. So is the entropy

$$S = N \ln \left( \frac{V}{N} \sigma \right) + \frac{N(d+2)}{2}. \quad (\text{VI.22})$$

Note that whether we treat particles as identical or distinguishable is a matter of convenience as long as our measurements (or interactions) are insensitive to differences between them. Taking different isotopes should not result in any physical difference as long as there is nothing which tells us that the isotopes are different. And indeed we saw that measurable quantities like energy, heat capacity, pressure do not care about this extra term coming from  $N!$ . We will return to this issue again when we will study quantum gases.

Let us compute heat capacity. From  $C_V = dE/dT|_V$  we find that

$$C_V = N \frac{d}{2}. \quad (\text{VI.23})$$

Sometimes it can be of interest to know heat capacity when we fix pressure rather than volume fixed. Note that the heat is defined as  $TdS$  (it is equal to  $dE$  if we fix the volume) then

$$C_P = T \frac{dS}{dT}|_P = \left( \frac{\partial E}{\partial T}|_P + P \frac{\partial V}{\partial T}|_P \right) = \frac{\partial(E + PV)}{\partial T}|_P = N \frac{d+2}{2}. \quad (\text{VI.24})$$

Note the expression  $E + PV$ , which is called enthalpy is convenient thermodynamic potential if we work at constant pressure.

## B. Thermodynamic potentials. Relations between derivatives.

We already encountered energy and free energy  $F = E - TS$ . We know that they satisfy

$$dE = TdS - PdV, \quad dF = -SdT - PdV \quad (\text{VI.25})$$

From these relations we see that

$$P = -\left.\frac{\partial E}{\partial V}\right|_S = -\left.\frac{\partial F}{\partial V}\right|_T \quad (\text{VI.26})$$

Usually the relations (VI.25) are interpreted as that energy is the function of  $S$  and  $V$ , while free energy is the function of  $T$  and  $V$ . Of course this is not literary true since  $S$ ,  $T$  and  $V$  are not independent variables but rather they are connected by the equation of state (see Eq. (VI.22)). It is just the matter of convenience: if temperature is fixed (and volume changes) i.e. if we perform an isothermal process, then the free energy change is equal to  $-PdV$ . On the other hand if the entropy is fixed (adiabatic process) then the change of energy is equal to  $-PdV$ . On the other hand change of the energy in the first case and change of the free energy in the second are more complicated. For example

$$E = F + TS = F - T\left.\frac{\partial F}{\partial T}\right|_V \quad (\text{VI.27})$$

is explicitly defined as a function of temperature and volume.

We can assume that there is some other external parameter  $\lambda$ . Then obviously if we change it infinitesimally we have

$$dE = TdS - PdV + \Lambda d\lambda, \quad (\text{VI.28})$$

where  $\Lambda = (\partial E/\partial\lambda)|_{S,V}$ . Similarly

$$dF = -SdT - PdV + \Lambda d\lambda. \quad (\text{VI.29})$$

Thus we see that  $\Lambda = (\partial F/\partial\lambda)_{T,V}$ . We can interpret these equalities also in the following way

$$\delta E|_{S,V} = \delta F|_{T,V} \quad (\text{VI.30})$$

I.e. if we infinitesimally change some external parameter in the adiabatic process then the change of the energy would be identical to the change of the free energy in the corresponding isothermal process.

One can also introduce other potentials like enthalpy  $H = E + PV$  and Gibbs free energy  $G = H - TS = E - TS + PV$ . We will obviously get  $dH = TdS + VdP$  and  $dG = -SdT + VdP$ . These two potentials are convenient if we use  $S, P$  or  $T, P$  as independent variables respectively.

Using general thermodynamic relations we can obtain identities between various quantities. For example

$$\left.\frac{\partial C_V}{\partial V}\right|_T = T\left.\frac{\partial^2 S}{\partial V \partial T}\right|_T = -T\left.\frac{\partial^3 F}{\partial T^2 \partial V}\right|_T = T\left.\frac{\partial^2 P}{\partial T^2}\right|_V \quad (\text{VI.31})$$

Similarly we can find

$$\left. \frac{\partial C_P}{\partial P} \right|_T = -T \left. \frac{\partial^2 V}{\partial T^2} \right|_P. \quad (\text{VI.32})$$

One can derive many similar relations like this.

Very often if we analyze various derivatives it is convenient to go from one set of variables to another e.g. from  $S$  and  $V$  to  $T$  and  $P$ . This can be done using Jacobians:

$$\frac{\partial(x, y)}{\partial(u, v)} \equiv \begin{vmatrix} \partial x / \partial u & \partial x / \partial v \\ \partial y / \partial u & \partial y / \partial v \end{vmatrix} \quad (\text{VI.33})$$

Jacobians have a number of properties:

$$\frac{\partial(x, y)}{\partial(x, v)} = \left. \frac{\partial y}{\partial v} \right|_x \quad (\text{VI.34})$$

also

$$\frac{\partial(x, y)}{\partial(f, g)} = \frac{\partial(x, y)}{\partial(u, v)} \frac{\partial(u, v)}{\partial(f, g)}. \quad (\text{VI.35})$$

In particular

$$1 = \frac{\partial(x, y)}{\partial(x, y)} = \frac{\partial(x, y)}{\partial(u, v)} \frac{\partial(u, v)}{\partial(x, y)}. \quad (\text{VI.36})$$

Using these properties we can easily derive various thermodynamic relations. E.g.

$$\begin{aligned} C_V &= T \left. \frac{\partial S}{\partial T} \right|_V = T \frac{\partial(S, V)}{\partial(T, V)} = T \frac{\partial(S, V)}{\partial(T, P)} / \partial(T, V) / \partial(T, P) \\ &= T \left( \left. \frac{\partial S}{\partial T} \right|_P \left. \frac{\partial V}{\partial P} \right|_T - \left. \frac{\partial S}{\partial P} \right|_T \left. \frac{\partial V}{\partial T} \right|_P \Big) / (\partial V / \partial P)|_T \end{aligned} \quad (\text{VI.37})$$

Next note that

$$\left. \frac{\partial S}{\partial P} \right|_T = \frac{\partial^2 G}{\partial T \partial P} = - \left. \frac{\partial V}{\partial T} \right|_P. \quad (\text{VI.38})$$

Thus we find

$$C_P - C_V = -T \left( \left. \frac{\partial V}{\partial T} \right|_P \right)^2 / (\partial V / \partial P)|_T \quad (\text{VI.39})$$

Because as we found out earlier  $\partial P / \partial V|_T \leq 0$  we find that  $C_P \geq C_V$  in accord to Eqs. (VI.23) and (VI.24) for ideal gases. But now we see that this inequality is a general result of thermodynamics. It is valid for quantum or classical systems, interacting or not.

### C. Le Chatelier principle.

Le Chatelier principle: any external action stimulates process which reduces the action. This principle is so general that it often goes beyond the realm of equilibrium statistical mechanics. The idea is very simple if no opposition to a certain external action is expected then the corresponding process would likely happen by itself, without any need of the external action. Look into society, biology. In some sense a third Newton law is in accord with this principle. Let us see how this principle agrees with the main postulate of thermodynamics.

Consider a system consisting of two parts with e.g. volumes  $V_1$  and  $V_2$  such that  $V_1 + V_2 = V$ . There is no particle exchange but there is a membrane so that  $V_1$  and  $V_2$  can change keeping the total volume fixed. Instead of volume we can use any other parameter: temperature, magnetization, etc. Now suppose we rapidly change  $V_1$ :  $V_1 \rightarrow V_1 + \Delta V_1$ . Then we let the system relax back to thermal equilibrium. Le Chatelier principle tells us that after the system equilibrates  $\Delta V_1(t = \infty) < \Delta V_1$ . Let us prove this is the case. After the initial change we have  $V_2$ ,  $P_2$  and  $T_2$  are unchanged while  $V_1$ ,  $P_1$ , and  $T_1$  do change. After the system relaxes to the equilibrium the pressures in both sides of the container will equilibrate. During this process the total entropy of the system must increase. The volume  $V_1$  will then have an additional change  $\delta V_1 = \Delta V_1(\infty) - \Delta V_1$ . Let us compute changes in the entropy of subsystems 1 and 2 after the system re-equilibrates

$$\begin{aligned}\delta S_1 &= \left. \frac{\partial S_1}{\partial E_1} \right|_{V_1} \delta E_1 + \left. \frac{\partial S_1}{\partial V_1} \right|_{E_1} \delta V_1 \\ \delta S_2 &= - \left. \frac{\partial S_2}{\partial E_2} \right|_{V_2} \delta E_1 - \left. \frac{\partial S_2}{\partial V_2} \right|_{E_2} \delta V_1\end{aligned}\tag{VI.40}$$

So we get

$$\delta S = \delta E_1 \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \delta V_1 \left( \frac{P_1}{T_1} - \frac{P_2}{T_2} \right).\tag{VI.41}$$

Let us assume for simplicity that  $T_1 = T_2 = T$ , i.e. we initially expanded the volume isothermally. Then  $\delta S = (P_1 - P_2)/T \delta V_1 \geq 0$ . Let us note that

$$P_1 = P_2 + \left. \frac{\partial P_1}{\partial V_1} \right|_{T_1} \Delta V_1\tag{VI.42}$$

The derivative  $\partial P_1 / \partial V_1|_T$  is always negative so we find that  $\Delta V_1 \delta V_1 < 0$  i.e. the system counter reacts on changing the volume by reducing this change.

Let us consider somewhat more complicated situation where we initially increase volume in the subsystem 1 adiabatically (as a result decreasing pressure) and prove after the relaxation

the pressure will increase in agreement with the Le-Chatelier principle. It is convenient to rewrite Eq. (VI.41) in the following way

$$\delta S \approx -\delta E_1 \frac{\Delta T}{T^2} - \frac{\Delta T}{T^2} P_1 \delta V_1 + \frac{\Delta P}{T} \delta V_1 = -\frac{\Delta T}{T} \delta S_1 + \frac{\Delta P}{T} \delta V_1. \quad (\text{VI.43})$$

Here we used the notation  $\Delta T = T_1 - T_2$  is the temperature change due to initial change of volume.

Let us now note that

$$\Delta T = \left( \frac{\partial T}{\partial V} \right)_S \Delta V, \quad \Delta P = \left( \frac{\partial P}{\partial V} \right)_S \Delta V. \quad (\text{VI.44})$$

From the Maxwell's relation (obvious from  $dE = TdS - PdV$ ) we have

$$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \quad (\text{VI.45})$$

Thus we obtain

$$\delta S \approx \frac{\Delta V}{T} \left[ \left( \frac{\partial P_1}{\partial S_1} \right)_V \delta S_1 + \left( \frac{\partial P_1}{\partial V_1} \right)_S \delta V_1 \right] = \frac{\Delta V \delta P_1}{T} \geq 0 \quad (\text{VI.46})$$

Now we see that because  $\Delta P$  and  $\Delta V$  have opposite signs (it follows from the Eq. (VI.47) and the fact that compressibility is positive as well as  $C_V$  and  $C_P$  are also positive)  $\delta P$  and  $\Delta P$  must have opposite signs.

Finally we can discuss how  $C_P > C_V$  follows from the Le-Chatelier principle (we had a formal proof before in Eq. (VI.39)). Assume that we have a gas at a fixed volume  $V$  and we heat it by temperature  $\Delta T$ . Then we increase its energy by the amount  $\Delta Q = C_V \Delta T$ . By doing this we also increase its pressure. Now assume the system is in the contact with the environment (no energy exchange). Then it will expand and cool until the pressures become identical. So in order to heat at constant pressure by the same amount  $\delta T$  we need to do additional heating. Thus  $C_P > C_V$ .

The formal proof of the Le-Chatelier principle, which is adopted from the book by Landau and Lifshitz, Statistical Physics.

#### D. Problems for Sec. VI

1. Consider a system of spins in a magnetic field. Define the magnetization as  $m = -1/V(\partial F/\partial H)$ . Illustrate explicitly that this magnetization is indeed proportional to average  $S_z$ . Now define the magnetization in a different way using entropy. Assume that the magnet is split into two subsystems and the total magnetic flux coming through this subsystems is fixed, i.e.  $H_1 A_1 + H_2 A_2 = \text{const}$ . Here  $A_1$  and  $A_2$  are the surface areas of the

subsystems. Now demand that the entropy is maximum of possible partitionings of the flux between the subsystem. Show this should leave to a quantity which is identical between the two subsystems. Show that this quantity (up to a prefactor) is the magnetization defined in the beginning of the problem.

2. Prove that

$$\left. \frac{\partial V}{\partial P} \right|_S = \frac{C_V}{C_P} \left. \frac{\partial V}{\partial P} \right|_T. \quad (\text{VI.47})$$

Give a physical interpretation of this result. What does it mean? Check this relation explicitly for an ideal gas.

3. Consider the problem discussed in Sec. VI.C, but now assume that we heat the subsystem one at constant volume increasing its temperature by  $\delta T$ . Prove that after re-equilibration the temperature in the subsystem one will reduce. (Hint you can use Eq. (VI.43), the Maxwell relation that  $\partial P/\partial T = \partial S/\partial V$ , and the fact that specific heat is non-negative, i.e.  $\partial E/\partial T \geq 0$ .)
4. Consider the Ising spin system in equilibrium at some fixed magnetization  $M$ . You may assume that  $M \ll N$ , where  $N$  is the total number of spins. Now imagine that in the subsystem one consisting of half of the spins we increased the average magnetization by the amount  $\Delta M$ , which is not necessarily much smaller than  $M$ , such that the subsystem one is in local thermal equilibrium (but not in equilibrium with the subsystem two). Calculate the new magnetization and temperature in the system after the two subsystems re-equilibrate. Do your results agree with the Le Chatelier principle?

## VII. INTERACTING SYSTEMS. HIGH TEMPERATURE EXPANSION

So far we were dealing with, in some sense, trivial situations of non-interacting systems. In reality we always have to deal with systems with interactions. Then the partition function can not be written as a product of partition functions corresponding to different degrees of freedom. What shall we do in this situations? Of course one can try to do numerical simulations. However, this is not always possible because we can simulate only a limited number of degrees of freedom and in quantum systems we have to sample over the exponentially large Hilbert space. It is often efficient to use a Monte-Carlo algorithm. There are however subtleties in using Monte-Carlo. E.g. in quantum systems sometimes Monte-Carlo simulations are not efficient because of the sign problem

(one needs to evaluate average over many terms with opposite signs). Also we generally understand better qualitative properties if we have analytic results.

### A. Ising model.

We will try to use a different route of using perturbation theory. For now we stick purely to classical systems. Suppose we have an ensemble of interacting spins with the Hamiltonian (energy):

$$\mathcal{H} = -h \sum_j \sigma_j - \frac{1}{2} \sum_{ij} J_{ij} \sigma_i \sigma_j = \mathcal{H}_0 + \mathcal{H}_{int}, \quad (\text{VII.1})$$

where  $\sigma_j = \pm 1$  is the  $z$ -component of the spin. For practical purposes we will mostly deal with the nearest neighbor interaction where  $J_{ij} = J$  if  $i$  and  $j$  form pairs of nearest neighbors in a  $d$ -dimensional lattice and zero otherwise. The factor of  $1/2$  is to avoid double counting of all bonds. Note that for  $J = 0$  our model reduces to the one we studied earlier in Sec. IV.A (we now use slightly different notations).

We need to evaluate the partition function

$$Z = \sum_{\{\sigma_j\}} \exp[-\beta \mathcal{H}], \quad (\text{VII.2})$$

which as we know contains all the information about equilibrium properties of our system. Let us note that we expect qualitatively different behavior of the system depending on the value of the product  $\beta J$  (for simplicity we assume for now that  $h = 0$ ). At high temperatures when  $\beta J \ll 1$  we expect that the interaction will be a small perturbation over the equilibrium noninteracting state where all spins have random orientation independent of each other. In the opposite limit we expect that all spins will align to minimize the energy and the state will be ordered. So we can expect that as one changes  $\beta J$  there can be a qualitative change in behavior characterized by a spontaneous formation of magnetization  $\langle \sigma \rangle$  will spontaneously acquire some expectation value at small  $T$ . This qualitative change in behavior is called a phase transition and we will come back to this important example later on.

For now we will be interested in a simpler question of understanding what happens when  $\beta J \ll 1$ . Let us rewrite the partition function in the following way

$$\begin{aligned} Z &= \sum_{\{\sigma_j\}} \exp \left[ \frac{\beta}{2} \sum_{\langle ij \rangle} J_{ij} \sigma_i \sigma_j \right] \exp[-\beta \mathcal{H}_0(\{\sigma_j\})] \\ &= Z_0 \left\langle \exp \left[ \frac{\beta}{2} \sum_{\langle ij \rangle} J_{ij} \sigma_i \sigma_j \right] \right\rangle_0 \equiv Z_0 \langle \exp[-\beta \mathcal{H}_{int}] \rangle_0, \end{aligned} \quad (\text{VII.3})$$

where  $Z_0$  is the noninteracting partition function, and  $\langle \dots \rangle_0$  is the expectation value weighted with the noninteracting equilibrium probability distribution. We basically found an exact identity that the interacting partition function  $Z$  is the product of the interacting partition function  $Z_0$  and the average of the exponent of  $-\beta$  times interaction energy weighted with non-interacting probability distribution. There is a similar expression in quantum mechanics, but it is more subtle because  $\mathcal{H}_0$  and  $\mathcal{H}$  in general do not commute.

Since we assumed that  $\beta J$  is small we can expand the exponent in Eq. (VII.3) into the Taylor series and find

$$Z \approx Z_0 \left( 1 + \frac{\beta}{2} \sum_{\langle ij \rangle} J_{ij} \langle \sigma_i \sigma_j \rangle_0 + \frac{1}{2!} \frac{\beta^2}{4} \sum_{\langle ij \rangle_0} \sum_{\langle kl \rangle} J_{ij} J_{kl} \langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle_0 + \dots \right) \quad (\text{VII.4})$$

So the partition function can be written in terms of series of moments of  $\mathcal{H}_{int}$ . Likewise we can write the expansion for the free energy

$$F = -T \ln Z = F_0 - T \ln \langle \exp[-\beta \mathcal{H}_{int}] \rangle_0 = F_0 - T \sum_n \frac{(-\beta)^n}{n!} \langle \mathcal{H}_{int}^n \rangle_0^c. \quad (\text{VII.5})$$

So expansion of the free energy is the cumulant expansion.

First let us evaluate  $Z$  and  $F$  to the leading order in  $J$ . Note that for  $i \neq j$  we have  $\langle \sigma_i \sigma_j \rangle_0 = \langle \sigma_i \rangle_0 \langle \sigma_j \rangle_0$ , for  $i = j$  on the other hand  $\langle \sigma_i^2 \rangle_0 = 1$ . Therefore

$$Z \approx Z_0 \left( 1 + \frac{\beta}{2} [\langle \sigma \rangle_0]^2 \sum_{i \neq j} J_{ij} + \frac{\beta}{2} \sum_j J_{jj} \right), \quad (\text{VII.6})$$

where  $N$  is the total number of spins. For the nearest neighbor model on the cubic lattice (with  $2d$  nearest neighbors) we can simplify the expression above further

$$Z \approx Z_0 \left( 1 + \beta N J d [\langle \sigma \rangle_0]^2 \right). \quad (\text{VII.7})$$

Note that in the absence of external magnetic field  $\langle \sigma \rangle_0 = 0$  and there is no correction to the partition function to the linear order in  $J$ . Likewise for the free energy we have

$$F \approx F_0 - J d N [\langle \sigma \rangle_0]^2. \quad (\text{VII.8})$$

Using results from Sec. IV.A we find

$$F \approx -TN \ln 2 \cosh \beta h - J d N \tanh^2 \beta h. \quad (\text{VII.9})$$

So for example the magnetization (recall last lecture: either differentiate the energy with respect to  $h$  at a constant entropy or the free energy with respect to  $h$  at a constant temperature)

$$M = - \frac{1}{V} \frac{\partial F}{\partial h} \Big|_T = n \tanh \beta h + 2 J d n \beta \frac{\sinh \beta h}{\cosh^3 \beta h}. \quad (\text{VII.10})$$

At high temperatures this yields

$$M \approx n\beta h(1 + 2Jd/T) \quad (\text{VII.11})$$

at low temperatures the correction to the magnetization due to  $J$  is exponentially small. Can you explain these results? What is the effective magnetic field each spins sees due to interactions with other spins? Try to argue that at small  $\beta h$  the effective field is  $h_{eff} = h + 2Jd\beta h$ . This should explain this result for the magnetization.

