Moderne Theoretische Physik II

Statistical Physics

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Contents

I. INTRODUCTION

This course will consist of two parts:

1) The first, smaller part will be about axiomatic thermodynamics. This is a closed and very sucsessful theory based on a few axioms (Laws of Thermodynamics).

2) The main part will be statistical physics, which provides the justification for the first part.

II. THERMODYNAMICS

A. Definitions

The thermodynamic systems have a very large number of degrees of freedom. The typical number is the Avogadro number $N_A \approx 6.023 \times 10^{23}$ particles per mole. Frequently one is interested in the so called thermodynamic limit. In this limit the number of particles $N \to \infty$ and the volume $V \to \infty$, but the density N/V remains constant.

The state of the system in thermodynamics is characterised by several macroscopic state functions (or state variables). One distinguished *extensive* and *intensive* state functions. The extensive ones are proportional to the number of particles $\propto N$, the intensive ones $\propto N^0$.

Extensive: Volume V, number of particles N, internal energy U, entropy $S \propto N$.

Intensive: Pressure P, temperature T, chemical potential $\mu \propto N^0$.

Equations of state describe *equilibrum*. They connect several state functions/variales. Example: in an ideal monoatomic gas the following equations hold $PV = Nk_{\mathrm{B}}T$, $U = \underline{\frac{3}{2}Nk_{\mathrm{B}}T}$. Here $k_{\mathrm{B}} \approx 1.38 \times 10^{23}\,\mathrm{J/K}$ is the Boltzmann constant.

$\hookrightarrow U = \frac{f}{2} N k_B T$ | f = dof

B. Laws of thermodynamics

1. Zeroth law : temp definition

There exists an intensive state variable called "temperature". Two systems at equilibrium with each other have equal temperatures.

2. *First law*

Conservation of energy (Robert Mayer, 1814-1878)

$$dU = \delta Q - \delta W + \mu dN \ . \tag{1}$$

Here δQ is the differential of heat flowing into the system. It is not a total differential, therefore we use δ and not d. That is heat is not a state function. Similarly δW is the differential of work performed by the system. In case of gas expanding mechanically $\delta W = PdV$. Also work is not a state function. However, the inner energy U and the number of particles N are state functions. We have also introduced the chemical potential μ. This is amount of energy needed to add one particle to the system provided no heat transfer and no work performed.

it's a process variable/func.

3. *Second law*

There is no thermodynamic change of state, the *only* effect of which is that

(I) an amount of heat is removed from a heat reservoir and fully converted into work.

(Ii) an amount of heat is removed from a colder heat reservoir and transferred to a warmer heat reservoir.

$$\Rightarrow \quad \Delta S = \frac{\Delta Q}{T} + \Delta S_{\text{irreversible}} \qquad / \ \Delta S \geq \frac{\Delta Q}{T}$$

C. Carnot Process

The following reversible cycle is performed:

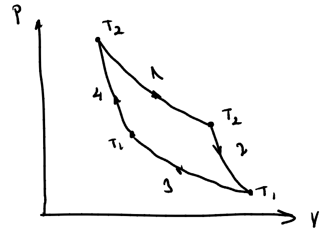
1. The system is in thermal contact with the reservoir T_2. In an isothermic process (e.g. expansion of the gas), the heat Q_2 flows into the system.

2. The system is thermally insulated. During an adiabatic process (e.g. further expansion) the temperature drops from T_2 to T_1.

3. The system is in thermal contact with the reservoir T_1. In an isothermic process (e.g. compression of the gas), the heat Q_1 flows out of the system.

4. The system is thermally insulated. During an adiabatic process (e.g. further compression) the temperature rises from T_1 to T_2.

The first law tell us that the amount of work performed by the Carnot machine is given



by

$$\Delta W = |Q_2| - |Q_1| = Q_2 + Q_1 \ . \tag{2}$$

The efficiency (energy conversion efficiency) is then given by

$$\eta \equiv \frac{\Delta W}{|Q_2|} = 1 - \frac{|Q_1|}{|Q_2|} \ . \tag{3}$$

Carnot theorem: for given temperatures T_2 and T_1 the efficiency of the Carnot machine is maximal possible.

D. Entropy

For the Carnot process we get

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \ . \tag{4}$$

Reminder: the sign of the amount of heat Q depends on whether if flows into the system (> 0) or out of the system (< 0). For the usual direction of the Carnot process ($T_2 > T_1$, heat is partially transformed into work) we have $Q_2 > 0$ and $Q_1 < 0$.

An arbitrary reversible cyclic process can be presented as a combination of many Carnot processes, therefore

$$\oint \frac{\delta Q}{T} = 0 \ . \tag{5}$$

Thus we can introduce a new state variable called **entropy** (this is the most important object in thermodynamics and statistical physics). It is usually denoted by S. The (total) differential of the entropy (for a reversible process) is given by

$$dS = \left.\frac{\delta Q}{T}\right|_{revers.} \ . \tag{6}$$

For irreversible processes

$$\oint \frac{\delta Q}{T} < 0 \ , \tag{7}$$

as follows from Carnot theorem, i.e., in a machine which is not reversible $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0$. In Fig. 1 the Carnot process is shown in the (S,T) coordinates.

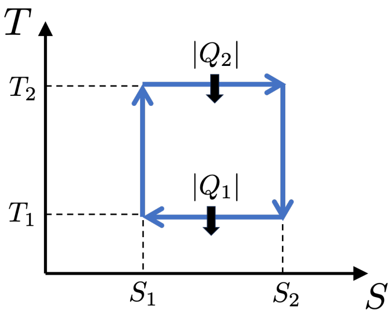


FIG. 1: Carnot process in (S,T) coordinates.

E. Fundamental relation of thermodynamics

We use $\delta Q = TdS$ (for reversible processes). Then the first law reads

$$dU = \delta Q - PdV + \mu dN = TdS - PdV + \mu dN \ . \tag{8}$$

We find for the differential of the entropy

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN \ . \tag{9}$$

From this we observe that S should be considered a function of U, V, N, i.e.

$$\boxed{S = S(U, V, N)} \tag{10}$$

For the partial derivatives Eq. 9 gives

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N} \quad , \quad \frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N} \quad , \quad \frac{\mu}{T} = -\left.\frac{\partial S}{\partial N}\right|_{U,V} \ . \tag{11}$$

For irreversible processes $dS > \frac{\delta Q}{T}$, i.e., $dS > \frac{1}{T}\,dU + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN$. Thus, for fixed U, V, N the entropy is *maximal* in equilibrium.

This should be understood as follows. Assume the entropy depends not only on U, V, N but also on some other parameters (see, e.g., the discussion of the thermodynamic stability in Section II H). The equilibrium corresponds to maximisation of the entropy with respect to these other parameters with fixed U, N, V. In equilibrium the other parameters will take the optimal values, which depend on U, V, N. Thus, the equilibrium entropy is a function of U, V, N only.

1. *Euler equation*

Since the entropy is a function of extensive variables only and is also itself extensive we have

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) \ . \tag{12}$$

This gives

$$\frac{d}{d\lambda}(\lambda S) = S = \frac{d}{d\lambda} S(\lambda U, \lambda V, \lambda N) \overset{\lambda \to 1}{=} \frac{\partial S}{\partial U} U + \frac{\partial S}{\partial V} V + \frac{\partial S}{\partial N} N \ . \tag{13}$$

Substituting (11) we get

$$\boxed{ST = U + PV - \mu N} \tag{14}$$

F. Thermodynamic potentials

Thermodynamic potential is an extensive state function expressed via its natural (controlled) variables. All other state functions can be found by differentiating the thermodynamic potential with respect to the controlled variables.

1. *Internal Energy*

Internal energy is the first example of a thermodynamic potential. To understand which variables are the natural (controlled) ones we use again

$$dU = TdS - PdV + \mu dN \ . \tag{15}$$

We observe that the natural variables for U are S, V, N. That is we just invert the function $S(U, V, N)$ with respect to U and obtain

$$\boxed{U = U(S, V, N)} \tag{16}$$

Then for the partial derivatives Eq. 15 gives

$$T = \frac{\partial U}{\partial S}\Big|_{V,N} \quad , \quad P = -\frac{\partial U}{\partial V}\Big|_{S,N} \quad , \quad \mu = \frac{\partial U}{\partial N}\Big|_{S,V} \ . \tag{17}$$

For irreversible processes $dU < TdS - PdV + \mu dN$. Thus, for fixed S, V, N the internal energy U is minimal.

Since dU is a total differential, we obtain the Maxwell relations. For example

$$\left.\frac{\partial T}{\partial V}\right|_{S,N} = \frac{\partial}{\partial V}\left(\left.\frac{\partial U}{\partial S}\right|_{V,N}\right)_S = -\left.\frac{\partial P}{\partial S}\right|_{V,N} = \frac{\partial}{\partial S}\left(\left.\frac{\partial U}{\partial V}\right|_{S,N}\right)_V \ . \tag{18}$$

2. Helmholtz free energy

The internal energy is inconvenient since it depends on entropy, which is hardly controllable. Thus one performs a Legendre transformation with respect to the pair S, T and defines the free energy as

$$F = U - TS \ . \tag{19}$$

With the help of the Euler equation we also obtain $F = -PV + \mu N$. Differentiating $F = U - TS$ we obtain

$$dF = -SdT - PdV + \mu dN \ . \tag{20}$$

Thus, the natural variables for the free energy are T, V, N:

$$\boxed{F = F(T, V, N)} \tag{21}$$

All three variables can be controlled in experiment, therefore the free energy is very useful as a thermodynamic potential. For the partial derivatives Eq. 20 gives

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} \quad , \quad P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} \quad , \quad \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} \ . \tag{22}$$

For fixed T, V, N the free energy F is minimal.

3. Enthalpy

Enthalpy is frequently used in chemistry because in chemical reactions the pressure and not the volume is usually controlled. Enthalpy is obtained from the internal energy by a Legendre transformation with respect to the pair P, V:

$$H = U + PV \ . \tag{23}$$

Differentiating we obtain

$$dH = TdS + VdP + \mu dN \ . \tag{24}$$

Thus, the natural variables for the entalpy are S, P, N:

$$\boxed{H = H(S, P, N)} \tag{25}$$

For the partial derivatives Eq. 24 gives

$$T = \frac{\partial H}{\partial S}\bigg|_{P,N} \quad , \quad V = \frac{\partial H}{\partial P}\bigg|_{S,N} \quad , \quad \mu = \frac{\partial H}{\partial N}\bigg|_{S,V} \ . \tag{26}$$

For fixed S, P, N the enthalpy H is minimal.

4. Gibbs free enthalpy

→ $\Delta G > 0$ → the chemical process isn't favored
$\Delta G < 0$ → " " " " energetically favoreble

The free enthalpy is even more important and used in chemistry. It is obtained from the enthalpy exactly as free energy from the internal energy by a Legendre transformation with respect to the pair S, T:

$$G = H - TS = U + PV - TS = F + PV \ . \tag{27}$$

Differentiating we obtain

$$dG = -SdT + VdP + \mu dN \ . \tag{28}$$

Thus, the natural variables for the free enthalpy are T, P, N:

$$\boxed{G = G(T, P, N)} \tag{29}$$

For the partial derivatives Eq. 28 gives

$$T = -\frac{\partial G}{\partial S}\bigg|_{P,N} \quad , \quad V = \frac{\partial G}{\partial P}\bigg|_{T,N} \quad , \quad \mu = \frac{\partial G}{\partial N}\bigg|_{T,V} \ . \tag{30}$$

For fixed T, P, N the free enthalpy G is minimal.

5. Grand potential

Another very useful thermodynamic potential

$$\Omega = F - \mu N = U - TS - \mu N \ . = \Phi_G \text{ in my notation} \tag{31}$$

$$d\Omega = -SdT - PdV - Nd\mu \ . \tag{32}$$

$$\boxed{\Omega = \Omega(T, V, \mu)} \tag{33}$$

For the partial derivatives Eq. 32 gives

$$S = -\frac{\partial \Omega}{\partial T}\Big|_{V,\mu} \quad , \quad P = -\frac{\partial \Omega}{\partial V}\Big|_{T,\mu} \quad , \quad N = -\frac{\partial \Omega}{\partial \mu}\Big|_{T,V} \; . \tag{34}$$

G. Response functions

Heat capacitance. The influx of heat into a system usually causes an increase of temperature. The latter depends, of course, on whether the volume or the pressure is controlled (fixed). This is because part of the heat can go to work. The heat capacitance C is the proportionality coefficient in

$$\delta Q = C dT \; . \tag{35}$$

Since, on the other hand $\delta Q = T dS$ we obtain

$$C_x \equiv T \left(\frac{\partial S}{\partial T}\right)_x \; , \tag{36}$$

where x can be either V or P.

For $V = const.$ one obtains

$$S = -\frac{\partial F}{\partial T}\Big|_{V,N} \quad \rightarrow \quad C_V = -T \left(\frac{\partial^2 F}{\partial T^2}\right)\Big|_{V,N} \; . \tag{37}$$

?

For $P = const.$ one obtains

$$S = -\frac{\partial G}{\partial T}\Big|_{P,N} \quad \rightarrow \quad C_P = -T \left(\frac{\partial^2 G}{\partial T^2}\right)\Big|_{P,N} \; . \tag{38}$$

An alternative way to calculate the heat capacitance is to say that for fixed V, N we have $\delta Q = dU$. Thus

$$C_V = \frac{\partial U}{\partial T}\Big|_{V,N} \; . \tag{39}$$

This, however, requires expressing the inner energy U in "unnatural coordinates" $U(T, V, N)$. For this one uses the relation $T = \frac{\partial U}{\partial S}\Big|_{V,N} = T(S, V, N)$. Inverting with respect to S one gets $S = S(T, V, N)$. Finally $U(T, V, N) = U(S(T, V, N), V, N)$. Frequently the inner energy is given in "unnatural" coordinates, e.g., $U = \frac{3}{2} N k_{\mathrm{B}} T$ for an ideal monoatomic gas.

Similarly

$$C_P = \frac{\partial H}{\partial T}\Big|_{P,N} \; . \tag{40}$$

H. Thermodynamic stability

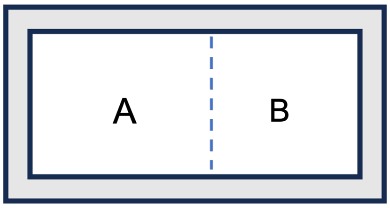


FIG. 2: Two subsystems A and B isolated from the rest of the world and connected by a movable, thermally conducting and permeable wall.

