Statistical Physics A

winter term 2020-21

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Tutors:

dr Maciej Lisicki, Thursday 14:15-17:00 dr Marta Wacławczyk, Wednesday 13:15-16:00

Rules

Lectures will be carried out online via Zoom. Every lecture is split into 3 parts with 45 minutes. In the end of each part there will be a quick test or quiz. If anyone will not get 80% of correct answers in total then such a student has to undertake an obligatory oral exam. Otherwise the oral exam is only for those students who are allowed to and want to upgrade their final mark by one step.

Tutorials will be performed online. There will be few problems to be solved in groups and presented online by each group and discussed by the tutor. Problems will be given in one week ahead.

Home problems will be given but will not be checked by tutors. However, some of these problems might occur during a colloquium or an exam.

- Standard way of passing the course
 - Activity, group working on tutorials, online, 40 pt.
 - Colloquium one, 2 problems, online, 20 pt.
 - Colloquium two, 2 problems, online, 20 pt.
 - Exam, 2 problems, online, 20 pt. (plus oral exam online, see above)
- Retaking to pass the course
 - Exam, 4 problems, online, 100 pt. (plus oral exam online, see above)

Final grade is based on total score points normalized to 100 and determined as follows:

5+ for 99-100 pt. 5 for 90-98 pt. 4+ for 81-89 pt. 4 for 72-80 pt. 3+ for 62-71 pt. 3 for 50-61 pt. 2 for 0-49 pt.

Warning: points from the first and second exams do not sum up.

Permanent link for lectures:

Krzysztof Byczuk https://zoom.us/j/4899364871?pwd= YWJrQlZ4ems2WWV6R1ZBSERvUy9ZUT09 Meeting ID: 489 936 4871 Passcode: 3XTpkb

Permanent links for tutorials:

Maciej Lisicki https://zoom.us/j/98076111296?pwd= WDJnZkp5STJtK0ZYTWhXWVRLbDJ1UT09 Meeting ID: 980 7611 1296 Passcode: EbHa0C

Marta Wacławczyk https://zoom.us/j/98822265791?pwd= TWMybjZ1UzZ1WkN5bk9KSDE4ZTI1Zz09 Meeting ID: 988 2226 5791 Passcode: 58D7k5

Dates of colloquia and exams:

colloquium I, 30/11/2020, 9:15-12:00, online

colloquium II, 18/01/2021, 9:15-12:00, online

written exam I, 08/02/2021, 9:15-13:00, online

oral exam I 10-12/02/2021, 10:00-16:00, online

written exam II, 25/02/2021, 9:15-13:00, online

oral exam II, 26/02/2021, 10:00-16:00, online

1 Week I, 15-21/10/2020

1.1 Lecture

I. Microcanonical ensemble:

&1. Foundations of statistical physics - a goal of statistical physics, few examples, a large number of components in macroscopic systems, the definition of mol and Avogadro number $N_a = 6,02214076 \cdot 10^{23}$, few examples, (the mol's day: October 23, from 6:02 am to 6:02 pm), discrete energy levels in quantum systems, e.g. quantum well and harmonic oscillator, very small distances between energy levels in macroscopic systems and very fast time of transition between neighboring levels, microscopic (mechanical) description of manybody system on quantum and classical levels, Schrodinger and Newton equations, a problem with huge number of possible information about macroscopic systems, in thermodynamic equilibrium only a small number of variables is sufficient to characterize a macroscopic system, thermodynamic (hydrodynamic) description as an alternative to mechanical ones, statistical physics aims to derive thermodynamics from mechanics, concepts of

microstates and macrostates, extensive and intensive variables, two-level system as an example to illustrates micro and macrostates.

&2. basic postulates of statistical mechanics - hypothesis of molecular chaos due to Ludwik Boltzmann, for an isolated system in thermal equilibrium all possible microstates realizing any macrostates are equally probable, hypothesis of equal probability a priori, two heuristic justifications (element of ignorance and selfaveraging hypothesis), definition of statistical ensemble, equivalence between averaging in time and averaging over a statistical ensemble (ergodic hypothesis), a prescription how to find corresponding probabilities, $p_i = \Omega_i / \Omega$, where Ω_i is the number of states realizing a given macrostate $y = y_i$ and Ω is the total number of microstates, short remainder of formulae in the probability theory.

1.2 Quizes

1.2.1 Quiz 1

The value of Avogadro number is

- 1. $6.02214076 \cdot 10^{26}$ 1/mol
- 2. $6.02214076 \cdot 10^{23}$ 1/mol
- 3. $1.602176634 \cdot 10^{-19}$ 1/mol
- 4. $6.62607015 \cdot 10^{-34}$ 1/mol

Your answer is 2.

1.2.2 Quiz 2

In thermal equilibrium

- 1. positions of particles are constant in time.
- 2. momenta of particles are constant in time.
- 3. density of particles is constant in time.
- 4. wave function of particles is constant in time.

Your answer is 3.

1.2.3 Quiz 3

The correct sentence is

- 1. a macrostate can be realized by many microstates.
- 2. a microstate can be realized by many macrostates.
- 3. a microstate is only a state of a small system.
- 4. a macrostate is too big to be observed.
- Your answer is 1.

1.3 Tutorial

- 1. Gaussian integrals Compute the integral $I = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx$ by firstly computing I^2 in the polar coordinates. By taking a derivative of I over α determine the integral $J = \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx$.
- 2. Gamma function Gaussian integrals in the form $I_m = 2 \int_0^\infty x^m e^{-\alpha x^2} dx$, with m > -1, formulate in terms of the gamma function $\Gamma(z) = \int_0^\infty y^{z-1} e^{-z^2} dz$. Show the recursion relation $\Gamma(n+1) = n\Gamma(n)$. Compute explicitly $\Gamma(1/2)$, $\Gamma(l+1/2)$, $\Gamma(1)$, $\Gamma(l+1)$, for l = 1, 2, 3, ...
- 3. Ball in n-dimensions Find the volume of a ball and the area of a sphere with radius r in n dimensions. The results express in terms of the Gamma function (generalized factorial function).
- 4. Stirling approximation Show that for $n \gg 1$ we can approximate $n! \approx \sqrt{2\pi n} n^n e^{-n+1/(12n)+O(1/n^2)}$. Write this approximation for $\ln n!$. Discuss the role of leading terms, 1/n corrections, and compare with an asymptotic of the gamma function.
- 5. *Probability theory* We throw two dice. What is a probability that a sum of results is six? What is the average sum of the results and its variance? What is the probability distribution function. (Using this example recollect: probability space, frequency definition of probability, axiomatic definition of probability, discrete random variables, probability distribution function of a random variable, moments of a random variable).
- 6. Probability theory A stone is falling down from a shelf at a height h. This event is registered by a photo camera at discrete and random times. On each photograph we measure the distance, which the stone has gone. Find a probability distribution function for these distances. Compute the average distance and the standard deviation. What is a probability that the stone was registered at a distance lower then one standard deviation from the average. (Using this example recollect: continuous random variables and their probability distributions, averages and other means).

1.4 Homework problems

- 1. COVID test A large group of people is tested for COVID-19 disease. The proportion of ill people that are correctly identified with positive test result equals 0.9. Tests' specificity (i.e. the percentage of healthy people who are correctly identified as not having some illness) equals 0.95. It is known that 10% of people from the group get positive COVID test result. Determine the true proportion of sick individuals in this group.
- 2. *Stirling's formula* Use the Stirling's formula to estimate the term:

$$1 \cdot 3 \cdot 5 \cdot \cdots \cdot (2n+1)$$

Use the Stirling's formula to estimate the term:

$$2 \cdot 4 \cdot 6 \cdot \cdots \cdot (2n)$$

Use the two to calculate

$$\prod_{n=1}^{\infty} \frac{2n}{2n-1} \frac{2n}{2n+1}$$

- 3. Tennis players Father, trying to motivate his Son to practice her tennis skills, promises him a prize if he wins at least two games in a row with the Father and the Club Master playing according to one of the schemes: Father – Club Master – Father or Club Master – Father – Club Master. Which order should the clever Son choose to maximise the probability of winning the prize if the chance to with with the Father is $p_f = 0.8$, while for the Club Master it is $p_m = 0.4$?
- 4. Bertrand's box paradox There are three boxes: a box containing two gold coins, a box containing two silver coins, a box containing one gold coin and one silver coin. We choose one of the boxes at random and withdraw one of the coins from it, which happens to be a gold coin. What is the probability that theother coin from the same box is also gold?
- 5. *Gaussian distribution* For a Gaussian distribution, given by

$$\mathcal{N}(x;\mu,\sigma) = N \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

(a) Find the normalising constant N. Hint: the integral is easier to do in polar coordinates

(b) Find the mean and the standard deviation.(c) Find the cumulative distribution function for the normal distribution.