Let us move to the next order in  $J$ . We need to evaluate

$$\left\langle \sum_{ij} \sum_{kl} J_{ij} J_{kl} \sigma_i \sigma_j \sigma_k \sigma_l \right\rangle_0 \quad (\text{VII.12})$$

To simplify our life we consider  $h = 0$ . Then note that the expectation value is non zero only if  $i = k, j = l$  or  $i = l$  and  $j = k$ . This term gives a trivial contribution since  $\langle \sigma_i^2 \rangle_0 = 1$ . So to the second order in  $\beta J$  and at  $h = 0$  for the nearest neighbor case we find

$$Z \approx Z_0 \left( 1 + \frac{\beta^2}{8} N 4d J^2 \right) = 2^N \left( 1 + \frac{\beta^2 J^2 N d}{2} \right) \quad (\text{VII.13})$$

Here we used the fact that there are  $2d$  neighbors for each site and we have two possible allowed permutations with  $i = k$  and  $i = l$ . For the free energy the expansion is similar because at  $h = 0$  the second cumulant of  $\mathcal{H}_{int}$  is the same as the second moment.

$$\mathcal{F} \approx -TN \ln(2) - N \frac{J^2 d}{2T}. \quad (\text{VII.14})$$

From free energy we can compute quantities like entropy, energy, and specific heat.

$$S = -\frac{\partial \mathcal{F}}{\partial T} \approx N \ln(2) - N \frac{dJ^2}{2T^2}. \quad (\text{VII.15})$$

The entropy decreases with  $J$  which indicates that the system is more ordered. Note that this is true for both signs of  $J$ .

$$E = \mathcal{F} + TS \approx -TN \ln(2) - N \frac{J^2 d}{2T} + TN \ln(2) - N \frac{J^2 d}{2T} = -N \frac{J^2 d}{T}. \quad (\text{VII.16})$$

Finally for the specific heat we have

$$C = \frac{1}{V} \frac{\partial E}{\partial T} = n \frac{J^2 d}{T^2} \quad (\text{VII.17})$$

As an exercise let us compute the next correction. It is easy to convince oneself that there is no contribution to  $Z$  and  $F$  in the order of  $J^3$ . In the order of  $J^4$  we need to compute

$$\frac{1}{4! 2^4} (J\beta)^4 \sum_{ij} \sum_{kl} \sum_{mn} \sum_{pq} \langle \sigma_i \sigma_j \sigma_k \sigma_l \sigma_m \sigma_n \sigma_p \sigma_q \rangle_0. \quad (\text{VII.18})$$

This some is non-zero if and only if indices coincide pairwise. It is convenient to compute all various contractions graphically (we will do in only in two dimensions). Each bond is represented by the line, horizontal or vertical. One can show that only loops matter everything else combines into  $2^N (\cosh \beta J)^{2N}$  and the expansion parameter is not  $\beta J$  but  $\tanh \beta J$ .

Note that the only closed loops that matter are squares. There are 8 ways to arrange for a square (four ways to choose the direction of the first bond and two ways to choose the direction of the second bond) and there are  $6 * 2^3 = 48$  ways to make various contractions  $j = k, l = m, n = p, i = q$  (first choose the bond then each bond except the first one can be oriented in an arbitrary way) like. So in total squares give the contribution  $8 * 48 = 384$ . And up to the fourth order we get

$$Z \approx [\cosh(\beta J)]^{2N} 2^N (1 + N \tanh^4 \beta J) \quad (\text{VII.19})$$

One can check that this result agrees with what one can get by brute force calculation up to the order  $(\beta J)^4$ .

To see that only closed loops matter let us observe that

$$\exp[\beta J \sigma_i \sigma_j] = \cosh(\beta J) + \sinh(\beta J) \sigma_i \sigma_j = \cosh \beta J (1 + \sigma_i \sigma_j \tanh \beta J). \quad (\text{VII.20})$$

So the partition function is indeed written as

$$Z = \cosh^{Nd}(\beta J) \sum_{\{\sigma_j\}} \prod_{\langle ij \rangle} (1 + \tanh(\beta J) \sigma_i \sigma_j). \quad (\text{VII.21})$$

Note that each link in the product appears once and thus repeated links are excluded.

It is interesting to note that the term proportional to  $J^3$  will appear in a triangular lattice. The corresponding contribution to the partition function is

$$\frac{\beta^3}{3!2^3} \sum_{\langle ij \rangle} \sum_{\langle kl \rangle} \sum_{\langle mn \rangle} \langle \sigma_i \sigma_j \sigma_k \sigma_l \sigma_m \sigma_n \rangle. \quad (\text{VII.22})$$

The only nonvanishing configuration from this term is such where sites are arranged in triangles. There are  $N$  possibilities for site  $i$ , 6 possibilities for site  $j$ , 2 possibilities for the next link, 4 possibilities to choose  $j = k, l, m, n$  and two more possibilities to orient the last link. So the corresponding contribution to the partition function is  $2N\beta^3 J^3$ . So up to the third order in  $J$  in zero magnetic field we find that the partition functions is

$$Z \approx Z_0 \left( 1 + \frac{4N}{3} J^2 \beta^2 + 2N J^3 \beta^3 + \dots \right). \quad (\text{VII.23})$$

Note that the second term appears because there is a factor of  $12 = 6 \times 2$  to arrange two links so that they form a single double link. Thus for the free energy we have

$$\mathcal{F} \approx -TN \ln(2) - N \frac{4J^2}{3T} - 2N \frac{J^3}{T^2} + \dots \quad (\text{VII.24})$$

and for the entropy

$$S \approx N \left( \ln(2) - \frac{4J^2}{3T^2} - 4 \frac{J^3}{T^3} \right). \quad (\text{VII.25})$$

The last term is very interesting. For positive  $J$ , i.e. ferromagnetic interactions it decreases the entropy: the system wants to be more ordered. However, for antiferromagnetic interactions  $J < 0$  it increases the entropy. The reason is that in this case the system is frustrated. If two neighboring spins want to arrange so that they are opposite to each other, the third spin does not know what to do. So there are more equal low-energy configurations in the antiferromagnetic case than in the ferromagnetic. So there is more entropy.

Computing the partition function in a non-zero magnetic field is not a very pleasant exercise (see homework). This is so because once we introduce nonzero  $h$  the spin inversion symmetry is gone and many terms, which are zero at  $h = 0$  become nonzero. However, very often we are not interested in full statistical information for arbitrary  $h$ . For example we can be interested the response of the system to a weak magnetic field, which is characterized by the magnetic susceptibility (per particle):

$$\chi = \frac{1}{N} \frac{\partial M}{\partial h} \Big|_{h=0} = -\frac{1}{N} \frac{\partial F^2}{\partial h^2} \Big|_{h=0} = -\frac{T}{N} \frac{1}{Z^2} \left( \frac{\partial Z}{\partial h} \Big|_{h=0} \right)^2 + \frac{T}{N} \frac{1}{Z} \frac{\partial^2 Z}{\partial h^2} \Big|_{h=0}. \quad (\text{VII.26})$$

Note that the first term in the sum is zero, because it is proportional to the square of magnetization at  $h = 0$ , which is zero by symmetry. The second term gives

$$\chi = \frac{1}{NT} \frac{1}{Z} \sum_{\{\sigma_{ij}\}} \sum_{ij} \sigma_i \sigma_j \exp[-\beta H] = \frac{1}{T} \sum_j \langle \sigma_j \sigma_0 \rangle = \frac{1}{T} + \frac{1}{T} \sum_{j \neq 0} \langle \sigma_j \sigma_0 \rangle, \quad (\text{VII.27})$$

where we used the fact the the system is translationally invariant. Note that the expectation value is taken with respect to the full partition function. We know how to expand the denominator in terms of  $J$ . We also need to expand the nominator in a similar fashion and read the result.

In the zeros order in  $J$  we recover usual Curie susceptibility:

$$\chi = \frac{1}{T} \quad (\text{VII.28})$$

In the first order in  $J$  there is no correction to  $Z$  so we do not worry about the denominator. In nominator only  $j$  which is the nearest neighbor contributes:

$$\chi \approx \frac{1}{T} + \frac{J}{2T^2} \sum_j \sum_{k,l} \langle \sigma_j \sigma_0 \sigma_k \sigma_l \rangle_0 = \frac{1}{T} + \frac{2Jd}{T^2}. \quad (\text{VII.29})$$

This is of course what we had before. Let us go to the second order. In numerator we will have to evaluate sums with six spins:

$$\frac{J^2}{8T^3} \sum_j \sum_{kl} \sum_{mn} \langle \sigma_j \sigma_0 \sigma_k \sigma_l \sigma_m \sigma_n \rangle_0. \quad (\text{VII.30})$$

Note that in this sum each site should appear twice, otherwise the average is zero. There are two types of terms. The first type is  $j = 0$  and ( $k = m, l = n$  or  $k = n, l = m$ ) (these terms are automatically excluded if we restrict the summation to  $j \neq 0$ ). This would correspond to a disconnected graph where contractions in the sum coming from the partition function are independent of the external spins in the sum. Such terms are dangerous because they are not-extensive (they contain extra factor of  $N$ ). However such terms are precisely canceled by similar terms in denominator  $Z$ . So we should not worry about such terms. This is a general statement. The other terms are such where all indices are linked together. It is easy to check that in 1D there are only two possibilities to connect next nearest neighbors:  $j = 2, k = 0, m = 1, l = 1, n = 2$  (plus seven equivalent permutations) and similarly with  $j = -2$ . In two dimensions there are 12 different permutations, in three dimensions there are  $6 + 24 = 30$  permutations etc. So to the next order in  $J$  we find (to be specific let us stick to two dimensions)

$$\chi \approx \frac{1}{T} \left( 1 + \frac{4J}{T} + \frac{12J^2}{T^2} + \dots \right) \quad (\text{VII.31})$$

## B. High temperature expansion for the interacting gas.

Let us assume that we have a gas of weakly interacting particles described by the Hamiltonian:

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i < j} U(q_i - q_j) \quad (\text{VII.32})$$

For simplicity we assume that we include only two-body interactions. In dilute limit particles are unlikely to meet at one point. Long range coulomb interactions can also be written in this two-body form. To shorten the notations we will denote the last sum (interaction energy) by  $U(\mathbf{q})$ , where  $\mathbf{q}$  spans coordinates of all particles.

We are going to use the same procedure as for the Ising model:

$$Z(T, V, N) = Z_0(T, V, N) \langle \exp[-\beta U(\mathbf{q})] \rangle_0 = Z_0(T, V, N) \sum_n \frac{(-\beta)^n}{n!} \langle U(\mathbf{q})^n \rangle_0 \quad (\text{VII.33})$$

and similarly

$$F(T, V, N) = F_0(T, V, N) - T \sum_n \frac{(-\beta)^n}{n!} \langle U(\mathbf{q})^n \rangle_0^c. \quad (\text{VII.34})$$

Let us now compute the first and the second order corrections to the free energy. In the first order in  $U$  the cumulant is equal to the expectation value:

$$\langle U \rangle_0^c = \sum_{i < j} \int \frac{d^d q_i}{V} \frac{d^d q_j}{V} U(q_i - q_j) = \frac{N(N-1)}{2V} \int d^d q U(q). \quad (\text{VII.35})$$

Note that the factors of  $1/V$  come from  $Z_0$  and since there is no coordinate dependence of the non-interacting weight all coordinates are equally probable. So in the leading order in interaction we are getting only the uniform shift.

The second order correction is written as the sum

$$\langle U^2 \rangle_0^c = \sum_{i < j, k < l} \int \dots \int \frac{d^d q_i}{V} \dots \frac{d^d q_l}{V} [\langle U(q_i - q_j) U(q_k - q_l) \rangle_0 - \langle U(q_i - q_j) \rangle_0 \langle U(q_k - q_l) \rangle_0]. \quad (\text{VII.36})$$

Note that there is no contribution to this sum if all indices  $i, j, k, l$  are different because all coordinates are equally probable. If there is a one common index, e.g.  $i = k$  then the same situation is again true. This is because we can choose this coordinate ( $q_i = q_k$ ) to be equal to zero (by changing variables) and the two remaining coordinates  $j$  and  $l$  are again uniformly distributed. So the average of the product again factorizes into the product of averages (cf. with Ising model). The only nontrivial contribution comes from the situations where  $i = k$  and  $j = l$  (note that because  $i < j$  and  $k < l$  there are no additional permutations (alternatively we can include them adding extra factors of  $1/2$ )). So we find

$$\langle U^2 \rangle_c^0 = \frac{N(N-1)}{2} \left[ \int \frac{d^d q}{V} U^2(q) - \left( \int \frac{d^d q}{V} U(q) \right)^2 \right]. \quad (\text{VII.37})$$

Note that the second term is smaller than the first one by a factor of  $1/V$  and can be ignored in thermodynamic limit.

So up to the second order in  $U$  we have

$$F(T, V, N) \approx F_0(T, V, N) + \frac{N^2}{2V} \left[ \int d^d q U(q) - \frac{\beta}{2} \int d^d q U(q)^2 \right]. \quad (\text{VII.38})$$

This expression already allows us to calculate pressure, entropy, etc. Unfortunately it is not very useful because interatomic potentials are typically very strong when particles are close to each other (they behave essentially as hard spheres). So the integrals diverge at short distances. In these situations instead of expansion in  $U$  it is much better to expand in terms of density (small density corresponds to the dilute noninteracting limit). The problem can be addressed by partially resumming the series or by equivalently using the trick similar to the one we used for the Ising

model:

$$\exp \left[ - \sum_{i < j} \beta U_{ij} \right] = \prod_{i < j} (1 - 1 + \exp[-\beta U_{ij}]) \equiv \prod_{i < j} [1 + f_{ij}], \quad (\text{VII.39})$$

where  $f_{ij} = \exp[-\beta U_{ij}] - 1$ . Note that  $f_{ij}$  is a much better expansion parameter than  $U_{ij}$  because when the interaction is weak then  $f_{ij}$  essentially coincides with  $U_{ij}$  (up to the sign) while if interaction is strong  $f_{ij}$  approaches  $-1$  instead of  $\infty$ . Clearly each order in the expansion in  $f_{ij}$  brings us the extra factor of  $1/V$  - we need to integrate over more points, and extra factor of  $N$  because there are more permutations, so we have the expansion in density as wanted. Physically this cluster expansion means that we solve two particle problem exactly and expand only in the number of events where more and more particles meet together within the interaction range. For example in the leading order on density one sums only over the clusters consisting of two different points  $i$  and  $j$ :

$$\begin{aligned} \ln Z &= \ln Z_0 + \sum_{n \geq 1} \frac{(-\beta)^n}{n!} \frac{N(N-1)}{2} \int \frac{d^d q}{V} U(q)^n + O\left(\frac{N^3 \beta^2 U^3}{V^2}\right) \\ &= \ln Z_0 + \frac{N(N-1)}{2V} \int d^d q f(q) + O\left(\frac{N^3 \beta^2 U^3}{V^2}\right) \end{aligned} \quad (\text{VII.40})$$

So we see that indeed the first term in the density expansion from re-summation of the series coincides with the first term in the cluster expansion.

In higher orders in density we will find terms of the order of  $Nn^2$  etc. See Kardar for formal rules and diagrams. We will stop our expansion at this order and find corrections to the equation of state. We have

$$F(T, V, N) \approx F_0(T, V, N) - \frac{TN^2}{2V} \int d^d q f(q) \quad (\text{VII.41})$$

Note that if the potential is weak and we expand  $f(q)$  to the second order in  $U$  we will reproduce Eq. (VII.38). Let us use the following model (van der Waals) potential:

$$U(r) = \begin{cases} \infty & r < r_0 \\ -u_0(r_0/r)^6 & r > r_0 \end{cases} \quad (\text{VII.42})$$

Then we find that

$$- \int d^3 q f(q) \approx \frac{4\pi r_0^3}{3} (1 - \beta u_0), \quad (\text{VII.43})$$

where we used high temperature expansion  $\beta u_0 \ll 1$  to evaluate the integral. Therefore

$$F \approx F_0 + \frac{N^2}{V} \frac{2\pi r_0^3}{3} (T - u_0) = F_0 + N \frac{\Omega N}{2V} (T - u_0), \quad (\text{VII.44})$$

where  $\Omega = 4\pi r_0^3/3$  is the excluded volume. Note that our expansion relies on the fact that the integral over the potential converges at long distances. So the potential should decrease faster than  $1/r^3$ . Otherwise the virial expansion does not work. We see that for short ranged potential the small parameter is the ratio of the excluded volume and the volume.

From the free energy we can get pressure, entropy etc. In particular

$$P = -\left.\frac{\partial F}{\partial V}\right|_T = \frac{NT}{V} + \frac{N^2\Omega}{2V^2}(T - u_0) + \dots = nT + \frac{\Omega}{2}n^2(T - u_0) + \dots \quad (\text{VII.45})$$

This we can rearrange as

$$P + \frac{u_0\Omega}{2}n^2 \approx \frac{nT}{1 - \Omega n/2} \quad (\text{VII.46})$$

The correction in the denominator in the second term can be interpreted as the correction to the volume. The factor of one half implies that this is the total excluded volume for all particles: for the first nothing is excluded, for the last  $N\Omega$  is excluded so we have  $\Omega/2$  on average per particle (remember the homework.) The correction to the pressure comes from the interactions: the particles attract to each other so there is a lower pressure on the boundaries. The equation above is the van der Waals equation with parameters  $a = u_0\Omega/2$  and  $b = \Omega/2$ . (See hand-waving derivation of the van der Waals equation in Kardar).

Van der Waals isotherms have a fundamental flaw that they have a region of negative compressibility: the isotherm  $P(V)$  can be non-monotonic. Thus we can find that

$$\frac{1}{\kappa} = -V \left( \frac{\partial P}{\partial V} \right)_T = \frac{nT}{(1 - nb)^2} - 2an^2 \quad (\text{VII.47})$$

If  $b$  is negligible we see that at  $T \approx 2an$  we get unstable regions.

The correct phase diagram can be obtained from these isotherms using Maxwell's construction. Note that the Gibbs free energy

$$G = E - TS + PV \quad (\text{VII.48})$$

is the function of  $T$ ,  $P$ , and  $N$  (in the sense as we discussed earlier). This implies that

$$\mu = \left. \frac{\partial G(P, T, N)}{\partial N} \right|_{T, P} \quad (\text{VII.49})$$

Because  $T$  and  $P$  are not extensive we can integrate this equality and we see that  $\mu N = E - TS + PV$ . Therefore  $\Omega = E - TS - \mu N = -PV$ . Note that  $d\Omega = -SdT - PdV - Nd\mu = -PdV - VdP$  therefore

$$SdT + Nd\mu = VdP \quad (\text{VII.50})$$

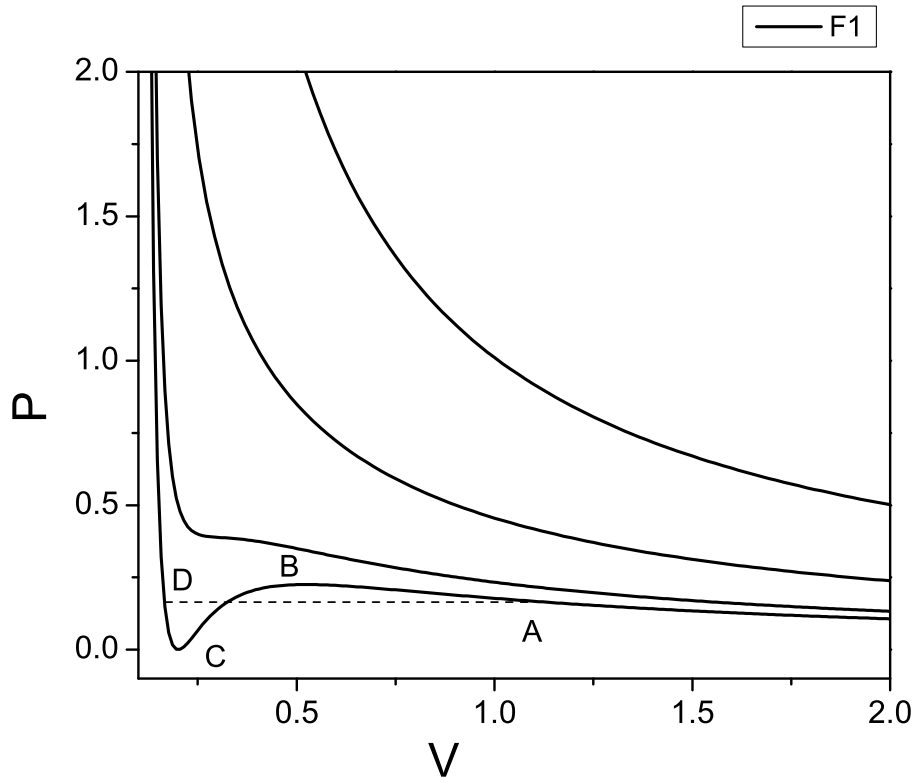


FIG. 4 Van der Waals isotherm for a particular set of parameters  $a = b = 0.1$ ,  $N = 1$ . The dashed line illustrates Maxwell construction.

If we consider an isotherm (temperature is fixed) we can obtain the chemical potential and thus  $G$  by integrating

$$d\mu = \frac{V}{N}dP. \quad (\text{VII.51})$$

Because the curve is nonmonotonic we will get three possible values for the chemical potential at the same value of  $T$  and  $P$ . So the chemical potential is not a unique function of  $T$  and  $P$ . This indicates there is a phase coexistence (another possibility of course is that van der Waals equations are not very accurate). Which of the phases is correct? In equilibrium if we keep  $T$  and  $P$  fixed then  $G$  should be minimal (we will prove this statement later). So we want to choose the minimal  $\mu$ . The phase transition occurs when two values of the chemical potential intersect:

$$\Delta\mu = \int \frac{V}{N}dP = 0, \quad (\text{VII.52})$$

where the integral is taken along the path  $A \rightarrow B \rightarrow C \rightarrow D$ , which is nothing but the difference of the areas above and below straight line connecting points  $A$  and  $D$ . This is the value of the

pressure where the phase transition between liquid and gas occurs. This construction implies that for fixed pressure below  $T_c$  the volume changes discontinuously. In turn this means that if we choose the volume between points  $A$  and  $D$  in the figure the system must phase separate and we will have a coexistence region. So real isotherms are obtained from Van Der Waals isotherms by connecting points  $A$  and  $D$  with straight lines.