Consider two subsystems A and B isolated from the rest of the world and connected by a movable, thermally conducting and permeable wall (Fig. 2). The total entropy is the sum $S = S_A(U_A, V_A, N_A) + S_B(U_B, V_B, N_B)$. Here we assumed that each subsystem is in its own equilibrium, but the combined system not necessarily and the total entropy depends not only on $U = U_A + U_B$, $V = V_A + V_B$, $N = N_A + N_B$. Varying these parameters we obtain

$$\begin{aligned} dS = dS_A + dS_B = & \left.\frac{\partial S_A}{\partial U_A}\right|_{V_A,N_A} dU_A + \left.\frac{\partial S_B}{\partial U_B}\right|_{V_B,N_B} dU_B \\ & + \left.\frac{\partial S_A}{\partial V_A}\right|_{U_A,N_A} dV_A + \left.\frac{\partial S_B}{\partial V_B}\right|_{U_B,N_B} dV_B \\ & + \left.\frac{\partial S_A}{\partial N_A}\right|_{U_A,V_A} dN_A + \left.\frac{\partial S_B}{\partial N_B}\right|_{U_B,V_B} dN_B \ . \end{aligned} \tag{41}$$

Since $U = U_A + U_B = const.$ we have $dU_A = -dU_B$. In equilibrium the entropy must be maximal, i.e. $dS = 0$. Therefore

$$\left.\frac{\partial S_A}{\partial U_A}\right|_{V_A,N_A} = \left.\frac{\partial S_B}{\partial U_B}\right|_{V_B,N_B} \quad \rightarrow \quad \frac{1}{T_A} = \frac{1}{T_B} \quad \rightarrow \quad T_A = T_B \ . \tag{42}$$

Similarly from $V = V_A + V_B = const.$ follows

$$\left.\frac{\partial S_A}{\partial V_A}\right|_{U_A,N_A} = \left.\frac{\partial S_B}{\partial V_B}\right|_{U_B,N_B} \quad \rightarrow \quad \frac{P_A}{T_A} = \frac{P_B}{T_B} \quad \rightarrow \quad P_A = P_B \ . \tag{43}$$

Finally, since $N = N_A + N_B = const.$ we get

$$\left.\frac{\partial S_A}{\partial N_A}\right|_{U_A,V_A} = \left.\frac{\partial S_B}{\partial N_B}\right|_{U_B,V_B} \quad \rightarrow \quad \frac{\mu_A}{T_A} = \frac{\mu_B}{T_B} \quad \rightarrow \quad \mu_A = \mu_B \ . \tag{44}$$

The condition dS ensures only that the entropy has an extremum. To have a maximum we should ensure that the "second differential" is negative. Varying the internal energies (with $V_{A/B}$ and $N_{A/B}$ fixed) we obtain

$$d^{(2)}S = \frac{1}{2}\sum_{i=A,B}\frac{\partial^2 S_i}{\partial U_i^2}\,(dU_i)^2 = -\frac{1}{2T^2}\sum_{i=A,B}\frac{\partial T_i}{\partial U_i}\,(dU_i)^2 \tag{45}$$

Thus, from $d^{(2)}S < 0$ follows

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} > 0 \ . \tag{46}$$

Since

$$C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N} > 0 \ , \tag{47}$$

we conclude that the free energy must be a convex functions, i.e., $(\partial^2 F/\partial T^2)_{V,N} < 0$.

I. Mixing entropy and Gibbs paradox

We postulate here the expression for the entropy of an ideal gas (this is exactly the task of the statistical physics to provide such expressions):

$$S(U,V,N) = Ns_0 + Nk_{\mathrm{B}}\ln\left(\frac{V}{N}\left(\frac{U}{N}\right)^{\frac{f}{2}}\right) \ . \tag{48}$$

Here s_0 is some constant, f is the number of degrees of freedom per molecule, e.g., $f = 3$ for a mono-atomic gas. This expressions produces the well-known equations of state for an ideal gas:

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_{U,N} &= \frac{P}{T} \quad \rightarrow \quad PV = Nk_{\mathrm{B}}T \ , \\ \left(\frac{\partial S}{\partial U}\right)_{V,N} &= \frac{1}{T} \quad \rightarrow \quad U = \frac{f}{2}\,Nk_{\mathrm{B}}T \ . \end{aligned} \tag{49}$$

Consider now two containers with volumes V_1 and V_2 filled with two distinct gases (Fig. 3). Assume also the gases have the same temperature T. If we remove the wall between the containers both gases expand to volume $V = V_1 + V_2$ but keep their internal energies in accordance with $U = \frac{f}{2}\,Nk_{\mathrm{B}}T$. The entropy change of each of the gases is then given by

$$\Delta S_i = N_i k_{\mathrm{B}}\ln\frac{V}{V_i} \quad , \quad i = 1,2 \ . \tag{50}$$

Thus we obtain a positive entropy of mixing $\Delta S = \Delta S_1 + \Delta S_2 > 0$.

Gibbs Paradox tekrar + not al!
- Neden $\Delta S = 0$ doğru olan?
- Distinguishable particle considerlasak sonuç ne olur?

Me

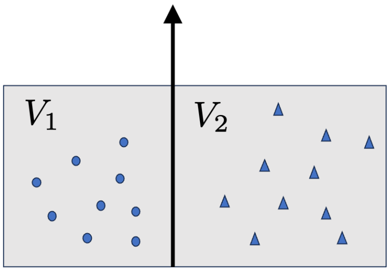


FIG. 3: Two gas containers with volumes V_1 and V_2.

Consider now identical gases in two containers. Assume also that before removing the wall the density, the temperature and the pressure were the same. Namely

$$\frac{V_1}{N_1} = \frac{V_2}{N_2} = \frac{V}{N} \quad , \quad \frac{U_1}{N_1} = \frac{U_2}{N_2} = \frac{U}{N} \ . \tag{51}$$

Here $U \equiv U_1 + U_2$ and $N \equiv N_1 + N_2$. Under these conditions removing the wall does not change the state, thus the entropy should not change. On the other hand, if we consider separately the gas particles that were initially in V_1, an expansion took place and the entropy should grow as before $\Delta S = \Delta S_1 + \Delta S_2 > 0$. This is Gibbs paradox. Of course, the correct answer is $\boxed{\Delta S = 0.}$ To explain one has to take into account that the particles are identical.

III. FOUNDATIONS OF STATISTICAL PHYSICS

A. Classical mechanics of N particles

The state of N particles is described by a point is a $6N$ dimensional phase space ($3N$ coordinates and $3N$ momenta):

$$\mathbf{x} = (\mathbf{p}, \mathbf{q}) = (p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N}) \ . \tag{52}$$

The dynamics is governed by the Hamilton function $H(\mathbf{p}, \mathbf{q})$. The equations of motion read

$$\dot{p}_j = -\frac{\partial H}{\partial q_j} \quad , \quad \dot{q}_j = \frac{\partial H}{\partial p_j} \ . \tag{53}$$

Thus, the phase space velocity $(\dot{\mathbf{p}}, \dot{\mathbf{q}})$ is an unambiguous (single valued) function of the position in the phase space $(\mathbf{p}, \mathbf{q})$. One obtains a velocity field in the phase space. This, in particular, means that the trajectories in the phase space never cross (see Fig. 4). Certain restrictions are placed by the conservation laws. So, for the example, the energy is

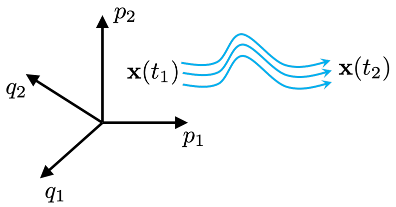


FIG. 4: Velocity field in the phase space.

conserved. Thus we might consider only the trajectories corresponding to a given energy E, i.e., $H(\mathbf{p},\mathbf{q}) = E$. This would be still a $6N-1$ dimensional space. Sometimes other quantities are also conserved, e.g., total momentum or total angular momentum.

$\rho(x,t)$
NE
TAM
OLARAK?
????
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B. Gibbs distribution

One considers an ensemble of equivalent systems characterised by the distribution function $\rho(\mathbf{x},t)$. The physical meaning is as follows: one introduces an infinitesimal volume element in the phase space dx. Then $\rho(\mathbf{x},t)dx$ is the probability that the state of the system is described by a point of the phase space inside of dx. Obviously, the distribution should be normalised: $\int dx \rho(\mathbf{x}) = 1$. If we have an observable quantity $O(\mathbf{x}) = O(q_j, p_j)$ the Gibbs distribution allows calculating the expectation value of O:

$$\bar{O}(t) = \int dx\, \rho(\mathbf{x},t) O(\mathbf{x}) \ . \tag{54}$$

It is sometimes convenient to define dx with a normalisation factor

$$dx = C_N \underline{d^{3N}q}\, \underline{d^{3N}p} \ , \tag{55}$$

$6D \to d^3\underline{x}\, d^3p$, $\underline{x} \to q$

$6ND \to d^{3N}x\, d^{3N}p$. $\frac{C_N}{\text{norm}}$.

so that dx and $\rho(\mathbf{x},t)$ become dimensionless. Once we consider the classical case as a limit of the quantum description, we observe (see below) that the natural choice is $C_N = (2\pi\hbar)^{-3N}$.

1. *Justification of the normalisation factor* $C_N = (2\pi\hbar)^{-3N}$

.

Consider free quantum particles in a box with dimensions L_x, L_y, L_z, volume $V = L_x L_y L_z$. The wave functions are plane waves

$$\psi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \exp\left[\frac{i}{\hbar}\mathbf{p}\mathbf{r}\right] \ . \tag{56}$$

To take into account the finite size of the box it is convenient to assume the periodic boundary conditions

$$\psi_{\mathbf{p}}(\mathbf{r} + L_x\mathbf{e}_x) = \psi_{\mathbf{p}}(\mathbf{r}) \tag{57}$$

and similarly for L_y and L_z. Then, the allowed momenta are given by

$$(p_x, p_y, p_z) = \left(\frac{2\pi\hbar n_x}{L_x}, \frac{2\pi\hbar n_y}{L_y}, \frac{2\pi\hbar n_z}{L_z}\right) \ , \tag{58}$$

where n_x, n_y, n_z are integer numbers.

We count the quantum states of one particle (with some condition), introduce $dp_x = 2\pi\hbar/L_x$, $\ \ldots$ and transform to an integral

for N particles

$$\sum_{n_x,n_y,n_z} = \frac{L_xL_yL_z}{(2\pi\hbar)^3}\int dp_xdp_ydp_z = \left[\int \frac{dxdydzdp_xdp_ydp_z}{(2\pi\hbar)^3} .\right]^N \tag{59}$$

$\Rightarrow (2\pi\hbar)^{3N}$

C. Liouville equation

The aim is to derive an equation of motion for $\rho(\mathbf{x}, t)$, i.e., we want to calculate $\frac{\partial\rho(\mathbf{x},t)}{\partial t}$. The partial derivative means that we fix the point in the phase space $\mathbf{x}$ and follow the evolution of the ρ in time. However we can think of our chosen point $\mathbf{x}$ as point reached at time t by a phase space trajectory $\mathbf{x}(t)$, i.e., $\mathbf{x} = \mathbf{x}(t)$. At the initial time t_0 this trajectory was at $\mathbf{x}_0 = \mathbf{x}(t_0)$. Obviously the probability density to be at $\mathbf{x}$ at time t is equal to the probability density to be at $\mathbf{x}_0$ at time t_0. More precisely we should equate the probabilities

$$\rho(\mathbf{x}, t)dx_t = \rho(\mathbf{x}_0, t_0)dx_{t_0} \ , \tag{60}$$

and use the Liouville theorem stating that the volume element is conserved $dx_t = dx_{t_0}$. Thus we obtain

$$\rho(\mathbf{x}, t) = \rho(\mathbf{x}(t), t) = \rho(\mathbf{x}_0, t_0) \ . \tag{61}$$

We differentiate with respect to t and obtain

$$\frac{d}{dt}\rho(\mathbf{x}(t), t) = \frac{\partial\rho(\mathbf{x}, t)}{\partial t} + \frac{d\mathbf{x}}{dt}\cdot\vec{\nabla}\rho(\mathbf{x}, t) = 0 \ . \tag{62}$$

Explicitly in coordinates we get

$$\frac{\partial\rho}{\partial t} + \sum_j \frac{dq_j}{dt}\frac{\partial\rho}{\partial q_j} + \sum_j \frac{dp_j}{dt}\frac{\partial\rho}{\partial p_j} = 0 \ . \tag{63}$$

Using the Hamiltonian equations of motion we obtain

$$\frac{\partial\rho}{\partial t} + \sum_j \frac{\partial H}{\partial p_j}\frac{\partial\rho}{\partial q_j} - \sum_j \frac{\partial H}{\partial q_j}\frac{\partial\rho}{\partial p_j} = 0 \; . \tag{64}$$

Finally, this gives the Liouville equation

$$\frac{\partial\rho}{\partial t} = \{H,\rho\} \;\; , \tag{65}$$

where $\{\dots\}$ denote the Poisson brackets. In particular, it is now easy to show, that if $\rho(\mathbf{q},\mathbf{p}) = \rho(H((\mathbf{q},\mathbf{p})))$, then $\partial\rho/\partial t = 0$.

D. Microcanonical ensemble, ergodic hypothesis

It is convenient to introduce the volume of the phase space corresponding to energies smaller than some chosen energy E:

$$\Omega(E) = \int dx\, \theta(E - H(\mathbf{x})) \; . \tag{66}$$

Niye $6N\boxed{-1}$?
??

Me

We define the $6N-1$ dimensional "surface area" of this volume

$$\Sigma(E) = \frac{d\Omega(E)}{dE} = \int dx\, \delta(E - H(\mathbf{x})) \; . \tag{67}$$

Then $\Sigma(E)dE$ is the "number of states" of the system with energies $E < H(\mathbf{x}) < E + dE$.

In the statistical physics one postulates the Gibbs distribution of a "microcanonical ensemble", which describes an isolated physical system (a system with a given energy) in equilibrium:

$$\begin{array}{rcl} \rho(\mathbf{x})^{eq} = \dfrac{1}{\Sigma(E)dE} & , & \text{for} \quad E < H(\mathbf{x}) < E + dE \\ \rho(\mathbf{x})^{eq} = 0 & , & \text{otherwise} \end{array} \tag{68}$$

That is one takes a small interval of energies and postulates that all "states" in this interval have equal probabilities to be realised. This distribution is stationary in time, since it can be presented as $\rho(H(\mathbf{x}))$.

A expectation value of a physical observable $O(\mathbf{x})$ in the microcanonical ensemble reads

$$\bar{O}_E = \frac{1}{\Sigma(E)dE}\int_{E<H(\mathbf{x})<E+dE} dx\, O(\mathbf{x}) \; . \tag{69}$$

Consider a trajectory in the phase space $\mathbf{x}(t)$, such that $H(\mathbf{x}(\mathbf{t})) = E$. One can calculate a time average of the observable O on this trajectory over long (infinite) time T:

$$\bar{O}_T = \lim_{T\to\infty} \frac{1}{T} \int_0^T O(\mathbf{x}(t)) \ . \tag{70}$$

Tekrar? ?

