Thermodynamics and ideal gas of bosons

After recalling the classical free scalar field and its canonical quantization in Lecture I, we briefly present here the principles of thermodynamics and derive properties of an ideal gas of bosons.

Thermodynamics

- Thermodynamics makes no reference to microscopic structure of matter but it uses well defined concepts like exact differential, state function, integrating factor. It offers a universal description of various equilibrium systems, and approximate approach to static or quasi-static systems.

- A thermodynamic description of any system employs the three laws of thermodynamics that form an axiomatic basis.

- The **first law of thermodynamics** states that the system's energy U is the state function and

$$dU = dQ - pdV, \tag{1}$$

  where dQ is the heat transfer, p is the pressure and V is the system's volume. The differential dU is exact even so dQ is not.

- The **second law of thermodynamics** states that $dS = \frac{dQ}{T}$, where dQ is the heat transfer in reversible process and T is the temperature, is the exact differential. Consequently, the entropy S is the state function. In general

$$dS \geqslant \frac{dQ}{T}, \tag{2}$$

  where the inequality holds for irreversible processes.

- The second law is often written as

$$S(B) - S(A) \geqslant \int_A^B \frac{dQ}{T}. \tag{3}$$

  When $dQ = 0$ we have $S(B) \geqslant S(A)$ which says that the entropy of an isolated system is a non-decreasing function of time.

- According to the **third law of thermodynamics**, the entropy of any system in the temperature of absolute zero is a universal constant which can be chosen as zero.

- We will often use the free energy $F = U - TS$ the minimum of which determines a system's state at fixed T and V. Using the first and second principle of thermodynamics (for reversible processes), one writes

$$dF = dU - SdT - TdS = -pdV - SdT, \tag{4}$$

  As seen $dF = 0$ if $dV = 0$ and $dT = 0$. So, there is extremum of F if T and V are fixed. Since in general $dQ \leqslant TdS$, we get

$$dF = dQ - TdS \leqslant 0 \tag{5}$$

  for $dV = dT = 0$. So, there is a minimum of F if T and V are fixed.

- The pressure is given as

$$p = -\left(\frac{\partial F}{\partial V}\right)_T,$$

(6)

where the derivative is taken at fixed T.

From statistical mechanics to thermodynamics

- In statistical mechanics we usually deal with quantities which are averaged over an interval of time which is long in a microscopic scale.

- The average over time is replaced by the average over ensemble. One assumes here the ergodic hypothesis which states that all accessible microstates are equiprobable over a long period of time.

- When the system under consideration is isolated, we use the microcanonical ensemble.

- When the system under consideration is in contact with a heat bath and there is an exchange of energy, we use the canonical ensemble.

- When the system under consideration is in contact with a heat bath and there is an exchange of energy and charges, we use the grand canonical ensemble.

- Further on, we will mostly use the canonical ensemble and we will compute the partition function defined as

$$Z(T) \equiv \sum_\alpha \langle \alpha | e^{-\beta \hat{H}} | \alpha \rangle,$$

(7)

where $\beta \equiv T^{-1}$ is the inverse temperature and $\hat{H}$ is the system's Hamiltonian.

- Since the system's average energy U equals

$$U = \frac{1}{Z(T)} \sum_\alpha \langle \alpha | e^{-\beta \hat{H}} \hat{H} | \alpha \rangle,$$

(8)

one defines the energy as

$$U \equiv -\frac{d}{d\beta} \ln Z(T).$$

(9)

- The second relation with thermodynamics is postulated to be

$$F(T) \equiv -T \ln Z(T),$$

(10)

where $F = U - TS$ is the free energy. It allows one, in particular, to compute the pressure using Eq. (6).

Partition function of ideal boson gas

- We are going to use the states $|n_1, n_2, n_3, \dots\rangle$ to derive a partition function of an ideal boson gas which is defined as

$$Z(T) \equiv \sum_\alpha \langle \alpha | e^{-\beta \hat{H}} | \alpha \rangle = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{n_3=0}^{\infty} \dots \langle n_1, n_2, n_3, \dots | e^{-\beta \hat{H}} | n_1, n_2, n_3, \dots \rangle,$$

(11)

where is the Hamiltonian $\hat{H}$ equals

$$\hat{H} = \sum_i \omega_i \hat{a}_i^\dagger \hat{a}_i.$$

(12)

- Since $|n_1, n_2, n_3, \dots \rangle$ is the energy eigenstate and

$$e^{-\beta \hat{H}} |n_1, n_2, n_3, \dots \rangle = e^{-\beta(\omega_1 n_1 + \omega_2 n_2 + \omega_3 n_3 + \dots)} |n_1, n_2, n_3, \dots \rangle, \tag{13}$$

we have

$$\langle n_1, n_2, n_3, \dots | e^{-\beta \hat{H}} |n_1, n_2, n_3, \dots \rangle = e^{-\beta(\omega_1 n_1 + \omega_2 n_2 + \omega_3 n_3 + \dots)}, \tag{14}$$

and the partition function (11) equals

$$Z(T) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{n_3=0}^{\infty} \dots e^{-\beta(\omega_1 n_1 + \omega_2 n_2 + \omega_3 n_3 + \dots)}$$

$$= \sum_{n_1=0}^{\infty} e^{-\beta \omega_1 n_1} \sum_{n_2=0}^{\infty} e^{-\beta \omega_2 n_2} \sum_{n_3=0}^{\infty} e^{-\beta \omega_3 n_3} \dots \tag{15}$$