(c) If X is a random variable with a standard normal distribution, i.e. $X \sim \mathcal{N}(x; 0, 1)$, what is the distribution of the variable X^2 (known as the chisquared distribution)?

2 Week II, 22-28/10/2020

2.1 Lecture

&3. Microcanonical ensemble - isolated system with constant internal energy, U as an independent macroscopic (thermodynamic) variable, a model of classical ideal gas, microstates $\{\vec{x}_1, ..., \vec{x}_N, \vec{p}_1, ..., \vec{p}_N\}$ and macrostates $\{U, V, N\}$, an expression $\Omega(U, V, N)$ for the total number of microstates at a given $\{U, V, N\}$, role of constants in integration measure, probability distribution $P(\vec{x}_1, ..., \vec{x}_N, \vec{p}_1, ..., \vec{p}_N)$, the total number of microstates $\Gamma(U, V, N)$ up to energy U, units of Γ and Ω , density of states (DOS) in many-body system $\Omega(U, V, N = \partial \Gamma(U, V, N) / \partial U)_{V,N}$, explicit calculation of Γ and Ω for the ideal classical gas at finiet N and in the large N limit, monotonicity of Γ and Ω vs. U for systems with unbound energy spectrum, a remark on systems with bounded energy spectrum and negative absolute temperatures", $\ln \Gamma$ and $\ln \Omega$ and their equivalence in large N limit, holographic principle in thermal physics.

&4. Subsystems in thermal equilibrium - two subsystems with a thermal interaction in the microcanonical ensemble, the most probable state in equilibrium, the thermal equilibrium condition, the Boltzmann definition of an entropy $S(U, V, N) = k_B \ln \Omega(U, V, N)$, the Boltzmann constant $k_B = 1,380649 \cdot 10^{-23} \text{ J} \cdot \text{K}$, absolute temperature $1/T = (\partial S(U, V, N)/\partial U)_{V,N}$, the entropy as a measure of microstates and the most probable macrostate, an information entropy and its properties, additivity of the entropy, an energy transfer from a hotter to a colder system, increase of the entropy in spontaneous processes as a consequence of approaching the system toward the most probable state, the probabilistic interpretations of the second law of thermodynamics, different examples of processes leading to increasing the entropy, equilibrium conditions with thermal, mechanical and chemical interactions, a pressure $p/T = (\partial S(U, V, N)/\partial V)_{U,N}$ and a chemical potential $\mu/T = -(\partial S(U, V, N)/\partial N)_{U,V}$.

2.2 Quizes

2.2.1 Quiz 4

In the microcanonical ensemble a conserved quantity is

- 1. temperature.
- 2. pressure.
- 3. internal energy.
- 4. ideal gas.

Your answer is 3.

2.2.2 Quiz 5

A correct integral measure in the phase space is

1. $\prod_{i=1}^{N} \frac{d_{3}x_{i}d_{3}p_{i}}{h^{3N}N!}.$ 2. $\frac{1}{h^{3N}N!} \prod_{i=1}^{N} d_{3}x_{i}d_{3}p_{i}.$ 3. $\frac{1}{h^{N}N!} \prod_{i=1}^{N} d_{3}x_{i}d_{3}p_{i}.$ 4. $\frac{1}{h^{3N}N} \prod_{i=1}^{N} d_{3}x_{i}d_{3}p_{i}.$ Your answer is 2.

2.2.3 Quiz 6

The Boltzmann entropy is given by

1. $S = k_B \ln \Omega$. 2. $S = k_B \ln \Gamma$. 3. $S = -k_B \ln \Omega$. 4. $S = \frac{1}{k_B} \ln \Gamma$.

Your answer is 1.

2.3 Tutorial

- 1. Identical particles in a box Consider N balls, which can occupy the left or the right half of the container. In the case of N = 4 write down all possible microstates. Let the macrostate be defined by the number of balls in the left half. What are the possible macrostates in this case? How many microstates can realize a given macrostate? What is a probability to find a given macrostate? In the case of N = 10 find all possible macrostates and probabilities of them occurring. Which macrostate is the most probable? Assume that in every second the system changes its microstate and all particles are distributed among the left and the right half with equal probabilities. What is the average time after which we would see all particles in the left half if $N = 10, 40, 10^9$, and 10^{23} ? Compare with other natural time scales.
- 2. Two-level system It is a very popular model describing localized spins 1/2, photons with polarization or atoms in certain states. For spins 1/2 it is visualized that each particle has a magnetic moment pointing up or down. Write down all possible microstates in the case of N = 2, 3, and 4 particles. For the spin system the natural variables describing different macrostates are the total number of particles N and the "magnetization" $M = N_{+} N_{-}$, where N_{\pm} is the numer of moments pointing up and down, respectively. Derive a formula for the number of microstates $\Omega(N, M)$, realizing a given macrostate with N and M. Find the total number of states $\Omega(N) = \sum_{M} \Omega(N, M)$. In the limit of large N show that $\Omega(N, M) \approx \Omega(N, 0) e^{-M^2/2N}$ is Gaussian. Show that $\Omega(N,0) \approx \sqrt{2/\pi N} 2^N$ and estimate its value for N = 100. Which are the most probable microstates?
- 3. Distribution of particles in a container Consider N identical, distinguishable particles occupying k cells. It is a model of a discrete space with particles in it. Microstates are given by the distribution of particles in each cell. Macrostates are characterized by providing numbers of particles n_i in each cell *i*. Derive the formula for the number of microstates for a given macro-state $\Omega(n_1, n_2, ..., n_k) = N!/n_1!n_2! \dots n_k!$. With a fixed number of particles $N = \sum_i n_i$ show that the most probable distribution of particles is such that in each cell there is $n_i = N/k$ of them. In other words, the distribution is uniform.
- 4. Transition times in classical systems A mean free length (the mean length of a path between two consecutive collisions) in one mole of H_2 in atmospheric pressure and temperature T = 300 K is

 $l = 2.7 \cdot 10^{-7}$ m. The mean speed of particles is v = 500 m/s. Estimate a number of collision in one second. How frequently does this system undergo from one micro-state to the other?

5. Transition times in quantum systems - First consider two spins 1/2 in a quantum state $|+-\rangle$. At time t = 0 the Heisenberg interaction $H' = J(S_1^+S_2^- + S_1^-S_2^+)$ is switched on with J = 0.00014 eV. In the lowest order of time-dependent perturbation theory estimate the time that the system transits to the state $|-+\rangle$. Next consider $N = 10^{23}$ spins with the total magnetization equal to zero. Estimate how frequently the system undergoes from one micro-state to the other without changing the zero magnetization macro-state.

2.4 Homework problems

1. *The Cauchy distribution* - Find the normalization and the first two moments (mean and the second moment) for the Cauchy distribution

$$p(x) = \mathcal{N} \frac{\kappa}{(x-a)^2 + \kappa^2}$$

- 2. Rare fluctuation in the air An air in a room of dimensions $3m \times 3m \times 3m$ is under a normal conditions (atmospheric pressure and T = 300K). Estimate a probability that at a given time in a cubic volume a) 1cm³, b) 1A° (angstrom) at any place in this room there is no air due to a statistical fluctuation. Hint: $p \sim \exp(-N(v/V))$, where N is a number of particles, V is a volume of the room, and v is a volume of the small cube.
- 3. Chain of rods N rods o length a are connected together one to each other (the end of one to the beginning of the next) forming a chain. The first rod and the last one are hung on walls remote by a distance l, where l < Na. Find the number of possible microstates Ω . Estimate $\ln \Omega$ at large N. Hints: rods are infinitely thin and placed parallel to each other. If N_{\pm} is the number of rods pointed to the right/left then we must have $l = |N_{+} N_{-}|$ and a number of possible combinations we can find similarly as in the problem with spins.
- 4. Checkerboard Suppose we have a 6×6 checkerboard. Each square of the board represents a localized spin -1/2 particle with two possible spin orientations, one spin-up marked by X and the other spin-down marked by O. We assume that every configuration of the checkerboard is equally likely. The macrostate is defined by a number of X's. What is a probability of a single microstate? How many microstates correspond to the macrostate "15 up spins"?

3 Week III, 28/10-04/11/2020

3.1 Lecture

II. Canonical ensemble:

&1. Canonical ensemble - A system and its reservoir, thermal equilibrium, definition of the canonical ensemble.