### C. Problems for Sec. VII.

1. Find expansion of the partition function and the free energy for the Ising model up to the order  $J^2$  in non-zero magnetic field in one and two dimensions. Pay special attention to how various terms scale with  $N$ . You should find some non-extensive contributions, proportional to  $N^2$  in the partition function, but if you do algebra correctly then such contributions should cancel out in the cumulant expansion for the free energy. So that the free energy remains extensive. You can assume  $N \gg 1$ . From your expansion find to the same order magnetization and magnetic susceptibility. Interpret your results.
2. Using Eq. (VII.21) compute the lowest non vanishing contribution to the partition function of the Ising model in the honeycomb lattice (consisting of hexagons) at zero magnetic field. Argue what will be the second non-vanishing order (you do not have to compute the coefficient explicitly). Do odd powers of  $\tanh bJ$  appear in the expansion? Why or why not? In the leading order in  $\tanh bJ$  find corrections to the entropy and specific heat.
3. Find the expression for the susceptibility  $\chi$  at zero magnetic field in the first two non-vanishing orders in  $\beta J$  for the triangular lattice (analogue of Eq. (VII.31)). You can use the trick similar to Eq. (VII.21) for the partition function or calculate it straightforwardly.

## VIII. BROKEN SYMMETRY: MEAN-FIELD AND VARIATIONAL APPROACH.

### A. Mean-field theory.

Let us return back to the classical Ising model:

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i. \quad (\text{VIII.1})$$

Recall that the magnetization

$$m = -\frac{1}{V} \frac{\partial F}{\partial h} = \frac{T}{V} \frac{\partial \ln Z}{\partial h} = \frac{1}{V} \sum_j \sigma_j \quad (\text{VIII.2})$$

In the absence of magnetic field the model has the spin-inversion symmetry  $\sigma_j \rightarrow -\sigma_j$ : two directions of spins are equivalent. However in the presence of magnetic field this symmetry is broken. So  $h$  is the symmetry-breaking field.

Now let us introduce a very important concept of spontaneous symmetry breaking. When  $h = 0$  we must have  $m = 0$ . But what happens if  $h \rightarrow 0$  and  $V \rightarrow \infty$ . We can have two possible limits

$$\lim_{h \rightarrow 0} \lim_{V \rightarrow \infty} m \tag{VIII.3}$$

and

$$\lim_{V \rightarrow \infty} \lim_{h \rightarrow 0} m \tag{VIII.4}$$

The latter limit is always zero. But this is not true about the first one. If the first limit is not-zero the system is said to be in spontaneously broken symmetry state. Clearly the order of limits can be different if the free energy is a non-analytic function of  $h$  in the limit  $V \rightarrow \infty$ .

To illustrate the idea let us consider spin system at very low temperature. First start from two spins. Assume that  $J$  is very large both compared to  $h$  and to  $T$ . The two favorable spin configurations are  $|\uparrow, \uparrow\rangle$  and  $|\downarrow, \downarrow\rangle$ . The energy difference between them is  $\Delta\mathcal{E} = 4h$ . Once this energy difference becomes much smaller than temperature (at least according to naive criterion) we obviously have  $m \rightarrow 0$ . This happens at  $h \sim T/4$ . Now consider instead 4 spins. By the same argument the energy difference between two favorite configurations  $|\uparrow, \uparrow, \uparrow, \uparrow\rangle$  and  $|\downarrow, \downarrow, \downarrow, \downarrow\rangle$  is  $\Delta\mathcal{E} = 8h$  so the spins become disordered at  $h \approx T/8$ . We see that as the number of spins increases the “naive” argument predicts that spins remain ordered up to smaller and smaller fields, which vanish as the number of spins become macroscopic. Similarly one can imagine that the times required to go from one macroscopic configuration to another become exponentially long.

We will see later that the naive argument is qualitatively correct in dimensions higher than one, where at small temperatures entropy is not important and we can focus only on the two optimal-energy configurations. The ordering is clearly a *collective* effect. Noninteracting spins will never order! At high temperatures  $T \gg J$  on the other hand spins are almost independent from each other and weak magnetic field can not have a pronounced effect. So we expect that there is a transition between ordered regime (where symmetry is spontaneously broken) and disordered regime. How do we find this transition? There are several available tools: meanfield approach, variational approach, numerical simulations, analysis of asymptotics of high-temperature expansion, renormalization group, exact solution for solvable models, ... In this course we will focus on the first two methods.

1. Self-consistent meanfield approach.

When we did high temperature expansion in the Ising model we argued that each spin feels an effective magnetic field  $h_{eff} = h(1 + 2Jd/T)$  (see Eq. (VII.11)). Note that this result can be understood from self-consistent arguments: without interactions the average magnetization per spin is  $h$ . Therefore to the lowest order the effect of interactions on a given spin with say  $j = 0$  is:

$$-J \sum_{\langle j0 \rangle} \sigma_j \sigma_0 \approx -2Jdh\sigma_0. \quad (\text{VIII.5})$$

Let us extend this argument below perturbation theory in  $J/T$  and assume that we can substitute the true interaction term by the mean-field one:

$$-J \sum_{\langle j0 \rangle} \sigma_j \sigma_0 \rightarrow -h_{eff}\sigma_0 \quad (\text{VIII.6})$$

so the only result of all other spins on spin 0 is that the latter feels some effective average field from the other neighboring spins. Clearly we are making an approximation because the problem is correlated: the state of nearest neighbors of site 0 depends on the spin  $\sigma_0$  itself in a complicated way. However, it is intuitively clear that in high-dimensions (large coordination numbers) this effect should be small. Other spins have too many nearest neighbors to care a lot about what a single spin is doing. However, at low dimensions, especially in 1D this approximation is very crude, and in fact incorrect.

Clearly  $h_{eff} = 2Jd\langle\sigma\rangle$  (assuming there is no external field) and

$$\langle\sigma_0\rangle = \tanh(\beta h_{eff}) \quad (\text{VIII.7})$$

To be consistent we must have

$$h_{eff} = 2Jd \tanh(\beta h_{eff}). \quad (\text{VIII.8})$$

because all spins should have the same average magnetization. Denoting  $\beta h_{eff}$  as  $x$  we see that this equation becomes:

$$x = 2Jd\beta \tanh x \quad (\text{VIII.9})$$

It can be solved graphically. Clearly for  $2Jd\beta < 1$  (high temperatures) we find that the only solution is  $x = 0$ . While for  $2Jd\beta > 1$  there are two additional solutions corresponding to non-zero magnetization. In the limit  $\beta \rightarrow 0$  we obviously have the nonzero solutions at  $x \approx \pm 2Jd\beta$  corresponding to  $\langle\sigma\rangle \approx \pm 1$ . It is intuitively clear that non-zero solutions are the correct ones by continuity argument. In the next section we will give a more rigorous justification to this statement.

## B. Variational approach

From quantum mechanics we know that the energy of the ground state is larger than the expectation value of the Hamiltonian in any state:

$$E_{gs} \leq \langle \psi | \mathcal{H} | \psi \rangle \quad (\text{VIII.10})$$

for any  $\psi$ . This statement serves as the basis for the variational principle, where we choose any trial state with some unfixed parameters and minimize the expectation value of the Hamiltonian with respect to this state. Can we generalize this principle to finite temperatures? Obviously we are no longer minimizing energy because the entropy should play the role.

It turns out that the generalization does exist and it can be formulated as follows. Let us choose some arbitrary trial Hamiltonian  $\mathcal{H}_0$ . Then the corresponding grand potential (free energy in the canonical case) satisfies the following inequality:

$$\Omega \equiv -T \ln Z \leq \Omega_{\text{tr}} = \Omega_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0, \quad (\text{VIII.11})$$

where the expectation value is taken with respect to the equilibrium partition function corresponding to  $\mathcal{H}_0$ . Let us check that this variational principle reduces to (VIII.10) in the zero temperature limit. In this case  $\Omega = E_{gs}$ ,  $\Omega_0 = E_{gs}^0$  so we have  $E_{gs} \leq \langle \mathcal{H} \rangle_0$ , which indeed follows from Eq. (VIII.10). The only difference is that the trial state is not assumed to be the ground state of some particular trial Hamiltonian. This Hamiltonian can be always found for any  $|\psi\rangle$  by an appropriate choice of potential.

Let us prove this statement, first in the classical case.

$$Z = \int dx dp \exp[-\beta(\mathcal{H}_0(x, p) - V(x, p))] = \frac{1}{Z_0} \langle \exp[-\beta V(x, p)] \rangle_0, \quad (\text{VIII.12})$$

where by  $x, p$  we schematically denoted all multi-dimensional phase space and  $V = \mathcal{H}(x, p) - \mathcal{H}_0(x, p)$ . The function  $\exp[-\beta v]$  is convex (it has a positive second derivative). For any convex function we have  $f(\bar{v}) \leq \overline{f(v)}$  (this is called Jensen's inequality) in particular  $f((v_1 + v_2)/2) \leq (f(v_1) + f(v_2))/2$ . This most easily can be seen from the picture. The general prove is beyond the purpose of this course, but for a particular exponential function we are interested in the proof is very simple. Let us prove that

$$g(\beta) = \langle \exp[-\beta(V - \langle V \rangle_0)] \rangle_0 \geq 1 \quad (\text{VIII.13})$$

To do this we note that

$$\begin{aligned}
g(\beta) &= g(0) + \int_0^\beta \frac{dg}{d\beta'} d\beta' = g(0) - \int_0^\beta \left\langle (V - \langle V \rangle_0) e^{-\beta'(V - \langle V \rangle_0)} \right\rangle_0 d\beta' \\
&= g(0) - \int_0^\beta \left\langle (V - \langle V \rangle_0) \left( e^{-\beta'(V - \langle V \rangle_0)} - 1 \right) \right\rangle_0 d\beta'. \tag{VIII.14}
\end{aligned}$$

The integrand in the last expression is never positive so we see that  $g(\beta) \geq g(0) = 1$ . The proof in the quantum case is similar if  $V$  commutes with  $\mathcal{H}_0$ . Otherwise it is more complicated but still correct (to prove the statement in general quantum case one can invoke the matrix generalization of Jensen's inequality for convex function:  $\text{Tr}(f(A) - f(B)) \leq \text{Tr}[(A - B)f'(B)]$ ).

We can use Eq. (VIII.11) to build a variational approach at finite temperature: choose a simple trial Hamiltonian with free parameters, from this find a trial thermodynamic potential  $\Omega_{\text{tr}}$ . Minimize this partition function. The state where it is equal to minimal is closest to the true equilibrium state of the system.

Let us apply this method to the Ising model

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j. \tag{VIII.15}$$

Let us choose a trial Hamiltonian to be noninteracting:

$$\mathcal{H}_0 = -\lambda \sum_j \sigma_j, \tag{VIII.16}$$

where  $\lambda$  is the variational parameter. Then

$$\Omega_0 = -TN \ln[2 \cosh \beta\lambda], \quad \langle \mathcal{H}_0 \rangle_0 = -\lambda N \tanh(\beta\lambda), \quad \langle \mathcal{H} \rangle_0 = -\frac{NJ2d}{2} \langle \sigma \rangle_0^2 = -NJd \tanh^2(\beta\lambda). \tag{VIII.17}$$

Therefore

$$\Omega_{\text{tr}} = -TN \ln[2 \cosh(\beta\lambda)] + \lambda N \tanh(\beta\lambda) - NJd \tanh^2(\beta\lambda) \tag{VIII.18}$$

Minimize with respect to  $\lambda$ :

$$-N \tanh(\beta\lambda) + N \tanh(\beta\lambda) + \frac{N\lambda\beta}{\cosh^2(\beta\lambda)} - 2NJd\beta \frac{\tanh(\beta\lambda)}{\cosh^2(\beta\lambda)} = 0 \Leftrightarrow \beta\lambda = 2Jd\beta \tanh(\beta\lambda). \tag{VIII.19}$$

The last equality exactly reproduces the mean field equation (VIII.9) with  $\lambda$  playing the role of  $h_{\text{eff}}$ . But now we can immediately see that for  $2Jd\beta > 1$  the broken symmetry solution corresponds to the minimum of free energy. Indeed if we expand  $\Omega_{\text{tr}}(\lambda)$  around  $\lambda = 0$  we will find

$$\Omega_{\text{tr}} \approx \text{const} + N\lambda^2 \left[ -\frac{\beta}{2} + \beta - \frac{J2d\beta^2}{2} \right] = \text{const} + \frac{N\lambda^2\beta}{2} [1 - 2Jd\beta] \tag{VIII.20}$$

So we find that indeed for  $2Jd\beta > 1$  the symmetry broken state has lower (trial) free energy and thus this would be closer to the true equilibrium state). We can make the expansion to the fourth order in  $\lambda$  and get that

$$\frac{\Omega_{\text{tr}}\beta}{N} \approx \text{const} + \frac{\alpha}{2}\lambda^2 + \frac{\gamma}{4}\lambda^4, \quad (\text{VIII.21})$$

where  $\alpha = 1 - 2\beta Jd$  and  $\gamma = 8\beta Jd/3 - 1$ . Note that near the transition  $2\beta Jd = 1$  the coefficient  $\gamma$  is positive  $\gamma \approx (1/3)$  so the effective free energy has a Mexican-hat type form. Because physically  $\lambda$  plays the role of magnetization we can view  $\Omega_{\text{tr}}(\lambda)$  as the expansion of free energy as a function of magnetization, which is a particular example of phenomenological Landau theory of phase transitions.

### C. Break down of mean-field approach in one dimension. Absence of broken symmetry.

In the previous sections two equivalent methods were developed to analyze the Ising model. Both showed that in any dimension there is a phase transition from a paramagnetic (symmetric) phase to the ferromagnetic phase which breaks spin inversion symmetry. In low dimensions (1D being lowest) the mean field theory is least reliable because it relies on the assumption that many surrounding spins of a given spin create average non-fluctuating mean-field acting on that spins. Thus we need to find independent argument proving the existence of both phases.

At high temperatures we can use the high temperature expansion which is valid in all dimensions. This expansion shows that if the ratio  $J/T$  is small then the magnetization still vanishes at the zero magnetic field (see Eq. (VII.11)). Thus the existence of paramagnetic phase is proven, at least perturbatively. Proving existence of ferromagnetic phase is more subtle. We already established its existence at zero temperature. Indeed in this case the system goes into one of the two lowest energy states with all spins parallel to each other with infinitesimal external magnetic field vanishing in the thermodynamic limit breaking the degeneracy. Now we need to check that this symmetry broken state survives small temperatures. We start from a one-dimensional spin chain and then analyze what happens in two and higher dimensions.

#### 1. Low temperature limit of a one-dimensional Ising chain.

It is intuitively clear that at low temperatures ( $T \ll J$ ) the chain will consist from large intervals with uniform magnetization with possibly rare defects. The elementary excitation in a one dimensional chain is a domain wall (see Fig. 5. It is intuitively clear that existence of domain

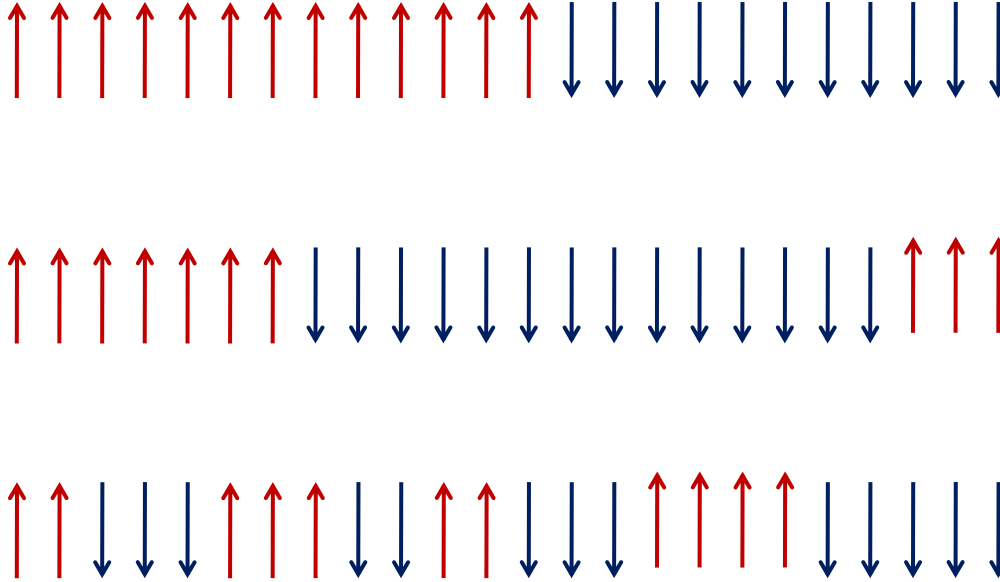


FIG. 5 Domain walls - elementary excitations in a one-dimensional Ising model. From the figure it is clear that many domain walls lead to rapid decay of spin-spin correlations and destruction of the long range order.

walls destroys long range correlations and thus the broken symmetry. To see this let us compare free energies of the two configurations: (i) uniform ferromagnetic state and (ii) a state with a one domain wall. In the former case clearly the entropy is zero and the free energy (== energy) is

$$\mathcal{F}_i = -JN. \quad (\text{VIII.22})$$

In the latter case with one domain wall the entropy of the system is  $\ln(N)$  thus the free energy is

$$\mathcal{F}_{ii} = -J(N - 1) + h - T \ln(N) \quad (\text{VIII.23})$$

It is clear that the free energy of the configuration with a single domain wall is lower for sufficiently long chains

$$L \geq \xi = \exp 2J/T. \quad (\text{VIII.24})$$

Note that the correlations length  $\xi$  exponentially depends on temperature and can be very large at small temperatures effectively leading to a ferromagnetic state in finite size systems. To find equilibrium density of domain walls at finite temperature we can use a trial state where the domain

walls are randomly distributed. It is convenient to assign a plus sign (positive charge) to a domain wall where spin flips from  $\uparrow$  to  $\downarrow$  and minus sign for the opposite domain wall. Then the domain wall configuration is described by a series of effective  $+$  and  $-$  charges with the constraint that a “ $+$ ” charge always follows a “ $-$ ” charge. Note the each domain wall contributes energy  $2J$ . Let us assume for simplicity that we have even number of domain walls  $2n$ . Then the entropy of a dilute gas of  $2n$  domain walls is approximately

$$S \approx \ln \left[ \frac{N!}{(N-2n)! 2n! \frac{1}{2^{2n-1}}} \right] \approx N \ln N - (N-2n) \ln(N-2n) - 2n \ln 2n - 2n \ln 2, \quad (\text{VIII.25})$$

where the factor  $1/2^{2n-1}$  appears because only two configurations of domains walls with alternating charges satisfy the constraint. From this we find

$$\mathcal{F} \approx 4Jn - TN \ln N + T(N-2n) \ln(N-2n) + 2nT \ln(2n) + 2nT \ln(2). \quad (\text{VIII.26})$$

Maximizing the free energy with respect to  $n$  we find

$$\frac{2J}{T} \approx \ln \left( \frac{N-2n}{4n} \right) \Rightarrow n \approx \frac{N}{4\xi + 2}. \quad (\text{VIII.27})$$

Thus  $2\xi$  is the mean distance between the domain walls. It is straightforward to check that  $\xi$  also sets the characteristic decay length of the correlations between the different spins.

## 2. Exact solution for the one-dimensional Ising model.

Actually the one-dimensional Ising model is simple enough can be solved exactly using transfer matrices. Let us assume for simplicity that we have periodic boundary conditions, i.e.  $N+1=1$ . The partition function for the Ising model is

$$Z = \sum_{\sigma_i} \exp \left[ \beta J \sum_j \sigma_j \sigma_{j+1} + \beta h \sum_j \sigma_j \right] \quad (\text{VIII.28})$$

Let us note that this partition function can be also written as a product of  $2 \times 2$  transfer matrices  $T_{ij}$  with the matrix elements

$$T_{11} = \exp[\beta(h+J)], \quad T_{22} = \exp[\beta(-h+J)], \quad T_{12} = T_{21} = \exp[-\beta J]. \quad (\text{VIII.29})$$

Then it is easy to check that

$$Z = \sum_{i_1, i_2, \dots, i_N=1,2} T_{i_1, i_2} T_{i_2, i_3} \dots T_{i_N, i_1} = \text{tr}[T^N] = \lambda_1^N + \lambda_2^N, \quad (\text{VIII.30})$$

where  $\lambda_{1,2}$  are the two eigenvalues of the matrix  $T$ . Those can be straightforwardly found solving  $2 \times 2$  secular equation:

$$\lambda_{1,2} = \exp[\beta J] \left[ \cosh(\beta h) \pm \sqrt{\sinh^2(\beta h) + \exp(-4\beta J)} \right]. \quad (\text{VIII.31})$$

If we take an infinite  $N$  limit then only the largest eigenvalue contributes to the partition function:  $Z \approx \lambda_1^N$ . In this limit we find that the magnetization per spin is

$$m = \frac{T}{N} \frac{\partial \ln(Z)}{\partial h} \approx \frac{\sinh(\beta h)}{\sqrt{\sinh^2(\beta h) + \exp[-4\beta J]}} \quad (\text{VIII.32})$$

We see that at zero magnetic field the magnetization is zero so the symmetry is not broken. However at small temperatures the magnetization rapidly increases with  $h$  reaching the saturation at exponentially small magnetic fields  $h^* \approx T \exp[-4J/T]$ . This is consistent with our previous observation that the symmetry is almost spontaneously broken in this system. Instead of finite magnetic field one can consider the effect of finite system size and reach the same conclusion as in the previous section.

#### D. Low temperature limit of the Ising model in two and higher dimensions.

Having established that there is no symmetry breaking in one dimensions we next check whether similar situation occurs in two and higher dimensions. Let us first consider defects which are domain walls (see Fig. 6). These defects, if present, clearly destroy long range order. Let us check whether they proliferate at low temperatures. We will proceed as in the one-dimensional case. Clearly the entropic gain in the free energy from creating such a defect is  $-T \ln(2L)$  (for simplicity we assume square lattice so there are  $2L$  possibilities to place the domain wall. This contribution is basically the same as in one dimensions. However, the energy cost for a domain wall now is  $2JL$  instead of  $2J$ . So the change in the free energy due to insertion of a single domain wall is

$$\delta \mathcal{F} = 4JL - T \ln(2L). \quad (\text{VIII.33})$$

Clearly domain walls are very costly in two dimensions and they are not spontaneously created. In higher dimensions the energy cost scales as  $L^{d-1}$  so they are even more suppressed.