The ergodic hypothesis states:

$$\bar{O}_E = \bar{O}_T \ . \tag{71}$$

E. Entropy (classical)

One defines (postulates) entropy to be

$$S = -k_{\rm B} \int dx\, \rho(\mathbf{x})\, \ln \rho(\mathbf{x}) \ . \tag{72}$$

It is an additive quantity. Namely, if we have two independent subsystems A and B, the phase space is a direct product of two phase spaces $x = (x_A, x_B)$. If the two are not correlated the Gibbs distributions of the combined system is given by

$$\rho(x) = \rho_A(x_A)\rho_B(x_B) \ . \tag{73}$$

Then

$$S = -k_{\rm B} \int dx_A dx_B \rho_A(x_A)\rho_B(x_B)\ [\ln\rho_A(x_A) + \ln\rho_B(x_B)] = S_A + S_B \ . \tag{74}$$

For the microcanonical Gibbs distribution (68) we readily obtain

$$S = k_{\rm B} \ln\left[\Sigma(E) dE\right] \ . \tag{75}$$

For large number of particles N one can approximately replace the volume of the energy window dE, i.e., $\Sigma(E)dE$ by the volume of the whole sphere $H(x) < E$. Thus we use

$\rho(x) \ln(x) \approx> \ln(\Sigma E dE) \approx> \ln(\Omega(E))$

$$S = k_{\rm B} \ln\left[\Sigma(E) dE\right] \approx k_{\rm B} \ln\left[\underline{\Omega(E)}\right] \ . \tag{76}$$

?

↳ microstates? Grand pot?? Spherical Volume??

The justification for this approximation is as follows: at least for non-interacting particles the volume $\Omega(E) \propto E^{aN}$, where a is a number of order 1. For example for non-relativistic particles with dispersion relation $\mathbf{p}^2/2m$ one obtains $a = 3/2$ (see below). Then, $\Sigma(E) \propto aNE^{aN-1}$. We thus have $\ln[\Omega(E)] \propto aN \ln E$, whereas $\ln[\Sigma(E)] \propto (aN-1)\ln E + \ln(aN)$. For $N \approx 10^{23}$ the leading term $aN \ln E$ clearly dominates.

$\Omega(E) = \overset{\nearrow \text{macrostates}}{\omega?} \approx \Omega \rightarrow \text{microstates}$

aynı mı??

F. Ideal classical gas (Maxwell-Boltzmann gas)

1. *Entropy of M.-B. gas*

We consider N identical particles in volume V. The Hamilton function reads

$$H = \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m} \ . \tag{77}$$

For the volume $\Omega(E)$ in the phase space we obtain

$$\Omega(E) = \int dx\, \theta(E - H(\mathbf{x})) = V^N \int \frac{d^{3N}p}{(2\pi\hbar)^{3N}}\, \theta\left(E - \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m}\right) \ . \tag{78}$$

The integral corresponds to the volume of a $3N$-dimensional sphere (in the p space) with the radius of $\sqrt{2mE}$. We use the well known mathematical formula for the volume of an N-dimensional sphere with radius R

$$V_N(R) = \frac{\pi^{\frac{N}{2}} R^N}{\Gamma\left(\frac{N}{2}+1\right)} \ , \tag{79}$$

which gives

$$\Omega(E) = V^N \frac{1}{\Gamma\left(\frac{3N}{2}+1\right)} \left(\frac{mE}{2\pi\hbar^2}\right)^{\frac{3N}{2}} \tag{80}$$

Here $\Gamma(\dots)$ is the Gamma-function defined as

$$\Gamma(z) \equiv \int_0^{\infty} t^{z-1} e^{-t}\, dt \ . \tag{81}$$

The important properties of these function are $\Gamma(1) = 0$ and $\Gamma(z+1) = z\Gamma(z)$, which means $\Gamma(n) = (n-1)!$ for n being a positive integer. We will also need the Stirling formula for large N:

$$N! \approx 2\pi\sqrt{N} \left(\frac{N}{e}\right)^N \ . \tag{82}$$

We will need only the logarithm of $N!$, which gives

$$\ln N! \approx N \ln(N/e) + O(\ln N) \ . \tag{83}$$

Clearly the last term can be omitted for $N \sim 10^{23}$.

Finally, we identify the inner energy with E, i.e., $U = E$. Calculating the entropy with Eq. 80 we would get

$$S(U,V,N) = k_{\mathrm{B}} \ln\left[\Omega(E)\right] = k_{\mathrm{B}} N \ln\left[V\, e^{\frac{3}{2}} \left(\frac{mU}{3\pi\hbar^2 N}\right)^{\frac{3}{2}}\right] \tag{84}$$

Although this result would produce the correct equations of state, it is not satisfactory because the function $S(U,V,N)$ is not extensive, $S(\lambda U, \lambda V, \lambda N) \neq \lambda S(U,V,N)$. We would also not be able to solve the Gibbs paradox.

Instead we invoke our knowledge from the quantum mechanics about the identical particles. If the volume $\Omega(E)$ should represent the number of quantum states, then for identical particles it has to be divided by $N!$ in order to take into account the permutations corresponding to the same quantum state. Thus we define

$$\tilde{\Omega}(E) = \frac{\Omega(E)}{N!} = \frac{V^N}{N!} \frac{1}{\Gamma\left(\frac{3N}{2}+1\right)} \left(\frac{mE}{2\pi\hbar^2}\right)^{\frac{3N}{2}} \quad . \tag{85}$$

For the entropy this gives

$$S(U,V,N) = k_{\mathrm{B}} \ln\left[\tilde{\Omega}(E)\right] = k_{\mathrm{B}} N \ln\left[\frac{V}{N}\, e^{\frac{5}{2}} \left(\frac{mU}{3\pi\hbar^2 N}\right)^{\frac{3}{2}}\right] \tag{86}$$

This function is extensive, i.e., $S(\lambda U, \lambda V, \lambda N) = \lambda S(U,V,N)$.

2. Equations of state

Using

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N} \tag{87}$$

we obtain $1/T = k_{\mathrm{B}} N (3/2)(1/U)$. This gives

$$U = \frac{3}{2} N k_{\mathrm{B}} T \; . \tag{88}$$

Similarly, using

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{U,N} \tag{89}$$

we get $P/T = k_{\rm B} N (1/V)$. This gives

$$PV = N k_{\rm B} T \ . \tag{90}$$

Finally, using

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N}\Big|_{U,V} \tag{91}$$

we obtain

$$\mu = -k_{\rm B} T \ln\left[\frac{V}{N}\left(\frac{mU}{3\pi\hbar^2 N}\right)^{\frac{3}{2}}\right] = -k_{\rm B} T \ln\left[\frac{V}{N}\left(\frac{m k_{\rm B} T}{2\pi\hbar^2}\right)^{\frac{3}{2}}\right] \ . \tag{92}$$

The chemical potential is an intensive quantity, as it should be.

3. Failure at $T = 0$

Substituting $U = (3/2) N k_{\rm B} T$ into (86) we obtain

$$S = k_{\rm B} N \ln\left[\frac{V}{N}\, e^{\frac{5}{2}} \left(\frac{m k_{\rm B} T}{2\pi\hbar^2}\right)^{\frac{3}{2}}\right] \tag{93}$$

We observe that for $T \to 0$ we get $S \to -\infty$ instead of zero. This is, of course, nonsense. In particular, this contradicts the third law. Related is the fact that the heat capacity

$$C_V \equiv T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3}{2} k_{\rm B} N \tag{94}$$

does not go to zero at $T = 0$ as it should. We observe a failure of classical physics near $T = 0$.

G. Mixed states, density matrix

In quantum mechanics the Gibbs distribution is replaced by a mixed state. A general mixed state can be presented as a set of states Ψ_α (not necessarily orthonormal) with the probabilities W_α for this state to be realised. Obviously $\sum_\alpha W_\alpha = 1$. An average of an observable is then given by

$$\langle O \rangle = \sum_\alpha W_\alpha \langle \Psi_\alpha | O | \Psi_\alpha \rangle \tag{95}$$

It is convenient to encode the mixed state using the so-called density matrix:

$$\rho \equiv \sum_\alpha W_\alpha |\Psi_\alpha\rangle\langle\Psi_\alpha| \tag{96}$$

We can now use an orthonormal basis $|j\rangle$, such that $\langle j|\, j'\rangle = \delta_{j,j'}$, to expand

$$|\Psi_\alpha\rangle = \sum_j c_{\alpha j}|j\rangle \tag{97}$$

This gives

$$\rho = \sum_{\alpha,j,j'} W_\alpha c_{\alpha j} c^*_{\alpha j'} |j\rangle\langle j'| = \sum_{j,j'} |j\rangle \rho_{j,j'} \langle j'| \ , \tag{98}$$

where

$$\rho_{j,j'} = \sum_\alpha W_\alpha c_{\alpha j} c^*_{\alpha j'} \ . \tag{99}$$

We observe that $\rho_{j,j'}$ is a hermitian matrix. Indeed $\rho_{j,j'} = \rho^*_{j',j}$. Thus, an orthonormal basis $|\Psi_n\rangle$, i.e., $\langle \Psi_n|\, \Psi_{n'}\rangle = \delta_{n,n'}$, can always be found, in which ρ is diagonal, i.e.,

$$\rho = \sum_n W_n \left|\Psi_n\right\rangle \left\langle \Psi_n\right| \ . \tag{100}$$

An expectation value of an observable O can be written as

$$\langle O\rangle = \sum_\alpha W_\alpha \langle \Psi_\alpha|O|\Psi_\alpha\rangle = \sum_{\alpha j} W_\alpha \langle\Psi_\alpha|O|j\rangle\langle j|\Psi_\alpha\rangle = \sum_{\alpha j}\langle j|W_\alpha|\Psi_\alpha\rangle\langle\Psi_\alpha|O|j\rangle = \mathrm{Tr}(\rho O) \ . \tag{101}$$

A density matrix evolves in time in accordance with the von Neumann equation:

$$i\hbar\frac{\partial}{\partial t}\rho = [H,\rho] \ . \tag{102}$$

Niye time dependence duruyor ?

Indeed, if at $t = 0$ we have $\rho = \sum_\alpha W_\alpha \left|\Psi_\alpha\right\rangle \left\langle\Psi_\alpha\right|$, then

$$\begin{aligned}\rho(t) &= \sum_\alpha W_\alpha \left|\Psi_\alpha(t)\right\rangle \left\langle\Psi_\alpha(t)\right| = \sum_\alpha W_\alpha \underbrace{\overset{u^\dagger}{e^{-iHt/\hbar}} \overset{\rho}{\left|\Psi_\alpha(\boxed{t})\right\rangle \left\langle\Psi_\alpha(\boxed{t})\right|} \overset{u}{e^{iHt/\hbar}}}_{e^{-iHt/\hbar}\,|\Psi_\alpha(\underset{0}{t_0})\rangle\langle\Psi_\alpha(0)|\,e^{iHt/\hbar}} \\ &= e^{-iHt/\hbar}\rho e^{iHt/\hbar} \ .\end{aligned} \tag{103}$$

??

Differentiating with respect to t we obtain (102). Generalisation to the case of a time-dependent Hamiltonian is straightforward.

In particular, if ρ is a function of the Hamiltonian $\rho(H)$, then $\frac{\partial}{\partial t}\rho = 0$.

If the density matrix represents a pure state, i.e., $\rho = \left|\Psi\right\rangle\left\langle\Psi\right|$, then $\rho^2 = \rho$. For a mixed state $\rho^2 \neq \rho$ and $\mathrm{Tr}[\rho^2] < \mathrm{Tr}[\rho]$.

H. Microcanonical ensemble (quantum)

The microcanonical density matrix is given by

$$\rho \equiv \sum_n W_n |\Psi_n\rangle\langle\Psi_n| \; . \tag{104}$$

Here $|\Psi_n\rangle$ are the eigenvectors of the Hamiltonian $H\,|\Psi_n\rangle = E_n\,|\Psi_n\rangle$. We choose an energy interval $[E, E+dE]$ and count the number $dN(E)$ of quantum states satisfying $E < E_n < E + dE$. The probabilities W_n are then given by

$$W_n = \begin{cases} 1/dN(E) & \text{for} \quad E < E_n < E + dE \\ 0 \quad \text{otherwise} \end{cases} \tag{105}$$

I. Entropy (quantum)

The quantum version of the entropy is defined as

$$S = -k_{\mathrm{B}} \mathrm{Tr}(\rho \ln \rho) \; . \tag{106}$$

If the density matrix is diagonalised (in an orthonormal basis), i.e., $\rho = \sum_n W_n |\Psi_n\rangle\langle\Psi_n|$, then

$$S = -k_{\mathrm{B}} \mathrm{Tr}(\rho \ln \rho) = -k_{\mathrm{B}} \sum_n W_n \ln W_n \; . \tag{107}$$

As in the classical case entropy is additive. For two independent systems A and B, $\rho = \rho_A \otimes \rho_B$. This means that the probability to be in state $\left|\Psi_n^A\right\rangle \left|\Psi_m^B\right\rangle$ is given by $W_n^A W_m^B$. Then

$$S = -k_{\mathrm{B}} \sum_{n,m} W_n^A W_m^B \left[\ln W_n^A + \ln W_m^B\right] = S_A + S_B \; . \tag{108}$$

For the microcanonical ensemble defined above (105) we readily obtain

$$S = k_{\mathrm{B}} \ln[dN(E)] \; . \tag{109}$$

1. *Problem with entropy*

One can show (exercise) that the Liouville equation in the classical limit or the von Neumann equation in the quantum case lead directly to a conclusion that $dS/dt = 0$, i.e., the entropy of an isolated system is constant. Thus, an isolated system does not relax to equilibrium. → Sheet 10 Problem 3 (?)

J. Canonical ensemble

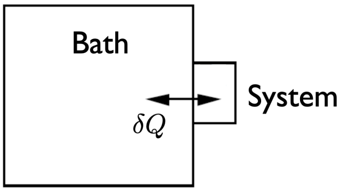

FIG. 5: System coupled to a thermal bath

We consider a system thermally coupled to a much bigger reservoir (thermal bath) (see Fig. 5). Only the heat exchange is allowed between the system and the bath. We assume the density matrix diagonal in the eigenbasis of the Hamiltonian, i.e., $\rho \equiv \sum_n W_n |\Psi_n\rangle\langle\Psi_n|$ and $H|\Psi_n\rangle = E_n |\Psi_n\rangle$. We demand the entropy to be maximal under the constraint of a given internal energy U, which we identify with the average value of the energy

$$U = \langle E \rangle = \mathrm{Tr}(\rho H) = \sum_n W_n E_n \ . \tag{110}$$

We use the method of Lagrange multipliers

$$\boxed{S_L = -k_\mathrm{B} \sum_n W_n \ln W_n - \lambda \left(\sum_n W_n - 1 \right) - \alpha \left(\sum_n W_n E_n - U \right)} \tag{111}$$

and demand

$$\frac{\partial S_L}{\partial W_n} = -k_\mathrm{B}(\ln W_n + 1) - \lambda - \alpha E_n = 0 \tag{112}$$

This gives

$$W_n = const. \cdot e^{-\frac{\alpha E_n}{k_\mathrm{B}}} \ . \tag{113}$$

We rename $\alpha = \beta k_\mathrm{B}$ and introduce a normalisation constant $1/Z$, which gives

$$\boxed{W_n = \frac{1}{Z} e^{-\beta E_n}} \ . \tag{114}$$

From the normalisation condition $\sum_n W_n = 1$ we obtain $Z = \sum_n e^{-\beta E_n}$. The quantity Z plays a central role is the statistical physics and is called **partition function** (German: Zustandssumme).

