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Chapter 5

Applications of quantum statistical physics

We now turn to first applications of quantum statistical physics. We will first have a look at one of the simplest quantum systems: The quantum harmonic oscillator. We will then turn to the situation of having many coupled oscillators, and encounter the anyway interesting concept of decoupling oscillators. A big proportion of the chapter will be spent with discussing bosons and fermions, so indistinguishable quantum many-body systems. We assume a basic knowledge of bosonic and fermionic systems already, but not too much.

5.1 Harmonic systems

5.1.1 Statistical mechanics of single harmonic oscillators

Harmonic systems are ubiquitous in physics, surely in theoretical physics. This is true for two reasons:

- a) Many problems can be modelled by harmonic oscillators. This is true for the mechanical motion of a micro-cantilever or a mirror in opto-mechanics, the motion of ions in a trap, of motions of ions in a crystal structure in condensed matter physics. It is also true for discrete versions of free fields and many other systems. This is no surprise: To first approximation, one can often take the Hamiltonian to be quadratic in positions and momenta, and couplings to be linear. Non-linearities can then be treated as a perturbation.
- b) The other reason is that they can be exactly solved. This is a merit that should not be underestimated. To be fair, most of what is published concerns both (i) what is genuinely interesting and (ii) what can be actually treated. Since harmonic systems can be studied in all generality, one can

often answer quite elaborate questions for these systems and hence use them as a kind of “theoretical laboratory”.

Quantum harmonic oscillator: The Hamiltonian of a harmonic oscillator is given by

$$H = \frac{1}{2m}P^2 + \frac{D}{2}Q^2, \quad (5.1)$$

where P and Q are the operators of momentum and position, $m > 0$ is the mass and $D > 0$ the spring constant.

It is not difficult to see that this oscillator can always be brought into the normal form

$$H = \frac{\omega}{2}(P^2 + Q^2), \quad (5.2)$$

where $\omega = (D/m)^{1/2} > 0$ is its frequency. This can be done by means of a unitary transformation, we will get back to that. We already know how the Hamiltonian looks like in the energy eigenbasis, it is

$$H = \sum_{n=0}^{\infty} E_n |E_n\rangle \langle E_n|, \quad (5.3)$$

where

$$E_n = \left(n + \frac{1}{2}\right)\omega. \quad (5.4)$$

The ground state energy is $E_0 = \omega/2$, while the spectrum is not bounded from above. Taking this knowledge into account, it is not difficult to compute the partition function of the quantum canonical ensemble. It is

$$\begin{aligned} Z &= \text{tr}(e^{-\beta H}) = \sum_{n=0}^{\infty} e^{-\beta\omega(n+1/2)} \\ &= \frac{e^{-\beta\omega/2}}{1 - e^{-\beta\omega}} \\ &= \frac{1}{2 \sinh(\beta\omega/2)}. \end{aligned} \quad (5.5)$$

This was easy! For comparison, let us also compute the classical partition function of a harmonic oscillator. Also here we could have considered the simplified Hamiltonian as in Eq. (5.2), only that now, of course, the classical instance is now taken. But let us keep the mass and the spring constant for a moment. We

have

$$\begin{aligned}
 Z &= \int d\gamma e^{-\beta H} \\
 &= \int dp \int dq \exp\left(-\beta\left(\frac{p^2}{2m} + \frac{D}{2}q^2\right)\right) \\
 &= \left(\frac{2\pi m}{\beta}\right)^{1/2} \left(\frac{2\pi}{\beta D}\right)^{1/2} = \frac{2\pi}{\beta\omega}.
 \end{aligned} \tag{5.6}$$

Remember that we have taken $\hbar = 1$, remember, and in the quantum mechanical description, we should have replaced ω by $\hbar\omega$ in SI-units, we have to divide the classical partition function by h such that it corresponds to the quantum mechanical one at high temperatures. From this, we can compute the thermodynamical potentials and functions. We rather state the results here, for

$$F = -\frac{1}{\beta} \log Z, \tag{5.7}$$

$$U = \langle H \rangle_\beta = \frac{\partial}{\partial \beta} \log Z, \tag{5.8}$$

$$\tag{5.9}$$

as well as S and C :

