Statistical Physics A

winter term 2022-23

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Team

Lecture:
prof. dr hab. Krzysztof Byczuk, Tue. 10:15-13:00 (2.03)
Tutorials:
dr hab. Maciej Lisicki, Thursday, 14:15-17:00 (2.23)
dr hab. Marta Wacławczyk, Wednesday, 8:15-11:00 (1.01)

Consultations:
Possible with each of us, on-line or stationary, at any convenient time after earlier e-mail notice and arrangement.

Rules

Lectures and tutorials will be carried out in classrooms. Home problems will be given every week and are not obligatory to solve. However, one of them you might expect on exams.

- Standard way of passing the course (in the end points are normalized to 100)
  - Activity, group working on tutorials, 10 pt.
  - Mid-term written exam (Colloquium), 3 problems, 30 pt.
  - Final written exam, 3 problems, 30pt.
- Retaking to pass the course
  - Exam, 4 problems, total number of points scaled to 100pt.

Final grade is 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 (retaking) exams do not sum up. In case of switching to on-line teaching, due to COVID19, some rules need to be modified.

Dates of mid term and final exams:

1. Mid term written exam (kolokwium): December 5th, 2022, 9:15-13:00, room B0.14
2. Final written exam (egzamin pisemny): February 6th, 2023, 9:15-13, room B0.14
3. Second final written exam (egzamin pisemny poprawkowy): February 20th, 2023, 9:15-13:00, room 1.03

1 Week I, 03-09/10/2022

1.1 Lecture

I. Basics of Thermodynamics:

&1. *Thermodynamic laws* - Primary definitions: thermodynamic variables, thermodynamic state (macrostate), conditions of equilibrium, extensive and intensive variables, equation of state, example ideal gas and thermometer. Thermodynamic laws: the Zero-th law of thermodynamics, definitions of thermodynamic process, to be continued...

1.2 Tutorial

1. *Equation of state* - From an experiment it is known that
$$\left(\frac{\partial p}{\partial V}\right)_T = -nRTf(V),$$
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} - 2nRTa,$$
where n - number of mole, a - a constant, $f(V)$ - an arbitrary function. Find the equation of state.
2. *Exact and inexact differentials*
   (a) Show that $\not{d}F(x,y) = xdx + xdy$ is inexact differential because the integral from $(0,0)$ to $(1,1)$ depends on a path. Consider two paths A: $(0,0)-(1,0)-(1,1)$ and B: $(0,0)-(0,1)-(1,1)$.
   (b) Derive the condition for the differential $dF(x,y)$ to be exact.
   (c) Introduce an integrating factor $dG(x,y) = r(x,y)\not{d}F(x,y)$. Consider $\not{F}(x,y) = ydx + dy$ and find its integrating factor.
3. *Thermodynamic potentials and Maxwell relations* - For a gas described by the fundamental relation $dU = TdS - pdV$ derive corresponding thermodynamic potentials: internal energy $U(S,V)$, entalpy $H(S,p)$, Helmholtz free energy $F(T,V)$, and Gibbs free energy $G(T,p)$ by choosing proper independent variables. Derive all possible Maxwell relations. Discuss equivalence and usefulness of different thermodynamic potentials in description a system.

4. *Engine efficiency* - Find efficiency of an engine working in
    (a) Carnot's cycle,
    (b) Otto's cycle. (optionally, if time allows)

   Remind students the heat capacity and specific heat at constant V and p.

1.3 Homework

1. A gas is described by the fundamental relation $U = \frac{AS^3}{nV}$, where $A = const$. Find the equation of state $p(T, V, n)$.

2. A gas fulfills the van der Waals equation of state: $p(T, v) = \frac{RT}{v-b} - \frac{a}{v^2}$, where a, b, R are positive constants, and $v = V/n$. Demonstrate that the specific heat c_v of this gas does not depend on volume V.

3. Evaluate $c_p - c_v$ for a gas fulfilling the Clapeyron equation of state $p = nRT/V$.

4. The internal energy of a certain one-component gas involving $n = 2$ moles fulfills the equation $U = ApV^2$, where A is a known constant. Find $U(p, V, n)$ for any n.