&2. Boltzmann distribution - description of the system coupled thermally to the reservoir with temperature T, derivation of the Boltzmann distribution, $p(\epsilon) = e^{-\beta\epsilon}/Z$, $\beta = k_B T$.

&3. Partition function - normalization factor $Z = \sum_{\epsilon} e^{-\beta\epsilon}$, derivation of internal energy from Z, energy fluctuations and the specific heat at constant volume.

&4. *Pressure* - microscopic force and microscopic pressure, the average pressure and its thermodynamic definition, different expressions for pressure.

&5. Heat and the laws of thermodynamics - thermodynamic reminder, reversible and irreversible processes, second law of thermodynamics i n four equivalent formulations, heat and entropy, first law of thermodynamics, work and heat, microscopic understanding of work and of heat.

&6. Helmholtz free energy - definition of Helmholtz free energy F(T, V, N) = U - TS, minimization of the free energy at isothermal processes, different thermodynamic relations from the free energy, physical interpretation of the free energy as an accessible work in isothermal processes, relation between the free energy and the partition function.

3.2 Quizes

3.2.1 Quiz 7

In the canonical ensemble a set of independent thermodynamic variable is

- 1. S, U, V.
- 2. U, V, N.
- 3. T, S, N.
- 4. N, V, T.

Your answer is 4.

3.2.2 Quiz 8

In reversible processes the pressure is expressed by

1.
$$p = -\left(\frac{\partial U}{\partial V}\right)_S$$
.
2. $p = -\left(\frac{\partial U}{\partial V}\right)_T$.
3. $p = -\left(\frac{\partial V}{\partial U}\right)_S$.
4. $p = -\left(\frac{\partial V}{\partial U}\right)_T$.

Your answer is 1.

3.2.3 Quiz 9

Work and heat changes in reversible processes are given by

1. $\delta W = \sum_s \epsilon_s dP(\epsilon_s)$ and $\delta Q = -\sum_s p_s P(\epsilon_s) dV$, respectively.

- 2. $\delta W = -\sum_s p_s dP(\epsilon_s)$ and $\delta Q = \sum_s \epsilon_s P(\epsilon_s) dV$, respectively.
- 3. $\delta W = \sum_{s} p_{s} P(\epsilon_{s}) dV$ and $\delta Q = -\sum_{s} \epsilon_{s} dP(\epsilon_{s})$, respectively.
- 4. $\delta W = -\sum_{s} p_{s} P(\epsilon_{s}) dV$ and $\delta Q = \sum_{s} \epsilon_{s} dP(\epsilon_{s})$, respectively.

Your answer is 4.

3.3 Tutorial

- 1. Microcanonical ensemble equilibrium conditions - An isolated system of the energy U, volume V, and number of particles N (microcanonical ensemble) is split with a partition that allows to exchange the energy and particles and change the volumes of subsystems, i.e. U_i , V_i and N_i , with i = 1, 2, are random variables which are constrained $U_1 + U_2 = U$, $V_1 + V_2 = V$ and $N_1 + N_2 = N$. Let $\Omega_i(U_i, V_i, N_i)$ be the number of microstates corresponding to a given macrostate (U_i, V_i, N_i) of each subsystem. Compute the total number of microstates for a given macrostate of the whole system. Maximizing the corresponding probability, find the equilibrium conditions for those subsystems. Hints: Introduce an entropy $S = k_B \ln \Omega$, temperature $1/T = (\partial S/\partial U)_{V,N}$, pressure $p/T = (\partial S/\partial V)_{U,N}$ and a chemical potential $-\mu/T = (\partial S/\partial N)_{U,V}$.
- 2. One-particle density of states in quantum mechanics - One-particle density of states (DOS) is defined as $\rho(\epsilon) = (1/V) \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}})$, where $\epsilon_{\mathbf{k}}$ is a given dispersion relation and \mathbf{k} is a *d*-dimensional wave vector, accordingly quantized. Find an analytic expression for the DOS in the case of a free particle with the parabolic dispersion relation $\epsilon_{\mathbf{k}} = \hbar^2 \mathbf{k}^2/2m$, where \hbar is the Planck constant and *m* is the mass of a particle. Assume here periodic boundary conditions in a *d*-dimensional hypercube with the volume *V*. Discuss and plot important cases with d = 1, 2, and 3. Find the total number of states up to an energy *E*. Hints: $\delta(f(x)) = \sum_{x_0} \delta(x - x_0)/|f'(x_0)|$, where $f(x_0) = 0$.
- 3. Number of microstates for a classical ideal gas in microcanonical ensemble - For a classical ideal gas in three dimensions find $\Omega(U, V, N)$ and $\Gamma(U, V, N)$. Find the corresponding expansions in case of large N. Hints: $\Gamma(U, V, N) = \int d_{3N}x d_{3N}p/(h^{3N}N!)\Theta(p - \sum_{i=1}^{N} p_i^2/2m),$ $\Omega(U, V, N) = (\partial \Gamma(U, V, N)/\partial U)_{V,N} \delta U$, and apply the Stirling formula $n! = n^n e^{-n}$. A schematic derivation and final results will be shown at the lecture.
- 4. Thermodynamics of an ideal classical gas from microcanonical ensemble - Applying results of the previous problem, also discussed at the lecture, determine the temperature T, the pressure p and the chemical potential μ for an ideal classical gas in

three dimensions. Show the energy equipartition theorem in this example and derive an equation of state for this system.

5. Generalized coordinates and the number of degrees of freedom - Discuss examples of generalized coordinates in mechanical systems and the number of degrees of freedom using a few examples.

3.4 Homework problems

- 1. Monoatomic crystal Atomic nuclei of a certain monoatomic crystal have spin j = 1. Each of them can be in one of the three states characterized by the values $m_j = -1, 0, \pm 1$ of the magnetic quantum number (i.e. the spin projection onto a chosen quantization axis). Energy of a single nucleus is equal $\epsilon > 0$, when $m_j = \pm 1$, and 0 in the state $m_j = 0$. Compute the number of microstates corresponding to a fixed value U of the total energy of the system of N such nuclei. Calculate the entropy of this system as a function of U and N.
- 2. Interfacial region between two fluids Consider two adjoining fluids (fluid 1 and fluid 2) which are homogeneous up to their common interface. In a thin interfacial region between the fluids the composition c of the fluid 1 changes from 1 to 0. Let us assume the interfacial region can be treated as a lattice composed of P flat layers of assigned composition. The layers cannot be interchanged. Each layer contains N molecules. Calculate the entropy of the interfacial region as a function of N and c_p , where c_p is an assigned composition of the p-th layer (for this make use of the Stirling's formula).
- 3. One-particle density of states in quantum mechanics - One-particle density of states (DOS) is defined as $\rho(\epsilon) = (1/V) \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}})$, where $\epsilon_{\mathbf{k}}$ is a given dispersion relation and \mathbf{k} is a *d*-dimensional wave vector, accordingly quantized. Find an analytic expression for the DOS in the case of a free particle with the parabolic dispersion relation $\epsilon_{\mathbf{k}} = c |\mathbf{k}|^{\alpha}$, where *c* is a constant in an appropriate unit (find it), and $\alpha > 0$ is a constant. Assume here periodic boundary conditions in a *d*-dimensional hypercube with the volume *V*. Discuss and plot important cases with d = 1, 2, and 3. Find the total number of states up to an energy *E*.
- 4. Six particles with quantized energies A system contains N = 6 particles with a total energy $U = 6\epsilon$. Distribution of particles among quantized energy levels, $0, \epsilon, 2\epsilon, 3\epsilon, 4\epsilon, 5\epsilon$, and 6ϵ is arbitrary. Find all possible macrostate with a fixed total energy, their number of microstates, and find the average occupation of each energy level.

4 Week IV, 05-11/11/2020

4.1 Lecture

&7. Ideal gas in canonical ensemble - A partition function for the classical ideal gas, de Broglie thermal wave length, different formulations and its interpretation $\lambda_{dB} = \sqrt{2\pi\hbar^2/mk_BT}$ and $\lambda_{dB} = \sqrt{\hbar^2/mk_BT}$, quantum concentration $n_Q = 1/\lambda_{dB}^3$, indistinguishable particles $Z = (n_Q V)^N/N!$, quantum and classical limits $n/n_Q \ll 1$ or $n/n_Q \gg 1$, respectively, thermodynamics: internal energy, specific heat, Helmholtz free energy, pressure, Clapeyron equation of states, entropy, the role of N! term, Gibbs paradox, entropy of mixing.