Quantum	Classical
$F = \frac{1}{\beta} \log 2 \sinh(\beta\omega/2)$	$F = \frac{1}{\beta} \log(\beta\omega)$
$U = \frac{\omega}{2} + \frac{\omega}{e^{\beta\omega} - 1}$	$U = \frac{1}{\beta}$
$S = k \frac{\beta}{\omega} 2 \coth(\beta\omega/2) - k \log(2 \sinh(\beta\omega/2))$	$S = k - k \log(\omega)$
$C = k \left(\frac{\beta\omega}{2 \sinh(\beta\omega/2)} \right)^2$	$C = k$

We see that we need at least $\beta\omega \approx 1$, hence $kT \approx \hbar\omega$ such that the motional degrees of freedom contribute to the thermodynamics. Below that temperature, they do not contribute significantly and are “frozen in”, as one says. In fact, we have already implicitly made use of that fact earlier when counting degrees of freedom.

5.1.2 Many uncoupled oscillators

So far so good. In statistical physics, one is, however, usually less interested in studying the properties of a single harmonic oscillator. But rather of many of

them. This might sound scarier than it is: If they are not coupled at all, then we are already there. The Hamiltonian of many uncoupled oscillators is

$$H = \sum_j H_j = \sum_j \frac{\omega_j}{2} (P_j^2 + Q_j^2), \quad (5.10)$$

defined on the Hilbert space $\otimes_j \mathcal{H}_j$. Therefore, we partition function factors,

$$Z = \prod_j Z_j \quad (5.11)$$

and hence we get

$$F = \sum_j F_j, \quad (5.12)$$

$$U = \sum_j U_j, \quad (5.13)$$

$$S = \sum_j S_j. \quad (5.14)$$

Hence, the thermodynamics of many oscillators can be reduced to the thermodynamics of a single harmonic oscillator: We just have to take the sum in a last step. So there is nothing more to say. We already know the thermodynamics of many uncoupled oscillators.

5.1.3 Coupled oscillators and symplectic transformations

But this is not quite the situation one usually encounters yet. Often, the constituents are coupled, even though only slightly. Think of ions in a lattice structure of a crystal structure. Surely, the motions will to a good approximation be harmonic. But neglect couplings altogether would be ridiculous. After all, the ions are in a crystal structure. Let us hence consider Hamiltonians of the general form

$$H = \sum_{j,k=1}^m (A_{j,k} P_j P_k + D_{j,k} Q_j Q_k). \quad (5.15)$$

The matrices $A, B \in \mathbb{R}^{m \times m}$ are Hermitian (and hence symmetric, as they are real), $A = A^T$, $B = B^T$. The main diagonal elements take the above role, but the off-diagonal elements reflect couplings. How can we capture them? This seems like an impossible task.

It is not. In fact, it is very easy to relate this case again to the case of uncoupled harmonic oscillators. The key insight is that harmonic systems can always be decoupled. Let us think of the vector of position and momentum operators

$$\mathbf{R} = (Q_1, \dots, Q_m, P_1, \dots, P_m)^T \quad (5.16)$$

We can now transform the Hamiltonian to a new form: This can be done by canonical transformation, so by linear transformations from one set of coordinates to a new one, while keeping the canonical commutation relations invariant:

$$[Q_j, P_k] = i\delta_{j,k}, \quad (5.17)$$

$$[P_j, P_k] = 0, \quad (5.18)$$

$$[Q_j, Q_k] = 0, \quad (5.19)$$

for $j, k = 1, \dots, m$. Here, we have again set $\hbar = 1$. We can hence think of linear transformations

$$\mathbf{R} \mapsto S\mathbf{R} = \mathbf{R}' = (Q'_1, \dots, Q'_m, P'_1, \dots, P'_m)^T, \quad (5.20)$$

with $S \in \mathbb{R}^{m \times m}$. The obvious question now is: What are the allowed matrices S , such that the commutation relations between position and momentum operators are respected? Let us define the skew symmetric matrix

$$\sigma = \begin{bmatrix} 0 & \mathbb{1}_m \\ -\mathbb{1}_m & 0 \end{bmatrix}. \quad (5.21)$$

Now, a moment of thought reveals the following:

Symplectic transformations: The linear transformations $\mathbf{R} \mapsto S\mathbf{R}$ that preserve the canonical commutation relations are exactly those corresponding to matrices $S \in \mathbb{R}^{m \times m}$ that satisfy

$$S\sigma S^T = \sigma. \quad (5.22)$$

These matrices form a group, the real symplectic group $Sp(2m, \mathbb{R})$.