2 Week II, 10-16/10/2022

2.1 Lecture

I. Basics of Thermodynamics: ... cont. , reversible process (in general sense), reversible process (in narrow sense), pseudostatic process, quasistatic process, fact: reversible processes are quasistatic, definition of mechanical work$W$, in reversible processes $\text{đ}W = Fdx$, x generalized coordinate, F generalized force, meaning of đ, examples: $\text{đ}W = -pdV$, $\text{đ}W = \mu dN$, definition of heat Q, definition of internal energy U as a state function, meaning of the state function, conservation energy, the First law of thermodynamics, $dU = \text{đ}W + \text{đ}Q$, definition of entropy S as a state function, properties, the Second law of thermodynamics, for isolated system $\Delta S \geqslant 0$, for arbitrary system $\text{đ}Q \leqslant TdS$, T absolute temperature, fundamental relation in quasistatic processes (so U and S are defined) $dU = TdS - \sum_k F_k dx_k$, equation of state $T = (\partial U/\partial S)_{x_i}$ and $F_k = -(\partial U/\partial x_k)_{x_i \neq x_k}$, in reversible processes $\text{đ}Q = TdS$ and $\text{đ}W = -\sum_k F_k dx_k$, (S, x_i) generalized coordinates, (T, F_k) generalized forces, entropy coordinate is related with a motion in microscopic scale, third law of thermodynamics $\lim_{T\to 0} S = S_0$ - a universal constant, usually taken to be zero.

&2. *Thermodynamic response functions* - Heat capacity $C_x(\text{đ}Q/dT)_x$, specific heat, different expressions to determine heat capacity, vanishing of heat capacity at zero temperature, compressibility $\kappa_x = -(\partial V/\partial p)_x/V$, coefficient of thermal expansion $\alpha == -(\partial V/\partial T)_p/V$, relations between different response functions.

&3. *Magnetic and electric systems* - Magnetic work $\text{đ}W = \mu_0 H dM$, fundamental relation for magnetic system $dU = TdS = \mu_0 H dM$, magnetic heat capacity, total magnetic moment, magnetization, magnetic susceptibility, electric work $\text{đ}W = Ed\mathcal{P}$, electric heat capacity, electric susceptibility.

2.2 Tutorial

1. *Entropy change* - An n mole of water at temperature T_1 is in a thermal contact with a very large environment at temperature T_2. Find changes of entropy: a) in the water, b) in the environment, and c) in the whole system, when the temperature of both gets equal. Mole specific heat is given c_V. Discuss the importance of the assumption that the environment must be infinitely large.

2. *Heat capacity* - Show that heat capacities are expressed by the two state functions
$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$
   and
$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p.$$

3. *Response functions* - Show that
$$\kappa_T(C_p - C_V) = TV\alpha^2$$
   and
$$C_p(\kappa_T - \kappa_S) = TV\alpha^2.$$

4. *Magnetic wok* - Derive the expression for work in magnetic systems
$$\text{đ}W = \mu_0 H dM.$$

5. *Electric work* - Derive the expression for work in electric systems
$$\text{đ}W = Ed\mathcal{P}.$$

2.3 Homework

1. Consider a magnetic system subject to a magnetic field H. Its fundamental thermodynamic relation is given by
$$dU = TdS + \mu_0 H dM, \tag{1}$$
   where μ_0 is the vacuum magnetic permeability and M is the total magnetic moment of such a system. Derive the respective thermodynamic potentials for such a system, as well as the heat capacities at constant magnetic moment and constant magnetic field. What are the isothermal and adiabatic susceptibility?

   If you redo all steps above considering
$$dU = TdS - \mu_0 M dH, \tag{2}$$
   what are the changes? Comment on them.

2. Consider an electric system subject to an electric field E. ts fundamental thermodynamic relation is given by

   $$dU = TdS + Ed\mathcal{P}, \tag{3}$$

   where $\mathcal{P}$ is the dipole moment. Redo problem 1 for such a system.