Maxwell distribution-&8. derivation of Maxwell distribution for classical ideal gases $4\pi (m/2\pi k_B T)^{3/2} v^2 e^{-mv^2/2k_B T}$, average p(v)= and typical velocities, some numerical examples, other formulations of the Maxwell distributions, $p(v_x, v_y, v_z)$ and p(E), experimental ways to determine p(v), "Maxwell temperatureóf ultracold atomic gases in magneto-optical traps, derivation of Clapeyron equation from the Maxwell distribution.

III. Planck distribution and its applications

&1. Planck distribution - single mode vibration of mechanical or electromagnetic systems, Planck hypothesis, energy spectrum of the quantum harmonic oscillator $\epsilon_s = \hbar \omega (s + 1/2)$, dual role of s quantum number and number of modes with a given ω , to be continued.

4.2 Quizzes

4.2.1 Quiz 10

De Broglie thermal wave length can be expressed as

1.
$$\sqrt{\frac{\hbar}{mk_BT}}$$
.
2. $\sqrt{\frac{2\pi\hbar^2}{k_BT}}$.
3. $\sqrt{\frac{2\pi\hbar^2}{mk_BT}}$.
4. $\sqrt{\frac{mk_BT}{2\pi\hbar^2}}$.

Your answer is 3.

4.2.2 Quiz 11

Sakura-Tetrode formula reads

1. $S = nR[\ln(\frac{n_Q}{n}) + \frac{5}{2}].$ 2. $S = nR[\ln(\frac{n_Q}{n}) + \frac{3}{2}].$ 3. $S = nR[\ln(\frac{n}{n_Q}) + \frac{5}{2}].$ 4. $S = nR[\ln(\frac{n}{n_Q}) + \frac{3}{2}].$

Your answer is 1.

4.3 Tutorial

- 1. Spins in magnetic field, microcanonical ensemble -An isolated system on $N \gg 1$ localized spins $\hbar/2$ is in an external magnetic field *B* and is described within a microcanonical ensemble. Find the entropy, internal energy, temperature, magnetization, magnetic susceptibility, specific heat. Discuss results and plot them as a functions of temperature.
- 2. Negative absolute temperatures (This is an additional, not obligatory material for a group more advanced in time. It should be presented by tutors.) - Discuss a problem of the existence and a meaning of a negative absolute temperature in systems of localized spins and in systems with itinerant degrees of freedom. Discuss historical and recent experimental findings. Discuss thermodynamics and, in particular, an energy transfer between two systems if the negative temperatures are allowed. Literature:
 - N. Spisak, Foton 132, Wiosna 2016, p. 16;
 - S. Braun et al., Science 339, p. 52 (2013);
 - N. Ramsey, Phys. Rev. 103, p. 20 (1956);
 - M. Klein, Phys. Rev. 104, p. 589 (1956);
 - D. Frenkel et al., Am. J. Phys. 83, p. 163 (2015) (!!!);
 - E. Abraham, et al., Phys. Rev. E 95, p. 012125 (2017) (!!!);

4.4 Homework problems

- 1. Consider a classical gas in volume V. Gas consists of N particles, each of mass m. The internal energy of the gas equals U. Calculate the probability that the energy of a selected particle in this gas is contained within E and E + dE.
- 2. Gas fluctuations in a cubic box A cubic box with isolating (adiabatic) walls of length L contains N particles of an ideal gas. Find the dispersion of the centre of mass of the system in equilibrium. How does the dispersion behave with the increasing number of particles in the box?

5 Week V, 12-18/11/2020

5.1 Lecture

&1. Planck distribution - continued, Boltzmann distribution for quantized harmonic oscillator energies, the partition function as a sum of geometric series, the average occupation of a single mode $\langle s \rangle = 1/(e^{\hbar \omega/k_B T} - 1)$, Planck distribution, the internal energy, specific heat, free energy, and entropy of the harmonic oscillator, high- and low-temperature limits.

&2. Black body radiation - the resonance cavity and the solution of Maxwell equation for a simple cubic cavity box, Planck hypothesis about quantization of energy in the electromagnetic field, the internal energy and the density of internal energy, Stefan-Boltzmann law and their constant, thermodynamics of the electromagnetic radiation and the equation of state, the spectral energy density and the Planck law $u(\omega) = (\hbar/\pi^2 c^3) \omega^3/(e^{\hbar\omega/k_BT} - 1)$, the classical limit and the ultraviolet catastrophy, the average number of excited models and its temperature dependence, radiation from a cavity and the energy flux of radiation, total energy flux and the Stefan-Boltzmann law, photometric quantities: luminous intensity and candela [cd], luminous flux and lumen [lm], illuminance and lux [lx], to be continued.

5.2 Quizzes

5.2.1 Quiz 12

Planck distribution reads

- 1. $\frac{1}{e^{\beta\hbar\omega}+1}$. 2. $\frac{1}{e^{\beta\hbar\omega}-1}$. 3. $\frac{1}{e^{-\beta\hbar\omega}+1}$.
- 4. $\frac{1}{e^{-\beta\hbar\omega}-1}$.

Your answer is 2.

5.2.2 Quiz 13

Planck law for spectral energy density for a black body radiation is

1.
$$\frac{\hbar}{\pi^2 c^3} \frac{\omega^1}{e^{\beta \hbar \omega} - 1}.$$

2.
$$\frac{\hbar}{\pi^2 c^3} \frac{\omega^2}{e^{\beta \hbar \omega} - 1}.$$

3.
$$\frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta \hbar \omega} - 1}.$$

4.
$$\frac{\hbar}{\pi^2 c^3} \frac{\omega^4}{e^{\beta \hbar \omega} - 1}.$$

Your answer is 3.

5.2.3 Quiz 14

According to the Stefan-Boltzmann law the total energy flux is

1. $J(T) = \sigma T^4$. 2. $J(T) = \sigma T^3$. 3. $J(T) = \sigma T^2$. 4. $J(T) = \sigma T^1$.

Your answer is 1.

5.3 Tutorial

- 1. Classical ideal gas, the partition function Derive the partition function for the classical ideal gas starting from a) quantized energy levels, b) classical kinetic energy for particles. Compare results and pay attention on h and N! factors.
- 2. Thermodynamics of ideal gas derived microscopically - From the partition function of the classical gas derive: internal energy, specific heat, Helmholtz free energy, pressure and equation of states, internal anergy, entropy. Derive the same expression for the entropy using results from microcanonical ensemble.
- 3. Ising spins in canonical ensemble Consider a system of N Ising spins in a magnetic field. Derive the partition function and discuss thermodynamics of this system by deriving internal energy, magnetization, free energy, entropy, magnetic susceptibility.
- 4. Work microscopically and macroscopically in the canonical ensemble Assuming that the energy level $\epsilon_i(X)$ changes with the change of the control parameter X introduce a microscopic force $F_i = -d\epsilon_i/dX$ and a microscopic work $\delta W_i = F_i dX$. Derive an equation for the macroscopic work $\delta W = k_B T(\partial \ln Z/\partial X) dX$. Discuss this result for ideal gas in a box of volume ($\delta W = -pdV$) and for Ising spins in a magnetic field ($\delta W = MdB$).
- 5. Work, heat, entropy and exact forms Recollect the first and the second laws of thermodynamics $(dU + \delta W = \delta Q$, and $\delta Q = TdS$), where δW is the work performed by the system. Discuss the difference between the state function U and its differential dU and the not state functions δW and δQ . Provide a physical interpretation. Show that $dU + \delta W$ is not an exact form (use $\delta W =$ $k_B T(\partial \ln Z/\partial X) dX$ and $U = -(\partial \ln Z/\partial \beta)$. Show that $\beta(dU + \delta W)$ is an exact form with the integration factor $S/k_B = \ln Z - \beta(\partial \ln Z/\partial \beta)$. Show the equivalence of S with the thermodynamic entropy $S - -(\partial F/\partial T)_{X,N}$.

5.4 Homework problems

- 1. Based on the Boltzmann distribution $P(\epsilon) = e^{-\beta\epsilon}/Z(T, V, N)$ calculate the internal energy $U(T, V, N) = \langle \epsilon \rangle$ and its dispersion $\sigma(U)^2 = \langle \epsilon^2 \rangle \langle \epsilon \rangle^2 = k_B T^2 C_v$. Recall the definition of the heat capacity $C_x = (\delta Q/dT)_x$ at constant x and from the first law of thermodynamics, find the formula for $C_v = (\partial U/\partial T)_{VN}$.
- 2. Prove the Dalton's law (which states that in a mixture of non-reacting gases, the total pressure is equal to the sum of the partial pressures of the individual gases) for a mixture of classical gasses using the canonical ensemble. Hint: Calculate the statistical sum for the mixture of gasses and make

use of the definition of the pressure, as it was done during the lecture for one-component gas.