- Keeping in mind that

$$\sum_{n_i=0}^{\infty} e^{-\beta \omega_i n_i} = \frac{1}{1 - e^{-\beta \omega_i}}, \tag{16}$$

the partition function (15) becomes

$$Z(T) = \Pi_i \frac{1}{1 - e^{-\beta \omega_i}} = \exp\left[-\sum_i \ln(1 - e^{-\beta \omega_i}) \right]. \tag{17}$$

- In the final step we change the discrete momenta into continuous one by means of replacement

$$\frac{1}{L^3} \sum_i \dots \to \int \frac{d^3 k}{(2\pi)^3} \dots. \tag{18}$$

Thus, we get

$$Z(T, V) = \exp\left[-V \int \frac{d^3 k}{(2\pi)^3} \ln(1 - e^{-\beta \omega_{\mathbf{k}}}) \right], \tag{19}$$

where $V = L^3$ is the system's volume and $\omega_{\mathbf{k}} \equiv \sqrt{\mathbf{k}^2 + m^2}$.

<u>Exercise</u>: Derive the partition function of bosons of g internal degrees of freedom.

<u>Exercise</u>: Derive the partition function of fermions assuming that n_i equals 0 or 1.

<u>Exercise</u>: Derive the partition function of fermions of g internal degrees of freedom.

Gas of bosons

- The partition function (19) with the relation (9) provides the system's energy equal to

$$U = V \int \frac{d^3 k}{(2\pi)^3} \frac{\omega_{\mathbf{k}}}{e^{\beta \omega_{\mathbf{k}}} - 1} = \frac{V}{2\pi^2} \int_0^{\infty} \frac{dk \, k^2 \sqrt{k^2 + m^2}}{e^{\beta \sqrt{k^2 + m^2}} - 1}. \tag{20}$$

- The formula of system's energy suggests to introduce a bosonic distribution function

$$f(\mathbf{k}) \equiv \frac{1}{e^{\beta \omega_{\mathbf{k}}} - 1}, \tag{21}$$

and then

$$U = V \int \frac{d^3 k}{(2\pi)^3} \omega_{\mathbf{k}} \, f(\mathbf{k}). \tag{22}$$

- If $T \gg m$, the particles can be treated as massless and using the integration formula

$$\int_0^\infty \frac{dx\, x^3}{e^x - 1} = \frac{\pi^4}{15}, \tag{23}$$

  the energy density is found as

$$\varepsilon \equiv \frac{U}{V} = \frac{\pi^2}{30} T^4, \tag{24}$$

  which is an analog of the Stefana-Boltzmann law.

- Using Eqs. (10) and (6), the pressure is found to be

$$p = -T \int \frac{d^3k}{(2\pi)^3} \ln(1 - e^{-\beta \omega_{\mathbf{k}}}) = -\frac{T}{2\pi^2} \int_0^\infty dk\, k^2 \ln(1 - e^{-\beta \sqrt{k^2 + m^2}}). \tag{25}$$

  Performing the partial integration one finds

$$p = \frac{1}{6\pi^2} \int_0^\infty \frac{dk\, k^4}{\sqrt{k^2 + m^2}} \frac{1}{e^{\beta \sqrt{k^2 + m^2}} - 1}. \tag{26}$$

- If $T \gg m$, the particles can be treated as massless and

$$p = \frac{\pi^2}{90} T^4 = \frac{1}{3}\varepsilon, \tag{27}$$

  which is the well-known equation of state.

Exercise: Derive the energy density and pressure of gas of bosons of g internal degrees of freedom.

Exercise: Derive the energy density and pressure of fermions of g internal degrees of freedom.

Relativistic covariance

- In quantum field theory we usually tend to write down all expressions in a Lorenz covariant way as it facilitates going from one reference frame to another.

- When we deal with many-body systems there is usually a preferred reference frame. In case on an equilibrium system this is the frame of a heat bath. Nevertheless formulas can be still written in a formally covariant way.

- Let us introduce the four-velocity of the heat bath u^μ which in the heat bath rest frame equals

$$u^\mu = (1, 0, 0, 0). \tag{28}$$

- One also introduces the four-vector of inverse temperature

$$\beta^\mu \equiv \beta u^\mu. \tag{29}$$

- Then, the partition function (7) can be formally written as a Lorenz scalar

$$Z(\beta^\mu) \equiv \sum_\alpha \langle \alpha | e^{-\beta^\mu \hat{P}_\mu} | \alpha \rangle, \tag{30}$$

where $\hat{P}_\mu$ is the four-momentum operator.

- One can also write down the energy-momentum tensor of the ideal boson gas as

$$T^{\mu\nu} = \int \frac{d^3k}{(2\pi)^3\omega_{\mathbf{k}}} k^\mu k^\nu f(k), \tag{31}$$

where $k^\mu \equiv (\omega_{\mathbf{k}}, \mathbf{k})$ and the distribution function, which is a Lorenz scalar, equals

$$f(k) \equiv \frac{1}{e^{\beta^\mu k_\mu} - 1}. \tag{32}$$

- One observes that

$$u_\mu u_\nu T^{\mu\nu} = \epsilon, \qquad (g_{\mu\nu} - u_\mu u_\nu)T^{\mu\nu} = -3p. \tag{33}$$

- In case of massless particles $T^\mu_{\ \mu} = 0$, which actually shows a conformal symmetry of the system, the equations (33) provide the equation of state

$$\epsilon = 3p. \tag{34}$$