1. *The physical meaning of β*

We want to understand what is β. Since the eigenenergies of the Hamiltonian depend on the volume and the number of particles we can consider the partition function as a function of β, V, N, i.e.,

$$Z(\beta, V, N) = \sum_n e^{-\beta E_n} \ . \tag{115}$$

Analogously for the internal energy

$$U(\beta, V, N) = \frac{1}{Z} \sum_n E_n e^{-\beta E_n} \ . \tag{116}$$

Finally, we get for the entropy

$$\begin{aligned} S(\beta, V, N) &= -k_\mathrm{B} \sum_n W_n \ln W_n = -k_\mathrm{B} \sum_n \frac{e^{-\beta E_n}}{Z} \left[-\ln Z - \beta E_n \right] \\ &= k_\mathrm{B} \ln Z + k_\mathrm{B} \beta U \ . \end{aligned} \tag{117}$$

We observe from Eqs. (115) and (116) a useful relation

$$U = -\frac{\partial}{\partial \beta} \ln Z \ . \tag{118}$$

We fix V and N and invert Eq. (116). Namely, Eq. (116) gives $U(\beta)$. We assume this function to be invertible, which would give $\beta(U)$. Then Eq. (117) gives (V and N fixed)

$$S(U, V, N) = k_\mathrm{B} \ln Z(\beta(U)) + k_\mathrm{B} U \beta(U) \ . \tag{119}$$

From this and (118) we get (V and N fixed)

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \left(k_\mathrm{B} \frac{\partial \ln Z}{\partial \beta} + k_\mathrm{B} U \right) \frac{\partial \beta}{\partial U} + k_\mathrm{B} \beta = k_\mathrm{B} \beta \ . \tag{120}$$

Thus $\beta = 1/(k_\mathrm{B} T)$. The final form of the canonical density matrix is thus

$$W_n = \frac{1}{Z} \exp\left(-\frac{E_n}{k_\mathrm{B} T} \right) \quad , \quad Z = \sum_n \exp\left(-\frac{E_n}{k_\mathrm{B} T} \right) \ . \tag{121}$$

In the matrix form the same reads

$$\rho = \frac{1}{Z} \exp\left(-\frac{H}{k_\mathrm{B} T} \right) \quad , \quad Z = \mathrm{tr} \left[\exp\left(-\frac{H}{k_\mathrm{B} T} \right) \right] \ . \tag{122}$$

2. *Free energy*

Eq. (117) can be rewritten as

$$U - TS = F = -k_{\mathrm{B}} T \ln Z \ . \tag{123}$$

Since Eq. (117) gives the partition function as function of β, V, and N, i.e., T, V, and N we have

$$F(T, V, N) = -k_{\mathrm{B}} T \ln Z(T, V, N) \ . \tag{124}$$

This relation allows, using (22), obtaining the thermodynamic state functions directly from the partition function.

3. *Alternative derivation*

Alternatively to maximising the entropy under the condition of a fixed internal energy $U = \mathrm{Tr}(\rho H)$, one can consider the combined system of the system and the thermal bath being described by a micro canonical state with energy E. We split this energy into the energy of the system E^S and the energy of the bath E^B. More accurately, we consider the product states $\left|n^S\right\rangle \left|m^B\right\rangle$ of the combined system and associate the energy $E_{n,m} = E_n^S + E_m^B$ with these states (neglecting the energy related to the interaction between the system and the bath). Since the system is much smaller than the bath, we expect $E_n^S \ll E_m^B$. The probability of the combined system to be in the state $\left|n^S\right\rangle \left|m^B\right\rangle$ is given by

$$W_{n,m} = \frac{1}{dN(E)} \quad \text{for} \quad E < E_{n,m} < E + dE \ , \tag{125}$$

and zero otherwise. Here $dN(E)$ is the number of states of the combined system with energies between E and $E + dE$. Next, we calculate the probability of the system to be in the state $\left|n^S\right\rangle$:

$$W_n = \sum_m W_{n,m} = \frac{dN^B(E - E_n)}{dN(E)} \ . \tag{126}$$

Here $dN^B(E)$ is the number of states of the bath with energies between E and $E + dE$. Thus we obtain

$$\begin{aligned} k_{\mathrm{B}} \ln W_n &= k_{\mathrm{B}} \ln \left[dN^B(E - E_n) \right] - k_{\mathrm{B}} \left[dN(E) \right] \\ &= S^B(E - E_n) - S = S^B(E) - E_n \frac{\partial S^B(E)}{\partial E} - S = const. - \frac{E_n}{T} \ . \end{aligned} \tag{127}$$

We have used the relation

$$\frac{\partial S^B(E)}{\partial E}\Big|_{V,N} = \frac{1}{T} \ . \tag{128}$$

(The bath is microcanonical, $E = U$). Thus T is the temperature of the bath enforced upon the much smaller system. This again gives the canonical distribution

$$W_n = \frac{1}{Z}\exp\left(-\frac{E_n}{k_{\rm B}T}\right) \quad , \quad Z = \sum_n \exp\left(-\frac{E_n}{k_{\rm B}T}\right) \ . \tag{129}$$

4. Canonical ensemble: fluctuations of the energy. Equivalence of the canonical and the microcanoincal ensembles.

We use again the relation

$$U = \langle E\rangle = \frac{1}{Z}\sum_n E_n e^{-\beta E_n} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\ln Z \ . \tag{130}$$

Differentiating once again we obatin

$$\frac{\partial U}{\partial\beta} = -\frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 \ . \tag{131}$$

This gives

$$\frac{\partial U}{\partial\beta} = -\frac{1}{Z}\sum_n E_n^2 e^{-\beta E_n} + \langle E\rangle^2 = -\langle E^2\rangle + \langle E\rangle^2 \ . \tag{132}$$

Finally,

$$\langle E^2\rangle - \langle E\rangle^2 = (\Delta E)^2 = -\frac{\partial U}{\partial\beta} = k_{\rm B}T^2\frac{\partial U}{\partial T} = k_{\rm B}T^2 C_V \tag{133}$$

Since $C_V \propto N$ and $U \propto N$ we obtain $\frac{\Delta E}{\langle E\rangle} \propto \frac{1}{\sqrt{N}} \to 0$. We see that in the thermodynamic limit ($N \to \infty$) the relative fluctuations of energy vanish. Thus the canonical ensemble should be equivalent to the microcanonical one.

K. Grand canonical ensemble

We consider a system coupled to a much bigger reservoir (thermal bath) (see Fig. 6). The heat exchange and the particle exchange are allowed between the system and the bath. We assume the density matrix diagonal in the eigenbasis of the Hamiltonian, i.e., $\rho \equiv$

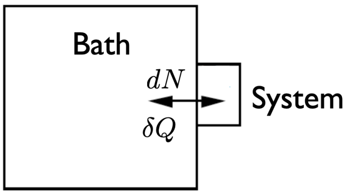

FIG. 6: System coupled to a thermal bath, exchange of particles is allowed.

$\sum_n W_n|\Psi_n\rangle\langle\Psi_n|$ and $H|\Psi_n\rangle = E_n\,|\Psi_n\rangle$. Moreover, we assume that the number of particles operator commutes with the Hamiltonian, $[\hat{N}, H] = 0$. Thus, they have a mutual basis of eigenstates. Therefore $\hat{N}\,|\Psi_n\rangle = N_n\,|\Psi_n\rangle$. We demand the entropy to be maximal under the constraint of a given internal energy U,

$$U \equiv \langle E\rangle = \mathrm{Tr}(\rho H) = \sum_n W_n E_n \ , \tag{134}$$

and a given average number of particles

$$N \equiv \langle \hat{N}\rangle = \mathrm{Tr}(\rho \hat{N}) = \sum_n W_n N_n \ . \tag{135}$$

We use the method of Lagrange multipliers

$$S_L = -k_\mathrm{B}\sum_n W_n \ln W_n - \lambda\left(\sum_n W_n - 1\right) - \alpha\left(\sum_n W_n E_n - U\right) - \gamma\left(\sum_n W_n N_n - N\right) \ . \tag{136}$$

and demand

$$\frac{\partial S_L}{\partial W_n} = -k_\mathrm{B}(\ln W_n + 1) - \lambda - \alpha E_n - \gamma N_n = 0 \tag{137}$$

This gives

$$W_n = const. \cdot e^{-\frac{\alpha E_n}{k_\mathrm{B}}} \cdot e^{-\frac{\gamma N_n}{k_\mathrm{B}}} \ . \tag{138}$$

We rename $\alpha \equiv k_\mathrm{B}\beta$, $\gamma = -k_\mathrm{B}\beta\mu$ (we anticipate μ to be the chemical potential, but this is not yet proven) and introduce a normalisation constant $1/Z_G$, which gives

$$W_n = \frac{1}{Z_G}\, e^{-\beta(E_n - \mu N_n)} \ . \tag{139}$$

From the normalisation condition $\sum_n W_n = 1$ we obtain $Z_G = \sum_n e^{-\beta(E_n-\mu N_n)}$. The quantity Z_G is called **grand canonical partition function**.

It is a straightforward exercise (very similar to the calculation provided above for the canonical ensemble) to show that again $k_{\rm B}\beta = 1/T$ and μ is indeed the chemical potential. Moreover, it is possible to relate the grand canonical partition function Z_G with the grand canonical thermodynamic potential $\Omega(T, V, \mu) = U - TS - \mu N$. Namely

$$\Omega = -k_{\rm B} T \ln Z_G \ . \tag{140}$$

Then, Eqs. (34) provide the connection to the thermodynamics.

1. *Alternative derivation*

Alternatively to maximising the entropy under the condition of a fixed internal energy $U = \mathrm{Tr}(\rho H)$ and fixed average number of particles $N = \mathrm{Tr}(\rho \hat{N})$, one can consider the combined system of the system and the thermal bath being described by a micro canonical state with energy E and number of particles N. We split this energy into the energy of the system E^S and the energy of the bath E^B. Similarly we split N into N^S and N^B. More accurately, we consider the product states $\left|n^S\right\rangle \left|m^B\right\rangle$ of the combined system and associate the energy $E_{n,m} = E_n^S + E_m^B$ and the number $N_{n,m} = N_n^S + N_m^B$ with these states (neglecting the energy related to the interaction between the system and the bath). Since the system is much smaller than the bath, we expect $E_n^S \ll E_m^B$ and $N_n^S \ll N_m^B$. The probability of the combined system to be in the state $\left|n^S\right\rangle \left|m^B\right\rangle$ is given by

$$W_{n,m} = \frac{1}{dN(E)} \quad \text{for} \quad E < E_{n,m} < E + dE \ , \tag{141}$$

and zero otherwise. Here $dN(E)$ is the number of states of the combined system with energies between E and $E + dE$. Next, we calculate the probability of the system to be in the state $\left|n^S\right\rangle$:

$$W_n = \sum_m W_{n,m} = \frac{dN^B(E - E_n, N - N_n)}{dN(E)} \ . \tag{142}$$

Here $dN^B(E, N)$ is the number of states of the bath with energies between E and $E + dE$ and with N particles. Thus we obtain

$$\begin{aligned} k_{\rm B} \ln W_n &= k_{\rm B} \ln \left[dN^B(E - E_n, N - N_n)\right] - k_{\rm B} \left[dN(E)\right] \\ &= S^B(E - E_n, N - N_n) - S = S^B(E) - E_n \frac{\partial S^B(E, N)}{\partial E} - N_n \frac{\partial S^B(E, N)}{\partial N} - S \\ &= const. - \frac{E_n}{T} + \frac{\mu N_n}{T} \ . \end{aligned} \tag{143}$$

We have used the relations

$$\frac{\partial S^B(E,N)}{\partial E}\Big|_{N,V} = \frac{1}{T} \quad , \quad \frac{\partial S^B(E,N)}{\partial N}\Big|_{E,V} = -\frac{\mu}{T} \ . \tag{144}$$

(The bath is microcanonical, $E = U$.) Thus T is the temperature of the bath enforced upon the much smaller system. Similarly, μ is the chemical potential of the bath enforced upon the system by the bath. This again gives the grand canonical distribution

$$W_n = \frac{1}{Z_G} \exp\left(-\frac{E_n - \mu N_n}{k_{\mathrm{B}} T}\right) \quad , \quad Z_G = \sum_n \exp\left(-\frac{E_n - \mu N_n}{k_{\mathrm{B}} T}\right) \ . \tag{145}$$

2. Grand canonical ensemble: fluctuations of the energy and number of particles. Equivalence of the grand canonical, canonical and the microcanonical ensembles.

It is a straightforward exercise, very similar to the derivation provided for the canonical ensemble to show that the fluctuations of the energy and of the number of particles in the grand canonical ensemble can be estimated as $\frac{\Delta E}{\langle E \rangle} \propto \frac{1}{\sqrt{N}} \to 0$ and $\frac{\Delta N}{\langle N \rangle} \propto \frac{1}{\sqrt{N}} \to 0$. Thus, in the thermodynamic limit all three ensembles are equivalent.

L. Summary of three ensembles

We summarise the thermodynamic potentials and their relation to the statistical physics for the three ensembles:

Microcanonical

$$-S(U,V,N) = -k_{\mathrm{B}} \ln Z_M \ , \tag{146}$$

where Z_M is the microcanonical partition function, which we define as

$$Z_M = dN(E=U) = \sum_{E<E_n<E+dE} 1 \ . \tag{147}$$

Note that Z_M was not introduced before. We introduce it here for similarity with the other ensembles. We also take as a thermodynamic potential minus the entropy, which then is minimal in equilibrium, similar to the other ensembles.

Canonical

$$F(T,V,N) = -k_{\mathrm{B}} T \ln Z_C \ , \tag{148}$$

where $Z_C = Z$ is the canonical partition function,

$$Z_C = \sum_n e^{-\beta E_n} \ . \tag{149}$$

Grand canonical

$$\Omega(T,V,\mu) = -k_{\mathrm{B}} T \ln Z_G \ , \tag{150}$$

where Z_G is the grand canonical partition function,

$$Z_G = \sum_n e^{-\beta (E_n - \mu N_n)} \ . \tag{151}$$

IV. MAXWELL-BOLTZMANN GAS

A. Canonical calculation

We consider again the Maxwell-Boltzmann gas with N particles in a box of size L_x, L_y, L_z. The Hamiltonian reads

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \tag{152}$$

The partition function reads

$$Z = \frac{1}{N!} \sum_{\{\mathbf{p}_i\}} e^{-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}} \tag{153}$$

The factor $N!$ takes into account the fact that the particles are identical.

The periodic boundary conditions allow the following momenta

$$(p_x, p_y, p_z) = \left(\frac{2\pi\hbar}{L_x} n_x, \frac{2\pi\hbar}{L_y} n_y, \frac{2\pi\hbar}{L_z} n_z \right) \tag{154}$$

We reduce the sum over micro-states $\{\mathbf{p}_i\}$ (eigen state of H with N particles) to a sum over one-particle-states:

$$Z = \frac{1}{N!} \sum_{\{\mathbf{p}_i\}} e^{-\beta \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}} = \frac{1}{N!} \left(\sum_{\mathbf{p}} e^{-\beta \frac{\mathbf{p}^2}{2m}} \right)^N = \frac{1}{N!} (Z_1)^N \tag{155}$$

Here Z_1 is the single particle partition function:

$$Z_1 \equiv \sum_{\mathbf{p}} e^{-\beta \frac{\mathbf{p}^2}{2m}} = V \int \frac{dp_x dp_y dp_z}{(2\pi\hbar)^3}\, e^{-\beta \frac{\mathbf{p}^2}{2m}} = \frac{V}{\lambda_{\mathrm{T}}^3} \tag{156}$$

Here

$$\frac{1}{\lambda_{\mathrm{T}}} = \frac{1}{2\pi\hbar}\sqrt{\frac{2m\pi}{\beta}} \quad \text{or} \quad \lambda_{\mathrm{T}} = \sqrt{\frac{2\pi\hbar^2}{mk_{\mathrm{B}}T}} \tag{157}$$

is the thermal de Broglie wavelength.