What are these symplectic transformations? They are the canonical transformations, as they appear also in classical physics. Still, what elements are contained in it? Let us consider the situation of a single harmonic oscillator first, so $Sp(2, \mathbb{R})$. Clearly, any rotation

$$\begin{bmatrix} Q'_1 \\ P'_1 \end{bmatrix} = \begin{bmatrix} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{bmatrix}, \quad (5.23)$$

with $\theta \in [0, 2\pi)$ is a symplectic transformation: The canonical commutation relations between the new position and momentum operator are the same one as before. Such operations are called “passive”, in that they preserve the number of excitations.

But the symplectic group contains also other elements: One can also “squeeze” the coordinates: One can stretch the position variables and compress the momentum ones and the other way around. For our oscillator, this means that

$$\begin{bmatrix} Q'_1 \\ P'_1 \end{bmatrix} = \begin{bmatrix} x & 0 \\ 0 & 1/x \end{bmatrix} \quad (5.24)$$

for $x \in \mathbb{R} \setminus \{0\}$ is an allowed map of this kind, as one can easily verify. Such operations are called “active”, as the number of excitations is not preserved. For a single oscillator, this is also it: The symplectic group is generated by such elements.

For a larger number of modes things are more complicated: It is still true that squeezers are the only non-passive transformations, but the passive ones are more than simple rotations. In fact, if $O \in O(m)$ is an orthogonal map, then

$$O \oplus O \in Sp(2m, \mathbb{R}). \quad (5.25)$$

But there are more than those as well. In fact, the passive subgroup is isomorphic to $U(m)$, for the group theory experts in the audience. A homework here: Can you, with these tools, decouple the above general Hamiltonian defined in Eq. (5.15)?

5.1.4 Quantum statistics of the harmonic chain

But let us rather turn to an important example, the linear harmonic chain. Such a harmonic chain is a model for phonons of a solid body in the condensed matter context. Here, we allow for $N + 2$ chain units, of which the left and the right ones cannot move and are fixed. We also consider only the motion in one direction, so only longitudinal motion. If Q_j and P_j are the positions and momenta of the j -th oscillator, then the Hamiltonian can be written as follows.

Hamiltonian of the harmonic chain:

$$H = \sum_{j=0}^N \left(\frac{P_j^2}{2m} + \frac{D}{2} (Q_j - Q_{j+1})^2 \right), \quad P_0 = 0, \quad Q_0 = Q_{N+1} = 0. \quad (5.26)$$

We expect wave solutions, but since the ends are fixed, the amplitude of the wave is forced to zero at the boundary. We can hence have a good guess of the above symplectic transformation. We take

$$Q_j = \sqrt{\frac{2}{N+1}} \sum_{k=1}^N \sin\left(\pi \frac{jk}{N+1}\right) Q'_k, \quad (5.27)$$

$$P_j = \sqrt{\frac{2}{N+1}} \sum_{k=1}^N \sin\left(\pi \frac{jk}{N+1}\right) P'_k. \quad (5.28)$$

In order to check that this really amounts to a symplectic transformation, we use the discrete orthogonality

$$\sum_{j=1}^N \sin\left(\pi \frac{jk}{N+1}\right) \sin\left(\pi \frac{jl}{N+1}\right) = \frac{N+1}{2} \delta_{l,k}. \quad (5.29)$$