In two and higher dimensions there is another type of point defects (see Fig. 7). The energy cost of these defects is lower  $4Jd$  while the entropy gain for a single defect is  $d \ln(L)$ . So the free energy change due to creating a point defect is

$$\delta F = 4Jd - dT \ln(L). \quad (\text{VIII.34})$$

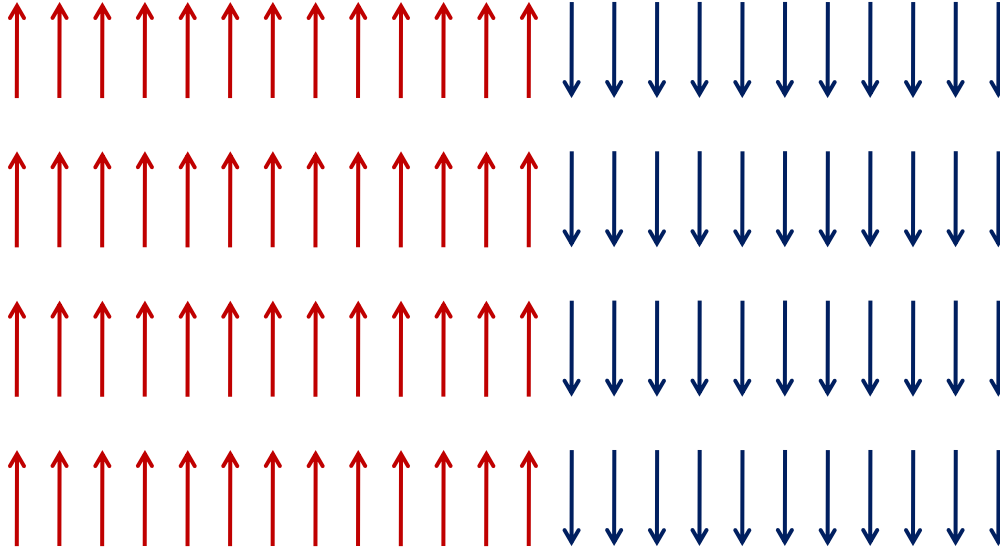


FIG. 6 Domain walls in two-dimensional Ising model.

we see that for  $L > \xi = \exp[4J/T]$ . These defects start to enter the system as soon as its size exceeds the characteristic length  $\xi$ . It is easy to check by the same argument as in 1D that at low temperatures the equilibrium density of these point defects is  $1/\xi^d$ . It is also easy to see that other clusters where spins join into small clusters are not important at low temperatures because they have higher energy cost (more neighbors) but essentially the same entropy gain as a single cluster.

The crucial difference between point defects and domain walls is that point defects do not destroy long range order and thus do not destroy spontaneous symmetry breaking. Indeed the average magnetization per spin is clearly

$$m \approx 1 - n \approx 1 - \frac{C}{\xi^d}, \quad (\text{VIII.35})$$

where  $C$  is a coefficient of the order of one. As long as  $\xi \gg 1$  the magnetization remains non-zero. So we see that in two and higher dimensions the mean-field phase diagram is qualitatively correct. It turns out that in two and three dimensions the mean-field approximation still does not describe correctly the behavior of the system near the critical temperature and only in four dimensions and above all qualitative (universal) predictions of the mean-field theory become accurate. Let us also point that the mean-field assumption always overestimates the ordering temperature, fluctuations

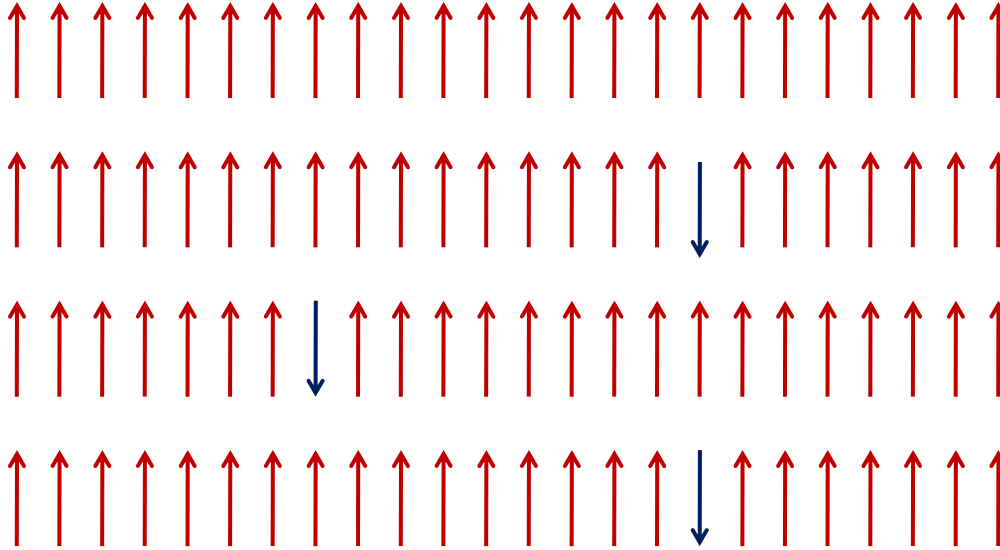


FIG. 7 Point defects in two-dimensional Ising model.

beyond mean-field tend to destroy long range order. This difference between the mean-field transition temperature and true transition temperature also tends to decrease with the dimensionality. E.g. in 2D  $T_c^{\text{mf}} = 4J$  while  $T_c \approx 2.27J$ . In 3D  $T_c^{\text{mf}} = 6J$ , while  $T_c \approx 4.51J$ .

Let us finally point that it is high dimensionality, not coordination number, is important for validity of the predictions of the mean-field theory. Indeed let us consider the system plotted in Fig. 6 where now there are exactly four coupled spin chains. If we assume periodic boundary conditions then clearly this system has the same coordination number as in a fully two-dimensional situation. So the free energy costs of creating the point defect is the same in both situations (as long as number of spins is the same). However, the energy cost of creating a domain wall now does not scale with  $L$ , it is rather  $8J$ . So we see that when  $L > \exp[8J/T]$  the domain walls are spontaneously created and destroy long range order. However, note that as the number of chains in the system increases the corresponding length scale where domain walls become important becomes exponentially bigger than the length scale for creating isolated defects. Thus at low temperatures such domains walls are important only for extremely long systems, which can be irrelevant for experimental setups.

### E. Systems with continuous symmetry. Mermin-Wagner theorem.

The scenario that in low dimensions fluctuations can destroy long-range correlations is very general. It is generally related to enhanced entropic contribution of the defects to the free energy compared with the energy cost and to the lower energy cost of creating topological excitations like domain walls. However, the discrete symmetry like spin inversion in the Ising model, is not very common in nature. In most situations it is continuous symmetry, which is broken. E.g. in solids it is translational symmetry, in ferromagnets - it is spin rotational symmetry, in superfluids it is a continuous gauge symmetry. To get some intuition into the systems with continuously broken symmetries let us consider a simple generalization of the Ising model, which is called  $O(2)$  rotor model or XY-model. This model represents a  $d$ -dimensional array of spins which are now

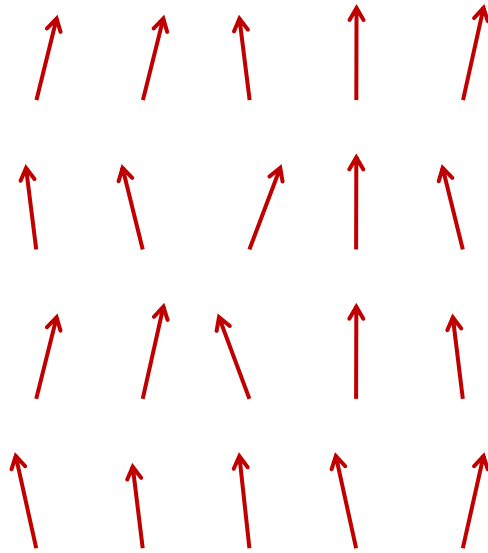


FIG. 8 Two-dimensional XY model.

represented by arrows of unit length confined to a plane (see Fig. 8). The name *XY*-model comes from the fact that the spins can not point to third the  $z$ -direction. Despite this model is very simple it will correctly explain qualitative features of generic systems with continuously broken symmetry.

The Hamiltonian for this system is

$$\mathcal{H}_{XY} = -J \sum_{\langle \mathbf{ij} \rangle} \vec{n}_{\mathbf{i}} \vec{n}_{\mathbf{j}} = -J \sum_{\langle \mathbf{ij} \rangle} \cos(\theta_{\mathbf{i}} - \theta_{\mathbf{j}}), \quad (\text{VIII.36})$$

where  $J$  is the coupling constant (positive  $J$  favors ferromagnetic state),  $\langle \mathbf{ij} \rangle$  denote nearest neighbors on a  $d$ -dimensional square lattice (we use bold notations to highlight that the site indices are  $d$ -dimensional vectors),  $\vec{n}_{\mathbf{i}}$  are the unit vectors representing the spins, and  $\theta_{\mathbf{i}}$  are the angles describing the direction of the spin  $\mathbf{i}$  with respect to the  $x$ -axis. It is easy to check (see homework) that the the mean-field or variational treatment of this model predicts paramagnetic to ferromagnetic transition for this model at  $T_c = dJ$  (a factor of two smaller than in the Ising case). It is also straightforward to check from the high-temperature expansion that the paramagnetic phase is stable at high temperatures, as in the Ising case the Curie magnetic susceptibility acquires small corrections of the order of  $J/T$  due to interactions. What we need to check is the stability of the low-energy phase. To do this we assume the the symmetry is broken and analyze whether the small fluctuations destroy the long-range order. To be specific we write that  $\theta_{\mathbf{i}} = \theta_0 + \delta\theta_{\mathbf{i}}$  and assume that  $\delta\theta_{\mathbf{i}}$  is small. Then we check whether this assumption is consistent with the Hamiltonian (VIII.36).

If the fluctuations are small we can clearly use the quadratic expansion for the XY-Hamiltonian:

$$\mathcal{H}_{XY} = -J \sum_{\langle \mathbf{ij} \rangle} \cos(\theta_{\mathbf{i}} - \theta_{\mathbf{j}}) \approx \frac{J}{2} \sum_{\langle \mathbf{ij} \rangle} (\theta_{\mathbf{i}} - \theta_{\mathbf{j}})^2. \quad (\text{VIII.37})$$

Note that this approximation does not actually require the long range order. It only relies on the assumption of small changes of the spin-direction from cite to cite. This is always the case at low-temperatures since large gradients are very costly. It is convenient to make the Fourier transformation of  $\theta_i$ :

$$\theta_j = \frac{1}{\sqrt{L^d}} \sum_{\mathbf{k}} \theta_{\mathbf{k}} \exp[i\mathbf{k}\mathbf{j}] \quad (\text{VIII.38})$$

Then it is easy to see that the Hamiltonian in the quadratic approximation becomes

$$\mathcal{H} \approx -J \sum_{\mathbf{k}} \sum_{\mathbf{a}} \theta_{\mathbf{k}}^* \theta_{\mathbf{k}} (1 - \cos(\mathbf{ka})), \quad (\text{VIII.39})$$

where  $\mathbf{a}$  denotes the vectors connecting the nearest neighbors. E.g. in two-dimensional system with unit lattice spacing  $\mathbf{a} = \{(1,0); (0,1)\}$ . At small temperatures we can anticipate that only low-energy quadratic modes are important so we can further simplify the Hamiltonian

$$\mathcal{H} \approx Jd \sum_{\mathbf{k}} \theta_{\mathbf{k}}^* \theta_{\mathbf{k}} k^2 \quad (\text{VIII.40})$$

The latter form of the Hamiltonian is a very generic description of the low-energy sector in systems with a continuously broken symmetry. The corresponding modes are the static part of the so called Goldstone modes. They are gapless because at zero momentum one can freely change the order parameter without any energy cost (the continuous symmetry can be broken in any direction). Thus one can expect that there should be a very small energy cost if we create an excitation with the order parameter very slowly changing in space. By symmetry the lowest allowed term should be proportional to the square of the momentum (gradient). These Goldstone bosons are very familiar to us - these are phonons in solids, Bogoliubov excitations in superfluids, spin-waves in ferromagnets (like in our case).

The Hamiltonian (VIII.40) represents the sum of potential energies of independent harmonic oscillators. From the equipartition theorem we know that

$$Jd\langle k^2\theta_{\mathbf{k}}^*\theta_{\mathbf{k}}\rangle = T/2 \quad (\text{VIII.41})$$

therefore

$$\langle\theta_{\mathbf{k}}^*\theta_{\mathbf{k}}\rangle = \frac{T}{2Jdk^2}. \quad (\text{VIII.42})$$

Now we can check whether the assumption of broken symmetry is consistent with the small temperature fluctuations. For this purpose we need to compute the fluctuations of  $\delta\theta_{\mathbf{i}}$  and check that they remain finite at small temperatures:

$$\langle\delta\theta_{\mathbf{i}}^2\rangle = \frac{1}{L^d} \sum_{\mathbf{k}} \langle\delta\theta_{\mathbf{k}}^*\delta\theta_{\mathbf{k}}\rangle = \frac{T}{2Jd} \frac{1}{L^d} \sum_{\mathbf{k}} \frac{1}{k^2} \quad (\text{VIII.43})$$

Let us analyze how this sum behaves in various dimensions.

First let us analyze the one dimensional case. Note that  $k = 2\pi n/L$  with  $n = -L/2, -L/2 + 1, \dots, L/2$ . From this we see that

$$\langle\delta\theta_{\mathbf{i}}^2\rangle \approx \frac{TL}{2J} \sum_{n=-L/2, \dots, L/2} \frac{1}{n^2} \sim L\frac{T}{J} \quad (\text{VIII.44})$$

We clearly see that the assumption of broken symmetry is violated for  $L \gtrsim J/T$ . Thus in one-dimensional systems the fluctuations destroy long-range order even stronger than in the Ising model (the characteristic length scale is inversely proportional to temperature versus the exponential dependence on  $1/T$  in the Ising case).

Next let us analyze the fluctuations in two dimensions

$$\langle\delta\theta_{\mathbf{i}}^2\rangle = \frac{T}{4J} \sum_{n_x, n_y} \frac{1}{(n_x^2 + n_y^2)}, \quad (\text{VIII.45})$$

where  $n_x$  and  $n_y$  change in the interval  $-L/2, \dots, L/2$ . This sum clearly diverges if  $L \rightarrow \infty$ . To estimate this sum we approximate it by the integral

$$\sum_{n_x, n_y} \frac{1}{(n_x^2 + n_y^2)} \approx 2\pi \int_0^L \frac{ndn}{n^2} \approx 2\pi \ln L. \quad (\text{VIII.46})$$

Thus we see that

$$\langle \delta\theta_{\mathbf{i}}^2 \rangle = \frac{T\pi}{2J} \ln(L). \quad (\text{VIII.47})$$

We see that now even in two-dimensions the long-range order is destroyed by the fluctuations for large system sizes:  $L \gtrsim \xi = \exp[2J/\pi T]$ .

These two observations are the basis of the so called Mermin-Wagner theorem (also known as Mermin-Wagner-Hohenberg theorem or the Coleman theorem), which states that continuous symmetries cannot be spontaneously broken at finite temperatures in one and two dimensional theories with local interactions.

Finally in three and higher dimensions we can observe that the sums over momenta are dominated by high values of  $k$ . Then the summation over momenta in Eq. (VIII.43) can be substituted by the integration and thus

$$\langle \delta\theta_{\mathbf{i}}^2 \rangle \sim \frac{T\Omega_d}{2Jd} \int_0^1 \frac{n^{d-1}dn}{n^2} \sim \frac{T}{J}. \quad (\text{VIII.48})$$

So we see that the fluctuations of the angle  $\theta$  in three dimensions and above remain finite and the broken symmetry state survives small temperature fluctuations.

## F. Problems for Sec. VIII

1. Consider the  $d$ -dimensional XY model analyzed in Sec. VIII.E.

- Using high-temperature expansion calculate the lowest correction to the magnetic susceptibility in the system in  $J/T$ . Compare your answer with the Ising system.
- Calculate the mean-field phase diagram of the XY-model. (Hint you can assume that the effective magnetic field points along the  $x$ -direction).
- Using the variational ansatz similar to the Ising case calculate the trial free energy of the XY-model at finite temperature. By minimizing the free energy with respect to the variational parameter (magnetic field) determine the phase diagram and compare it with the mean field result. Prove which phases are stable within the mean field approximation.

- Solving the mean field (variational) equations analyze the scaling of the spontaneous magnetization with  $T - T_c$  when the temperature  $T$  is slightly below the critical temperature  $T_c$ .

## IX. NONINTERACTING QUANTUM SYSTEMS

Let us first compute the grand canonical partition function for a single degree of freedom:

$$\mathcal{Z}_k = \sum_{N_k=0}^{N_{max}} e^{-(\epsilon_k - \mu)\beta} \quad (\text{IX.1})$$

the upper limit of the sum really depends on whether our particles are fermions or bosons. For bosons the sum stretches to infinity, and we get:

$$\mathcal{Z}_k^B = \sum_{N_k=0}^{\infty} e^{-(\epsilon_k - \mu)\beta} = \frac{1}{1 - e^{-(\epsilon_k - \mu)\beta}} \quad (\text{IX.2})$$

For fermions we have to sum only up to 1, since there could be at most one particle in the same quantum state:

$$\mathcal{Z}_k^F = \sum_{N_k=0}^1 e^{-(\epsilon_k - \mu)\beta} = 1 + e^{-(\epsilon_k - \mu)\beta}. \quad (\text{IX.3})$$

For many particles we have to take the double sum over all states and all occupations of the states. Note that we are not summing over different permutations each quantum state is counted once. Therefore all many-body states (which span the Hilbert space) can be characterized by the occupation numbers of different single-particle states.

$$\Omega = -T \ln Z = \sum_k \Omega_k, \quad (\text{IX.4})$$

where  $\Omega_k = -T \ln(1 + \exp[-\beta(\epsilon_k - \mu)])$  for fermions and  $\Omega_k = T \ln(1 - \exp[-\beta(\epsilon_k - \mu)])$  for bosons.

From the thermodynamic potential  $\Omega$  we can find energy:

$$\mathcal{E} - \mu N = -\frac{\partial \ln Z}{\partial \beta} = \sum_k (\epsilon_k - \mu) n_k, \quad (\text{IX.5})$$

where

$$n_k = \frac{1}{\exp[\beta(\epsilon_k - \mu)] \pm 1} \quad (\text{IX.6})$$

is the distribution function of fermions “+” sign or bosons “-” sign. We can also find a similar expression for the average number of particles

$$N = \frac{\partial \Omega}{\partial \mu} = \sum_k n_k. \quad (\text{IX.7})$$

Therefore  $E = \sum_k \epsilon_k n_k$  and we thus associate  $n_k$  with the average occupation of the mode with momentum  $k$ . The two distributions given by (IX.6) are called Fermi-Dirac and Bose-Einstein respectively. From Eq. (IX.7) we see that  $\mu \leq 0$ , where 0 is the minimal possible energy. If the bosons are interacting this is no longer true. The classical Boltzmann's statistic is obtained when  $n_k \ll 1$  which means that the argument of the exponent is large and positive (large negative chemical potential). Then both for fermions and bosons we have

$$n_k \approx \exp[-\beta(\epsilon_k - \mu)]. \quad (\text{IX.8})$$

For bosons there is also another classical limit corresponding to classical waves. To be specific consider a single oscillator with the Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + \frac{m\omega^2}{2}q^2 \quad (\text{IX.9})$$

Then the classical partition function

$$Z_{vib} = \int \frac{dpdq}{2\pi\hbar} \exp[-\beta\mathcal{H}] = \frac{T}{\hbar\omega}. \quad (\text{IX.10})$$

This partition function gives e.g. equipartitioning of different energies: average energy per each degree of freedom is the same. The quantum partition function is

$$Z_{vib}^q = \frac{\exp[-\beta\hbar\omega/2]}{1 - \exp[-\beta\hbar\omega]} \quad (\text{IX.11})$$

In the limit  $\beta\hbar\omega \ll 1$  this function becomes identical to the classical one. So now the classical wave (vibrational) limit corresponds to large mode occupancy. The same is true if we have many modes. If the occupancy per mode is large we can treat these modes as classical waves. If the occupancy per mode is small we treat them as particles. We will be more specific later when we discuss superfluidity.