For the free energy we get

$$F(T,V,N) = -k_{\mathrm{B}}T \ln Z = -k_{\mathrm{B}}TN \ln\left[Z_1 N^{-1} e\right] = -k_{\mathrm{B}}TN \ln\left[\frac{V}{N}\,\frac{e}{\lambda_{\mathrm{T}}^3}\right] \; . \tag{158}$$

Here we have used the Stirling formula

$$\ln N! \approx N \ln(N/e) + O(\ln N) \; . \tag{159}$$

Differentiating the free energy with respect to T we obtain

$$S = -\frac{\partial F}{\partial T}\Big|_{V,N} = -\frac{F}{T} + \frac{3}{2}\,k_{\mathrm{B}}N \quad \rightarrow \quad U = \frac{3}{2}\,Nk_{\mathrm{B}}T \; . \tag{160}$$

Similarly

$$P = -\frac{\partial F}{\partial V}\Big|_{T,N} = \frac{Nk_{\mathrm{B}}T}{V} \quad \rightarrow \quad PV = Nk_{\mathrm{B}}T \; , \tag{161}$$

$$\mu = \frac{\partial F}{\partial N}\Big|_{T,V} = -k_{\mathrm{B}}T \ln\left[\frac{V}{N}\,\frac{1}{\lambda_{\mathrm{T}}^3}\right] = -k_{\mathrm{B}}T \ln\left[\frac{V}{N}\left(\frac{mk_{\mathrm{B}}T}{2\pi\hbar^2}\right)^{\frac{3}{2}}\right] \; . \tag{162}$$

The results are identical to those obtained using the microcanonical ensemble (Sec. III F 2).

1. *Validity of the Maxwell-Boltzmann approximation*

We calculate again the entropy:

$$S = -\frac{\partial F}{\partial T}\Big|_{V,N} = -\frac{F}{T} + \frac{3}{2}\,k_{\mathrm{B}}N = k_{\mathrm{B}}N \ln\left[\frac{V}{N}\,\frac{e}{\lambda_{\mathrm{T}}^3}\right] + \frac{3}{2}\,k_{\mathrm{B}}N \tag{163}$$

We use the estimate

$$\frac{V}{N} \sim a^3 \; , \tag{164}$$

where a is the typical distance between the particles. We observe that for $a \ll \lambda_{\rm T}$ one gets $S < 0$. Thus we get a failure of the classical physics. The Maxwell-Blotzmann regime is only valid if $a \gg \lambda_{\rm T}$. Two important examples: 1) for hydrogen gas H_2, at $T = 100$K, one obtains $\lambda_{\rm T} \approx 1\AA \ll a$ (for typical densities). Thus, the Maxwell-Boltzmann approximation is good for H_2. 2) for electrons in a typical metal, at $T = 100$K, one gets $\lambda_{\rm T} \approx 70\AA \gg a$. Maxwell-Boltzmann approach fails for electrons.

B. Grand canonical calculation

We calculate the grand canonical partition function

$$Z_G(T,V,\mu) = \sum_n e^{-\beta(E_n - \mu N_n)} = \sum_N e^{\beta\mu N} \sum_j e^{-\beta E_j(N)} = \sum_N e^{\beta\mu N} Z(N) \ . \tag{165}$$

Using $Z(N) = Z_1^N/N!$ we get

$$Z_G(T,V,\mu) = \sum_N \frac{1}{N!} \left(e^{\beta\mu} Z_1\right)^N = \exp\left(e^{\beta\mu} Z_1\right) \ . \tag{166}$$

For the grand canonical potential we obtain

$$\Omega(T,V,\mu) = -k_{\rm B}T \ln Z_G = -k_{\rm B}T e^{\beta\mu} Z_1 = -k_{\rm B}T e^{\beta\mu} \frac{V}{\lambda_{\rm T}^3} \ . \tag{167}$$

The thermodynamic relations give

$$N = -\frac{\partial\Omega}{\partial\mu}\Big|_{T,V} = e^{\beta\mu}\frac{V}{\lambda_{\rm T}^3} = -\frac{\Omega}{k_{\rm B}T} \quad \rightarrow \quad \Omega = -Nk_{\rm B}T \ . \tag{168}$$

$$S = -\frac{\partial\Omega}{\partial T}\Big|_{V,\mu} = -\frac{5}{2}\frac{\Omega}{T} - \frac{\mu N}{T} \quad \rightarrow \quad U = -\frac{3}{2}\Omega = \frac{3}{2}k_{\rm B}TN \ . \tag{169}$$

$$P = -\frac{\partial\Omega}{\partial V}\Big|_{T,\mu} = -\frac{\Omega}{V} \quad \rightarrow \quad PV = Nk_{\rm B}T \ . \tag{170}$$

Note, that in the grand canonical case the chemical potential μ is controlled and the average number of particles can be obtained as a function of μ, i.e. $N = N(T,V,\mu)$, using Eq. (168). Inverting this equation we clearly obtain (162). We observe again the equivalence of the canonical and grand canonical ensembles.

V. QUANTUM GASES

Our Maxwell-Boltzmann calculation, although looking quantum, was not correct. The problem was counting the number of states properly. We have used the factor $1/N!$ to account for identical particle, but that was too simple.

Consider once again the grand canonical partition function

$$Z_G = \sum_N e^{\beta\mu N} Z(N) \ . \tag{171}$$

For the canonical partition function with N particles, $Z(N)$ we have taken

$$Z(N) = \frac{1}{N!}\sum_{\{\mathbf{p}_i\}} e^{-\beta\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m}} = \frac{1}{N!}\left(\sum_{\mathbf{p}} e^{-\beta\frac{\mathbf{p}^2}{2m}}\right)^N = \frac{1}{N!}\left(Z_1\right)^N \ . \tag{172}$$

Here

$$Z_1 = \sum_{\mathbf{p}} e^{-\beta\frac{\mathbf{p}^2}{2m}} \tag{173}$$

is a 1-particle partition function. We introduce a more general notation for 1-particle states. Instead of $\mathbf{p}$ we will write λ (later λ will encode the spin in addition to the momentum). The index λ will run over all possible 1-particle states. Instead of $\frac{\mathbf{p}^2}{2m}$ we will write ϵ_λ, i.e., the energy of the 1-particle state λ. This gives

$$Z(N) = \frac{1}{N!}\sum_{\{\lambda_i\}} e^{-\beta\sum_{i=1}^{N}\epsilon_{\lambda_i}} = \frac{1}{N!}\left(\sum_{\lambda} e^{-\beta\epsilon_\lambda}\right)^N = \frac{1}{N!}\left(Z_1\right)^N \ , \tag{174}$$

where

$$Z_1 = \sum_{\lambda} e^{-\beta\epsilon_\lambda} \ . \tag{175}$$

Where is the mistake? The sets of 1-particle states $\{\lambda_i\}$ ($i = 1, \ldots, N$) taken by N particles can be of different nature. If all λ_i are different, i.e., the N particles occupy N different 1-particle states, dividing by $N!$ is correct. However, if at list 2 particles occupy the same 1-particle state (assume they are bosons), we overestimate the number of permutations. If the particles are fermions, the double occupations are not allowed at all. Thus, in both cases our calculation fails.

1. *Bosons*

The logic thus far was: say which particle (particle number i) occupies which 1-particle state (λ_i) and then count permutations (divide by the number of permutations). New logic: count only how many particles occupy a 1-particle state λ and sum over all possible 1-particle states λ. In the new logic there are no permutations at all. We get for the canonical partition function

$$Z(N) = \sum_{\substack{\{n_\lambda\} \\ \sum_\lambda n_\lambda = N}} e^{-\beta \sum_\lambda n_\lambda \epsilon_\lambda} \; . \tag{176}$$

Here $\{n_\lambda\}$ denotes a set of occupation numbers for each 1-particle state. In the canonical ensemble this set is restricted to satisfy $\sum_\lambda n_\lambda = N$. This is not so simple to calculate due to the constraint $\sum_\lambda n_\lambda = N$. It is much simpler to calculate the grand canonical partition function

$$Z_G(\mu) = \sum_{\{n_\lambda\}} e^{-\beta \sum_\lambda n_\lambda (\epsilon_\lambda - \mu)} \; , \tag{177}$$

where the set of occupation numbers $\{n_\lambda\}$ is unrestricted.

Simple combinatorics gives

$$Z_G(\mu) = \prod_\lambda \sum_{n_\lambda = 0}^{\infty} e^{-\beta n_\lambda (\epsilon_\lambda - \mu)} = \prod_\lambda Z_\lambda \; . \tag{178}$$

Here

$$Z_\lambda = \sum_{n_\lambda = 0}^{\infty} e^{-\beta n_\lambda (\epsilon_\lambda - \mu)} \tag{179}$$

is a partition function related to a particular 1-particle state λ. This is not the same as the above introduced Z_1, which was a partition function for 1-particle occupying any possible state.

Summing the geometric series we get

$$Z_\lambda = \frac{1}{1 - e^{-\beta(\epsilon_\lambda - \mu)}} \; . \tag{180}$$

Note that the series converges only if $\epsilon_\lambda > \mu$. Thus, for bosons the chemical potential is not arbitrary. It has to satisfy $\mu < \min(\epsilon_\lambda)$. In the simplest case $\epsilon_\lambda = \mathbf{p}^2/2m$ we have $\mu < 0$.

The probability that a 1-particle state λ is occupied by n_λ particles is obviously given by

$$W_\lambda(n_\lambda) = \frac{1}{Z_\lambda} e^{-\beta n_\lambda(\epsilon_\lambda - \mu)} \tag{181}$$

For the average occupation of the state λ this gives

$$\langle n_\lambda \rangle = \sum_{n_\lambda=0}^{\infty} W_\lambda(n_\lambda) n_\lambda = \frac{1}{Z_\lambda} \sum_{n_\lambda=0}^{\infty} n_\lambda e^{-\beta n_\lambda(\epsilon_\lambda - \mu)} = \frac{1}{e^{\beta(\epsilon_\lambda - \mu)} - 1} \tag{182}$$

The simplest way to prove this is to introduce $x \equiv \beta(\epsilon_\lambda - \mu)$. Then

$$Z_\lambda = \sum_{n_\lambda=0}^{\infty} e^{-x n_\lambda} = \frac{1}{1 - e^{-x}} \ . \tag{183}$$

Then

$$\langle n_\lambda \rangle = \frac{1}{Z_\lambda} \sum_{n_\lambda=0}^{\infty} n_\lambda e^{-x n_\lambda} = -\frac{1}{Z_\lambda} \frac{\partial Z_\lambda}{\partial x} = \frac{1}{e^x - 1} \ . \tag{184}$$

Thus we obtain the famous Bose function

$$\langle n_\lambda \rangle = n_B(\epsilon_\lambda) \ , \tag{185}$$

where

$$n_B(\epsilon) \equiv \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \ . \tag{186}$$

The condition $\mu < \epsilon$ is again clearly seen. Indeed, it ensures that the average occupation number is positive.

2. Fermions

For fermions the occupation numbers n_λ can only have two values: 0 and 1. Thus

$$Z_G(\mu) = \sum_{\{n_\lambda=0,1\}} e^{-\beta \sum_\lambda n_\lambda(\epsilon_\lambda - \mu)} \ , \tag{187}$$

This gives

$$Z_G(\mu) = \prod_\lambda \sum_{n_\lambda=0}^{1} e^{-\beta n_\lambda(\epsilon_\lambda - \mu)} = \prod_\lambda Z_\lambda \ , \tag{188}$$

where

$$Z_\lambda = \sum_{n_\lambda=0}^{1} e^{-\beta n_\lambda(\epsilon_\lambda - \mu)} = 1 + e^{-\beta(\epsilon_\lambda - \mu)} \ . \tag{189}$$

For the average occupation of the state λ this gives

$$\langle n_\lambda \rangle = \sum_{n_\lambda=0}^{1} W_\lambda(n_\lambda) n_\lambda = \frac{1}{Z_\lambda} \sum_{n_\lambda=0}^{1} n_\lambda e^{-\beta n_\lambda(\epsilon_\lambda - \mu)} = \frac{1}{e^{\beta(\epsilon_\lambda - \mu)} + 1} \tag{190}$$

Thus we obtain the famous Fermi function

$$\langle n_\lambda \rangle = n_F(\epsilon_\lambda) \ , \tag{191}$$

where

$$n_F(\epsilon) \equiv \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \ . \tag{192}$$

Unlike for bosons, there is no restriction on the chemical potential μ.

3. Maxwell-Boltzmann

For comparison we provide here the average occupation number of a 1-particle state λ in the Maxwell-Boltzmann approximation. The grand canonical partition function in this case reads

$$Z_G = \sum_N \frac{1}{N!} \left(e^{\beta\mu} Z_1\right)^N = \exp\left(e^{\beta\mu} Z_1\right) \ , \tag{193}$$

where

$$Z_1 = \sum_\lambda e^{-\beta\epsilon_\lambda} \ . \tag{194}$$

Thus we obtain

$$Z_G = \prod_\lambda Z_\lambda \ , \tag{195}$$

where

$$Z_\lambda = \exp\left(e^{-\beta(\epsilon_\lambda - \mu)}\right) = \exp\left(e^{-x}\right) \ , \tag{196}$$

where $x \equiv \beta(\epsilon_\lambda - \mu)$. As above

$$\langle n_\lambda \rangle = -\frac{1}{Z_\lambda}\frac{\partial Z_\lambda}{\partial x} = -\frac{\partial \ln Z_\lambda}{\partial x} = e^{-x} = e^{-\beta(\epsilon_\lambda-\mu)} \ . \tag{197}$$

All three distributions (Bose-Einstein, Fermi-Dirac, Maxwell-Boltzmann) are shown in Fig. 7. They give approximately the same when $\langle n_\lambda \rangle \ll 1$, i.e., for $\epsilon_\lambda - \mu \gg k_B T$ (see Fig. 7).

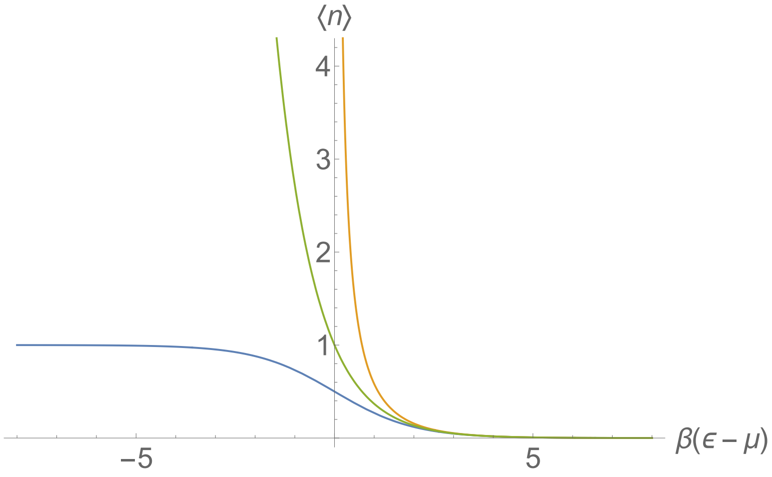

FIG. 7: Average occupation number: Bose-Einstein (upper curve), Maxwell-Boltzmann (middle curve), Fermi-Dirac (lower curve).