3. A magnetic compound behaves according to the Curie law, $m = CH/T$, where C is a constant, H is the applied magnetic field, m is the magnetization per particle, and T is temperature. In a quasi-static process, we have

   $$du = Tds + Hdm, \tag{4}$$

   where $u = u(s, m)$ plays the role of an internal energy. For an infinitesimal adiabatic process, show that we can write

   $$\Delta T = \frac{CH}{c_H T}\Delta H, \tag{5}$$

   where c_H is the specific heat at constant magnetic field.

4. The chemical potential of a simple fluid of a single component is given by

   $$\mu = \mu_o(T) + k_B T \log(p/p_o(T)), \tag{6}$$

   where μ_o and p_o are well behaved functions of T. Show that this system obeys Boyle's law. Obtain expressions for c_p, c_v, κ_T (isothermal compressibility), α (thermal expansion coefficient), and the Helmholtz free energy $f(T, v)$.

3 Week III, 17-23/10/2022

3.1 Lecture

II. Foundations of statistical physics:

&1. *Main observations* - A goal of statistical physics, few examples, a large number of components in macroscopic systems, the definition of *mole* and Avogadro number $N_a = 6,02214076 \cdot 10^{23}\mathrm{mol}^{-1}$, few examples, (the mole'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 many-body 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 physics* - 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 self-averaging 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.

III. Microcanonical ensemble:

&1. *Isolated system in microcanonical ensembe* - 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 finite N, to be continued...

3.2 Tutorial

1. (If time allows) *Change of entropy in ideal gas* - Find the entropy change of an n mole of ideal gas in a reversible process from a state A (p_A, V_A, T_A) to a state B (p_B, V_B, T_B). Specific heats c_V and c_p are given.

2. *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 $J = \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx$.

3. *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 $l = 1, 2, 3, ...$.

4. *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).

5. *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.

3.3 Homework

1. *Entropy change of van der Waals gas*

A van der Waals gas for which

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

changes its state from (T_1, V_1) to (T_2, V_2). Derive expression for changes in entropy of n moles of this gas corresponding to this change in state. The specific heat c_V is given.

2. *Stirling's formula* - Use the Stirling's formula to estimate the term:

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

   Use the Stirling's formula to estimate the term:

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

   Use the two to calculate

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

3. *n-dimensional ball* - Volume of n-dimensional ball is expressed by the formula

   $$V_n = \frac{\pi^{n/2} r^n}{\Gamma(n/2+1)}$$

   ($n > 0$ is a natural number). Prove that the non-dimensional parameter V_n/r^n attains its maximum value for $n = 5$.

4. *Gamma function* - Express the following integral in terms of the Gamma function

   $$I = \int_0^1 \mathrm{d}x x^2 \left(\ln \frac{1}{x}\right)^3 .$$

4 Week IV, 24-30/10/2021

4.1 Lecture

III. Microcanonical ensemble:

&1. *Isolated system in microcanonical ensembe* - ...continued, 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 ńegative absolute temperatures", $\ln \Gamma$ and $\ln \Omega$ and their equivalence in large N limit, holographic principle in thermal physics.

&2. *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 $k_B = 1,380649 \cdot 10^{-23}$ J $\cdot$ 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 $\mu/T = -(\partial S(U,V,N)/\partial N)_{U,V}$.

IV. Canonical ensemble:

&1. *Canonical ensemble* - A system and its reservoir, thermal equilibrium, definition of the canonical ensemble, (T,V,N) as independent thermodynamic variables.

&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 $Z(T,V,N) = \sum_\epsilon e^{-\beta\epsilon}$, derivation of internal energy from Z, $U(T,V,N) = T^2 \partial/\partial T(k_B \ln Z(T,V,N))$, energy fluctuations and the specific heat at constant volume, $\langle \epsilon^2 \rangle - \langle \epsilon \rangle = k_B T^2 C_V$.

...to be continued

4.2 Tutorial

1. *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).

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 $f(x_0) = 0$.

4.3 Homework

1. *Probability theory* - We roll two dice. What is the probability that the sum of the results is six? What is the average sum of the results and its variance? What is the probability distribution function?

2. *Particles in a box* - Consider N balls, each of which can be placed in the left or the right half of a 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 the probability to find a given macrostate? In the case of $N = 10$ find all the possible macrostates and probabilities of their occurrence. Which macrostate is the most probable? Assume that 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 expected 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. Treat the balls as distinguishible objects throughout the analysis.