### A. Noninteracting Fermions

Let us now focus on noninteracting fermions. It turns out that despite Coulomb interactions the free fermion model is very adequate for describing metals. First let us analyze the zero temperature limit What does the distribution function look like at zero temperature? Assuming that our energy spectrum stretches from zero up, (which we can always do by setting the lowest energy eigenvalue in the problem to zero), if  $\mu < 0$  then:

$$f(\epsilon_k) = \frac{1}{e^{(\epsilon_k - \mu)/T} + 1} \rightarrow 0 \quad (\text{IX.12})$$

since the exponent is large. For positive  $\mu$  it becomes:

$$f(\epsilon_k) = \frac{1}{e^{(\epsilon_k - \mu)/T} + 1} = \begin{cases} 1 & \epsilon_k < \mu \\ 0 & \epsilon_k > \mu \end{cases} \quad (\text{IX.13})$$

It is a step like function. Only states below the chemical potential are occupied, we call the chemical potential in this case - the Fermi energy. Let's calculate it requiring that the total number of fermions is  $N$ . In the case of a spherically-symmetric dispersion, we can write the k-integral very simply:

$$n = (2s + 1) \int_0^{k_F} \frac{d^d k}{(2\pi)^d} = (2s + 1) \int_0^{E_F} \rho(\epsilon) d\epsilon = (2s + 1) \frac{\Omega_d k_F^d}{(2\pi)^d}, \quad (\text{IX.14})$$

where we included the factor of  $2s + 1$  to take into account spin degeneracy,  $\rho(\epsilon)$  is the single particle density of states:

$$\rho(\epsilon) = \int \frac{d^d k}{(2\pi)^d} \delta(\epsilon - \epsilon_k) = \Omega_d \left( \frac{\sqrt{2m}}{2\pi\hbar} \right)^d \epsilon^{d/2-1} \quad (\text{IX.15})$$

and  $\Omega_d$  is the volume of a  $d$ -dimensional unit sphere. Sometimes the spin factor  $2s + 1$  is included in  $\rho$ . In two dimensions we have

$$n = \frac{(2s + 1)}{4\pi} k_F^2 \quad (\text{IX.16})$$

We can of course write this in terms of energy:

$$n = \frac{(2s + 1)}{4\pi} \frac{2mE_F}{\hbar^2} \quad (\text{IX.17})$$

This defines the Fermi energy through density. Note that up to a factor of  $\pi$  and the spin-related degeneracy, the Fermi wave vector,  $k_F$ , is just the inverse inter-particle distance (by the Pauli principle). In a metal, usually there is just one particle per atom. The distance between atoms is of the order of  $5\text{\AA}$ . What is the Fermi energy? In three dimensions instead of Eq. (IX.16) we find

$$n = \frac{1}{(2\pi)^3} \frac{4\pi}{3} k_F^3 \cdot 2 \approx \frac{1}{3\pi^2} k_F^3 \quad (\text{IX.18})$$

The final result is then:

$$k_F \approx \pi \frac{1}{a} = \frac{\pi}{5 \cdot 10^{-10} \text{m}} \text{m}^{-1} \quad (\text{IX.19})$$

This defines the energy:

$$E_F = \frac{\hbar^2 \pi^2}{2 \cdot 10^{-30} \text{kg} (5 \cdot 10^{-10} \text{m})^2} \approx 2 \cdot 10^{-19} \text{J} \approx 1.25 \text{eV} \approx 1.5 \cdot 10^4 \text{K}. \quad (\text{IX.20})$$

Indeed the fermi energy of most metals is very high, and is of the order of between  $10^4$  and  $10^5$  K. A more amazing number is the fermi velocity:

$$v_F = \frac{\hbar k_F}{m} = \frac{\pi \hbar}{ma} \approx 10^6 m/s \quad (\text{IX.21})$$

Quite fast for something that is actually at zero temperature!

Let us next compute pressure:

$$-PV = \Omega(T, \mu, V) = -T(2s+1) \sum_{\vec{k}} \ln(\mathcal{Z}_k) = -V(2s+1) \int \frac{d^d k}{(2\pi)^d} \ln\left(1 + e^{-(\epsilon_k - \mu)\beta}\right) \quad (\text{IX.22})$$

At very small temperatures the integrand in the expression above is 0 for  $\epsilon_k > \mu = E_F$  and is dominated by the exponent in the opposite case so we find that in three dimensions

$$P \approx (2s+1) \int_{\epsilon_k < E_f} \frac{d^3 k}{(2\pi)^3} (E_f - \epsilon_k) \approx \frac{2}{5} n E_f. \quad (\text{IX.23})$$

To find this result we used that

$$n = (2s+1) \int \int_{\epsilon_k < E_f} \frac{d^3 k}{(2\pi)^3} \quad (\text{IX.24})$$

Another useful property of the ideal Fermi gas is the isothermal compressibility:

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N} = \frac{1}{n} \left( \frac{\partial n}{\partial P} \right)_{T,N} = \frac{1}{n} \left( \frac{\partial n}{\partial \mu} \right)_T \left( \frac{\partial \mu}{\partial P} \right)_T. \quad (\text{IX.25})$$

Recall that  $SdT + Nd\mu = VdP$  therefore

$$\kappa = \frac{1}{n^2} \left( \frac{\partial n}{\partial \mu} \right)_T. \quad (\text{IX.26})$$

At zero temperature the compressibility is equal to

$$\kappa(T=0) = \frac{1}{n^2} \rho_0(E_f) = \frac{3}{2nE_f} = \frac{3}{5} \frac{1}{P}. \quad (\text{IX.27})$$

It is very hard to compress fermions at high densities.

We can relate compressibility also to number fluctuations. Recall that (see Eq. (V.35))

$$\left. \frac{\partial n}{\partial \mu} \right|_T = \frac{1}{TV} (\langle N^2 \rangle - \langle N \rangle^2) \Rightarrow \kappa = \frac{1}{Tn} \frac{\delta N^2}{N} \quad (\text{IX.28})$$

For the ideal Fermi gas we have

$$\delta N^2 = \sum_k f(\epsilon_k) - f^2(\epsilon_k) \quad (\text{IX.29})$$

Clearly the fluctuations come only from energies close to  $E_f$  because if  $f(\epsilon_k) = 0$  and  $f(\epsilon_k) = 1$  we have  $f - f^2 \approx 0$ . Another important quantity is the entropy:

$$S = -\left. \frac{\partial \Omega}{\partial T} \right|_{\mu, V} \quad (\text{IX.30})$$

Using the explicit form of the thermodynamic potential we can find

$$\begin{aligned} S &= V \int d\epsilon \rho_0(\epsilon) [\ln(1 + \exp[-\beta(\epsilon - \mu)]) + \beta(\epsilon - \mu)f(\epsilon - \mu)] \\ &= -V \int d\epsilon \rho_0(\epsilon) [f(\epsilon) \ln(f(\epsilon)) + (1 - f(\epsilon)) \ln(1 - f(\epsilon))]. \end{aligned} \quad (\text{IX.31})$$

One can recognize that this is indeed the usual von-Neumann entropy where  $f(\epsilon)$  serves as the probability that the state is occupied and  $1 - f(\epsilon)$  corresponds the probability of having the empty state. It is clear that at small temperatures, where  $f(\epsilon)$  is like a step function the entropy is very close to zero. The only nonzero contribution comes from  $\epsilon \approx \mu$  where  $f(\epsilon) \approx 1/2$ . So we can estimate entropy at small temperatures as  $S \approx VT\rho_0(E_F)$  so at small temperatures the entropy of free fermions linearly vanishes with temperature (recall that for Boltzmann gas (VI.22) the entropy was decreasing logarithmically with temperature without bound).

Specific heat:

$$c_v = \left. \frac{T}{V} \frac{\partial S}{\partial T} \right|_V = \left. \frac{\partial E}{\partial T} \right|_V = - \int d\epsilon \rho_0(\epsilon) (\epsilon - \mu)^2 \frac{\partial f(\epsilon)}{\partial \epsilon}. \quad (\text{IX.32})$$

The specific heat is also determined by energies close to  $\mu$ . It vanishes in the zero-temperature limit.

*Sommerfeld expansion.* Suppose now we want to analyze our thermodynamic functions at small but finite temperature. We need to be able to evaluate integrals like

$$I = - \int_0^\infty d\epsilon G(\epsilon) \frac{\partial f(\epsilon)}{\partial \epsilon}. \quad (\text{IX.33})$$

There is a general way to do this using Sommerfeld expansion. Note that if we have a low temperature  $T \ll E_F$  then the Fermi-Dirac distribution is 1 or 0 outside a region  $|E - \mu| \lesssim 2T$  so that the derivative of the Fermi function is essentially zero. If the temperature is small compared to  $E_f$  then this region is very narrow. Note that in metals where  $E_f \sim 10^4 K$  room temperatures satisfy this criterion  $T \ll E_f$ . So it makes sense to expand various smooth quantities into Taylor series around  $E = \mu$ :

$$G(\epsilon) \approx G(\mu) + G'(\mu)(\epsilon - \mu) + \dots \quad (\text{IX.34})$$

With the exponential accuracy in  $E_F/T$  the integral over  $\epsilon$  can be extended to  $-\infty$ . Then it is easy to see that

$$I(T) \approx \sum_{n \geq 0} b_n T^n \left. \frac{\partial G^n}{\partial \epsilon^n} \right|_{\epsilon=\mu}, \quad (\text{IX.35})$$

where

$$b_n = -\frac{1}{n!} \int_{-\infty}^{\infty} dx x^n \frac{\partial f(x)}{\partial x}. \quad (\text{IX.36})$$

The integrals above are tabulated:

$$b_0 = 1, \quad b_2 = \frac{\pi^2}{6}, \quad b_4 = \frac{7\pi^4}{360}. \quad (\text{IX.37})$$

As an example of using the Sommerfeld expansion let us compute energy (per unit volume) as a function of temperature and from this heat capacity and entropy:

$$E = \int d\epsilon \rho(\epsilon) \epsilon f(\epsilon) \quad (\text{IX.38})$$

Let us integrate by parts. Introduce the notation

$$G(\epsilon) = \int_0^{\epsilon} \epsilon' \rho(\epsilon') d\epsilon' \quad (\text{IX.39})$$

Then

$$E = G(\epsilon) f(\epsilon) \Big|_0^{\infty} - \int_0^{\infty} d\epsilon G(\epsilon) \frac{\partial f}{\partial \epsilon} \quad (\text{IX.40})$$

The first term is clearly zero and the second is of precisely the form (IX.33). So we find

$$E \approx G(\mu) + \frac{\pi^2}{6} T^2 \left. \frac{d^2 G}{d\epsilon^2} \right|_{\mu} = \int_0^{\mu} \epsilon \rho(\epsilon) d\epsilon + \frac{\pi^2}{6} T^2 (\rho(\mu) + \mu \rho'(\mu)) \quad (\text{IX.41})$$

Note that the second term is of the order  $T^2$  so there we can safely substitute  $\mu$  by  $E_F$ . In the first term we can not do it because  $\mu$  itself also acquires corrections of the order of  $T^2$ . Indeed

$$n = \int d\epsilon \rho(\epsilon) f(\epsilon) \approx \int_0^{\mu} \rho(\epsilon) d\epsilon + \frac{\pi^2}{6} T^2 \rho'(\mu) \quad (\text{IX.42})$$

But  $n$  is independent of temperature (we want to find energy vs. temperature at fixed  $N$  and  $V$ ).

Note that  $\int_0^{E_F} \rho(\epsilon) d\epsilon = n$  and writing  $\mu = E_f + \delta\mu$  we find

$$n \approx n + \rho(E_F) \delta\mu + \frac{\pi^2}{6} T^2 \rho'(E_F). \quad (\text{IX.43})$$

Therefore up to  $T^2$  we have

$$\delta\mu \approx -\frac{\pi^2}{6} T^2 \frac{\rho'(E_F)}{\rho(E_F)} \quad (\text{IX.44})$$

Note that if the density of states increases with  $E$  then the correction to the chemical potential is negative. This is so because if we keep chemical potential constant, by broadening Fermi function, we would populate more higher energy states than deplete lower energy states. Now we can find energy (per unit volume)

$$E \approx E_F + \delta\mu E_F \rho(E_F) + \frac{\pi^2}{6} T^2 (\rho(E_F) + E_F \rho'(E_F)) \approx E_F + \frac{\pi^2}{6} T^2 \rho(E_F) \quad (\text{IX.45})$$

Thus the heat capacity is

$$c_v = \left. \frac{\partial E}{\partial T} \right|_{V,N} \approx \frac{\pi^2}{3} T \rho(E_F) = \frac{\pi^2}{2} n \frac{T}{E_F}, \quad (\text{IX.46})$$

where the last equality is true for the free fermions in three dimensions. This is in accord with our previous estimates. Note that

$$c_v = T \frac{\partial S}{\partial T}. \quad (\text{IX.47})$$

Because  $c_v$  is linear in  $T$  we find that at low temperatures  $S \approx c_v$ .

## B. Noninteracting electrons in magnetic field.

### 1. Pauli Susceptibility of an electron gas

There are two effects of the magnetic field on electrons: orbital - vector potential couples to the momentum via the term  $(\mathbf{p} - e/c\mathbf{A})^2/2m$  and to the spin via the term

$$\hat{\mathcal{H}}_{spin} = -g\mu_B \vec{h} \cdot \hat{\vec{\sigma}} = -g\mu_B h \sigma_z, \quad (\text{IX.48})$$

where we chose the spin-quantization axis along the magnetic field. Now, spin up has less energy than spin down. The chemical potential of the electron gas is still the same for the two spins, but this implies that the fermi energy - which here we distinguish from the chemical potential by saying that it is the *kinetic* energy up to which electron states are filled - is not the same for the two electron flavors.

For down electrons, the total energy is:

$$E_{\downarrow} = \epsilon_k + hg\mu_B \quad (\text{IX.49})$$

while

$$E_{\uparrow} = \epsilon_k - hg\mu_B \quad (\text{IX.50})$$

Now we need to find the chemical potential at which the up and down systems are at equilibrium. Formally we can do this by requiring that

$$n = \int_0^\infty \rho(\epsilon) \frac{1}{\exp[\beta(\epsilon + g\mu_B h - \mu)] + 1} + \int_0^\infty \rho(\epsilon) \frac{1}{\exp[\beta(\epsilon - g\mu_B h - \mu)] + 1} \quad (\text{IX.51})$$

Here  $\rho(\epsilon)$  is the density of states for spinless particles (i.e. not multiplied by  $2s + 1 = 2$ ). Note that at zero temperature and small magnetic fields the density of states can be treated as a constant so

$$n \approx \rho(E_F)(\mu - g\mu_B h + \mu + g\mu_B h) = 2\mu\rho(E_F). \quad (\text{IX.52})$$

Therefore there is no correction to the chemical potential in the linear order in  $h$  therefore  $\mu \approx E_F$ . This means  $E_{F\uparrow} \approx E_F + g\mu_B h$  and  $E_{F\downarrow} \approx E_F - g\mu_B h$ . This relations can be understood also in the following way. Since the energy shift for up is minus that of down, some electrons from the high-energy down spins, would flip to point in the direction of the magnetic field. This will happen until we have

$$E_{F\uparrow} - E_{F\downarrow} = 2hg\mu_B \quad (\text{IX.53})$$

After that it is already energetically unfavorable to flip flop electrons.

So we have an excess of upspins, and we can easily calculate how many:

$$n_\uparrow - n_\downarrow = \int_{\mu - hg\mu_B}^{\mu + hg\mu_B} \rho(\epsilon) d\epsilon = 2\rho(E_F)hg\mu_B \quad (\text{IX.54})$$

and the excess spin magnetization is:

$$g\mu_B(n_\uparrow - n_\downarrow) = 2\rho(E_F)h(g\mu_B)^2 \quad (\text{IX.55})$$

So the susceptibility per unit volume is:

$$\chi_{Pauli} = 2\rho(E_F)(g\mu_B)^2 = 3n \frac{(g\mu_B)^2}{E_F}. \quad (\text{IX.56})$$

This susceptibility is a direct measure of the density of states at the Fermi surface. Free electron spins tend to point in the direction of the field, but don't actually have magnetization at zero field. Hence this is called **paramagnetism**.

Now, in addition to this effect there is also going to be an orbital effect on the general magnetization, and the question rises - how do we measure the Pauli susceptibility alone? This is done using the Knight shift - The energy level of nuclear spins are coupled to the electronic spins

through the contact term of the hyper-fine hamiltonian of an atom. This coupling is much stronger than the coupling of nuclei to a raw magnetic field (since their Bohr magneton is three orders of magnitude smaller than that of the electron's). Using NMR one can get very accurate readings of nuclear energy levels, and there one see's precisely this quantity.

## 2. Orbital effects of a magnetic field - Shubnikov-De-Haas-van Alpen oscillations and Landau diamagnetism

Note that classically there is no diamagnetism. The partition function of free classical electron gas is

$$Z = \frac{1}{N!} \left[ \int \frac{d\mathbf{p}d\mathbf{q}}{(2\pi\hbar)^3} \exp[-\beta(\mathbf{p} - e/c\mathbf{A})^2/2m] \right]. \quad (\text{IX.57})$$

The vector potential or the magnetic field can be removed by a simple change of variables  $\mathbf{p} \rightarrow \mathbf{p} + e/c\mathbf{A}$ . However, quantum mechanically the situation is quite different. Quantum mechanically we can introduce a new energy scale  $\hbar\omega_c$ , where

$$\omega_c = \frac{eB}{mc} \quad (\text{IX.58})$$

is the cyclotron frequency, which is the frequency of rotation of a classical particle in a magnetic field (recall  $m\omega^2 R = e/c\omega RB$  so that  $\omega = eB/(mc)$ ). In SI units there is no  $c$  in denominator. Since the energies must be quantized into multiples of that frequency we expect that at least at small temperatures  $T \ll \hbar\omega_c$  there will be a strong difference between quantum and classical pictures. The discrete energy levels of electrons in magnetic field are called Landau-levels. Like in an Harmonic oscillator, the allowed energy eigenvalues of a particle in a magnetic field are:

$$E_n = \left( \frac{1}{2} + n \right) \hbar\omega_c \quad (\text{IX.59})$$

In two dimensions, instead of having a flat density of states, we suddenly have a comb like shape with spikes at these energies.

We can estimate the degeneracy of each level for each spin  $N_L$  from a simple argument. (Let us do it in 2D for simplicity). The total number of states with and without magnetic field should be the same therefore

$$N_L = A \int_{0 \leq \epsilon_k \leq \hbar\omega_c} \frac{d^2k}{(2\pi)^2} = \frac{A}{2\pi\hbar^2} m\hbar\omega_c = \frac{A}{2\pi\hbar^2} m\hbar \frac{eB}{mc} = \frac{\Phi}{\Phi_0}, \quad (\text{IX.60})$$

where  $\Phi = Ah$  is the total magnetic flux and

$$\Phi_0 = \frac{2\pi\hbar c}{e} \quad (\text{IX.61})$$

is the flux quantum. There is an alternative semiclassical explanation to why the Landau level degeneracy is such. When you let an electron go in a closed orbit, the phase of the wave function (by gauge invariance) acquires the value:

$$\varphi \sim \frac{e}{\hbar} \int d\vec{l} \cdot \vec{A} = 2\pi \frac{\Phi}{\hbar/e} \quad (\text{IX.62})$$

Whenever  $\varphi$  is a multiple of  $2\pi$ , the electron can be at rest. So each electron orbit should encircle at least one flux quantum. The area of each orbit is therefore  $\Phi_0/B$ . So the total number of electrons we can fit to area  $A$  is thus  $N_L = A/(\Phi_0/B) = \Phi/\Phi_0$ .

A magnetic field is like a flux density. The most useful way is to think about it as the field for a given 2d fluxon density:

$$B = \frac{\Phi_0}{b} \quad (\text{IX.63})$$

as it turns out, for each Landau level, there is a density of states which is exactly  $b$  - just as though there is one electronic state for each fluxon. This means that the density of states function for an electron gas in 2d is (ignoring spin) :

$$\rho(\epsilon) = \sum_{n=0}^{\infty} \delta\left(\epsilon - \left(\frac{1}{2} + n\right) \hbar\omega_c\right) \frac{B}{\Phi_0} \quad (\text{IX.64})$$

The integer quantum Hall effect occurs when the number of electrons fits exactly an integer number of Landau levels. We define the filling factor:

$$\nu = \frac{n}{B/\Phi_0} \quad (\text{IX.65})$$

$\nu$  tells us how many Landau levels are full. The Quantum-Hall effects occur when  $\nu$  hits the magic numbers 1, 2, 3... for integer, and a variety of rational fractions - most notably 1/3, for which Laughlin, Störmer and Tsui won their Nobel prize for.

But those regime of small  $\nu$ , ie, of high field, they are complex, and have a lot of structure, which, unfortunately, lies beyond the scope of this class. We will concentrate on the relatively simple, but nevertheless fascinating phenomena at low fields.

Recall that in the case of the Pauli susceptibility, everything happens near the edge of the Fermi surface. Looking at the 2d electron gas, when we turn on a magnetic field, the electronic states just bunch into delta-functions. All those states that are filled - instead of being a continuum, they are just bunched together. Even if we turn on a spin-field, as in the Pauli susceptibility, the depolarization occurs. It is clear that near the Fermi surface - the thing that really matters once a field is on, is how filled the last Landau level is. This is:

$$\text{mod}(\nu) \quad (\text{IX.66})$$

Every quantity of the system will depend strongly on  $mod(\nu)$ , but only weakly on what  $\nu$  is, or on the magnetic field. Thus, every quantity will undergo an oscillation, whenever  $\nu$  goes through 1. But This means:

$$\nu = \int_{\epsilon_k < E_F} \frac{d^2k}{(2\pi)^2} \frac{\Phi_0}{B} = \frac{1}{2\pi^2} \frac{V_K \Phi_0}{B}, \quad (\text{IX.67})$$

where  $V_K$  is the area of the Fermi surface in the momentum space. Note that in 3D the momentum orthogonal to magnetic field is conserved and thus we this area law for each  $z$ -component of the wave vector. The largest effect to the oscillations will be whenever the density of states is largest, i.e. when the area satisfying  $\nu = \text{integer}$  reaches extremum (maximum or minimum on the Fermi surface). So as a function of  $1/B$  we'll get oscillations in any quantity that are with 'wave-length':

$$\Delta(1/B) = \frac{(2\pi)^2}{V_K \Phi_0} \quad (\text{IX.68})$$

which corresponds to  $1/B$  changes that move  $\nu$  to  $\nu - 1$ . These oscillations are called Shubnikov-De-Haas-Van-Alpen oscillations. This result is remarkable - if you measure the resistance of a metal in a varying field, plot the result with respect to  $1/B$ , we'll see oscillations, which frequency, corresponds to the area enclosed in the fermi surface (note the shape of the Fermi surface may not be necessarily a sphere in real crystals).