VI. IDEAL FERMI-GAS

A. General relations

Fermions are particles with a half-integer spin. For example electrons have spin $s = 1/2$. Thus 1-particle states are $\lambda = \{\mathbf{p}, s_z\}$ with $s_z = -s, -s+1, \ldots, s$. For Fermions we have obtained

$$Z_G = \prod_\lambda Z_\lambda \ , \tag{198}$$

where

$$Z_\lambda = 1 + e^{-\beta(\epsilon_\lambda-\mu)} \ . \tag{199}$$

This gives for the grand canonical potential

$$\Omega(T,V,\mu) = -k_\mathrm{B}T\ln Z_G(T,V,\mu) = -k_\mathrm{B}T\sum_\lambda \ln\left[1+e^{-\beta(\epsilon_\lambda-\mu)}\right] \ . \tag{200}$$

We calculate first the average particle number (remember in the grand canonical ensemble the chemical potential is fixed, whereas the number of particles is not). The calculation gives an obvious result:

$$\langle N\rangle = -\frac{\partial\Omega}{\partial\mu}\Big|_{T,V} = \sum_\lambda \frac{e^{-\beta(\epsilon_\lambda-\mu)}}{1+e^{-\beta(\epsilon_\lambda-\mu)}} = \sum_\lambda \langle n_\lambda\rangle \ . \tag{201}$$

Here

$$\langle n_\lambda\rangle = n_F(\epsilon_\lambda) = \frac{1}{e^{\beta(\epsilon_\lambda-\mu)}+1} \ . \tag{202}$$

Thus we obtain the average number of particles as a function of the chemical potential $N(T,V,\mu)$. Even if the number of particles is given and, in principle, one should have used the canonical ensemble, one usually performs a grand canonical calculation. Then one inverts the function $N(T,V,\mu)$ into $\mu(T,V,N)$.

For the entropy we obtain

$$S = -\frac{\partial\Omega}{\partial T}\Big|_{V,\mu} = -k_\mathrm{B}\sum_\lambda \left[\langle n_\lambda\rangle\ln\langle n_\lambda\rangle + (1-\langle n_\lambda\rangle)\ln(1-\langle n_\lambda\rangle)\right] \ . \tag{203}$$

We observe that the 3-d law of thermodynamics is fulfilled, i.e., $S(T\to 0)\to 0$.

Out of all these quantities we can combine the internal energy. The result, obviously, reads

$$U = \Omega + TS + \mu N = \sum_\lambda \epsilon_\lambda n_F(\epsilon_\lambda) \ . \tag{204}$$

For the pressure we obtain

$$P = -\frac{\partial\Omega}{\partial V}\Big|_{T,\mu} = -\frac{\Omega}{V} \tag{205}$$

B. $T = 0$, Fermi energy

For $T=0$ we have

$$n_F(\epsilon_\lambda) = \frac{1}{e^{\beta(\epsilon_\lambda-\mu)}+1} = \theta(\mu-\epsilon_\lambda) = \begin{cases} 1 & \text{für} \quad \epsilon_\lambda < \mu \\ 0 & \text{für} \quad \epsilon_\lambda > \mu \end{cases} \tag{206}$$

Thus, $\mu(T=0)$ is the highest energy a particle can have. This energy is called the Fermi energy $\epsilon_F \equiv \mu(T=0)$. All states with energies below the Fermi energy are occupied. The states with energies above ϵ_F are empty.

$$\Omega(T,V,\mu) = -k_{\mathrm{B}}T\sum_\lambda \ln\left[1+e^{-\beta(\epsilon_\lambda-\mu)}\right] = \sum_\lambda(\epsilon_\lambda-\mu)\theta(\mu-\epsilon_\lambda) \tag{207}$$

$$N = \sum_\lambda n_F(\epsilon_\lambda) = \sum_\lambda \theta(\mu-\epsilon_\lambda) \tag{208}$$

$$N = \sum_\lambda \theta(\mu-\epsilon_\lambda) = (2s+1)V\int d\epsilon\,\nu(\epsilon)\,\theta(\mu-\epsilon) \tag{209}$$

We have introduced the (orbital) density of states, i.e., number of states per volume and per spin projection:

$$\nu(\epsilon) = \frac{1}{(2s+1)V}\sum_\lambda \delta(\epsilon-\epsilon_\lambda) = \frac{1}{V}\sum_{\mathbf{p}}\delta(\epsilon-\epsilon_{\mathbf{p}}) \tag{210}$$

For periodic boundary conditions

$$(p_x,p_y,p_z) = \left(\frac{2\pi\hbar}{L_x}n_x, \frac{2\pi\hbar}{L_y}n_y, \frac{2\pi\hbar}{L_z}n_z\right) \tag{211}$$

Then

$$\sum_{\mathbf{p}}\cdots = V\int\frac{dp_x dp_y dp_z}{(2\pi\hbar)^3}\cdots \; . \tag{212}$$

Thus the integration measure reads

$$\frac{d^3p}{(2\pi\hbar)^3} = \nu(\epsilon)d\epsilon \; . \tag{213}$$

This gives for $\epsilon_p = \frac{\mathbf{p}^2}{2m}$

$$\nu(\epsilon) = \frac{m^{3/2}\epsilon^{1/2}}{\sqrt{2}\pi^2\hbar^3} \tag{214}$$

Assume the density of particles is given. What is the chemical potential/Fermi energy?

$$n = \frac{N}{V} = (2s+1)\int\frac{d^3p}{(2\pi\hbar)^3}\theta(\epsilon_F-\epsilon_{\mathbf{p}}) = \frac{(2s+1)}{(2\pi\hbar)^3}\cdot\frac{4}{3}\pi p_F^3 \tag{215}$$

Here the Fermi momentum p_F is given by $p_F = \sqrt{2m\epsilon_F}$.

$$\mu(T=0) = \epsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{2s+1}\right)^{\frac{2}{3}} \tag{216}$$

In typical metals $\epsilon_F \sim 10\text{eV}$, which corresponds to the temperature $T_F \equiv \epsilon_F/k_{\text{B}} \sim 10^5\text{K}$. At usual temperatures we thus have $T \ll T_F$. This regime is called "degenerate Fermi gas". The Fermi sphere is almost the same as at $T = 0$. Only the occupation numbers around the Fermi energy change (see Fig. 8).

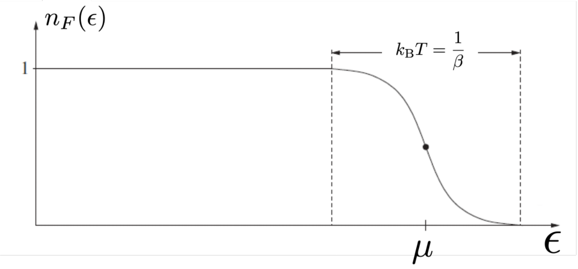

FIG. 8: Occupation numbers in the regime of degenerate Fermi gas.

C. Degenerate Fermi gas, Sommerfeld expansion

We consider the degenerate regime, $k_{\text{B}}T \ll \epsilon_F$. We calculate the gross canonical potential

$$\Omega(T,V,\mu) = -k_{\text{B}}T \ln Z_G(T,V,\mu) = -k_{\text{B}}T \sum_{\lambda} \ln\left[1 + e^{-\beta(\epsilon_\lambda - \mu)}\right] \ . \tag{217}$$

Transforming to integration we get

$$\Omega(T,V,\mu) = -k_{\text{B}}T(2s+1)V \int\limits_{-\infty}^{\infty} d\epsilon\, \nu(\epsilon) \ln\left[1 + e^{-\beta(\epsilon-\mu)}\right] \tag{218}$$

The integration runs from $-\infty$ as we define $\nu(\epsilon) = 0$ for $\epsilon < \epsilon_{min}$. Performing integration by parts we obtain

$$\Omega(T,V,\mu) = -(2s+1)V \int\limits_{-\infty}^{\infty} d\epsilon\, a(\epsilon) n_F(\epsilon) \ , \tag{219}$$

where

$$a(\epsilon) \equiv \int\limits_{-\infty}^{\epsilon} d\epsilon_1 \nu(\epsilon_1) \tag{220}$$

Another integration by parts gives

$$\Omega(T,V,\mu) = -(2s+1)V \int\limits_{-\infty}^{\infty} d\epsilon\, b(\epsilon)(-n_F'(\epsilon)) \ , \tag{221}$$

where

$$b(\epsilon) \equiv \int\limits_{-\infty}^{\epsilon} d\epsilon_1 a(\epsilon_1) \tag{222}$$

A simple calculation gives

$$-\frac{\partial n_F(\epsilon)}{\partial \epsilon} = \frac{1}{4k_\mathrm{B}T\cosh^2\frac{\epsilon-\mu}{2k_\mathrm{B}T}} \tag{223}$$

In the degenerate regime this function is substantially non-zero only in the $k_\mathrm{B}T$ vicinity of the chemical potential (see Fig. 9). To proceed, we expand $b(\epsilon)$ around $\epsilon = \mu$ and substitute the expansion into (221) . We obtain

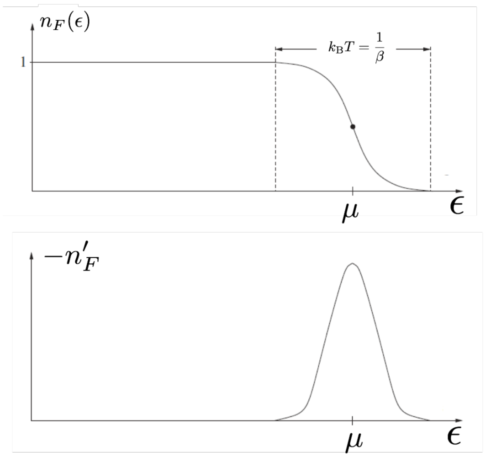

FIG. 9: Function $-\partial n_F(\epsilon)/\partial\epsilon$.

$$b(\epsilon) = b(\mu) + a(\mu)(\epsilon-\mu) + \frac{1}{2}\,\nu(\mu)(\epsilon-\mu)^2 + \dots \tag{224}$$

$$\Omega(T,V,\mu) = -(2s+1)V\left[b(\mu) + \frac{\pi^2}{6}\,(k_\mathrm{B}T)^2\,\nu(\mu) + \dots\right] \ . \tag{225}$$

In the calculation we have used

$$\int\limits_{-\infty}^{\infty} dx\,\frac{x^2}{\cosh^2 x} = \frac{\pi^2}{6} \ . \tag{226}$$

We now turn to the particle number

$$N = -\frac{\partial\Omega}{\partial\mu}\Big|_{T,V} = (2s+1)V\left[a(\mu) + \frac{\pi^2}{6}\left(k_{\mathrm{B}}T\right)^2\frac{d\nu(\mu)}{d\mu} + \dots\right] . \tag{227}$$

For $a(\mu)$ we have

$$a(\mu) \equiv \int\limits_{-\infty}^{\mu} d\epsilon_1\nu(\epsilon_1) = \frac{N(T=0,V,\mu)}{(2s+1)V} \tag{228}$$

Thus

$$N(T,V,\mu) = N(T=0,V,\mu) + (2s+1)V\frac{\pi^2}{6}\left(k_{\mathrm{B}}T\right)^2\frac{d\nu(\mu)}{d\mu} + \dots \tag{229}$$

We divide by V and obtain for the density

$$n(T,\mu) = n(T=0,\mu) + (2s+1)\frac{\pi^2}{6}\left(k_{\mathrm{B}}T\right)^2\frac{d\nu(\mu)}{d\mu} + \dots \tag{230}$$

1. Chemical potential $\mu(T)$

Equation (230) assumes the gross canonical logic: the chemical potential is given, the density depends on the temperature. If, instead, the density is given, we have to invert the logic and find $\mu(T,n)$. For this, we write Eq. (230) as $n(T,\mu) = n$ and try to find μ. For $n(T=0,\mu)$ we use Eq. (216), which we write here again

$$\mu(T=0) = \epsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{2s+1}\right)^{\frac{2}{3}} . \tag{231}$$

We invert this equation in two different ways. First we obtain the density at $T = 0$ as a function of μ (which is arbitrary):

$$n(T=0,\mu) = \frac{2s+1}{6\pi^2}\left(\frac{2m\mu}{\hbar^2}\right)^{\frac{3}{2}} . \tag{232}$$

Second, we express the density $n = n(T,\mu)$ via $\epsilon_F = \mu(T=0)$, i.e.,

$$n = \frac{2s+1}{6\pi^2}\left(\frac{2m\epsilon_F}{\hbar^2}\right)^{\frac{3}{2}} . \tag{233}$$

We also use Eq. 214 for the density of states $\nu(\epsilon) = \frac{m^{3/2}\epsilon^{1/2}}{\sqrt{2}\pi^2\hbar^3}$, which gives

$$\frac{d\nu(\mu)}{d\mu} = \frac{d\nu(\epsilon)}{d\epsilon}\Big|_{\epsilon\to\mu} = \frac{m^{3/2}}{\sqrt{8}\pi^2\hbar^3}\frac{1}{\sqrt{\mu}} . \tag{234}$$

Substituting all this into (230) we obtain

$$
\begin{aligned}
n = \frac{2s+1}{6\pi^2}\left(\frac{2m\epsilon_F}{\hbar^2}\right)^{\frac{3}{2}} &= n(T=0,\mu) + (2s+1)\frac{\pi^2}{6}\,(k_\mathrm{B}T)^2\,\frac{d\nu(\mu)}{d\mu} \\
&= \frac{2s+1}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left[\mu^{3/2} + \frac{\pi^2}{8\sqrt{\mu}}\,(k_\mathrm{B}T)^2 + \dots\right]
\end{aligned}
\tag{235}
$$

Simplifying we get

$$
\epsilon_F^{3/2} = \mu^{3/2} + \frac{\pi^2}{8\sqrt{\mu}}\,(k_\mathrm{B}T)^2 + \dots \tag{236}
$$

This equation can be inverted if we approximate $\mu \approx \epsilon_F$ in the second term of the RHS (we assume $k_\mathrm{B}T \ll \epsilon_F$, thus small correction):

$$
\mu = \epsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_\mathrm{B}T}{\epsilon_F}\right)^2 + \dots\right] \tag{237}
$$

The result is shown in Fig. 10.

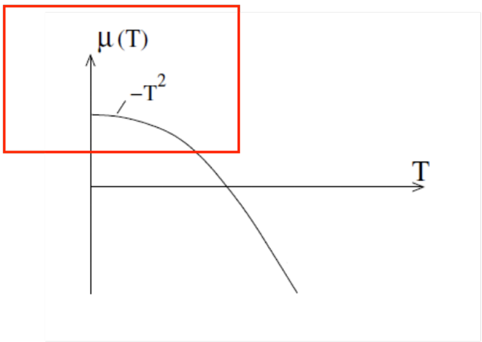

FIG. 10: $\mu(T)$ in Sommerfeld expansion. The function $\mu(T)$ is shown for all temperatures, but, thus far, we have obtained only the low temperature expansion (red box).