5 Week V, 31/10-06/11/2022

5.1 Lecture

No lecture in this week.

5.2 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. *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 are shown at the lecture.

3. *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.

5.3 Homework

1. *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 macrostates?

2. *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.

3. *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?

   Solution The system is isolated, so each state of a fixed energy E is equally probable (the distribution of states is microcanonical). Thus

$$p(\vec{r}_1, ..., \vec{r}_N, \vec{p}_1, ..., \vec{p}_N) = \frac{1}{\Omega(E, V, N, \delta E)},$$

where

$$\Omega(E, V, N, \delta E) = \int_{E<H<E+\delta E} d\Gamma.$$

Integrating over the momenta, we get the distribution for positions

$$p(\vec{r}_1, ..., \vec{r}_N) = \frac{1}{L^{3N}}$$

We introduce a coordinate system with the origin in the middle of the cube. The centre of mass is defined as $\vec{R} = \frac{\sum_i m_i \vec{r}_i}{\sum_i m_i}$, so by symmetry

$$\langle \vec{R} \rangle = \frac{\sum_i m_i \langle \vec{r}_i \rangle}{\sum_i m_i} = 0.$$

Now

$$\langle R^2 \rangle = \left\langle \frac{1}{N^2} \left(\sum_{i=1}^{N} r_i \right)^2 \right\rangle =$$

$$= \left\langle \sum_{i=1}^{N} \frac{1}{N^2} r_i^2 + \sum_{i \neq j}^{N} \frac{1}{N^2} r_i r_j \right\rangle$$

because the variables are independent and $\langle r_i \rangle = 0$, we have

$$\left\langle \sum_{i \neq j}^{N} \frac{1}{N^2} r_i r_j \right\rangle = 0$$

and thus

$$\langle R^2 \rangle = \frac{1}{N} \langle r_1^2 \rangle = \frac{3}{N} \langle x_1^2 \rangle = \frac{L^2}{4N}$$

so we find

$$\sigma = \frac{L}{2\sqrt{N}}.$$

6 Week VI, 07-13/11/2022

6.1 Lecture

IV. Canonical ensemble: continued ...

&4. *Pressure* - microscopic force and microscopic pressure $p_s = -d\epsilon_S(V)/dV$, the average pressure and its thermodynamic definition $p = -(\partial U/\partial V)_S$, different expressions for pressure $p = T(\partial S/\partial V)_U$.

&5. *Heat and the laws of thermodynamics* - thermodynamic reminder, reversible and irreversible processes, second law of thermodynamics and its 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.

&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 $\lambda_{dB} = \sqrt{h^2/mk_BT}$, 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.

... to be continued.

6.2 Tutorial

1. *Harmonic oscillator in microcanonical ensemble* - A system is described by a set of classical harmonic oscillators with the Hamiltonian

$$H = \sum_{i=1}^{N} \left(\frac{\vec{p}_i^2}{2m} + \frac{1}{2} m\omega^2 \vec{r}_i^2 \right).$$

   Compute $\Gamma(U, V, N)$, $\Omega(U, V, N)$, entropy, temperature, specific heat, pressure, and chemical potential. Why volume is not present?

2. *Spins in magnetic field, microcanonical ensemble* - An isolated system of $N \gg 1$ 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.

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. Compare microcanonical and canonical description.

4. *Negative absolute temperatures* (This is an additional material if time allowes, 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) (!!!);

6.3 Homework

1. *Rare fluctuation in the air* - An air in a room of dimensions 3m×3m×3m is under a normal conditions (atmospheric pressure and $T = 300$K). Estimate a probability that at a given time in a cubic volume a) 1cm^3, 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.

2. *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.

3. Statistical sum satisfies the relation $\ln Z = aT^{\alpha}V$, where a and α are positive constants. Calculate specific heat at constant volume of this system.

4. 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 $\sigma_M/M = \sqrt{\langle M^2\rangle - \langle M\rangle^2}/\langle M\rangle$.