There's another thing. Because the dispersion of the electrons changes, so does their energy. In fact it rises:

$$E = E_0 + \frac{1}{2} \chi_L B^2 \quad (\text{IX.69})$$

The extra kinetic energy due to the magnetic field means also that the electrons, in their orbits, produce a magnetization contrary to the external field and try to reduce it. This contribution to the magnetization is called Landau-diamagnetism. In the problem set you'll find:

$$\chi_L = -\frac{1}{3} \chi_{Pauli} \quad (\text{IX.70})$$

in a free electron gas.

A bit of terminology - free spins tend to point at the direction of the external field, but not to reorder ferromagnetically on their own - this is paramagnetism, and it implies a negative magnetic energy. Diamagnetism is the opposite - the magnetic moment tries to reduce the external field - which is diamagnetism. The difference between diamagnetism and AFM is that without a field there isn't any spontaneous canted internal field.

### C. Bose-Einstein statistics

The distribution for bosons is quite different from that of fermions, although the numerical expression is quite similar:

$$n(\epsilon) = \frac{1}{e^{(\epsilon-\mu)\beta} - 1} \quad (\text{IX.71})$$

The big difference comes from the minus sign. It is possible to have a divergence of the distribution. The properties of bosonic gasses are mostly determined by what happens near this divergence.

First consider two very typical bosonic systems. Photons and phonons. and we will derive the black body radiation formulas, and also the Debye theory for heat capacity. Both of these are important examples for the success of quantum mechanics in explaining deviations of experimental measurements from classical results.

#### 1. Black body radiation

The phenomena of black-body radiation requires little introduction. By the end of the nineteenth century, from observing hot metals, as well as stars, it was clear that:

- Hot bodies emit electromagnetic radiation that is unrelated to their spectrum.
- the wavelength corresponding to the maximum intensity of the radiation is inversely proportional to their temperature:

$$\lambda_m T = \text{constant} \quad (\text{IX.72})$$

which was known as Wien's law.

- The total radiation emitted per unit area of a hot body (body hotter than its environment) is given by:

$$I/A = \sigma T^4 \quad (\text{IX.73})$$

where  $\sigma = 5.67 \cdot 10^{-8} \text{W}/(\text{m}^2 \text{K}^4)$ , which is known as Stefan's law.

Let us try to understand this result classically. Like the wave function of a particle in a box, the electromagnetic field has solutions of the Maxwell equations, or the E-M wave equation:

$$\frac{\partial^2 \vec{A}}{\partial t^2} = \nabla^2 \vec{A} \quad (\text{IX.74})$$

which are  $e^{i\vec{k}\cdot\vec{x}}$ . There are two solutions for each  $k$  value - two polarizations  $\vec{n}\cdot\vec{k} = 0$ .

Each value of  $\vec{k}$  was considered to be a harmonic mode, and therefore, just like a spring, each mode, by equipartition theorem gets:

$$\langle \epsilon_k \rangle = T, \quad (\text{IX.75})$$

where  $\epsilon_k$  is the energy associated with each mode (It can be obtained from writing classical energy density  $(\mathbf{E}^2 + \mathbf{B}^2)/8\pi$  in terms of modes in the box. Note these are purely classical considerations.

The dispersion of light as we know:

$$\omega = c|\vec{k}| \quad (\text{IX.76})$$

and therefore the energy in the range  $\omega, \omega + d\omega$  is the number of modes in the spherical shell  $k = \omega/c$  to  $k + dk = (\omega + d\omega)/c$ , times  $T$ :

$$f(T, \omega)d\omega = 2 \cdot \frac{4\pi k^2}{(2\pi)^3} dk T = \frac{1}{\pi^2} T \frac{\omega^2}{c^3} d\omega \quad (\text{IX.77})$$

Now we need to integrate this expression over all modes and get

$$f(T) = \int_0^\infty d\omega \frac{1}{\pi^2} T \frac{\omega^2}{c^3} \rightarrow \infty \quad (\text{IX.78})$$

So there is something wrong in this purely classical formulation. We need to use correct Bose-Einstein distribution which does not give equipartition.

Instead of the equipartition theorem we need to put our better guess. Let's calculate quickly the partition function for a photonic state. A state can have one photon, two photons, etc. Each photon in state  $k$  has energy:

$$\epsilon_k = \hbar\omega_k = \hbar ck. \quad (\text{IX.79})$$

The partition function (ignoring zero point energy) is:

$$Z = 1 + e^{-\epsilon_k\beta} + e^{-2\epsilon_k\beta} \dots = \frac{1}{1 - e^{-\epsilon_k\beta}}. \quad (\text{IX.80})$$

Note that there is no chemical potential. The latter appeared because we needed to work with fixed (or slightly fluctuating number of particles). Alternatively we split the system into two subsystems and introduced chemical potential because we needed to maximize entropy with respect to exchanging particles between the two subsystems. That was the reason that  $\partial S/\partial N_1$  had to be maximized and that derivative we called chemical potential. Here number of photons is not

conserved (like number of quanta in an oscillator) so we automatically sum over all occupancies of all modes without any constraints.

The number of photons in the state, is therefore like the Bose-Einstein distribution, only with  $\mu = 0$ . We differentiate the log with respect to  $\beta$  and obtain:

$$\langle E_k \rangle = -\frac{\partial \ln Z}{\partial \beta} = \epsilon_k \frac{1}{e^{\epsilon_k \beta} - 1} = \epsilon_k n_k, \quad (\text{IX.81})$$

where

$$n_k = \frac{1}{e^{\beta \epsilon_k} - 1}. \quad (\text{IX.82})$$

At this point let us look at this expression. If  $\epsilon_k = \hbar \omega_k$  is much smaller than  $T$ ,

$$\epsilon_k = \hbar \omega_k \ll T, \quad (\text{IX.83})$$

we can expand the exponential in a power series, and get:

$$n_k \approx \frac{T}{\epsilon_k} \quad (\text{IX.84})$$

and therefore an energy:

$$\epsilon_k n_k \approx T, \quad (\text{IX.85})$$

which is indeed the equipartition. But if the energy is much larger than  $T$ :

$$\epsilon_k = \hbar \omega_k \gg T, \quad (\text{IX.86})$$

the exponent in the denominator of the BE distribution will dominant over the 1, and we would have:

$$\epsilon_k n_k \approx \epsilon_k e^{-\epsilon_k \beta} \quad (\text{IX.87})$$

Note that a very similar argument works in other situations. For instance, a diatomic molecule has a rotational degree of freedom and also a vibrational degree of freedom. The first excited state of the rotational degree of freedom is:

$$\frac{L^2}{2I} \sim \frac{\hbar^2}{2md^2} \sim \frac{10^{-68}}{10^{-26}(10^{-10})^2} = 10^{-22} J = 10K \quad (\text{IX.88})$$

So at room temperatures we can forget about quantization of angular momentum and treat them classically (equipartition works). The vibrational degrees of freedom, that have a spectrum very much like that of photons in a  $k$  state, will only get excited therefore when  $T$  is of order of their

energy. The frequency of chemical bonds is such, that they start playing a role at temperatures of the order of thousands of kelvins. So at room temperatures vibrational degrees of freedom are completely frozen and do not contribute to e.g. specific heat.

Using the correct Bose-Einstein distribution we find

$$f(T, \omega)d\omega = 2 \cdot \frac{4\pi k^2}{(2\pi)^3} dk \frac{1}{e^{\epsilon_k \beta} - 1} = \frac{1}{\pi^2} \frac{\omega^2}{c^3} d\omega \frac{\omega \hbar}{e^{\omega \hbar \beta} - 1} \quad (\text{IX.89})$$

This is the Planck formula for the power spectrum of the black body. To get the total energy density we need to integrate over all frequencies:

$$f(T) = \frac{1}{\pi^2} \int_0^{\infty} \frac{\omega^2}{c^3} d\omega \frac{1}{e^{\omega \hbar \beta} - 1} \quad (\text{IX.90})$$

by changing variables we can get all the dependencies outside the integral. The change of variables is dictated by the exponent, and we define

$$x = \omega \beta \hbar \quad (\text{IX.91})$$

we then obtain

$$f(T) = \frac{1}{\pi^2} \int_0^{\infty} \frac{\omega^2}{(\hbar \beta c)^3} d\omega \frac{1}{e^x - 1} \frac{1}{\beta} = \frac{T^4}{\pi^2 \hbar^3 c^3} \int_0^{\infty} dx x^3 \frac{1}{e^x - 1} \quad (\text{IX.92})$$

The integral above can be evaluated exactly:

$$\int_0^{\infty} dx x^3 \frac{1}{e^x - 1} = \frac{\pi^4}{15} \quad (\text{IX.93})$$

so that

$$f(T) = \frac{\pi^2}{15} \frac{T^4}{c^3 \hbar^3}. \quad (\text{IX.94})$$

From this density we still need to get the radiance per unit area. Assume that we have a small hole in a black body. Then the average velocity of outgoing photons is

$$\langle c_{\perp} \rangle = \frac{c}{4\pi} \int_0^{\pi/2} d\theta \int_0^{2\pi} d\phi \sin \theta \cos \theta = \frac{c}{4}. \quad (\text{IX.95})$$

So the average flux of energy per unit area is

$$I = \frac{c}{4} f(T) = \sigma T^4, \quad (\text{IX.96})$$

where

$$\sigma = \frac{\pi^2}{60} \frac{k_B^4}{\hbar^3 c^2} = 5.67 \cdot 10^{-8} \frac{W}{m^2 K^4} \quad (\text{IX.97})$$

We can also compute pressure of the black body radiation:

$$P = -\left.\frac{\partial F}{\partial V}\right|_T, \quad (\text{IX.98})$$

where

$$F = 2TV \int \frac{d^3k}{(2\pi)^3} \left[ \frac{\beta\hbar ck}{2} + \ln(1 - e^{-\beta\hbar ck}) \right], \quad (\text{IX.99})$$

where the factor of 2 comes from two polarizations and the first term comes from the zero point motion:  $\epsilon_k = \hbar\omega_k(n_k + 1/2)$ . The first term leads to a (divergent) constant contribution and the second term can be integrated by parts leading to

$$F = 2V \int \frac{d^3k}{(2\pi)^3} \left[ \frac{\beta\hbar ck}{2} - \frac{1}{\pi^2} \int_0^\infty dk \frac{k^3}{3} \hbar cn_k \right]. \quad (\text{IX.100})$$

The second contribution is just  $-1/3$  of the energy so we find

$$P = P_0 + \frac{1}{3} \frac{E}{V} = P_0 + \frac{1}{3} f \approx 2.5 \cdot 10^{-18} T^4 \text{ Pa}, \quad (\text{IX.101})$$

where  $1/3$  comes from the relativistic dispersion. Note that normal atmospheric pressure is about  $10^5$  Pa. Note that  $P_0$  is actually regularized if we consider pressure difference between inside and outside of the body. This pressure difference leads to Casimir force which was actually observed.

## 2. Debye theory of heat-capacity of solids

Bose-Einstein statistics is closely related to the statistics of waves. Of course electro-magnetic waves are one of the primary examples. Another important example are the phonons or the sound waves in solids and liquids. We will concentrate on solid where phonons are just lattice vibrations or displacement waves. Let's consider a simple example of a chain of masses and springs in 1d. Each mass has the equation of motion:

$$m \frac{\partial^2 x_n}{\partial t^2} = -\kappa(x_{n+1} - x_n) + \kappa(x_n - x_{n-1}) \quad (\text{IX.102})$$

And let us assume periodic boundary conditions - like the particle in the box, this is solved by:

$$x_n = e^{iqna - i\omega t} \quad (\text{IX.103})$$

and the dispersion relation becomes:

$$\omega = \sqrt{\frac{\kappa}{m}(1 - \cos qa)} \quad (\text{IX.104})$$

where  $a$  is the lattice constant, and we use  $q$  as the wave vector.

Now, what is the range of  $q$ ? Note that if we add  $2\pi/a$  to  $q$  then the solution (IX.103) will not change so we can choose the range

$$-\pi < qa < \pi \quad (\text{IX.105})$$

There is another reason of why the domain of  $q$  is bounded. Let us compute the total number of allowed  $q$ . The latter is quantized in units

$$dq = \frac{2\pi}{L} \quad (\text{IX.106})$$

If the modes are restricted to be between  $\pm\pi/a$ , then we have:

$$g = \frac{2\pi/a}{2\pi/L} = \frac{L}{a} = N \quad (\text{IX.107})$$

with  $N$  being the number of particles. That's right! can't have more modes than particles!

Another feature of the dispersion is the low  $q$ , or low  $a$ , behavior. When  $qa$  is small, we can expand the cosine and obtain:

$$\omega = \sqrt{\frac{\kappa}{m}} qa \quad (\text{IX.108})$$

This implies that the force equation can also be approximated by:

$$m \frac{\partial^2 x}{\partial t^2} = a^2 \kappa \frac{\partial^2 x}{\partial r^2} \quad (\text{IX.109})$$

Note that here  $r$  is the physical location of the mass (instead of  $x_n$  we use  $x(r)$  in the continuum language) and  $x$  is its displacement from the equilibrium position. So e.g.  $x$  is always small while  $r$  can be arbitrary number between 0 and  $L$ . We see that at low frequencies, we can approximate lattice vibrations with sound waves.

This equation is easily generalizable to higher dimensional solids:

$$\frac{\partial^2 x}{\partial t^2} = c^2 \nabla^2 x, \quad (\text{IX.110})$$

with  $c$  the speed of sound. In a solid though, there would be three sound modes for every  $k$  - two transverse and one longitudinal. Except for that, sound is just like light!

Another comment before starting to work is that - every mode has its own frequency. therefore each mode is like a quantum harmonic oscillator, with energies:

$$E_n = (n + 1/2)\hbar\omega \quad (\text{IX.111})$$

This can be also understood if we work with momentum and coordinate operators and go to normal modes using the quantum Hamiltonian. The nice thing about hamronic systems is that quantum and classical equations of motion coincide. Now, let's discuss the energy stored in these vibrational modes in a 3d solid. We have the following info to go by:

- Generalizing from the 1-d example: we have a total number of  $3N$  vibrational modes - since we have  $3N$  degrees of freedom.
- At low wave numbers or frequency, the dispersion is linear, and we can approximate the vibrations as sound waves.
- each mode acts like a quantum harmonic oscillator:

$$E_n = (n + 1/2)\hbar\omega \quad (\text{IX.112})$$

$n$  is the number of *phonons* in the state.

Let's start with high temperatures. By high we mean temperature higher than the largest energy of the phonon (corresponding to  $q = \pi/a$  in our case). Let us call this energy scale as Debye temperature:

$$T_D = \alpha\hbar\frac{c}{a} \quad (\text{IX.113})$$

This is an approximation for the highest frequency that a vibrational mode can hold,  $\alpha$  is a numerical coefficient of order 1.

If  $T \gg T_D$ , we can forget about quantum mechanics, and we have equipartition,  $T$  energy in each mode.

$$U = 3NT \quad (\text{IX.114})$$

this is called the *Dulong and Petit law*. This what we would get for light if the spectrum of photons was bounded. The heat capacity at high-T is thus:

$$C_V = 3N \quad (\text{IX.115})$$

At very low temperatures we can use the sound-wave approximation because only small frequency modes corresponding to small  $q$  are populated. Let us assume, for simplicity, that the speed

of sound for all three sound modes is the same,  $c$ , although they are unlikely to be so. If we have three sound modes than, at low  $T$ , the energy density for phonons is just like it is for photons:

$$U/V = 3 \int_0^{\infty} \frac{4\pi\omega^2 d\omega}{(2\pi c)^3} \frac{\hbar\omega}{e^{\hbar\omega\beta} - 1} = \frac{\pi^4}{15} \frac{T^4}{\pi^2 c^3 \hbar^3}, \quad (\text{IX.116})$$

where the prefactor 3 corresponds to three different modes. This expression is very similar to what we got for photons. The heat capacity now is the famous Debye law:

$$C_V = \frac{\pi^4}{5} \frac{T^3}{\pi^2 c^3 \hbar^3} \quad (\text{IX.117})$$

So the heat capacity is constant and high temperatures and rapidly decreases to zero as  $T^3$  at low temperatures. In between we should get some kind of interpolation which is sensitive to the details of the dispersion relations.

### 3. Bose statistics in systems with conserved number of particles. Bose-Einstein condensation.

Recall that the occupation number per mode, according to Bose-Einstein statistics is

$$f_b(\epsilon) = \frac{1}{\exp[\beta(\epsilon - \mu)] - 1} \quad (\text{IX.118})$$

We need to find  $\mu$  by fixing the total density of particles  $n$ :

$$n = \int \frac{d^d q}{(2\pi)^d} \frac{1}{\exp[\beta(\epsilon_q - \mu)] - 1}. \quad (\text{IX.119})$$

At high temperatures we expect  $\mu$  to be large and negative. Indeed if this is so we have

$$n \approx e^{\beta\mu} \int \frac{d^d q}{(2\pi)^d} \exp\left[-\beta \frac{\hbar^2 q^2}{2m}\right] \approx e^{\beta\mu} \left(\frac{m}{2\pi^2 \hbar^2}\right)^{d/2} T^{d/2} \int d^d \xi \exp[-\xi^2] = C_d n e^{\beta\mu} \left(\frac{T}{T_D}\right)^{d/2} \quad (\text{IX.120})$$

So we see that at large temperatures  $T \gg T_D \approx \hbar^2 n^{2/d} / (2m) \sim \frac{\hbar^2}{2ma^2}$ , where  $a$  is the inter-particle distance, up to numerical coefficient

$$e^{-\beta\mu} \sim \left(\frac{T}{T_D}\right)^{d/2} \gg 1. \quad (\text{IX.121})$$

This justifies *a-posteriori* the Boltzmann's distribution in this limit. What happens as  $T$  approaches the degeneracy temperature? Note that  $T_D$  is the same object (up to various factors of  $\pi$ ) as the Fermi energy. This is the scale where de Broglie wavelength associated with the average energy of the particles  $T$  is comparable to inter-particle spacing. This is the regime when particles start to acquire wave-like phenomena, they can not be treated as point objects any more. This is also the regime where statistics bosonic vs. fermionic becomes important.

Obviously as  $T$  decreases chemical potential increases approaching zero. Eventually as  $T \rightarrow 0$  it should reach the asymptotic value, which for bosons must be zero (since contrary to fermions it can not cross it). So we must have

$$n \rightarrow \int \frac{d^d q}{(2\pi)^d} \frac{1}{\exp[\beta\hbar^2 q^2/(2m)] - 1} \quad (\text{IX.122})$$

Note that in  $1D$  and  $2D$  this integral diverges at small  $q$  meaning that we should introduce small negative chemical potential to make it convergent. As temperature goes to zero so does chemical potential as  $T^2$  in  $1D$  and as  $\exp[-1/T]$  in  $2D$ . However in  $3D$  this integral converges. So the chemical potential vanishes at finite temperature such that

$$n \approx \zeta_{3/2} \left( \frac{mT}{(2\pi\hbar)^2} \right)^{3/2}, \quad (\text{IX.123})$$

which defines the temperature of Bose-Einstein condensation:

$$T_c = \frac{(2\pi\hbar)^2}{m} \left( \frac{n}{\zeta_{3/2}} \right)^{2/3}, \quad (\text{IX.124})$$

here  $\zeta_{3/2} \approx 2.612$  is the zeta function:

$$\zeta_m = \frac{1}{\Gamma(m)} \int_0^\infty \frac{dx x^{m-1}}{\exp[x] - 1}. \quad (\text{IX.125})$$

As  $T$  becomes smaller than  $T_c$  we must have  $\mu = 0$  and one state (the ground state) gets macroscopic occupation. Recall that we have to sum over all states (different  $k$ ) rather than integrate over them. The summation is equivalent to integration only if the function  $f_b(\epsilon_k)$  is smooth. If one state is macroscopically occupied this is no longer true.

Below  $T_c$  the Bose gas has unusual properties. The population of excited modes does not depend on the number of particles. So we are essentially dealing with an ensemble where  $N$  is not conserved like phonons or photons. In other words the condensate is like a reservoir of particles out of which we can take particles for free: it does not cost any entropy or energy. The dispersion of this particles is quadratic (not linear) but it is an artifact of non-interacting model. With interactions the dispersion becomes linear. The low energy modes are macroscopically occupied so we can treat them as waves (in quantum mechanics such modes are described by the coherent states where both number and phase can be well defined). The gas pressure for  $T < T_c$  is

$$P = \frac{2}{3} \int \frac{d^3 q}{(2\pi)^3} \frac{\epsilon_q}{\exp[\beta\epsilon_q] - 1} = T \zeta_{5/2} \frac{1}{\lambda_D^3} \propto T^{5/2} \quad (\text{IX.126})$$

is independent on the number of particles. Here  $\lambda_D = \sqrt{2\pi\hbar/mT}$  is the de Broglie wavelength. This means for example that below  $T_c$  pressure is independent of volume (again like in the case of photons). We will discuss relation of Bose-Einstein condensation and superfluidity in the next chapter.