2. *Entropy $S(T)$ and heat capacitance $C_V(T)$*

Next we consider the entropy. Using (225) we get

$$
S(T,V,\mu) = -\frac{\partial\Omega}{\partial T}\Big|_{V,\mu} = (2s+1)V\frac{\pi^2\nu(\mu)}{3}\,k_\mathrm{B}^2T\ . \tag{238}
$$

First, we observe again the validity of the 3-d law, namely $S(T\to 0)\to 0$.

Further, we can calculate the heat capacitance $C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N}$. One has to be careful here as the partial derivative in the formula for C_V is taken with $N = cosnt.$ and not with $\mu = const.$. Therefore the correct result reads

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = T\left(\frac{\partial S(T, V, \mu(T, V, N))}{\partial T}\right)_{V,N} \ . \tag{239}$$

The chemical potential is in reality a function of temperature T and density $n = N/V$. This gives

$$C_V = T\left(\frac{\partial S(T, V, \mu)}{\partial T}\right)_{V,\mu} + T\left(\frac{\partial S(T, V, \mu)}{\partial \mu}\right)_{V,T}\left(\frac{\partial \mu(T, V, N)}{\partial T}\right)_{V,N} \ . \tag{240}$$

For the second term we can use the result (237). One can see that the second term $\propto T^3$, thus, at low temperatures, the first term dominates and we obtain

$$C_V \approx N k_\mathrm{B} \frac{\pi^2}{2} \frac{k_\mathrm{B} T}{\epsilon_F} + O(T^3) \ . \tag{241}$$

D. Pauli paramagnetism

To describe the ideal gas of electrons in a magnetic field we recall the Pauli Hamiltonian

$$H = \frac{\left(\vec{p} - \frac{q}{c}\vec{A}\right)^2}{2m} - \frac{\hbar q}{2mc}\vec{B}\cdot\vec{\sigma} + q\Phi \ , \tag{242}$$

where for electrons $q = -e$ (we use $e > 0$). Assuming $\Phi = 0$ (no electric field) we get

$$H = \frac{\left(\vec{p} + \frac{e}{c}\vec{A}\right)^2}{2m} + \mu_B \vec{B}\cdot\vec{\sigma} \ , \tag{243}$$

where we have introduced the Bohr magneton $\mu_B \equiv \frac{e\hbar}{2mc}$. The magnetic field $\vec{B} = \vec{\nabla}\times\vec{A}$ influences the electrons in two ways. The coupling via the kinetic energy $\frac{\left(\vec{p}+\frac{e}{c}\vec{A}\right)^2}{2m}$, called also the orbital coupling, is responsible for the Lorentz force, modifying the trajectories of the electrons and leading, finally, to the Landau levels and the diamagnetic response. The other coupling, Zeeman term, $\mu_B \vec{B}\cdot\vec{\sigma}$ acts on the spin and results in a paramagnetic response. We consider here the effect of the Zeeman coupling only. Thus we (artificially) assume the Hamiltonian to be

$$H = \frac{\mathbf{p}^2}{2m} + \mu_B \vec{B}\cdot\vec{\sigma} \ . \tag{244}$$

We choose, for simplicity, $\vec{B} = B\mathbf{e}_z$ and get the 1-particle states $\lambda = \{\vec{p}, \sigma\}$, where $\sigma = \sigma_z = \pm 1$. The 1-particle energies are

$$\epsilon_\lambda = \epsilon_{\vec{p},\sigma} = \epsilon_{\mathbf{p}} + \mu_B B\sigma = \frac{\mathbf{p}^2}{2m} + \mu_B B\sigma \ . \tag{245}$$

For the grand canonical potential we obtain

$$\begin{aligned}\Omega(T,V,\mu) &= -k_{\mathrm{B}}T\sum_\lambda \ln\left[1 + e^{-\beta(\epsilon_\lambda - \mu)}\right] \\ &= -k_{\mathrm{B}}T\sum_{\mathbf{p}} \ln\left[1 + e^{-\beta(\epsilon_{\mathbf{p}} + \mu_B B - \mu)}\right] - k_{\mathrm{B}}T\sum_{\mathbf{p}} \ln\left[1 + e^{-\beta(\epsilon_{\mathbf{p}} - \mu_B B - \mu)}\right] \ .\end{aligned} \tag{246}$$

We can formally rewrite this as

$$\Omega(T,V,\mu) = \Omega_0(T,V,\mu - \mu_B B) + \Omega_0(T,V,\mu + \mu_B B) \ , \tag{247}$$

where

$$\Omega_0(T,V,\mu) \equiv -k_{\mathrm{B}}T\sum_{\mathbf{p}} \ln\left[1 + e^{-\beta(\epsilon_{\mathbf{p}} - \mu)}\right] \tag{248}$$

is the grand canonical potential of "spin-less" fermions (electrons) with energies $\epsilon_{\mathbf{p}}$. We have already calculated Ω_0 above. One just has to remove the spin degeneracy factor $(2s+1)$. We observe that, effectively, the electrons with spin up ($\sigma = +1$) have the chemical potential $\mu_+ = \mu - \mu_B B$ and the electrons with spin down ($\sigma = -1$) have the chemical potential $\mu_- = \mu + \mu_B B$. Thus $\Omega(T,V,\mu) = \Omega_0(T,V,\mu_+) + \Omega_0(T,V,\mu_-)$.

Let us calculate (out of curiosity) the derivative

$$-\frac{\partial \Omega}{\partial B}\Big|_{T,V} = \mu_B \frac{\partial \Omega_0(\mu_+)}{\partial \mu}\Big|_{T,V} - \mu_B \frac{\partial \Omega_0(\mu_-)}{\partial \mu}\Big|_{T,V} = -\mu_B(N_+ - N_-) \ . \tag{249}$$

Here $N_{+/-}$ is the average number of particles with spin up/down. Taking into account that an electron has a magnetic moment $-\mu_B$ (negative charge), we obtain the magnetisation (in z-direction)

$$M = -\mu_B(N_+ - N_-) = -\frac{\partial \Omega}{\partial B}\Big|_{T,V} \ . \tag{250}$$

This relation is not accidental and will be discussed later in the context of the thermodynamics of magnetic systems.

For a degenerate gas, $k_B T \ll \epsilon_F$ it is easy to calculate

$$\frac{N_+ - N_-}{V} = \int d\epsilon\, \nu(\epsilon)\ \left[n_F(\epsilon, \mu_+) - n_F(\epsilon, \mu_-)\right] = -2\nu(\epsilon_F)\mu_B B \ . \tag{251}$$

Finally, for the magnetisation density we obtain $\frac{M}{V} = \chi B$, where χ is the Pauli magnetic susceptibility given by

$$\chi = 2\mu_B^2 \nu(\epsilon_F) \ . \tag{252}$$

At high temperatures it is possible to obtain

$$\chi = \frac{\mu_B^2 n}{k_B T} \ , \tag{253}$$

where n is the electron density.

VII. IDEAL BOSE-GAS

A. General relations

The partition function of an ideal Bose gas is given by

$$Z_G = \prod_\lambda Z_\lambda \ , \tag{254}$$

where λ denote the 1-particle states. In the simplest case $\lambda = \{\mathbf{p}, s_z\}$, $s_z = -s, -s+1, \ldots, s-1, s$. The spin s is now integer, i.e., $s = 0, 1, 2, \ldots$. The state λ can be occupied by an arbitrary number of particles, $n_\lambda = 0, 1, 2, \ldots$. Thus we obtain

$$Z_\lambda \equiv \sum_{n_\lambda=0}^{\infty} e^{-\beta(\epsilon_\lambda - \mu) n_\lambda} = \frac{1}{1 - e^{-\beta(\epsilon_\lambda - \mu)}} \ . \tag{255}$$

The grand canonical potential reads

$$\Omega(T, V, \mu) = -k_{\mathrm{B}} T \ln Z_G(T, V, \mu) = k_{\mathrm{B}} T \sum_\lambda \ln\left[1 - e^{-\beta(\epsilon_\lambda - \mu)}\right] \ . \tag{256}$$

For the average number of particles this gives

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu}\Big|_{T,V} = \sum_\lambda \langle n_\lambda \rangle \ , \tag{257}$$

where the average occupation number of a state λ is given by the Bose function

$$\langle n_\lambda \rangle = n_B(\epsilon_\lambda) = \frac{1}{e^{\beta(\epsilon_\lambda - \mu)} - 1} \ . \tag{258}$$

For the entropy we obtain

$$S = -\frac{\partial\Omega}{\partial T}\Big|_{V,\mu} = -k_{\mathrm{B}}\sum_{\lambda}\left[\langle n_\lambda\rangle \ln\langle n_\lambda\rangle - (1+\langle n_\lambda\rangle)\ln(1+\langle n_\lambda\rangle)\right] \ . \tag{259}$$

This allows calculating the inner energy as

$$U = \Omega + TS + \mu N = \sum_{\lambda}\epsilon_\lambda n_B(\epsilon_\lambda) \ . \tag{260}$$

B. Bose-Einstein condensation

Unlike in the Fermi gas, the ground state of the Bose gas seem to be very simple: all the particles are in the state with minimum energy. The spin degeneracy might make things a bit more complicated, but we will not address this here.

It is convenient to introduce a quantity $z \equiv e^{\beta\mu}$, which is called fugacity. Consider once again the thermodynamic potential

$$\Omega(T,V,\mu) = k_{\mathrm{B}}T\sum_{\lambda}\ln\left[1 - e^{-\beta(\epsilon_\lambda-\mu)}\right] = k_{\mathrm{B}}T\sum_{\lambda}\ln\left[1 - ze^{-\beta\epsilon_\lambda}\right] \ . \tag{261}$$

or the number of particles

$$N(T,V,\mu) = \sum_{\lambda}\frac{1}{e^{\beta(\epsilon_\lambda-\mu)}-1} = \sum_{\lambda}\frac{z}{e^{\beta\epsilon_\lambda}-z} \ . \tag{262}$$

Transforming these to integrals with the help of the density of states we obtain

$$\Omega(T,V,\mu) = k_{\mathrm{B}}T(2s+1)V\int_0^\infty d\epsilon\,\nu(\epsilon)\ln\left[1 - ze^{-\beta\epsilon}\right] \ , \tag{263}$$

and

$$N = -\frac{\partial\Omega}{\partial\mu}\Big|_{T,V} = (2s+1)V\int_0^\infty d\epsilon\,\nu(\epsilon)n_B(\epsilon) \ . \tag{264}$$

For the density this gives

$$n = \frac{N}{V} = (2s+1)\int_0^\infty d\epsilon\,\nu(\epsilon)n_B(\epsilon) \tag{265}$$

Assume we keep the temperature constant and increase the density. In order to accommodate the higher density the occupation numbers $n_B(\epsilon)$ must grow. The only way to achieve this is to increase the chemical potential. But the chemical potential is limited from above by $\epsilon_{\min}$. We assume, for simplicity, that $\epsilon_{\min} = 0$. We inspect, therefore, what happens at $\mu = 0$. The question is whether the following integral converges or diverges

$$\int_0^\infty d\epsilon\, \nu(\epsilon) n_B(\epsilon, \mu = 0) = \int_0^\infty d\epsilon\, \frac{\nu(\epsilon)}{e^{\beta\epsilon} - 1} \tag{266}$$

If it diverges, there is no problem to accommodate an arbitrary density by taking $\mu \to 0$. If this integral converges, there is a maximal density we can accommodate.

$$n_{\max}(T) \equiv (2s+1) \int_0^\infty d\epsilon\, \frac{\nu(\epsilon)}{e^{\beta\epsilon} - 1}\ . \tag{267}$$

What happens if we increase the density beyond this value? The problem is solved if we reexamine the transition from the sum to the integral in the expressions for Ω and N above. In any finite system the set of energies ϵ_λ is discrete and starts at $\epsilon_{\min} = 0$. We denote the distance to the next energy state by $\Delta\epsilon$. For example in a cubic box of linear size L and with $\epsilon_\lambda = \mathbf{p}^2/2m$ we have $\Delta\epsilon = \frac{1}{2m}\left(\frac{2\pi\hbar}{L}\right)^2 \propto L^{-2} \propto V^{-2/3}$. When we increase μ in order to accommodate more and more particles, we can at some stage get into the regime $-\mu = |\mu| \ll \Delta\epsilon$. Then, the first term in the sum $N = \sum_\lambda \frac{1}{e^{\beta(\epsilon_\lambda - \mu)} - 1}$, which corresponds to $\epsilon_\lambda = 0$ becomes much larger that the other contributions. We are forced to treat it separately. Thus we have

$$\Omega(T, V, \mu) = k_{\mathrm{B}}T\,(2s+1)\,\ln[1 - z] + k_{\mathrm{B}}T(2s+1)V \int_0^\infty d\epsilon\, \nu(\epsilon) \ln\left[1 - z e^{-\beta\epsilon}\right] \tag{268}$$

and

$$N = -\frac{\partial\Omega}{\partial\mu}\Big|_{T,V} = (2s+1)\,\frac{z}{1-z} + (2s+1)V \int_0^\infty d\epsilon\, \nu(\epsilon) n_B(\epsilon)\ . \tag{269}$$

The contribution treated separately

$$N_0 = (2s+1)\,\frac{z}{1-z} = (2s+1)\frac{1}{z^{-1} - 1} = (2s+1)\frac{1}{e^{-\beta\mu} - 1} \tag{270}$$

is just the number of particles in the state(s) with $\epsilon = \epsilon_{\min} = 0$. For the density we obtain

$$n = \frac{N}{V} = \frac{(2s+1)}{V}\,\frac{z}{1-z} + (2s+1) \int_0^\infty d\epsilon\, \nu(\epsilon) n_B(\epsilon)\ , \tag{271}$$

which can be rewritten as

$$n = n_0 + n_{\epsilon>0} \ . \tag{272}$$

Here

$$n_0 = \frac{(2s+1)}{V} \frac{z}{1-z} \tag{273}$$

is the density of particles with $\epsilon = \epsilon_{\rm min} = 0$ whereas $n_{\epsilon>0}$ is the density of particles with higher energies.

If the integral (266) converges, $n_{\epsilon>0}$ has a maximum value at a given temperature, i.e., $\max{[n_{\epsilon>0}]} = n_{\rm max}(T)$, which is reached at $\mu \to 0$. If we increase the density further, the rest of the particles must be accommodated in n_0, i.e., in the condensate. We obtain a finite density of particles in the condensate

$$n_0(T) = n - n_{\rm max}(T) \ . \tag{274}$$

This corresponds to a macroscopic occupation of the 1-particle ground state(s), i.e., $N_0 = Vn_0 \propto V$.