- 3. A system can be in states of energies $0, \epsilon, \epsilon, \epsilon, 2\epsilon$. Calculate the internal energy of this system and the specific heat at temperature T.
- 4. Statistical sum satisfies the relation $\ln Z = aT^{\alpha}V$, where a and α are positive constants. Calculate specific heat of this system.
- 5. Consider N magnetic moments, which have two allowed orientations $\pm \mu$ in an external magnetic field B (the energy of each dipole can take values $\pm \mu B$). Within the canonical ensemble, find the relative dispersion of the magnetisation $\sigma_M/M = \sqrt{\langle M^2 \rangle \langle M \rangle^2}/\langle M \rangle$.

6 Week VI, 19-25/11/2020

6.1 Lecture

&2. Black body radiation - continued, absorption and emission coefficients, the perfect mirror and the black body, the gray body, Kirhchoff's law and its proof, universality of black body radiation formula, (stimulated) absorption, spontaneuos emission, stimulated emission, Einstein coefficients, detailed balance.

&3. Specific heat of solids, phonons - definition of the heat capacity (extensive) and the specific heat (intensive), harmonic model of crystal lattices, normal modes of vibrations, classical theory of the specific heat of solids, experimental evidences at low temperatures for the specific heat, Einstein's model of the specific heat of crystals and its limitations, Debye's model of the specific heat, Debye length, Debye wave vector, Debye frequency, phonons, emergent particles, emergency vs determinizm.

6.2 Quizzes

6.2.1 Quiz 15

Absorption of a perfect mirror $A(\omega, T)$ is equal to

- 1. zero for all frequencies.
- 2. one for all frequencies.
- 3. zero for selected frequencies.
- 4. one for selected frequencies.

Your answer is 1.

6.2.2 Quiz 16

The heat capacity is

- 1. intensive.
- 2. proportional to the temperature.
- 3. extensive.
- 4. inversely proportional to the temperature.

Your answer is 3.

In the Debye model the specific heat at low temperatures behaves as

- 1. $C_V \sim \text{const.}$
- 2. $C_V \sim T^3$.
- 3. $C_V \sim T^4$.

4.
$$C_V \sim T^{-2} e^{-T_0/T}$$

Your answer 2.

6.3 Tutorial

- 1. Classical ideal gas of two-atom molecules Ideal gas is composed of molecules with two atoms of mas m_1 and m_2 . Atoms inside a molecule interact with each other with the potential of model (expanded) form $V(r) = V(r_0) + (1/2)m\omega_0\xi^2$, with $\xi = r - r_0$. For a single molecule find the kinetic energy in relative and center of mass coordinates. Then find the partition function and discuss each contributing terms. For the translationally invariant part use the earlier results for a monoatomic ideal gas. For rotational and vibrational degrees of freedom show that $Z_1^{\text{rot}} = 2Ik_BT/\hbar^2$ and $Z_1^{\text{vib}} = k_BT/\hbar\omega_0$, where $I = mr_0^2$.
- 2. Classical ideal gas of two-atom molecules thermodynamics - For a gas of diatomic molecules find: internal energy, specific heat at constant volume, Helmholtz free energy, pressure and equation of state, entropy.
- 3. Classical gas of electric dipoles in an electric field - For a classical gas of electric dipoles \vec{d} in the electric field \mathcal{E} find partition function, Helmholtz free energy, and polarization. The interacting potential between the dipoles and the field is $V = -\vec{d} \cdot \vec{\mathcal{E}}$ and masses of the ions are m_1 and m_2 . A dipol is made out of two atoms which charges are distributed such that on one ends there is a charge qand on the opposite end the charge is -q.
- 4. Maxwell distribution characteristics Find the typical (the most probable) velocity, the averaged velocity, the averaged square velocity and the dispersion form the Maxwell distribution in three dimensional space. Estimate those quantities for an oxygen gas at normal conditions.
- 5. Maxwell distribution equation of states Using the hypothesis of molecular chaos, where particles are moving chaotically with the velocity distribution given by the Maxwell formula, find the pressure and the equation of state for the ideal gas.
- 6. *Barometric formula* Find the formula describing how the pressure of the ideal gas in a uniform gravitational field changes with the altitude and the temperature.

6.4 Homework problems

- 1. A ball of radius R moves with velocity \mathbf{u} in a dilute ideal gas of temperature T and density n. Assuming that the collisions of gas particles with the ball are ellastic calculate the drag force exerted on the ball during its movement. Estimate the result for air at normal conditions and for a typical football.
- 2. A small hole of area S was drilled in a container with ideal gas. Estimate the number of particles per unit time that fall on a disc of radius R placed at a distance h from the hole. The disc plane is parallel to the hole plane. The centers of the disc and the hole are located along a straight line perpendicular to the hole plane. Assume that velocities of gas particles are described by the Maxwell distribution and the hole is so small that the leakage does not disturb the thermodynamic equilibrium state inside the container.
- 3. Two containers in which the pressures p_1 and p_2 , respectively and temperatures T_1 and T_2 are constantly maintained are connected by a small tube with a cross section S. Calculate the mass of the gas which flows from one container to the second one per unit time if the mass of a single gas particle equals m and $p_1 = 2p_2$, $T_1 = 2T_2$.
- 4. *The Maxwell distribution* For the Maxwell distribution of gas particle velocities in an ideal gas

$$\rho(\mathbf{v}) = \left(\frac{m}{2kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right),$$

where T is the temperature and m is the mass of a gas particle

(a) find the typical (average) velocity of a gas particle,

(b) find the average relative velocity of two particles $|\mathbf{v}_{12}| = |\mathbf{v}_1 - \mathbf{v}_2|$. Comment on the relation between the two results.

7 Week VII, 26/11-02/12/2020

7.1 Lecture

IV. Grand canonical ensemble

&1. Chemical potential - systems with chemical (diffusive) interaction (coupling), thermodynamic condition of equilibrium, definition of the chemical potential $\mu(T, V, N) = (\partial F / \partial N)_{T,V}$, direction of particle flow from higher to lower chemical potentials, the chemical potential for multicomponent systems, example: the chemical potential for ideal gas, internal and external chemical potential, electrochemical potential, magnetochemical potential, etc.

&2. Chemical potential and entropy - thermodynamic relations - thermodynamic derivation of $\mu = -T(\partial S/\partial N)_{U,V}$, first thermodynamic law for open systems. &3. Grand canonical ensemble - Gibbs distribution - definition of the grand canonical ensemble, derivation of Gibbs distribution from the equal probability hypothesis a priori, grand partition function, thermodynamic quantities from the grand partition function.

7.2 Quizzes

7.2.1 Quiz 18

The chemical potential is equal to

- 1. $(\partial F/\partial N)_{T,V}$ and is extensive.
- 2. $(\partial F/\partial N)_{U,V}$ and is intensive.
- 3. $(\partial F/\partial N)_{U,V}$ and is extensive.
- 4. $(\partial F/\partial N)_{T,V}$ and is intensive.

Your answer is 4.

7.2.2 Quiz 19

The chemical potential is equal to

1.
$$-T(\partial S/\partial N)_{T,V}$$
.

2.
$$-T(\partial S/\partial N)_{U,V}$$

3.
$$T(\partial S/\partial N)_{U,V}$$
.

4.
$$-T(\partial S/\partial U)_{T,V}$$
.

Your answer is 2.

7.2.3 Quiz 20

The grand partition function reads

1.
$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} \sum_{\epsilon_s(N)} e^{-\frac{\epsilon_s(N) + \mu N}{k_B T}}.$$

2.
$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} \sum_{\epsilon_s(N)} e^{-\frac{\epsilon_s(N) - \mu N}{k_B T}}.$$

3.
$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} \sum_{\epsilon_s(N)} e^{\frac{\epsilon_s(N) - \mu N}{k_B T}}.$$

4.
$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} \sum_{\epsilon_s(N)} e^{\frac{\epsilon_s(N) + \mu N}{k_B T}}.$$

Your answer is 2.

7.3 Tutorial

- 1. Discuss with students three problems from the colloquium one.
- 2. Rotated cylinder with the ideal gas An ideal gas is in the cylindrical container of height h and radius R, which rotates with the angular velocity ω with respect to symmetry axis. Fins the pressure acting on the cylinder wall. The number of particles Nand the temperature T are given.