#### D. Problems for Sec. IX

1. Show that Eqs. (IX.28) and (IX.29) reproduce the result (IX.27).
2. Assume that temperature is small compared to  $E_F$  but finite. Find the temperature correction to the magnetization (Eq. (IX.56)) still to the linear order in  $h$ . Argue that this result can be also understood using picture of two fermi gases (up and down) where we start from the unpolarized state and flip electrons until the free energy reaches the minimum.
3. Landau diamagnetism. The electrons are constrained to move in a plane, the electronic states become Landau levels. Using that their energies are  $\epsilon_n = \hbar\omega_c(n + 1/2)$  and the degeneracy of each level is  $AB/\Phi_0$  find the energy increase per area due to magnetic field:

$$\Delta E \approx -\frac{1}{2}\chi_L h^2 \quad (\text{IX.127})$$

(where  $\chi_L$ ) is the Landau diamagnetic susceptibility. In this problem we will calculate it.

(a) What is the energy of the electron gas in a magnetic field  $B$  in terms of its temperature and chemical potential? No need to evaluate the infinite sum yet. Ignore the Zeeman splitting due to the magnetic field. (b) To evaluate the total energy, it is necessary to convert the sum to an integral. Prove the following approximation:

$$\eta \sum_{n=0}^{\infty} f(\eta(n + 1/2)) \approx \int_0^{\infty} f(x)dx - \frac{\eta^2}{24} \int_0^{\infty} f''(x)dx = \int_0^{\infty} f(x)dx + \frac{\eta^2}{24} f'(0) \quad (\text{IX.128})$$

to second order in  $h$ . (c) Using the approximation of 1b, find  $\chi_L$  for a noninteracting electron gas. Assume  $T$  close to zero, but take the limit  $T \rightarrow 0$  only once you obtain an expression for  $\chi_L$ , i.e. consider the order of limits where the magnetic field vanishes first (at finite  $T$ ) and then temperature is set to zero.

#### X. INTERACTING QUANTUM MANY-PARTICLE SYSTEMS.

##### 1. Quick introduction to second quantization

When we work with many-particle systems it is usually not very convenient to deal with a many-body phase space. There is a much more convenient way to relabel many-particle basis using (complete) single-particle basis and distribution of different particles in this basis. So the eigenstates will be labeled by strings like this

$$|2, 0, 1, 3, 0, 0, 0, 1, \dots\rangle \quad (\text{X.1})$$

for bosons and by strings like

$$|1, 0, 1, 1, 0, 0, 1, \dots\rangle \quad (\text{X.2})$$

for fermions. The numbers here indicate that e.g. the first state contains two particles in the single-particle ground state, 0 particles in the first excited state, etc. If there are no interactions, this basis labels eigenstates of the many-particle system. We actually used this basis when we considered ideal quantum gases. However, if the systems are interacting this basis does not describe energy eigenstates. Any Hamiltonian in this basis can be described by matrix elements between different states. It turns out that the second quantized language allows us to write these matrix elements in a very compact form. Let us introduce the creation and annihilation operators denoted as  $a_j^\dagger$  and  $a_j$ , which are responsible for increasing or decreasing number of particles in a given single-particle state. In principle the choice of the matrix elements of this operators with other states is arbitrary. However, it is convenient and conventional to stick to the following rules:

- For bosons we require that creation and annihilation operators corresponding to different single particle states commute with each other. This automatically gives us symmetric wavefunctions. E.g.

$$\psi(1, 3) = |1, 0, 1, 0, \dots\rangle = a_1^\dagger a_3^\dagger |0, 0, 0, 0, \dots\rangle = a_3^\dagger a_1^\dagger |0, 0, 0, 0, \dots\rangle = \psi(3, 1). \quad (\text{X.3})$$

Equivalently we have  $a_1^\dagger a_3^\dagger = a_3^\dagger a_1^\dagger$ . Similarly for fermions it is convenient to choose creation and annihilation operators corresponding to different states as anti commuting

$$\psi(1, 3) = |1, 0, 1, 0, \dots\rangle = c_1^\dagger c_3^\dagger |0, 0, 0, 0, \dots\rangle = -c_3^\dagger c_1^\dagger |0, 0, 0, 0, \dots\rangle = -\psi(3, 1), \quad (\text{X.4})$$

or  $c_1^\dagger c_3^\dagger = -c_3^\dagger c_1^\dagger$ . It is easy to check that similar (anti)commutation relations between creation and annihilation operators, as well as annihilation and creation operators ensure that all basis functions are always properly symmetrized.

- Now we need to decide what to do with commutation relations for  $a_j$  and  $a_j^\dagger$  corresponding to the same single particle state. For bosons it is convenient to use the same convention as for harmonic oscillators, i.e.

$$[a_j, a_j^\dagger] = a_j a_j^\dagger - a_j^\dagger a_j = 1. \quad (\text{X.5})$$

This requirement immediately yields familiar matrix elements for the creation and annihilation operators in the harmonic oscillator:

$$a_j^\dagger |n_j\rangle = \sqrt{n_j + 1} |n_j + 1\rangle. \quad (\text{X.6})$$

This can be seen e.g. from normalization conditions:

$$\langle 1|1\rangle = \langle 0|a_j a_j^\dagger|0\rangle = \langle 0|1 - a_j^\dagger a_j|0\rangle = 1 \quad (\text{X.7})$$

and

$$\begin{aligned} \langle 1|a_j a_j^\dagger|1\rangle &= \langle 0|a_j a_j a_j^\dagger a_j^\dagger|0\rangle \langle 0| = |a_j(1 + a_j^\dagger a_j)a_j^\dagger|0\rangle \\ &= 1 + \langle 0|(1 + a_j^\dagger a_j)(1 + a_j^\dagger a_j)|0\rangle = 2 \end{aligned} \quad (\text{X.8})$$

From this and normalization  $\langle 2|2\rangle = 1$  we see that  $a_j^\dagger|1\rangle = \sqrt{2}|2\rangle$ . And so on. Similarly we can find that  $a_j|n_j\rangle = \sqrt{n_j}|n_j - 1\rangle$ . This commutation relations immediately yield that  $n_j = a_j^\dagger a_j$  is the number operator:  $a_j^\dagger a_j|n_j\rangle = a_j^\dagger \sqrt{n_j}|n_j - 1\rangle = n_j|n_j\rangle$ . So the Hamiltonian of any noninteracting bosonic system can be written as

$$\mathcal{H} = \sum_j \epsilon_j n_j = \sum_j \epsilon_j a_j^\dagger a_j \quad (\text{X.9})$$

Note that we never used any details of the Hamiltonian to write down this expression. Harmonic oscillator shows us an example how these operators can be explicitly constructed from the coordinate and momentum operators.

So bosonic operators satisfy

$$[a_i, a_j^\dagger] = \delta_{i,j} \quad (\text{X.10})$$

- For fermions it is convenient to choose creation and annihilation operators corresponding to the same state satisfying  $\{c_j, c_j^\dagger\} \equiv c_j c_j^\dagger + c_j^\dagger c_j = 1$ . We must also have  $c_j c_j = c_j^\dagger c_j^\dagger = 0$  because by Pauli exclusion principle it is impossible to have more than one particle in the same state. This choice automatically yields  $c_j^\dagger|0\rangle = |1\rangle$  and  $c_j|1\rangle = |0\rangle$ . Indeed then  $\langle 1|1\rangle = \langle 0|c_j c_j^\dagger|0\rangle = \langle 0|1 - c_j^\dagger c_j|0\rangle = 1$ . The quantity  $c_j^\dagger c_j$  also serves as the number operator so for the noninteracting particles the Hamiltonian still takes the form (X.9) with  $a_j \leftrightarrow c_j$ . Obtaining explicit form of the fermionic operators is much less trivial than the bosonic. However, there is such a representation of fermionic operators through products of  $2 \times 2$  matrices. This representation is non-local; it was derived by Jordan and Wigner (you can search for Jordan-Wigner transformation or look in e.g. Subir Sachdev, *Quantum Phase Transitions*).
- The form of the Hamiltonian (X.9) is consistent with our earlier expressions for the average energy:

$$E = \langle \mathcal{H} \rangle = \sum_j \epsilon_j f(\epsilon_j), \quad (\text{X.11})$$

where  $f(\epsilon_j)$  is the bosonic or fermionic distribution function. Similarly one can check that we can derive correct expressions for fluctuations of energy, etc.

- It is important to be able to change the basis and know how creation and annihilation operators transform. Let us consider the following single-particle transformation:

$$|j\rangle = \sum_k U_{jk} |k\rangle, \quad (\text{X.12})$$

where  $U$  is some unitary matrix. On the other hand this is equivalent to

$$a_j^\dagger |0\rangle = \sum_k U_{jk} b_k^\dagger |0\rangle \quad (\text{X.13})$$

We use notations  $b_k$  to denote annihilation operators in the different basis. So

$$a_j^\dagger = U_{jk} b_k^\dagger, \quad \Leftrightarrow \quad a_j = U_{kj}^\dagger b_k \quad (\text{X.14})$$

or in the compact matrix notation  $a = bU^\dagger$ . Note that this unitary transformation does not change commutation relations:

$$[a_j^\dagger, a_i] = U_{jk} U_{qi}^\dagger [b_k^\dagger, b_q] = U_{jk} U_{ki}^\dagger = \delta_{ji}. \quad (\text{X.15})$$

For example if  $j$  stands for the (discrete) position and  $k$  stands for the momentum we have

$$a_j = \frac{1}{\sqrt{L}} \sum_k a_k \exp[ikj] \quad (\text{X.16})$$

- If we now write the single-particle Hamiltonian (or any other single particle operator) in arbitrary basis than in the second quantized form it becomes:

$$\mathcal{H} = \sum h_{ij} a_i^\dagger a_j, \quad (\text{X.17})$$

where  $h_{ij}$  are the matrix elements of the single particle Hamiltonian between the states  $i$  and  $j$ . This can be obtained e.g. from the Eq. (X.9) and the unitary transformation (X.14). This expression has a very clear interpretation: single particle operators can annihilate a particle at one state and create at some other state, with which the matrix element of the corresponding operator is nonzero. For example if the Hamiltonian has a kinetic energy and some external potential then the off-diagonal part of  $H$  corresponds to scattering between different momentum states.

- Our final ingredient is to add interactions to this picture. Typically we deal with two body interactions corresponding to two-particle collisions. Then the corresponding contribution to the Hamiltonian reads:

$$\frac{1}{2} \sum_{ijkl} c_i^\dagger c_j^\dagger V_{ij,kl} c_k c_l, \quad (\text{X.18})$$

where  $V_{ij,kl}$  is the matrix element of the interaction between the properly symmetrized states where the two particles are in states  $|i\rangle, |j\rangle$  and  $|k\rangle, |l\rangle$  respectively. The factor of  $1/2$  is usually written for convenience. Let us prove that this is indeed the case for a stationary density density interaction:

$$V(x_1, x_2, \dots, x_N) = \sum_{i < j} v(x_j - x_i) = \frac{1}{2} \sum_{i,j} v(x_j - x_i) = \frac{1}{2} \int dx_1 dx_2 v(x_1 - x_2) \rho(x_1) \rho(x_2), \quad (\text{X.19})$$

where the sum is taken over all particle pairs and  $\rho(x) = \sum_i \delta(x - x_i)$ . In the second quantized language the density operator becomes simply  $a^\dagger(x)a(x)$ . This is obvious if we treat  $x$  as the discrete coordinate, then density is just the number operator (up to volume factors) corresponding to the given position. So we have

$$\begin{aligned} V &= \frac{1}{2} \int \int dx_1 dx_2 v(x_1 - x_2) a^\dagger(x_1) a(x_1) a^\dagger(x_2) a(x_2) \\ &= \frac{1}{2} v(0)N + \frac{1}{2} \int \int dx_1 dx_2 a^\dagger(x_1) a^\dagger(x_2) v(x_1 - x_2) a(x_2) a(x_1). \end{aligned} \quad (\text{X.20})$$

Note that in this form the expression works both for bosons and for fermions. The first term is trivial shift of energy and we can always eliminate it reabsorbing either into the chemical potential (in grand canonical systems) or to the redefinition of the ground state energy (in canonical systems). We will thus not worry about this term. In the second term in this often convenient to go to the momentum basis. Then

$$V = \frac{1}{2L^2} \sum_{q_1, q_2, q_3, q_4} a_{q_1}^\dagger a_{q_2}^\dagger a(q_3) a(q_4) \int dx_1 dx_2 v(x_1 - x_2) \exp[iq_1 x_1 + iq_2 x_2 - iq_3 x_2 - iq_4 x_1]. \quad (\text{X.21})$$

By changing variables to  $x = x_1 - x_2$  and  $X = (x_1 + x_2)/2$  we find that the integral over  $X$  gives  $q_1 + q_2 = q_3 + q_4$  - total momentum is conserved and the integral over  $x$  gives the Fourier transform of  $v(x)$  so

$$V = \frac{1}{2} \sum_{k,p,q} a_{k+q}^\dagger a_{p-q}^\dagger v(q) a_p a_k \quad (\text{X.22})$$

The physical interpretation of this term is very simple. Interaction takes two particles with momenta  $k$  and  $p$  and scatters them to the two-particles into two other states conserving the

total momentum (which is the consequence of the translational invariance of the interaction. Note again that Eq. (X.22) is valid again both for bosons and for fermions.

This is the end of our short introduction to the second quantization. We never used any details from the Schrödinger first-quantized picture. The second quantized approach is very powerful for the many-particle systems. It also gives very convenient way for seeing particle-wave duality. As we will see later for classical waves (phonons, photons, condensates,...) it is  $a_j$  which becomes a classical field:  $a_j \sim \sqrt{\rho_j} \exp[i\phi_j]$ , where  $\rho_j$  is the density and  $\phi_j$  is the phase. One should not be deceived, by the simplicity of the interaction term (X.22). It is a compact notation of the interaction operator in the exponentially large Hilbert space. The problem of solving the Schrödinger equation is not becoming easier if we just change notations. However, manipulations and building approximate schemes in the second quantized form becomes much more transparent.

## 2. Interacting Fermi systems.

Both mean-field principle and the variational approach are straightforwardly generalized to interacting quantum systems (in fact quantum or classical does not make a big difference, but quantum is more general). In general we are dealing not with ideal quantum or classical gases but rather with systems with interactions. In the second quantized language we are dealing with the Hamiltonians:

$$\mathcal{H} = K + U, \tag{X.23}$$

where

$$\mathcal{H} = \sum_k (\varepsilon_k - \mu) c_k^\dagger c_k \tag{X.24}$$

and

$$U = \frac{1}{2} \int dr dr' \rho(r) u(r - r') \rho(r') = \frac{1}{2} \sum_{k,p,q} c_{k+q}^\dagger c_{p-q}^\dagger u(q) c_p c_k. \tag{X.25}$$

Understanding the properties of the system with the general hamiltonian  $\mathbf{H}$  is the realm of the condensed matter physics. Here I will flash several examples, showing how from variational approach and mean-field theory we can understand many different phases and phase transitions, from theory of Fermi liquids to such phenomena as crystallization and superfluidity (superconductivity). The trick is to determine the possible broken phase and write a simple trial Hamiltonian (or simple

mean-field). For us simple means non-interacting. The most general noninteracting Hamiltonian we can write is

$$\mathcal{H}_0 = \sum_{k,k'} \Lambda_{k,k'} c_k^\dagger c_{k'} + \Gamma_{k,k'} c_k^\dagger c_{k'}^\dagger + \Gamma_{k,k'}^* c_k c_{k'}, \quad (\text{X.26})$$

where we treat  $\Lambda_{k,k'}$ ,  $\Gamma_{k,k'}$ , and  $\Gamma_{k,k'}^*$  as variational parameters. This is substantially more complicated than the simple Ising model because instead of one variational parameter we have many. Yet the variational problem is much simpler than the exact one because instead of exponentially large number of coefficients of the density matrix we have only a power law number of terms.

Let us see what are the symmetries which can be broken within this trial Hamiltonian. Let us write operators for the momentum and number:

$$P = \sum_k \hbar k c_k^\dagger c_k, \quad N = \sum_k c_k^\dagger c_k. \quad (\text{X.27})$$

Both operators commute with the full Hamiltonian. But note that

$$[P, \mathcal{H}_0] = \sum_{k,k'} \hbar(k - k') \Lambda_{k,k'} c_k^\dagger c_{k'} + \hbar(k + k') \Gamma_{k,k'} c_k^\dagger c_{k'}^\dagger + c.c. \quad (\text{X.28})$$

So we see that the translational symmetry is not broken if we insist that  $\Lambda_{k,k'} = \Lambda_k \delta_{k,k'}$ ,  $\Gamma_{k,k'} = \Gamma_k \delta_{k,-k'}$ . This is more or less intuitively clear we can either kill and create a particle with the same momentum or create or kill the pair of particles with opposite momenta so the total momentum is conserved. Similarly

$$[N, \mathcal{H}_0] = 2 \sum_{k,k'} \Gamma_{k,k'} c_k^\dagger c_{k'}^\dagger + c.c. \quad (\text{X.29})$$

So the total number of particles is conserved (or the corresponding symmetry is non-broken) is equivalent to having  $\Gamma \equiv 0$ .

### 3. Fermi liquid theory

Let us assume that there are no broken symmetries. Then the trial Hamiltonian is

$$\mathcal{H}_0 = \sum_k (\epsilon_k + \Sigma_k - \mu) c_k^\dagger c_k, \quad (\text{X.30})$$

where  $\Sigma_k$  is the self energy. For us it is just the variational parameter. Next we need to find a trial free energy. We have several ingredients:

$$\Omega_0 = -T \sum_k \ln[1 + \exp[-\beta(\epsilon_k + \Sigma_k - \mu)]], \quad (\text{X.31})$$

$$\langle \mathcal{H}_0 \rangle_0 = \sum_k (\epsilon_k + \Sigma_k - \mu) f(\epsilon_k + \Sigma_k - \mu), \quad (\text{X.32})$$

$$\langle K \rangle_0 = \sum_k (\epsilon_k - \mu) f(\epsilon_k + \Sigma_k - \mu) \quad (\text{X.33})$$

The last ingredient is

$$\langle U \rangle_0 = \frac{1}{2} \sum_{k,p,q} v_q \langle c_{k+q}^\dagger c_{p-q}^\dagger c_p c_k \rangle_0. \quad (\text{X.34})$$

The only two possibilities that the expectation value above is nonzero are i)  $q = 0$  and ii)  $q = p - k$  so

$$\langle U \rangle_0 = \frac{1}{2} v(0) \sum_{k,p} f(\epsilon_k + \Sigma_k - \mu) f(\epsilon_p + \Sigma_p - \mu) - \frac{1}{2} \sum_{k,p} v(k-p) f(\epsilon_k + \Sigma_k - \mu) f(\epsilon_p + \Sigma_p - \mu). \quad (\text{X.35})$$

For bosons we will get the same result but with a “+” sign. Next we need to minimize the trial free energy with respect to  $\Sigma_k$ . It is easy to verify that this minimization yields

$$\Sigma_k = v(0) \sum_p f(\epsilon_p + \Sigma_p - \mu) - \sum_p v(p-k) f(\epsilon_p + \Sigma_p - \mu). \quad (\text{X.36})$$

For bosons there will be gain a “+” sign. This is a system of self-consistent equations which needs to be solved. Still hard but much easier than the original problem. Combining all ingredients we find that

$$\Omega_{\text{tr}} = -T \sum_k \ln[1 + \exp[-\beta(\epsilon_k + \Sigma_k - \mu)]] + \frac{1}{2} \sum_k \Sigma_k f(\epsilon_k + \Sigma_k - \mu). \quad (\text{X.37})$$

The trial free energy (thermodynamic potential) depends only on the combination  $\epsilon_k + \Sigma_k$ . Finding  $\Sigma_k$  requires solving complicated coupled nonlinear equations. Yet it is much easier than solving the full problem. One can anticipate that at small  $k$  we have  $\Sigma_k = \text{const} + \alpha k^2$ : the linear term in  $k$  must vanish because of inversion symmetry. Thus at small  $k$  we can write that

$$\epsilon_k + \Sigma_k \approx \frac{\hbar^2 k^2}{2m^*}, \quad (\text{X.38})$$

where

$$\frac{m}{m^*} = 1 + \left. \frac{\partial \Sigma_k}{\partial \epsilon_k} \right|_{\epsilon_k=0}. \quad (\text{X.39})$$

The quantity  $m^*$  is called the effective mass. For liquid  ${}^4\text{He}$  it is equal to  $1.58m$ . Similar expansion can be made for interacting nearly degenerate fermions:

$$\epsilon_k + \Sigma_k \approx E_f + \frac{\hbar^2 k_f k}{m^*}, \quad (\text{X.40})$$

where

$$\frac{m}{m^*} = 1 + \left. \frac{\partial \Sigma_k}{\partial \epsilon_k} \right|_{\epsilon_k = E_f}. \quad (\text{X.41})$$

Note that the same equation (X.36) can be obtained using meanfield approach.

$$\begin{aligned} U &= \frac{1}{2} \sum_{k,p,q} c_{k+q}^\dagger c_{p-q}^\dagger u(q) c_p c_k \rightarrow U_{mf} \\ &= \frac{1}{2} \sum_{k,p,q} u(q) [c_{k+q}^\dagger \langle c_{p-q}^\dagger c_p \rangle c_k + \langle c_{k+q}^\dagger c_k \rangle c_{p-q}^\dagger c_p - c_{k+q}^\dagger c_p \langle c_{p-q}^\dagger c_k \rangle - \langle c_{k+q}^\dagger c_p \rangle c_{p-q}^\dagger c_k]. \end{aligned} \quad (\text{X.42})$$

Note that if the translational symmetry is not broken the averages are non-zero only if  $q = 0$  in the first two terms and  $p = k + q$  in the last two. So we have

$$U_{mf} = u(0) \sum_k [c_k^\dagger c_k \sum_p f(p) - c_k^\dagger c_k \sum_p u(k-p) f(p)]. \quad (\text{X.43})$$

From this we easily recover the equation (X.36) for the self energy. Note that the first term in Eq. (X.43) is the classical mean-field potential: electrons feel effective potential from the average density of other electrons surrounding it. This term called after Hartree. The second (named after Fock) is the exchange contribution (negative for electrons and positive for bosons). Note that for short range interactions  $v(q) = \text{const}$ . The Hartree and Fock terms exactly cancel each other for fermions (electrons do not see each other due to Pauli principle) and these two terms are equal to each other for bosons. So interactions for bosons are enhanced compared to classical particles: Bose bunching, they like to be with each other.