7 Week VII, 14-20/11/2022

7.1 Lecture

IV. Canonical ensemble: continued ...

&8. *Maxwell distribution* - derivation of Maxwell distribution for classical ideal gases $p(v) = 4\pi(m/2\pi k_BT)^{3/2}v^2e^{-mv^2/2k_BT}$, average 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 temperature' of ultracold atomic gases in magneto-optical traps, derivation of Clapeyron equation from the Maxwell distribution.

V. 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,

&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 $u(\omega) = (\hbar/\pi^2c^3)\omega^3/(e^{\hbar\omega/k_BT} - 1)$, the classical limit and the ultraviolet catastrophy, the average number of excited models and its temperature dependence, to be continued ...

7.2 Tutorial

1. *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 $\text{đ}W_i = F_idX$. Derive an equation for the macroscopic work $\text{đ}W = k_BT(\partial\ln Z/\partial X)dX$. Discuss this result for ideal gas in a box of volume ($\text{đ}W = -pdV$) and for Ising spins in a magnetic field ($\text{đ}W = MdB$).

2. *Work, heat, entropy and exact forms* - Recollect the first and the second laws of thermodynamics ($dU + \text{đ}W = \text{đ}Q$, and $\text{đ}Q = TdS$), where $\text{đ}W$ is the work performed by the system. Discuss the difference between the state function U and its differential dU and the not state functions $\text{đ}W$ and $\text{đ}Q$. Provide a physical interpretation. Show that $dU + \text{đ}W$ is not an exact form (use $\text{đ}W = k_BT(\partial\ln Z/\partial X)dX$ and $U = -(\partial\ln Z/\partial\beta)$. Show that $\beta(dU + \text{đ}W)$ 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 $S = -(\partial F/\partial T)_{X,N}$.

7.3 Homework

1. 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.

2. 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.

3. *Tonk's gas* – 1D system consists of N small segments, each of them of mass m and length σ moving along a section of length L ($L >> N\sigma$). The segments do not pass through each other. Treating the system as classical, calculate the canonical statistical sum, Helmholz free energy and equation of state of the gas created by such segments.

4. The probability density function of measuring the value E of an internal energy of a classical ideal gas, which remains in the thermal equilibrium with a thermostat of temperature T, can be written as

$$\rho(E) = \frac{E^a\exp(-\beta E)}{\int_0^\infty E^a\exp(-\beta E)\mathrm{d}E},$$

where

$$a = \frac{3N}{2} - 1, \quad \beta = \frac{1}{k_BT}.$$

Using this function calculate the mean energy and derive the most probable value of the energy. Show that the two are indistinguishable for the classical ideal gas.

8 Week VIII, 21-27/11/2022

8.1 Lecture

&2. *Black body radiation* - ...continued, radiation from a cavity and the energy flux of radiation, total energy flux and the Stefan-Boltzmann law, 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, spontaneous 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 of crystals, T^3 law for the specific heat, Debye length, Debye wave vector, Debye frequency, phonons, emergent particles, emergency vs determinizm.

8.2 Tutorial

1. *Classical ideal gas, the partition function in canonical ensemble* - 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 in canonical ensemble* - 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. *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 $Z_1^{\mathrm{rot}} = 2Ik_BT/\hbar^2$ and $Z_1^{\mathrm{vib}} = k_BT/\hbar\omega_0$, where $I = mr_0^2$.

4. *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.

8.3 Homework

1. Suppose there are two systems I and II in thermal contact with a heat bath at temperature T and there exists some mechanism enabling the two systems to exchange particles. Obtain the expression for the probability of having a distribution (N_I, N_{II}) of particles into I and II in terms of the partition functions $Z_I(N_I, T)$ and $Z_{II}(N_{II}, T)$, and derive the condition for finding the most probable distribution.

2. The three lowest energy levels of a certain molecule are $E_1 = 0$, $E_2 = \epsilon$, $E_3 = 10\epsilon$. Show that at sufficiently low temperatures (how low?) only levels E_1 and E_2 are populated. Find the average energy of the molecule at temperature T. Find the contributions of these levels to the specific heat (per mole). Sketch the specific heat as a function of temperature.