7.4 Homework problems

1. Correlations in an ideal gas The measure of (in)dependence of two random variables is their correlation. Find the correlation function between two components of velocity

$$C(v_x, v_y) = \langle v_x v_y \rangle - \langle v_x \rangle \langle v_y \rangle$$

for an ideal gas assuming a Maxwell velocity distribution. Can you guess the result before calculating?

- 2. Find the center of gravity of an ideal gas in the cylinder in the uniform gravity field g at the temperature T. An atomic mass m is given.
- 3. A mixture of l ideal gases, with different atomic masses $m_{i=1,...,l}$ are closed in a cylinder of the radius R and the height h in a gravitational field of the Earth. Find the position of the center of gravity of this mixture.

8 Week VIII, 03-09/12/2020

8.1 Lecture

&4. Grand canonical potential - thermodynamic definition of the grand canonical potential, definition of the grand canonical potential in statistical physics in grand canonical ensemble, differential form of the grand canonical potential, the first thermodynamic law for system exchanging energy and particles, summary of the three ensembles, mathematical definition of Legendre transform, summary of the most relevant thermodynamical potentials (state functions): internal energy, entropy, Helmholtz free energy, entalpy, Gibbs free energy, grand canonical potential, example of ideal classical gas in the grand canonical ensemble, the partition function, activity, thermodynamic quantities and derivation of the equation of state, the chemical potential in explicit form.

V. Ideal quantum gases

&1. Wave function of many-body particles - quantum mechanics reminder: a single particle in a box with the periodic boundary condition, two non-interacting ideal particles and they wave function, Heisenberg uncertainty principle and indistinguishability of identical quantum particles, symmetry of the many-body wave function under permutation of particles, symmetric and antisymmetric wave functions, fermions and bosons, spin-statistics theorem, some examples, Pauli exclusion principle.

8.2 Quizzes

8.2.1 Quiz 21

The first thermodynamical law in open systems is expressed by

1.
$$dU = SdT - pdV + \mu d\bar{N}$$
.
2. $dU = TdS + pdV + \mu d\bar{N}$.

3.
$$dU = TdS - pdV - \mu d\bar{N}.$$

4.
$$dU = TdS - pdV + \mu d\bar{N}.$$

Your answer 4.

8.2.2 Quiz 22

The grand canonical potential for an ideal gas is given by

- 1. $\Phi = -k_B T \alpha \frac{V}{\lambda_{dB}^3}.$ 2. $\Phi = +k_B T \alpha \frac{V}{\lambda_{dB}^3}.$
- 3. $\Phi = -k_B T \alpha \frac{\lambda_{dB}^3}{M}$.

$$\lambda = 1 - \lambda_{dB}^3$$

4.
$$\Phi = k_B T \alpha \frac{AB}{V}$$

Your answer 1.

8.2.3 Quiz 23

The true statement is:

- 1. All bosons have half-integer spins and all fermions have half-integer spins.
- 2. All bosons have integer spins and all fermions have half-integer spins.
- 3. All bosons have integer spins and all fermions have integer spins.
- 4. All bosons have half-integer spins and all fermions have integer spins.

Your answer 2.

8.3 Tutorial

- 1. Quantum harmonic oscillator For a single harmonic oscillator find the partition function, the average number of excitations, the internal energy, the specific heat, the free energy, the entropy, and discuss the low- and high- temperature limits.
- 2. Electromagnetic radiation of a resonance cavity An electromagnetic radiation is captured inside an resonance cavity of cubic shape with the length L and the temperature T, where metallic walls are perfect conductors. Find the partition function, the average number of excitations, the internal energy, the specific heat, the free energy, the entropy, and discuss the low- and high- temperature limits.
- 3. *Photons in the Universe* Estimate the average number per volume of photons in the Universe. Assume its temperature to be 3K. Estimate the entropy per volume of the Universe.

- 4. Two-atomic molecule and separation of degrees of freedom¹ On the quantum mechanical ground justify that the energy of a tow-atom molecule H_2^+ reads $E_{\mathbf{K},J,\nu} = \hbar^2 K^2 / 2m_s + \hbar \omega (\nu + 1/2) + \hbar^2 J (J + 1)/2I + V_0$, where m_s is a mass of the system, ω is the resonant frequency of oscillations, I is the moment of inertia, V_0 is the potential energy at the equilibrium. Quantum numbers: \mathbf{K} continuous wave vector, $\nu = 0, 1, 2, 3, ...$ and J = 0, 1, 2, 3, ... Forget the spins of electrons and nucleus and apply the Born-Oppenheimer approximation.
- 5. Quantum theory of specific heat for ideal gas of two-atomic molecules Assuming that one can separate different degrees of freedom in a twoatom molecule one can write the partition function as $Z = Z_{trans} Z_{vib} Z_{rot} Z_{electr}$, where each term represents contributions from translational, oscillation, rotation, and electronic degrees of freedom, respectively. Find contributions from oscillational and rotational degrees of freedom to the specific heat and discuss low and high temperature limits. Discuss the typical temperature dependence of the specific heat and characteristic energy/temperature scales.

8.4 Homework problems

- 1. The Sun constant is 1360 J/m²s and describes amount of energy approaching from Sun to Earth in a unit of time and per unit of area. The distance Sun-Earth is $1.3 \cdot 10^{11}$ m and the Sun radius is $7 \cdot 10^8$ m. Find the total power of the Sun and its temperature.
- 2. Find an approximate formula for the Wien's shift law.

9 Week IX, 10-16/12/2020

9.1 Lecture

&2. Fermi-Dirac and Bose-Einstein distribution functions - The grand partition functions for fermions and bosons, the grand canonical potential for fermions and bosons, the average number of particles in a given quantum states for fermions and bosons, Fermi-Dirac function, Bose-Einstein function.

&3. Quantum corrections to ideal gases - high temperature expansion of the grand canonical potential for fermions and bosons, the activity as a formal small control parameter of the expansion, the first quantum correction to the grand canonical potential, the quantum corrections to the equation of states in classical gases, corrections to pressure for fermions and bosons.

&4. Gas of ideal fermions at T = 0 - the ground state of non-interacting fermions, the main characteristics: Fermi energy, Fermi wave vector, Fermi momentum, Fermi wave length, Fermi velocity, Fermi temperature, the idea of Fermi sea, Fermi wave vector and

 $^{^1\}mathrm{Discuss}$ by the tutor if time allows, otherwise skip it, please. See also the next week IX.

the particle density, different numerical examples and some estimates, the internal energy of ideal fermions, the pressure in the ground state and its origin, additional factors to stabilize the fermionic systems, Pauli paramagnetism, Pauli susceptibility.

9.2 Tutorial

Only one group is going to have a tutorial in this week so the problems are supposed to be supplementary, i.e. this material is not obligatory during exams.

- 1. Two-atomic molecule and separation of degrees of freedom - On the quantum mechanical ground justify that the energy of a tow-atom molecule H_2^+ reads $E_{\mathbf{K},J,\nu} = \hbar^2 K^2 / 2m_s + \hbar \omega (\nu + 1/2) + \hbar^2 J (J + 1)/2I + V_0$, where m_s is a mass of the system, ω is the resonant frequency of oscillations, I is the moment of inertia, V_0 is the potential energy at the equilibrium. Quantum numbers: \mathbf{K} continuous wave vector, $\nu = 0, 1, 2, 3, ...$ and J = 0, 1, 2, 3, ...Forget the spins of electrons and nucleus and apply the Born-Oppenheimer approximation.
- 2. Quasiparticles and the specific heat Find the specific heat at low temperatures of quasiparticles in d-dimensions with the dispersion relation $\epsilon_{\mathbf{k}} = \epsilon_0 (k/k_0)^{\alpha}$, where $\mathbf{k} = 2\pi/L[n_1, n_2, ...n_d]$, L is the system length and n_i are integers. The exponent $\alpha > 0$ and ϵ_0 has energy unit and k_0 has momentum unit. In condensed matter systems one can design or tailor such excitations that at low energy limit their dispersion relation might have an arbitrary power law. One of such examples are excitations of one-dimensional interacting electrons, known as Luttinger liquids.
- 3. Thermal radiation of q-ons Consider a hypothetical excitations in three dimensions with linear dispersion relation $\epsilon_p = cp$, such that a maximal numer of excited quanta is $q \ge 1$. The case of $q = \infty$ corresponds to either photons or phonos. In case of magnetic excitations of a magnetic, so called a spin waves, the maximal number of excited modes is constrained by the spin and then q = 2s + 1. derive the partition function, the averaged number of excitations and discuss limits, the internal energy, the specific heat at constant V, the Helmholtz free energy, the entropy, the pressure, the equation of state, the average number of excitations in volume V. Discuss different limits of q and compare with known results for photons.