This equality can be simply deduced from the real part of the orthogonality relations of the Fourier transform

$$\sum_{j=0}^{2N+1} e^{\pi i j k / (N+1)} e^{\pm \pi i j l / (N+1)} = \sum_{j=0}^{2N+1} e^{2\pi i j \frac{j(k \pm l)}{2N+2}} = 2(N+1) \begin{cases} \delta_{k,0} \delta_{l,0} & +, \\ \delta_{k,l} & -, \end{cases} \quad (5.30)$$

for $0 \leq k, l \leq N$. Indeed, this is a passive symplectic transformation of the form as in Eq. (5.25). With $m = N + 2$, we have applied the same orthogonal transformation to the position and momentum coordinate, and this transformation hence corresponds to an element in $Sp(2(N+2), \mathbb{R})$. What is more, the kinetic part involving the momentum coordinates will remain the same: After all, the coupling matrix is simply an identity matrix which is left unchanged by this orthogonal transformation. The coupling in the position coordinates, however, now becomes

$$\sum_{j=0}^N (Q_j - Q_{j+1})^2 = \sum_{k=1}^N 4 \sin^2 \left(\frac{\pi}{2} \frac{k}{N+1} \right) Q_k'^2. \quad (5.31)$$

This is an uncoupled system! Let us digest for a moment what this means: We have transformed a system that is coupled to one that reflects the physics of simple harmonic oscillators. Hence, all we know on statistical mechanics will be applicable, quite an exciting state of affairs.

In this way, we hence have an uncoupled set of harmonic oscillators with frequencies

$$\omega_k = 2\sqrt{\frac{D}{m}} \sin \left(\frac{\pi}{2} \frac{k}{N+1} \right) = \Omega \sin \left(\frac{\pi}{2} \frac{k}{N+1} \right) \quad (5.32)$$

for $1 \leq k \leq N$, introducing

$$\Omega = 2\sqrt{\frac{D}{m}}. \quad (5.33)$$

So the harmonic oscillators are uncoupled, but all – except from some double degeneracies – have a different frequency now, which is sine modulated. One finds that they become dense for large N , so they better and better approximate a continuum function.

In this light of this observation, it makes sense to think of a “density of states” g , such that $g(\omega)$ denotes how many frequencies are around ω in the thermodynamic limit $N \rightarrow \infty$. We first compute the total number $N(\omega)$ of frequencies which are $\leq \omega$, for some ω . This gives

$$N(\omega) = \sum_{k: \omega_k \leq \omega} 1 \approx \int_{\Omega \sin(\frac{\pi}{2} \frac{k}{N+1}) \leq \omega} dk = (N+1) \frac{2}{\pi} \arcsin \left(\frac{\omega}{\Omega} \right). \quad (5.34)$$

The density of states is the derivative of this expression to ω . This exact derivative would be a sum of δ -distributions. We hence first take the thermodynamic limit and then take the derivative. There are good reasons for that, and this

can also be made rigorous. This leads to the definition

$$g(\omega) = \frac{d}{d\omega} \lim_{N \rightarrow \infty} \frac{N(\omega)}{N} = \frac{2}{\pi\sqrt{\Omega^2 - \omega^2}}. \quad (5.35)$$

This density of states is in a sense an intensive variable and estimates the value $Ng(\omega)\Delta\omega$ for the number of eigenfrequencies in the interval $\Delta\omega$ at ω . For small values of ω the function g becomes constant. At the value $\omega = \Omega$, when neighboring chain elements oscillate in opposite directions, g diverges.

Just in the same way as a system of finitely many oscillators the values ω_k determine the partition function and the thermodynamical functions, the function g contains it in the thermodynamical limit. For the energy density, for example, we get

$$u(\beta) = \lim_{N \rightarrow \infty} \langle H \rangle_\beta = \int_0^\Omega d\omega g(\omega) U(\beta\omega), \quad (5.36)$$

where U is the expression derived above, so

$$U = \frac{\omega}{2} + \frac{\omega}{e^{\beta\omega} - 1}. \quad (5.37)$$

Such formulas are also true in more general contexts, and also in higher dimensions, except that the function g needs to be altered then. Specifically, for d dimensions, one gets

$$\int d\omega g(\omega) = kd. \quad (5.38)$$

5.2 Bosons and fermions

5.2.1 Statistics in quantum theory

We now turn to quantum gases consisting of identical particles. There is a lot to say about identical particles in quantum mechanics, needless to say. Given that the course on advanced quantum mechanics is held at the same time, however, we will skip all the introduction and will jump right into the middle of the discussion. The presumably simplest quantum system of N particles is composed of N non-interacting members. Their Hamiltonian is given by