Instead of increasing the density at a given T, we can lower the temperature keeping the density constant. Then, assuming (266) converges, $n_{\rm max}(T)$ decreases with decreasing T. For high enough temperatures $n_{\rm max}(T) > n$ and there is no need to have a finite condensate density. At some critical temperature, which we denote T_c, one gets $n_{\rm max}(T_c) = n$. At $T < T_c$ we are forced to have $n_0(T) = n - n_{\rm max}(T) > 0$. This is an example of a second order phase transition with $n_0(T)$ being the order parameter.

1. Non-relativistic bosons in 3D

For $\epsilon_\lambda = \mathbf{p}^2/2m$ in 3D we have (see Eq. (214))

$$\nu(\epsilon) = \frac{m^{3/2}\epsilon^{1/2}}{\sqrt{2}\pi^2\hbar^3} = \alpha\epsilon^{1/2} \ . \tag{275}$$

We have introduced $\alpha \equiv \frac{m^{3/2}}{\sqrt{2}\pi^2\hbar^3}$ to simplify the notations. Then

$$n_{\rm max}(T) \equiv (2s+1)\int\limits_0^\infty d\epsilon \, \frac{\nu(\epsilon)}{e^{\beta\epsilon}-1} = \frac{\alpha(2s+1)}{\beta^{3/2}} \int dx \, \frac{x^{1/2}}{e^x - 1} = \gamma \, T^{3/2} \ . \tag{276}$$

We have introduced another constant $\gamma \equiv \alpha(2s+1)k_{\rm B}^{3/2} \int dx\, \frac{x^{1/2}}{e^x-1}$ to simplify the notations. This gives $\gamma T_c^{3/2} = n$, i.e.,

$$T_c = (n/\gamma)^{2/3} \,. \tag{277}$$

For the order parameter below the critical temperature, $T < T_c$, we obtain

$$n_0(T) = n - n_{\rm max}(T) = \gamma \left(T_c^{3/2} - T^{3/2}\right) \,, \tag{278}$$

$$\frac{n_0(T)}{n} = 1 - \frac{n_{\rm max}(T)}{n} = 1 - \left(\frac{T}{T_c}\right)^{3/2} \,. \tag{279}$$

This dependence is shown in Fig. 11

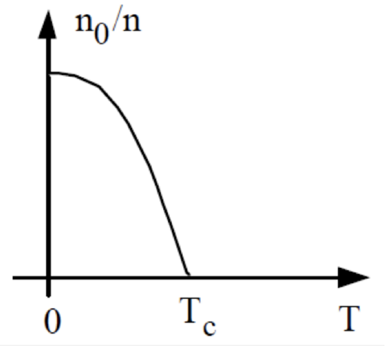

FIG. 11: Density of particles in condensate (divided by the total density) as a function of temperature.

2. Chemical potential for $T < T_c$, thermodynamic limit

From Eq. (273) one finds the fugacity as

$$z = \frac{1}{1 + \frac{2s+1}{Vn_0}} \,. \tag{280}$$

For $T < T_c$ the condensate density is finite, $Vn_0 = N_0 \gg 1$ and we get

$$z \approx 1 - \frac{2s+1}{Vn_0} \quad \rightarrow \quad \beta\mu = \ln(z) \approx -\frac{2s+1}{Vn_0} \,. \tag{281}$$

We obtain

$$\mu \approx -k_{\rm B}T\frac{2s+1}{Vn_0} \,. \tag{282}$$

In the thermodynamic limit $\mu \to 0$. We observe that $|\mu| \propto 1/V$ whereas the energy distance to the first positive energy state (discussed above) was $\Delta\epsilon \propto V^{-2/3}$. Thus, we indeed reach the limit $|\mu| \ll \Delta\epsilon$ when $V \to \infty$ and we must separate the $\epsilon = 0$ contribution from the integrals.

C. Black body radiation

We now consider a gas of photons in a cavity (Fig. 12). Such a cavity can be used as a model of a black body, i.e, a body at temperature T that absorbs all incoming light and radiates light in turn. Inside the cavity the photons are in thermal equilibrium with the walls, i.e., have temperature T.

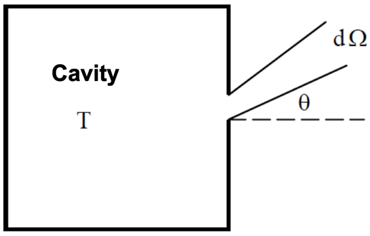

FIG. 12: Cavity as a model of a black body.

Photons are massless bosons (with spin 1). Since they are massless, only two spin states (polarisations) are allowed. Thus, the 1-particle states are given by $\lambda = (\mathbf{k}, \sigma)$, where $\mathbf{k}$ is the wave vector and $\sigma = \pm 1$ is the polarisation. The dispersion relation is linear $\epsilon_\lambda = c\hbar|\mathbf{k}| = c|\mathbf{p}|$.

For summations over the 1-particle states of the type

$$\sum_\lambda f(\epsilon_\lambda) = 2V \int d\epsilon\, \nu(\epsilon) f(\epsilon) \tag{283}$$

we obtain the density of states

$$\nu(\epsilon) = \frac{4\pi\epsilon^2}{(2\pi\hbar c)^3} \tag{284}$$

The very special property of phonons is that their number is not conserved. Indeed they can be freely emitted and absorbed. As we will see, this leads to a very important conclusion: the chemical potential must be identically zero, $\mu = 0$. Unlike with massive particles this does not lead to the macroscopic occupation of the zero-energy state, because photons of zero energy do not exist.

Justification for $\mu = 0$. We can argue similar to Eq. 127 and Eq. 143. The situation is on one hand similar to the canonical, since only heat and not particles is exchanged with the bath. On the other hand it is also grand canonical, since the number of particles in the system is not fixed and we sum over all occupation numbers. We conclude that the probability of a micro-state is given by

$$W_n \propto e^{-\beta E_n} \ , \tag{285}$$

where n is characterised by the occupation numbers $\{n_\lambda\}$, $E_n = \sum n_\lambda \epsilon_\lambda$, and the number of particles $N_n = \sum_\lambda n_\lambda$ is not restricted. The contribution $-\mu N_n$ in the exponent does not appear, as particles are not taken from the bath. Thus, indeed, $\mu = 0$. Another important detail: there are no particles with $\epsilon_\lambda = 0$. Every photon has to have some minimal energy. Thus, no Bose-Einstein condensation despite $\mu = 0$.

The grand canonical potential and the free energy are in this case the same since $\Omega = F - \mu N$ and $\mu = 0$. We obtain

$$\Omega(T, V, \mu = 0) = F(T, V) = -k_{\mathrm{B}} T \ln Z_G(T, V, \mu = 0) = k_{\mathrm{B}} T \sum_\lambda \ln\left[1 - e^{-\beta\epsilon_\lambda}\right] \ . \tag{286}$$

Transforming to integral we get

$$\Omega = 2 V k_{\mathrm{B}} T \int_0^\infty d\omega \, \nu(\omega) \ln\left[1 - e^{-\beta\hbar\omega}\right] \tag{287}$$

Here $\nu(\omega) d\omega = \nu(\epsilon) d\epsilon$, i.e., $\nu(\omega) = \hbar\nu(\epsilon \to \hbar\omega)$. Since $\nu(\omega) \propto \omega^2$ we can define $x = \beta\hbar\omega$ and extract all the dimension-full factors. We immediately observe $\Omega \propto T^4$. The remaining dimension-less integral reads

$$\int_0^\infty dx \, x^2 \ln\left[1 - e^{-x}\right] = -\frac{\pi^4}{45} \ . \tag{288}$$

Finally, we obtain

$$F = \Omega \ = -V \, \frac{\pi^2}{45} \, \frac{(k_{\mathrm{B}} T)^4}{(c\hbar)^3} \ . \tag{289}$$

We calculate the entropy

$$S = -\frac{\partial F}{\partial T}\Big|_V = -4\,\frac{F}{T} = k_{\mathrm{B}} V \, \frac{4\pi^2}{45} \, \frac{(k_{\mathrm{B}} T)^3}{(c\hbar)^3} \ . \tag{290}$$

For the inner energy this gives

$$U = F + TS = -3F \; . \tag{291}$$

Finally, for the heat capacitance we get

$$C_V = T \frac{\partial S}{\partial T}\bigg|_V = k_{\mathrm{B}} V \, \frac{4\pi^2}{15} \, \frac{(k_{\mathrm{B}}T)^3}{(c\hbar)^3} \; . \tag{292}$$

Finally, we can calculate the radiation pressure:

$$P = -\frac{\Omega}{V} = \frac{\pi^2}{45} \, \frac{(k_{\mathrm{B}}T)^4}{(c\hbar)^3} \; . \tag{293}$$

D. Planck formula

The average occupation number of a 1-photon state λ is given by by the Bose function with $\mu = 0$, i.e.,

$$\langle n_{\mathbf{k},\sigma} \rangle = \frac{1}{e^{\beta\hbar\omega_{\mathbf{k}}} - 1} \; , \tag{294}$$

where $\omega_{\mathbf{k}} = c|\mathbf{k}|$.

Next we calculate the number of photons in an interval of frequencies $d\omega$. This is given by

$$n_\omega d\omega = \langle n_{\mathbf{k},\sigma} \rangle 2V \, \frac{4\pi k^2 dk}{(2\pi)^3} = \langle n_{\mathbf{k},\sigma} \rangle \, 2V \nu(\omega) \, d\omega \; , \tag{295}$$

where

$$\nu(\omega) = \frac{4\pi\omega^2}{(2\pi c)^3} \; . \tag{296}$$

Finally, the radiation energy in a frequency window $d\omega$ pro unit of volume is given by

$$u(\omega, T) d\omega \equiv \frac{1}{V} \, n_\omega \hbar\omega d\omega \; . \tag{297}$$

We obtain the Planck formula (Max Planck, 1900), which gives the spectral density of radiation energy (per unit frequency, per unit volume)

$$u(\omega, T) = \frac{\hbar}{\pi^2 c^3} \, \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \; . \tag{298}$$

See Fig. 13. This formula interpolates between Reyleigh-Jeans-Law at low frequencies $\hbar\omega \ll k_\mathrm{B}T$

$$u(\omega,T) = \frac{1}{\pi^2 c^3}\, k_\mathrm{B}T\,\omega^2 \ , \tag{299}$$

and Wien-Law at high frequencies $\hbar\omega \gg k_\mathrm{B}T$

$$u(\omega,T) = \frac{1}{\pi^2 c^3}\, \hbar\omega^3\, e^{-\beta\hbar\omega} \ . \tag{300}$$

The maximum is achieved at $\hbar\omega_\mathrm{max} \approx 2,822\, k_\mathrm{B}T$.

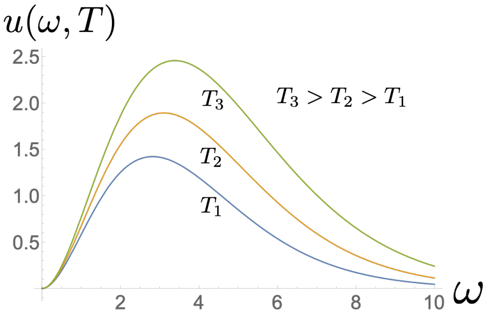

FIG. 13: Planck's spectral density of black body radiation.

VIII. THERMODYNAMICS OF MAGNETIC SYSTEMS

We recall the magnetic relations. The magnetic inductance is defined via $\mathbf{B} = \mathrm{rot}\mathbf{A}$, whereas the magnetic field is given by $\mathbf{H} \equiv \mathbf{B} - 4\pi\mathbf{M}$. Here $\mathbf{M}$ is the magnetisation.

$$dU_\mathrm{Feld} = \int dV \left(\frac{\mathbf{E}\cdot d\mathbf{D} + \mathbf{H}\cdot d\mathbf{B}}{4\pi} \right) \ . \tag{301}$$

A work performed by a magnetic system reads

$$\delta W = -dU_\mathrm{Feld} = -\int dV\, \frac{\mathbf{H}\cdot d\mathbf{B}}{4\pi} \ . \tag{302}$$

Assuming $\mathbf{H}$ is controlled, we have $d\mathbf{H} = 0$ and $d\mathbf{B} = 4\pi d\mathbf{M}$. Thus

$$\delta W = -\int dV\, \mathbf{H}\cdot d\mathbf{M} \ . \tag{303}$$

We will shorten this as

$$\delta W = -\mathbf{H}\cdot d\mathbf{M} \ . \tag{304}$$

The first law of thermodynamics reads

$$dU = \delta Q - dW = TdS + \mathbf{H} \cdot d\mathbf{M} \ . \tag{305}$$

Thus for the inner energy the proper variables are S and $\mathbf{M}$, i.e., $U(S, \mathbf{M})$. The usual Legendre transformation leads to free energy $F = U - TS$. We obtain

$$dF = dU - TdS - SdT = -SdT + \mathbf{H} \cdot d\mathbf{M} \ . \tag{306}$$

Since $\mathbf{M}$ is difficult to control, we prefer to control $\mathbf{H}$. To do so one has to perform another Legendre transformation leading to the free enthalpy: $G = F - \mathbf{H} \cdot \mathbf{M}$. We obtain

$$dG = -SdT - \mathbf{M} \cdot d\mathbf{H} \ . \tag{307}$$

The proper variables of G are $G(T, \mathbf{H})$ and

$$\mathbf{M} = -\left(\frac{\partial G}{\partial \mathbf{H}}\right)_T \ . \tag{308}$$

Usually the full field $\mathbf{H}$ is not controlled either. It is only the externally applied field that is controlled. The other part of $\mathbf{H}$, the so called demagnetising field (or the field created by $\mathbf{M}$) is not controlled. Here we neglect the demagnetising effects and approximate $\mathbf{H} \approx \mathbf{H}_{ext} = \mathbf{B}_{ext}$.

The Hamiltonian of the magnetic systems usually contains the term $-\mathbf{H} \cdot \mathbf{M}$. That is, usually, $H = H_U - \mathbf{H}_{ext} \cdot \mathbf{M}$, where H_U can be associated with the inner energy of the system. Thus H corresponds to enthalpy rather than to inner energy. That's why we have

$$G = -k_B T \ln Z \ , \tag{309}$$

where Z has been calculated with the full Hamiltonian, $Z = Tr\left[\exp\left(-\beta H\right)\right]$.

A. Example: spin 1/2, Curie susceptibility

Consider spin-1/2 with Hamiltonian

$$H = \mu_B B \sigma_z \ . \tag{310}$$

There are two eigenstates with energies $E_n = \pm \mu_B B$. The partition function reads

$$Z = \sum_n e^{-\beta E_n} = e^{\beta \mu_B B} + e^{-\beta \mu_B B} = 2 \cosh \frac{\mu_B B}{k_B T} \ . \tag{311}$$

The thermodynamic potential reads

$$G = -k_B T \ln Z = -k_B T \ln \left[2 \cosh \frac{\mu_B B}{k_B T} \right] \ . \tag{312}$$

For the magnetisation (in z-direction) we get

$$M = -\frac{\partial G}{\partial B}\bigg|_T = \mu_B \tanh \frac{\mu_B B}{k_B T} \ . \tag{313}$$

Linearising for $\mu_B B \ll k_B T$ we get $M \approx \chi B$, where the (Curie) susceptibility χ reads

$$\chi = \frac{\mu_B^2}{k_B T} \ . \tag{314}$$

IX. LITERATURE

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