9.3 Homework problems

1. Solve a classical model for 1D crystal with the Hook's interactions between atoms and with periodic boundary conditions. Calculate eigenmodes, disparsion relation and wavenumbers. Calculate the statistical sum, internal energy and specific heat. Hint: Recall the same problem from the quantum mechanics course. 2. Quantize the classical model from the previous task. Calculate the statistical sum, internal energy and the specific heat in the Debeye approximation.

10 Week X, 17-23/12/2020

10.1 Lecture

&4. Gas of ideal fermions at T = 0 - continued, a gas of ideal fermions in infinite dimensions.

&5. Gas of ideal fermions at low temperatures - general integrals involving the Fermi-Dirac function, the density of states in energy space, the heat capacity and the specific heat for fermions, the low-temperature Sommerfeld expansion, the low-temperature expansion of the specific heat, the effective mass and examples of different systems: liquid ³He, alkali and transition metals, heavy fermions.

&6. Landau quasiparticles - Foundation of the Landau Fermi liquid theory, concept of weakly interacting fermionic quasiparticles, the Landau energy functional, the effective mass and the renormalization factor, selected results from Fermi liquid theory: specific heat, Pauli susceptibility, compressibility, sound speed and they renormalizations.

11 Week XI, 07-13/01/2021

11.1 Tutorial

- 1. Chemical potential for ideal gas Using the Helmholtz free energy, find a chemical potential for an ideal gas assuming that the the energy of a molecule is a sum of kinetic, rotation, oscillation and electronic energies.
- 2. Chemical potential in chemical reactions In chemical reactions molecules can decay or can be created, this is symbolically described by the equation $\sum_{i=1}^{r} b_i B_i \leftrightarrow \sum_{i=r+1}^{M} b_i B_i$, where B_i is a molecule symbol and b_i is the smallest integer according to conservation of atomic numbers. Let $\nu_i = -b_i$ for i = 1, ..., r and $\nu_i = b_i$ for i = r+1, ..., M. Show that in thermodynamical equilibrium for isothermal (T = const) and isochoric (V = const) reactions $\sum_{i=1}^{M} \nu_i \mu_i = 0$, where μ_i is a chemical potential for the *i*th molecule. Illustrate with examples.
- 3. Law of mass action Derive the law of mass action (Guldberg, Waage, 1867) $\prod_{i=1}^{M} n_i^{\nu_i} = K(T)$, where $n_i = N_i/V$ is a density of the *i*th molecule, and find an explicit expression for the equilibrium constant K(T). Treat molecules as classical ideal gases. Illustrate with examples.
- 4. Changes of the free energy in chemical reactions - Show that in thermal equilibrium it is obeyed $\prod_{i=1}^{M} N_i^{\nu_i} = \exp(-\Delta F_0/k_B T)$ for any chemical reaction, where ΔF_0 is the change of the free energy of the system.

5. Model of adsorption - As a simple model of adsorption consider an ideal classical gas and a surface with N holes. In every hole there might be maximally one particle and then its energy is $-\epsilon < 0$. Find the covering coefficient $k = \bar{N}/M$, where \bar{N} is the average number of particles adsorbed on the surface. Hint: use grand canonical ensemble.

11.2 Homework problems

1. Give explicit formulas for the law of mass action and the equilibrium constant for the reactions:

$$N_2O_4 \leftrightarrow 2NO_2$$

$$2H_2 + O_2 \leftrightarrow 2H_2O$$

2. Calculate explicit form of the relation $\sum_{i=1}^{M} \nu_i \mu_i = 0$ for the reactions

$$ClNO_2 + NO \leftrightarrow NO_2 + ClNO$$

$$N_2O_4 \leftrightarrow 2NO_2$$

3. A neutral gas consists of N_e electrons e^- , N_p protons p^+ , and N_H Hydrogen atoms H. An electron and a proton can combine to form Hydrogen

$$e^- + p^+ \leftrightarrow H.$$

At fixed temperature and volume, the free energy of the system is $F(T, V; N_e, N_p, N_H)$. we can define a chemical potential for each of the three species as

$$\mu_i = \frac{\partial F}{\partial N_i}$$

By minimizing the free energy, together with suitable constraints on the particle numbers, show that the condition for equilibrium is

$$\mu_e + \mu_p = \mu_H.$$

Such reactions usually take place at constant pressure, rather than constant volume. What quantity should you consider instread of F in this case?

12 Week XII, 14-20/01/2021

12.1 Lecture

&7. Bose-Einstein condensation - 1926 Einstein's prediction of a macroscopic occupation oh the lowest energy state for bosons, negativity and temperature dependence of the chemical potential for ideal bosons, convergency issue of the boson partition function, occupations of the ground and excited states, physical understanding of the phase transition to condensed phase, critical temperature for condensation, temperature dependence of occupation of ground and excited states, microscopic and macroscopic properties of condensed bosons, indistinguishability and a common wave function with the same phase for all condensed bosons, macroscopic phase coherence, similarity in laser physics, experimental observation of Bose-Einstein condensation, bosonic alkali atoms, idea of a magnetic traps and cooling the system, signatures of experimental verification of the condensation: macroscopic occupation and interference, comparison of of condensed bosons in free space and in a harmonic potential, time of flight experiments.

&8. Superfluidity - phase diagram and unique properties of ⁴He atoms, lambda transition in a specific heat, frictionless capillary flow of HeII, infinite heat conductance and no biling in HeII, thermomechanical effect, mechanothermal effect, Andronikashvili effect, two fluid model of Tisza and Landau, special properties of superfluid component, quantization of vortices, twofluid thermodynamics, simple understanding of thermomechanical effect, to be continued,

12.2 Quizzes

12.2.1 Quiz 24

Number of bosons in the Bose-Einstein condensate depends on temperature as

1.
$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_{BEC}}\right)^{5/2}$$

2. $\frac{N_0}{N} = 1 - \left(\frac{T}{T_{BEC}}\right)^{2/3}$
3. $\frac{N_0}{N} = 1 - \left(\frac{T}{T_{BEC}}\right)^{2/5}$
4. $\frac{N_0}{N} = 1 - \left(\frac{T}{T_{BEC}}\right)^{3/2}$

Your answer is 4.

12.2.2 Quiz 25

The phases of bosons in the Bose-Einstein condensate are

- 1. arbitrary for each particle.
- 2. the same for each particle.
- 3. random for each particle.
- 4. zero or 2π for each particle.
- Your answer 2.

12.2.3 Quiz 26

To prove the existence of the Bose-Einstein condensation one has to observe

- 1. macroscopic occupation of a single level or interference fringes.
- 2. interference fringes.
- 3. macroscopic occupation of a single level and interference fringes.
- 4. macroscopic occupation of a single level.

Your answer 3.

12.3 Tutorial

- Grand canonical ensemble ideal gas Consider non-relativistic ideal classical gas in the grand canonical ensemble in three space dimensions. Find:

 (a) the partition function,
 (b) the grand canonical thermodynamic potential,
 (c) the average number of particles,
 (d) the pressure,
 (e) the entropy,
 (f) the internal energy.
- 2. Ideal gas in the grand canonical ensemble For an ideal classical gas show that: (a) $\bar{N} = -\beta \Phi(T, V, \mu)$, (b) the probability of finding exactly N particles is given by a Poisson law $P_N = e^{-\bar{N}} \bar{N}^N / N!$.
- 3. Ideal gas in the gravity field the grand canonical ensemble derive a formula expressing a density of particles at the level z = H with respect to the ground level z = 0 assuming the uniform gravity field U(z) = mgz. Derive the barometric formula for the pressure.
- 4. Ideal quantum gases grand canonical ensemble -Show explicitly that the averaged occupation of the orbital kth is given by $n_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} \pm 1}$, i.e. by Fermi-Dirac and Bose-Einstein distribution functions, respectively for fermions and bosons.

12.4 Homework problems

- Grand canonical ensemble ultra-relativistic ideal gas - Consider ultra-relativistic ideal classical gas in the grand canonical ensemble in three space dimensions. The dispersion relation is ε_p = cp, where c is a given velocity constant and p is a length of the momentum. Find: (a) the partition function, (b) the grand canonical thermodynamic potential, (c) the average number of particles, (d) the pressure, (e) the entropy, (f) the internal energy.
- 2. Fluctuation of particle number i grand canonical ensemble Derive the formula for the variance of particle number $\sigma_N^2 = \langle N^2 \rangle \langle N \rangle^2$ in the grand canonical ensemble and show that the relative fluctuation of the particle umber $\sigma_N / \langle N \rangle \sim 1 / \sqrt{\langle N \rangle}$ vanishes in the thermodynamic limit.