$$H = \sum_{j=1}^N \frac{P_j^2}{2m}, \quad (5.39)$$

where P_j denotes the momentum operator of the particle labelled j . Now systems consisting of N identical quantum systems come in two flavours. Bose systems and Fermi systems. The eigenfunctions of a Bose system are those eigenfunctions of H that are symmetric under interchange of the coordinates of any pair of particles. The eigenfunctions of Fermi systems are anti-symmetric,

in contrast. Examples of Bose systems are phonons, photons, and so on. Examples for fermions are electrons. We will not get too much into detail here, as this is something surely covered in the other course. We will discuss the situation of ideal Bose and Fermi gases, however, as far as their implications for quantum statistical mechanics are concerned, however.

5.2.2 Ideal quantum gases in the micro-canonical ensemble

We start with the micro-canonical ensemble for the ideal Bose gas. We fix the energy interval $[E - \epsilon, E]$ for some energy $E > 0$ (and some $\epsilon > 0$). In order to get the partition function of this ensemble, we simply have to count. The energy eigenvalues of an ideal system is a sum of single-particle energies, often referred to as energy levels. They are given by

$$E_p = \frac{p^2}{2m}, \quad (5.40)$$

where $p = |\mathbf{P}|$ is the momentum eigenvalue of the single particle,

$$\mathbf{p} = \frac{2\pi\hbar}{L} \mathbf{n}, \quad (5.41)$$

for which $\mathbf{n} \in \mathbb{Z}^3$ and L is the cube root of the volume of the system,

$$L = V^{1/3}. \quad (5.42)$$

In the limit of a large volume, it is possible to treat the possible values of \mathbf{p} as a continuum. The sum over \mathbf{p} is then replaced by an integral,

$$\sum_{\mathbf{p}} \mapsto \frac{V}{h^3} \int d^3p, \quad (5.43)$$

where $h = 2\pi\hbar$. We now recapitulate what we have learnt in the other course on second quantization: A basis state vector in second quantised form is defined by the occupation numbers $\{n_{\mathbf{p}}\}$, so by the numbers of particles $n_{\mathbf{p}}$ that have momentum \mathbf{p} . The total energy E and the total number of particles are given by

$$E = \sum_{\mathbf{p}} E_{\mathbf{p}} n_{\mathbf{p}}, \quad (5.44)$$

$$N = \sum_{\mathbf{p}} n_{\mathbf{p}}. \quad (5.45)$$

For spinless bosons and fermions – so particles that have no further internal degree of freedom – these numbers uniquely define the basis state of the system. The allowed values are

$$n_{\mathbf{p}} = \begin{cases} 0, 1, 2, \dots, & \text{for bosons,} \\ 0, 1, & \text{for fermions} \end{cases}. \quad (5.46)$$

For massless particles, state vectors can also be superpositions of such basis states, otherwise, a particle number super-selection rule is in action. Do you know what this is? If not, ask me.

We now turn to the computation of the partition function, so $Z(E)$. In the limit of large V , we can proceed as follows. The energy levels then form a continuum. We can divide the spectrum hence into groups of levels that contain c_1, c_2, \dots energy levels, each group having an average energy E_j . The occupation number of the j -th cell, denoted as n_j is the sum over all $n_{\mathbf{p}}$ over all levels in that cell. Let us denote with $W(n_1, n_2, \dots)$ the number of basis states of the system corresponding to the set of occupation numbers (n_1, n_2, \dots) . Then the partition function of the micro-canonical ensemble is given by

$$Z(E) = \sum W(n_1, n_2, \dots), \quad (5.47)$$

where the sum of performed over all configurations that satisfy both

$$E = \sum_j E_j n_j, \quad (5.48)$$

$$N = \sum_j n_j. \quad (5.49)$$

To find $W(n_1, n_2, \dots)$ for a Bose gas and a Fermi gas it is sufficient to identify the collection of all w_j , $j = 1, 2, \dots$, so the number of ways in which the n_j particles can be assigned to the j -th cell. Because then we simply have

$$W(n_1, n_2, \dots) = \prod_j w_j. \quad (5.50)$$

We have boiled down the problem to a combinatorical one, therefore.