#### 4. Examples of various broken symmetry states

We can now understand how to look into various symmetry broken states in interacting electron (or boson) systems.

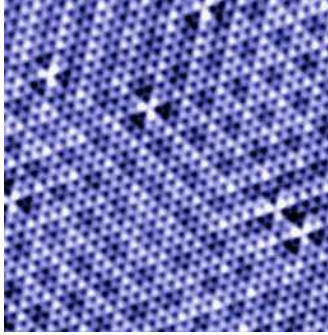
*Broken translational symmetry.* For example, if we use the trial Hamiltonian of the form

$$\mathcal{H}_0 = \sum_k (\epsilon_k - \mu) c_k^\dagger c_k + \sum_{k,k+Q} c_k^\dagger c_{k+Q} + c.c. \quad (\text{X.44})$$

If the variational state with non-zero  $\Sigma$  is better than with zero  $\Sigma$  then we have a transition to the charge density wave state. Within the mean-field approach this corresponds to nonzero expectation value of

$$c_k^\dagger c_{k+Q} \quad (\text{X.45})$$

In Fig. 9 we show the example of CDW in  $\text{NaSe}_2$ . In classical gases crystals provide us with the



**CDW in  $\text{NaSe}_2$ ,**  
K. Mc Elroy, U. of Colorado, Boulder

FIG. 9 Example of charge density wave transition  $\text{NaSe}_2$ .

example of systems with spontaneously broken translational symmetry. This phase is characterized by divergent response to the perturbation

$$\delta H = \lambda \int dx \rho(x) \cos(Qx + \theta) \quad (\text{X.46})$$

*Broken time reversal symmetry: ferromagnetism* We can break time reversal symmetry resulting in ferromagnetism. The trial Hamiltonian would be

$$\mathcal{H}_0 = \sum_k (\epsilon_k - \mu + \Sigma_k^+) (c_{k\uparrow}^\dagger c_{k\uparrow} + c_{k\downarrow}^\dagger c_{k\downarrow}) + \Sigma_k^- (c_{k\uparrow}^\dagger c_{k\uparrow} - c_{k\downarrow}^\dagger c_{k\downarrow}) \quad (\text{X.47})$$

When  $\Sigma_k^-$  becomes nonzero (or equivalently  $\langle c_{k\uparrow}^\dagger c_{k\uparrow} - c_{k\downarrow}^\dagger c_{k\downarrow} \rangle$  becomes nonzero in the meanfield language) then we have spontaneous magnetization. The ferromagnetism (as in the case of the Ising model) can be understood as the divergent response to the magnetic field:

$$\delta H = h \sum_k c_{k\uparrow}^\dagger c_{k\uparrow} - c_{k\downarrow}^\dagger c_{k\downarrow}. \quad (\text{X.48})$$

*Broken time reversal + translational symmetries: antiferromagnetism (or more generally spin density waves).* If we have a lattice then we can break both symmetries using the trial Hamiltonian

$$\mathcal{H}_0 = \sum_k (\epsilon_k - \mu + \Sigma_k^+) (c_{k\uparrow}^\dagger c_{k\uparrow} + c_{k\downarrow}^\dagger c_{k\downarrow}) \sum_j (-1)^j \Sigma_j (c_{j\uparrow}^\dagger c_{j\uparrow} - c_{j\downarrow}^\dagger c_{j\downarrow}), \quad (\text{X.49})$$

where  $j$  enumerates different positions in the lattice. When  $\Sigma_j$  is non-zero we have divergent response to a staggered magnetic field (which alternates signs between neighboring lattice sites).

### A. Broken number symmetry. Superfluids and superconductors

Before we were dealing with the situations where  $N$  was always conserved so that in all thermodynamic ensembles number was a diagonal operator. Also in all previous variational examples the trial Hamiltonian was commuting with  $N$  and in the meanfield Hamiltonians only number conserving quantities acquired expectation values.

#### 1. Weakly interacting Bose gases.

But are there situations where the number symmetry is broken? We had a hint from studying Bose-Einstein condensation in ideal Bose gases. Recall that active part of the particles, which participated in specific heat, entropy, pressure etc. was insensitive to the total number of particles which went to the condensate part. So for the active part of the Bose gas below the condensation temperature the number symmetry is effectively broken. Particles can appear from and disappear to the condensate.

Note that if the number of particles in the condensate is large then the corresponding creation and annihilation operators can be treated as classical (complex) numbers. For example

$$a|N\rangle \approx \sqrt{N}|N-1\rangle, \quad a^2|N\rangle \approx \sqrt{N(N-1)}|N-2\rangle \approx \sqrt{N^2}|N-2\rangle \sim N^2|N-2\rangle \quad (\text{X.50})$$

The last equality implies that the state with  $N-2$  particles is very similar to the original state of  $N$  particles. One can also introduce phase, which is conjugate to number

$$|\phi\rangle = \sum_{N \geq 0} \exp[i\phi N] |N\rangle \quad (\text{X.51})$$

Clearly phase and number are like coordinate and momentum: when one is defined the other is not. There is one subtlety that  $N \geq 0$  so the sum above is not the Fourier transform, but this subtlety is not important when average  $N$  is large. When the modes are highly occupied the best states to work with are the coherent states, where both number and phase are defined. These states are analogues of the minimum uncertainty (gaussian) states for coordinate-momentum. Formally these states are defined as eigenstates of annihilation operators:

$$a|\lambda\rangle_c = \lambda|\lambda\rangle_c \quad (\text{X.52})$$

One can check by explicit calculation that the state  $|\lambda\rangle_c$  can be written as the series:

$$|\lambda\rangle_c = |0\rangle + \frac{\lambda}{1} a^\dagger |0\rangle + \frac{\lambda^2}{2!} (a^\dagger)^2 |0\rangle + \dots = \exp[\lambda a^\dagger] |0\rangle. \quad (\text{X.53})$$

Properly normalized coherent states are  $|\lambda\rangle_c = \exp[-|\lambda|^2/2] \exp[\lambda a^\dagger] |0\rangle$ .

For the ideal Bose below  $T_c$  we concluded that all condensed particles should go to the zero momentum mode. But because there is so huge degeneracy between states with different  $N$  we can equally say that condensed particles are in the coherent state:  $|\sqrt{N_0} \exp[i\theta_0]\rangle_c$ , where  $\theta$  is some arbitrary phase. In this state  $a_0$  can be treated as a classical variable:

$$a_0 |\sqrt{N_0} \exp[i\theta_0]\rangle_c = \sqrt{N_0} \exp[i\theta_0] |\sqrt{N_0} \exp[i\theta_0]\rangle_c. \quad (\text{X.54})$$

In the meanfield language we can say that  $a_0$  spontaneously acquired expectation value. This corresponds to the broken global gauge symmetry. If we define the operator

$$S = \exp \left[ i\chi a_0^\dagger a_0 \right] = \exp [i\chi N], \quad (\text{X.55})$$

where  $N$  is the total number operator, then we have

$$S a_0 S^\dagger = \exp[-i\chi] a_0. \quad (\text{X.56})$$

Normally the equilibrium state should be invariant under the global gauge transformations since  $S$  commutes with the Hamiltonian. However, if the symmetry is broken then this is not longer the case and thus the equilibrium state can loose this invariance. This what happens if the system picks the coherent state with a fixed phase. We can still define a gauge-symmetry breaking perturbation

$$\delta\mathcal{H} = -\lambda \int dx (e^{i\theta} a^\dagger(\mathbf{r}) + e^{-i\theta} a(\mathbf{r})) \quad (\text{X.57})$$

and see when the response diverges, i.e. when this symmetry is spontaneously broken. Clearly for the ideal Bose gas below  $T_c$  these gauge symmetry is broken. For example at zero temperature the expectation value of the perturbation  $\delta H$  in the coherent state with phase  $\theta_0$  scales as  $-2\lambda\sqrt{N} \cos(\theta - \theta_0)$ , while the same expectation value of this perturbation in the number state is simply zero. In the limit  $N \rightarrow \infty$  the coherent (broken symmetry) state with  $\theta = \theta_0$  obviously wins at arbitrarily small  $\lambda$ .

Let us now consider an interacting system and proceed with the variational calculation. We assume that the zero momentum mode is in the coherent state  $|\phi\rangle_c$  and the rest are described by the Hamiltonian

$$\mathcal{H}_0 = \sum_{k \neq 0} \xi_k a_k^\dagger a_k + \lambda_k a_k^\dagger a_{-k}^\dagger + \lambda_k^* a_k a_{-k} \quad (\text{X.58})$$

The motivation for this (Bogoliubov) Hamiltonian is the following: (i) it is quadratic, (ii) it preserves translational invariance but it breaks global gauge symmetry, (iii) it incorporates our prior result that in the non-interacting limit bosons can condense into the lowest energy mode, which is macroscopically occupied. All parameters here are variational. Physically one can interpret the  $a_k^\dagger a_{-k}^\dagger$  terms as creating two particles from the condensate. They should be thus multiplied by  $a_0^2$ , but since the condensate is the coherent state these are just multiplication by  $\phi^2$ .

To simplify derivation even more we can first keep only the  $k = 0$  term and assume that all the modes with  $k \neq 0$  are empty. Since there is no entropy associated with one mode we have  $\Omega_0 = \langle H_0 \rangle_0$  and so

$$\Omega_{\text{tr}} = \langle H \rangle_0 = (\epsilon_0 - \mu)|\phi|^2 + \frac{u(0)}{2}|\phi|^4 \quad (\text{X.59})$$

By minimizing with respect to the variational parameter  $\phi$  we find

$$\mu = \epsilon_0 + u(0)|\phi|^2. \quad (\text{X.60})$$

Recall that  $|\phi|^2$  is actually the number of particles in the condensate.

If we include quadratic terms then we have to deal with the Bogoliubov Hamiltonian. It can be diagonalized by the Bogoliubov transformation

$$a_k^\dagger = \cosh \theta_k \alpha_k^\dagger - \sinh \theta_k \alpha_{-k}, \quad a_k = \cosh \theta_k \alpha_k - \sinh \theta_k \alpha_{-k}^\dagger \quad (\text{X.61})$$

and the inverse transformation

$$\alpha_k^\dagger = \cosh \theta_k a_k^\dagger + \sinh \theta_k a_{-k}, \quad \alpha_k = \cosh \theta_k a_k + \sinh \theta_k a_{-k}^\dagger \quad (\text{X.62})$$

Note that both  $\alpha_k^\dagger$  and  $a_k^\dagger$  increase momentum by  $k$ . One can check that  $\alpha_k$  and  $\alpha_k^\dagger$  still satisfy bosonic commutation relations.

**Homework, optional.** Prove that  $[\alpha_k^\dagger, \alpha_q^\dagger] = 0$  and  $[\alpha_k, \alpha_q^\dagger] = \delta_{k,q}$ .

Now we will try to choose  $\theta_k$  so that anomalous terms cancel so that

$$\mathcal{H}_0 = \sum_k E_k \alpha_k^\dagger \alpha_k. \quad (\text{X.63})$$

This is indeed possible if we choose

$$\tanh(2\theta_k) = -2 \frac{\lambda_k}{\xi_k} \quad (\text{X.64})$$

If we now express  $\Omega_{\text{tr}}$  through  $\theta_k$  and  $E_k$  (instead of  $\lambda_k$  and  $\xi_k$  and minimize it with respect to these parameters we find

$$\tanh 2\theta_k = \frac{-u|\phi|^2}{\epsilon_k - \mu + 2u|\phi|^2} = \frac{-u|\phi|^2}{\epsilon_k + u|\phi|^2} \quad (\text{X.65})$$

and

$$E_k = \sqrt{\epsilon_k^2 + 2u|\phi|^2\epsilon_k} \quad (\text{X.66})$$

At small  $k$  we get linear dispersion

$$E_k \approx \sqrt{\frac{\hbar^2 u_0 \rho_0}{m}} k, \quad (\text{X.67})$$

where  $u_0 = u(k=0)L^3$  and  $\rho_0 = |\phi|^2/L^3$ . The latter is the condensate density.

This mode is in fact collective Goldstone mode corresponding to the slow variation of phase. If we use  $a(r) \approx \sqrt{\rho(r)} \exp[i\theta(r)]$  and substitute this to the Hamiltonian then we will find

$$\mathcal{H} \approx \int d\mathbf{r} \frac{\hbar^2}{8m\rho_0} |\nabla\rho|^2 + \frac{\hbar^2}{2m} |\rho_0| |\nabla\theta|^2 + \frac{U}{2} \rho^2. \quad (\text{X.68})$$

One can check that  $a^\dagger(r)$  and  $a(r)$  being bosonic fields implies that  $\rho(r)$  and  $\theta(r)$  are conjugate variables like coordinate and momentum. There are some subtleties involved, which are not important for our purposes. Then the Hamiltonian above is equivalent to that of a coupled Harmonic oscillators with the dispersion (X.66).

Superfluids have many fascinating properties. They all basically originate from (i) non-dissipativity of the flow and (ii) flux (macroscopic phase) quantization: if we make a circle then the phase  $\theta$  should change by a multiple integer of  $2\pi$ . Let us give a simple Landau argument why there is no dissipation in superfluids. Assume that the fluid is flowing around an obstacle, or conversely an obstacle is moving in a still superfluid. In order to create excitation we need to satisfy energy and momentum conservation

$$\frac{Mv^2}{2} = \frac{Mv'^2}{2} + E_{\text{ex}}(k)M\mathbf{v} = M\mathbf{v}' + \hbar\mathbf{k} \quad (\text{X.69})$$

Solving these two and assuming that  $M$  is large we find

$$\mathbf{v}\hbar\mathbf{k} = E_{\text{ex}} \quad (\text{X.70})$$

so that

$$v \geq \frac{E_{\text{ex}}(k)}{\hbar k} \quad (\text{X.71})$$

If the ratio above has a minimum then the flow with velocities smaller than this minimum can not lead to dissipation. In conventional liquids this minimum is always zero because there are essentially zero energy transverse modes at arbitrary high momentum. In superfluids the minimum is nonzero, it is called the Landau critical velocity (above this velocity superfluidity becomes unstable). In the example we considered of a weakly interacting Bose gas the Landau critical velocity is the same as the sound velocity. In general this is not true.

## 2. Weakly attractive Fermi gas. BCS theory of superconductivity.

From what we considered above it may seem that the superfluidity is a feature of Bosonic particles. Indeed at zero temperature non-interacting Bose particles condense while the non-interacting Fermions form highly energetic Fermi sea. However, it turns out that at low temperatures many metals become superconducting (superfluid) and the superfluidity of fermions is very closely connected to superfluidity of bosons. It took many years before the mechanism of superconductivity was understood by Bardeen, Cooper, and Schrieffer. Basically the mechanism behind superconductivity is still bosonic: fermions join into Cooper pairs, i.e. weakly bound states, which in turn can superconduct. This is of course a very loose explanation since the size of Cooper pairs is typically much bigger than interparticle distance. So they can not be literally treated as bosonic particles. However, we won't care. We will just apply our standard mean field - variational argument and see what happens. Also we ignore that Fermions are charged. For electromagnetic response (Meissner effect) this fact is crucial. However for establishing the mechanism of the fermionic superfluidity and for the BCS theory the fact the fermions are charged is not important.

For simplicity we will assume that the interaction between fermions is local and the Hamiltonian can be written as

$$\mathcal{H} = \sum_{k,\sigma} (\epsilon_k - \mu) c_{k,\sigma}^\dagger c_{k,\sigma} - \frac{U}{2} \sum_r c_{\uparrow}^\dagger(r) c_{\downarrow}^\dagger(r) c_{\downarrow}(r) c_{\uparrow}(r), \quad (\text{X.72})$$

where  $\sigma = \uparrow, \downarrow$ . Note that for the local interaction potential only electrons with opposite spins can interact because of Pauli principle. The “-” sign in the Hamiltonian above explicitly tells that the interactions are attractive (usually such  $U$  originates from electron-phonon interactions). Similarly to the bosonic case we will consider the following trial Hamiltonian

$$\mathcal{H}_0 = \sum_k \xi_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_k (\lambda_k c_{k,\uparrow}^\dagger c_{-k,\downarrow}^\dagger + h.c.) \quad (\text{X.73})$$

This Hamiltonian preserves translational invariance and violates global gauge symmetry (or global number conservation). It can be shown that in the meanfield language this variational Hamiltonian

is equivalent to

$$\mathcal{H}_{mf} = \sum_k (\epsilon_k - \mu) c_{k,\sigma}^\dagger c_{k,\sigma} + \Delta c_{k,\uparrow}^\dagger c_{-k,\downarrow}^\dagger + h.c., \quad (\text{X.74})$$

where

$$\Delta = U/2 \langle c_\uparrow(r) c_\downarrow(r) \rangle. \quad (\text{X.75})$$

One can find the spectrum of this Hamiltonian using the Bogoliubov transformation similar to the bosonic case introducing new fermionic operators:

$$\gamma_{k,\uparrow}^\dagger = \cos \theta_k c_{k,\uparrow}^\dagger + \sin \theta_k c_{-k,\downarrow}, \quad \gamma_{k,\downarrow} = \cos \theta_k c_{k,\downarrow} + \sin \theta_k c_{-k,\uparrow}^\dagger \quad (\text{X.76})$$

and requiring that the Hamiltonian does not contain anomalous  $\gamma_{k,\uparrow}^\dagger \gamma_{-k,\downarrow}^\dagger$  terms. There is however a more elegant (but equivalent) way to find the spectrum using the Nambu notations:

$$\psi_{k,\uparrow} = c_{k,\uparrow}, \quad \psi_{k,\downarrow} = c_{-k,\downarrow}^\dagger. \quad (\text{X.77})$$

One can check that  $\psi$  is a proper fermionic operator satisfying correct commutation relations. In terms of  $\psi$  the mean field Hamiltonian is written as

$$\mathcal{H}_{mf} = \sum_k \mathcal{H}_k, \quad (\text{X.78})$$

where

$$\mathcal{H}_k = \psi_{k,\alpha}^\dagger [(\epsilon_k - \mu) \sigma_{\alpha,\alpha'}^z + \Delta \sigma_{\alpha,\alpha'}^x] \psi_{k,\alpha'}. \quad (\text{X.79})$$

The eigen energies are clearly the eigenvalues of the  $2 \times 2$  matrix:

$$E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta^2}. \quad (\text{X.80})$$

And finally the self-consistency condition (X.75) gives

$$\Delta = \frac{U}{V} \sum_k \langle \psi_{k,\uparrow}^\dagger \psi_{k,\downarrow} \rangle = \frac{U}{V} \sum_k \frac{\Delta \tanh(\beta(\epsilon_k - \mu)/2)}{(\epsilon_k - \mu)}. \quad (\text{X.81})$$

At zero temperature this reduces to

$$1 = U \rho(E_F) \int_0^{\hbar\omega_D} \frac{d\epsilon}{\sqrt{\epsilon^2 + \Delta^2}}, \quad (\text{X.82})$$

where  $\hbar\omega_D$  is some high energy cutoff, which is usually the highest energy of the phonons participating in the superconductivity. This gives

$$\Delta \approx 2\hbar\omega_D \exp \left[ -\frac{1}{U \rho(E_F)} \right] \ll \hbar\omega_D. \quad (\text{X.83})$$

Equation (X.81) can also be used to find the highest temperature above which there is no solution with  $\Delta \neq 0$ . Thus temperature is given by

$$T_c \approx 1.14\hbar\omega_D \exp\left[-\frac{1}{U\rho(E_F)}\right]. \quad (\text{X.84})$$

Let us make a couple of quick comments. By dimensional analysis (also analyzing the behavior of the correlation function  $c_{\uparrow}^{\dagger}(r)c_{\downarrow}^{\dagger}(r')$ ) one can estimate the size of the Cooper pair as

$$\xi \sim \frac{\hbar v_F}{\Delta} \gg n^{1/3} \quad (\text{X.85})$$

The parameter, which justifies the mean field approximation, is the number of particles within the coherent volume:  $n\xi^3$  in typical metal superconductors this is a huge number so the meanfield works very well.

## B. Problems for Sec. VIII

1. Consider the Ising model. Compare the result for magnetic susceptibility obtained from high temperature expansion and from meanfield approach up to the second order in  $J/T$ . For the meanfield approach you need to assume that there is a small magnetic field  $h$  and find the effective magnetic field (obtained self-consistently) to the linear order in  $h$  but including corrections in  $J/T$ .
2. For the Ising model use variational approach to find  $\Omega_{\text{tr}}$  at fixed magnetization. Essentially you need to repeat the steps but minimize  $\Omega_{\text{tr}}$  using magnetization  $m = 1/N \sum_{\langle j \rangle} \sigma_j$  as a Lagrange multiplier. Derive Taylor expansion of  $\Omega_{\text{tr}}(m)$  to the second order in  $m$ , discuss your result.

What you should derive is an example of Landau phenomenological theory of phase transitions, largely for which he got Nobel prize. The magnetization  $m$  plays the role of the order parameter and expansion of the free energy in  $m$  up to the fourth order is an example of the expansion phenomenologically proposed by Landau to characterize continuous second order phase transitions.

## XI. ACKNOWLEDGEMENTS

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