13 Week XIII, 21-27/01/2021

13.1 Lecture

&8. Superfluidity - continued, quasiparticles and superfluidity, Landau criterium for critical velocity of a superfluid.²

VI. Phase transitions:

&1. Phase and phase diagram - Definition of thermodynamical phases, examples of phases, phase diagrams for solid-liquid-gas phases, a triple point, a critical point, first order transition lines, melting-freezing transition, sublimation-resublimation, condensation-evaporation, discontinuous and continuous phase transitions, phase diagram for a magnetic phase transition.

&2. First order phase transition - continuous Gibbs entalpy G(T, p, N) = U - pV - TS at phase transition of first order, discontinuous first derivatives of the Gibbs entalpy $S = -(\partial G/\partial T)_p$ and $V = (\partial G/\partial p)_T$ at phase transition of first order, coexistence of phases solidliquid, liquid-vapor, latent heat $\Delta Q_L = T\Delta S$, condition for the phase coexistence $\mu_1(p, T0 = \mu_2(p, T))$, why does the salt melt the ice?, Clausius-Clapeyron equation - derivation and discussion.

&3. Ehrenfest classification of phase transitions - definition of the order of the phase transition with respect to discontinuity of the m-the order derivatives of the thermodynamical potential, 1-st order phase transition - characteristics, 2-nd order phase transitions - characteristics, example of specific hat jump in superconducting transition, divergence of response functions in case of infinite correlation length at 2-nd order phase transitions, continuous and discontinuous entropy, jump in the volume and density, jump in the magnetization and hysteresis.

&4. Mean field -theory I - van der Waals equation of state - role of interparticle interactions in phase transitions, heuristic modification of ideal gas equation of state to include finite radius of molecules and finite attractive interaction and longer distances, van der Waals equation, microscopic derivation of the van der Waals equation via virial expansion - sketch of derivation, virial coefficients, to be continued.

13.2 Quizzes

13.2.1 Quiz 27

At the critical point the phase transition is

- 1. 1st order.
- 2. 2nd order.
- 3. 3rd order.
- 4. 4th order.

Your answer 2.

13.2.2 Quiz 28

Clausius-Clapeyron relation reads

1.
$$\left(\frac{dT}{dp}\right)_{\Delta G=0} = \frac{\Delta Q_L}{T\Delta S}$$
.
2. $\left(\frac{dp}{dT}\right)_{\Delta G=0} = \frac{\Delta Q_L}{S\Delta T}$.
3. $\left(\frac{dp}{dT}\right)_{\Delta G=0} = \frac{\Delta Q_L}{T\Delta V}$.
4. $\left(\frac{dT}{dp}\right)_{\Delta G=0} = \frac{\Delta V}{T\Delta Q_L}$.

Your answer 3.

²Not presented.

Van der Waals equation of state reads

1. $(p + a \left(\frac{n}{V}\right)^2)(V - bn) = nRT.$ 2. $(p - a \left(\frac{n}{V}\right)^2)(V - bn) = nRT.$ 3. $(p + a \left(\frac{n}{V}\right)^2)(V + bn) = nRT.$ 4. $(p - a \left(\frac{n}{V}\right)^2)(V + bn) = nRT.$

Your answer 1.

13.3 Tutorial

- 1. Ideal quantum gases grand canonical ensemble - For ideal bosons and fermions derive integral expressions for: (a) the partition function, (b) the grand canonical thermodynamic potential, (c) the average number of particles, (d) the pressure, (e) the entropy, (f) the internal energy. Introduce the necessary polylogarithmic functions $g_n(z)$ and $f_n(z)$ for bosons and fermions, respectively.
- 2. Ideal quantum gases at hight temperature grand canonical ensemble - For ideal bosons and fermions we have derived integral expressions for: (a) the partition function, (b) the grand canonical thermodynamic potential, (c) the average number of particles, (d) the pressure, (e) the entropy, (f) the internal energy. In the high temperature limit find explicitly quantum corrections to the chemical potential, the internal energy and the pressure. Discuss the results and the role of quantum statistics on pressure.
- 3. Ideal fermions at low temperatures Sommerfeld expansion - Derive a low temperature expansion for the general integral $\int d\epsilon H(\epsilon) f(\epsilon)$, where $f(\epsilon)$ is the Fermi-Dirac function. Write down explicitly terms up to $(k_B T)^4$ order.
- 4. Ideal fermions at low temperatures thermodynamics - Derive expressions in the low temperature expansion up to $(k_BT)^2$ order for the chemical potential, the internal energy, the specific heat, the entropy, and the free Helmholtz free energy for ideal fermions.

13.4 Homework problems

1. Ideal quantum gases at hight temperature - grand canonical ensemble - For ideal bosons and fermions with ultrarelativistic dispersion relation $\epsilon_p = cp$ derive integral expressions for: (a) the partition function, (b) the grand canonical thermodynamic potential, (c) the average number of particles, (d) the pressure, (e) the entropy, (f) the internal energy. In the high temperature limit find explicitly quantum corrections to the chemical potential, the internal energy and the pressure. Discuss the results and the role of quantum statistics on pressure. 2. Ideal fermions at low temperatures - thermodynamics - Derive expressions in the low temperature expansion up to $(k_B T)^4$ order for the chemical potential, the internal energy, the specific heat, the entropy, and the free Helmholtz free energy for ideal fermions.

14 Week XIV, 28-31/01/2021

14.1 Lecture

&4. Mean field -theory I - van der Waals equation of state - continued, alternative mean-field derivation of the van der Waals equation, finding the critical point, phase separation, coexistence condition, free energy and Maxwell construction.

&5. Mean field theory II - Ising model - introduction to Ising model, exact partition function and magnetization, application of the Ising model, needs for approximate solution, mean-field approximation as neglection of correlation fluctuations, mean-field energy and the interpretation of the mean magnetic field, the menafield partition function and the self-consistent equation for the magnetization, solution of the mean-field equation at zero magnetic field, the critical temperature, critical behavior of the magnetization and the magnetic susceptibility, concept of universal critical exponents, free-energy expansion and Landau approach to phase transitions.

14.2 Quizzes

14.2.1 Quiz 30

At the critical point of the van der Waals gas the ratio pV/nRT is

- 1. 2/3.
- 2. 3/4.
- 3. 3/8.
- 4. -3/8.

Your answer is 3.

14.2.2 Quiz 31

The critical (Curie) temperature of the Ising model within the mena-field approximation is

1. $T_c = k_B/2zJ$. 2. $T_c = 2zJ/k_B$ 3. $T_c = 2zk_BJ$. 4. $T_c = 2zk_B/J$.

Your answer is 2.

14.2.3 Quiz 32

The universal critical exponent γ_{-} of the mean-field susceptibility is

- 1. -1.
- 2. +1.

3.
$$-1/2$$

4.
$$+1/2$$

Your answer is 2.

14.3 Tutorial

- 1. Complete solutions of problems from the previous week.
- 2. Bosons at low temperatures 1. represent a grand thermodynamical potential by a polilogarithmic function and derive formal expressions for the particle density, pressure, internal energy. Discuss properties of the $g_{\alpha}(z)$ functions vs. z - the activity. 2. find the explicit formula for the T_{BEC} condensation temperature, derive expression for the activity z, 3. derive an expression for the density of bosons inside the condensed fraction, 4. derive an equation for pressure and the equation of state.
- 3. If time allows, discuss all or selected solution to problems in the last mid-term exam (colloquium).

14.4 Homework problems

- 1. Consider tow dimensional bosons and show that the Bose-Einstein condensation occurs only at T = 0. Discuss thermodynamics of such bosons.
- 2. Show that in one dimension the Bose-Einstein is impossible.
- 3. Supposing that the dispersion relation is $\epsilon_k = ak^{\alpha}$ and the system is *d* dimensional, derive a condition for α when the Bose-Einstein condensation can occur at T > 0 case.

15 Literature

- Ch. Kittel, H. Kroemer, Thermal Physics.
- K. Huang, Statistical mechanics.
- F. Schwabl, Statistical mechanics.
- R.H. Swendsen, An introduction to statistical mechanics and thermodynamics.
- F. Reif, Statistical physics.
- F. Mandl, Statistical physics.
- H.B. Callen, Thermodynamics.