3. Consider a gas of noninteracting point-like particles of mass m and temperature T, enclosed in a huge container. In one of the container walls a small hole of area A was created, through which the particles may escape into vacuum. Consider a short time interval Δt. What is the probability of finding a particle of velocity between $\vec{v}$ and $\vec{v}+d\vec{v}$ among the particles leaving the container in this time interval? What is the rate of change $-dN/dt$ of the particle number in the container?

9 Week IX, 28/11-04/12/2022

9.1 Lecture

VI. 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.

&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, to be continued ...

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.

9.2 Tutorial

1. *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.

2. *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.

3. *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. Find the pressure acting on the cylinder wall. The number of particles N and the temperature T are given.

9.3 Homework

1. *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 q and on the opposite end the charge is $-q$.

2. *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?

3. 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.

4. A mixture of l ideal gases, with different atomic masses $m_{i=1,\ldots,l}$ 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.

5. *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.

10 Week X, 05-11/12/2022

10.1 Lecture

&4. *Grand canonical potential* ... continued, 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.

VII. 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.

&2. *Fermi-Dirac and Bose-Einstein distribution functions* - The grand partition functions for fermions and bosons, the grand canonical potential for fermions and bosons, ...to be continued.

the average number of particles in a given quantum states for fermions and bosons, Fermi-Dirac function, Bose-Einstein function.

10.2 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.

10.3 Homework

1. A one-dimensional quantum harmonic oscillator is in thermal equilibrium with a heat bath at temperature T.
   (a) What is the mean oscillator's free energy as a function of T?
   (b) What is the root mean-square fluctuation ΔE in energy?
   (c) How do the above quantities behave for low and high T?

2. The Sun constant is 1360 J/m^{2}s 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.

3. Find an approximate formula for the Wien's shift law.

4. Calculate the temperature of the surface of the Earth on the assumption that as a black body in thermal equilibrium it re-radiates as much thermal radiation as it receives from the Sun. Assume also that the surface of the Earth is at a constant temperature over the day-night cycle. Use $T_{sun} = 5800K$, $R_{sun} = 7 \cdot 10^8 m$ and the distance between the Earth and the Sun $D_{ES} = 15 \cdot 10^{10} m$. How this result compares with the measured average temperature on Earth equal to around $288K$ (or around 15° C)?

   What is the average temperature on the Mars planet, if the distance between the Mars and the Sun is ca. 1.5 times larger than the distance between the Earth and the Sun.

5. *Greenhouse effect.* Most of the Sun's radiation passes through the atmosphere. On the other hand, Earth's atmosphere contains gases which absorb most of the infrared radiation, emitted by the Earths surface. This leads to the increase of the Earth's temperature and is called the "greenhouse effect."

   Consider the atmosphere to be a thin layer transparent to the sun's radiation, and perfectly absorbent to all the Earth's radiation. Assume that the atmosphere radiates half of its energy outward to space and half of it inward back to Earth. The Earth is in radiative equilibrium with the Sun and the atmosphere. The atmosphere is in radiative equilibrium with the Earth (as it absorbs no Sun's radiation). The separation between the atmosphere and the Earth's surface is negligible. Calculate the temperature of the Earth. How result of this simple model compares with the measured average temperature on the Earth?

11 Week XI, 12-18/12/2022

11.1 Lecture

&2. *Fermi-Dirac and Bose-Einstein distribution functions* - ... continued, 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 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.

11.2 Tutorial

1. Two-atomic molecule and separation of degrees of freedom[1] - 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. *Quantum theory of specific heat for ideal gas of two-atomic molecules* - Assuming that one can separate different degrees of freedom in a two-atom 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.

3. *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.

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[1] Discussed by the tutor if time allows, otherwise skip it, please. In such a case give some intuitive introduction to problem 5.

4. *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 ith molecule. Illustrate with examples.

5. *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 ith molecule, and find an explicit expression for the equilibrium constant $K(T)$. Treat molecules as classical ideal gases. Illustrate with examples.

6. *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.

11.3 Homework

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 instead of F in this case?

12 Week XII, 19-22/12/2022

12.1 Lecture

&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 ^{3}He, 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.

&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.

Have a wonderful holiday time and happy New Year!

12.2 Tutorial

1. *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.

2. A metal surface can adsorb gas atoms of mass m. It requires work ϕ to remove a single atom from the metal. The adsorbed atoms may freely move on the metal surface, so that they constitute a two-dimensional gas. The metal was brought to a contact with a (three-dimensional) gas of fixed temperature T and pressure p. Find the (surface) density of atoms adsorbed in the metal. Treat both the metal and the environment as classical, monatomic ideal gases with atomic masses m.

13 Week XIII, 9-15/01/2023

13.1 Lecture

&8. *Superfluidity* - phase diagram and unique properties of ^{4}He 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, two-fluid thermodynamics, simple understanding of thermomechanical effect, quasiparticles and superfluidity, Landau criterium for critical velocity of a superfluid.

13.2 Tutorial

1. *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 kth orbital 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.

13.3 Homework

1. *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 $\epsilon_p = cp$, 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.

3. Show that the entropy in the grand canonical ensemble can be written as $S = -k_B\sum_j P_j \log P_j$, where $P_j = \Xi^{-1}\exp(-\beta E_j + \beta\mu N_j)$.

4. At a given temperature T, a surface with N_o adsorption centers has $N \leqslant N_o$ absorbed molecules. Suppose that there is no interaction between molecules. Calculate the chemical potential of the adsorbed gas.

14 Week XIV, 16-22/01/2023

14.1 Lecture

VIII. 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 solid-liquid, 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.

14.2 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 polylogaritmic 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 $(k_B T)^2$ order for the chemical potential, and optionally if time allows, for the internal energy, the specific heat, the entropy, and the Helmholtz free energy for ideal fermions. Hint, express everything for a general density of states $\rho(\epsilon)$ and in the end take it for free fermions in three dimensions.

14.3 Homework

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 Helmholtz free energy for ideal fermions. Hint, express everything for a general density of states $\rho(\epsilon)$ and in the end take it for free fermions in three dimensions.

3. *Pauli paramagnetism* - Derive expressions in the low temperature expansion up to $(k_B T)^2$ for the magnetic susceptibility of ideal fermions in three dimensions. Assume Zeeman type of interaction between magnetic moments of fermions and external magnetic induction. Hint, $T = 0$ case was discussed during the lecture.

15 Week XV, 23-29/01/2023

15.1 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.

15.2 Tutorial

1. *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.

2. *Vapor pressure* - Assuming that the vapor is an ideal gas and that the latent heat q is constant show tat on the coexistence line between a liquid and a gas on the phase diagram $p(T) \sim e^{-q/RT}$.

3. *Critical point* - Find the critical pressure p_c, temperature T_c and molar volume v_c when the gas becomes a liquid for the first time if the equation of states is

   (a) *van der Waals*

   $$p(V) = \frac{nRT}{V-nb} - \frac{an^2}{V^2},$$

   (b) *Dieterici (only if time allows)*

   $$p(V) = \frac{nRT}{V-nb} e^{-\frac{na}{RTV}}.$$

   Express those equation of states in therms of the reduced variables $\pi = p/p_2$, $\tau = T/T_c$, and $\phi = v/v_c$. Note $v = V/n$.

4. *Ising model - exact solution* - Solve $d = 1$ Ising model with a) open boundary condition, b) with periodic boundary condition. Compute the specific heat.

5. *Ising model - antiferromagnetic mean-field solution (only if time allows)* - Using mean-field approximation solve the Ising model with antiferromagnetic exchange coupling. Determine the Neel temperature.

15.3 Homework

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.

4. Show, that for a phase transition between the phase 1 to the phase 2 the latent heat changes with the temperature T as

$$\frac{dQ}{dT} = c_p^{(1)} - c_p^{(2)} - \frac{Q}{T} + Q\frac{v_2\alpha_p^{(2)} - v_1\alpha_p^{(2)}}{v_2 - v_1},$$

where $c_p^{(i)}$ is the heat capacity of the i-th phase at constant pressure and $\alpha_p^{(i)}$ is the thermal expansion coefficient of the i-th phase, and $v_i = V_i/n$. Show that the approximate expression if the phase 2 is an ideal gas is given by

$$\frac{dQ}{dT} = c_p^{(1)} - c_p^{(2)}.$$

(Hint, then $v_2 \gg v_1$).

16 Literature

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