For bosons, each level can be occupied by any number of particles, in principle even all particles, as it happens in perfect Bose-Einstein condensation. We find that

$$w_j = \frac{(n_j + c_j - 1)!}{n_j!(c_j - 1)!}. \quad (5.51)$$

Therefore,

$$W(n_1, n_2, \dots) = \prod_j \frac{(n_j + c_j - 1)!}{n_j!(c_j - 1)!}. \quad (5.52)$$

For fermions, the number of particles in each of the c_j subcells in the j -th cell is either 0 or 1. Therefore, w_j is given by the number of ways in which n_j items can be chosen from c_j things, so

$$w_j = \frac{c_j!}{n_j!(c_j - n_j)!}. \quad (5.53)$$

Again,

$$W(n_1, n_2, \dots) = \prod_j \frac{c_j!}{n_j!(c_j - n_j)!}. \quad (5.54)$$

We are not quite there, however. In order to get the partition function, we need to sum this expression over all those entries that satisfy both Eq. (5.48) and (5.49). In an exact fashion, this is not an easy task. Fortunately, this can simply be done in a very good approximation. One takes $W(\bar{n}_1, \bar{n}_2, \dots)$, where $(\bar{n}_1, \bar{n}_2, \dots)$ are the numbers that solve the problem of maximizing

$$W(\bar{n}_1, \bar{n}_2, \dots), \quad (5.55)$$

subject to the conditions

$$E = \sum_j E_j \bar{n}_j, \quad (5.56)$$

$$N = \sum_j \bar{n}_j. \quad (5.57)$$

This is again an optimisation problem that we can solve with the machinery of Lagrange multipliers that we have discussed before. The computation is straightforward and not too interesting. We state the results here: We find

$$\bar{n}_j = \frac{c_j}{z^{-1} e^{\beta E_j} - 1} \quad (5.58)$$

for bosons and

$$\bar{n}_j = \frac{c_j}{z^{-1} e^{\beta E_j} + 1} \quad (5.59)$$

for fermions. We can derive from this that

$$\bar{n}_{\mathbf{p}} = \frac{1}{z^{-1} e^{\beta E_{\mathbf{p}}} - 1} \quad (5.60)$$

for bosons and

$$\bar{n}_{\mathbf{p}} = \frac{1}{z^{-1} e^{\beta E_{\mathbf{p}}} + 1} \quad (5.61)$$

for fermions. Here, the parameters $z, \beta \in \mathbb{R}$ are two Lagrange parameters determined from

$$E = \sum_{\mathbf{p}} E_{\mathbf{p}} \bar{n}_{\mathbf{p}}, \quad (5.62)$$

$$N = \sum_{\mathbf{p}} \bar{n}_{\mathbf{p}}. \quad (5.63)$$

5.2.3 Bose and Fermi gases in the grand canonical ensemble

In principle, this is the solution to the problem. It is easier to progress, however, in a different picture, namely by referring to the grand canonical ensemble. This is yet another ensemble, and yet one that is equivalent to the known ones in the same sense as the micro-canonical ensemble and the canonical one are equivalent. Let us first state the canonical partition function again. In this second-quantised picture, this may not be entirely straightforward.

Canonical partition function of the ideal Bose and Fermi gas: For both fermions and bosons,

$$Z = \sum e^{-\beta \sum_{\mathbf{p}} E_{\mathbf{p}} n_{\mathbf{p}}}, \quad (5.64)$$

where the sum is performed over all $\{n_{\mathbf{p}}\}$ for which

$$\sum_{\mathbf{p}} n_{\mathbf{p}} = N. \quad (5.65)$$

For a Bose gas, $n_{\mathbf{p}} = 0, 1, 2, \dots$, for a Fermi gas $n_{\mathbf{p}} = 0, 1$.

This is one condition less compared to the micro-canonical ensemble. Still, the condition in Eq. (5.65) makes things a bit awkward. This is by we consider the grand canonical partition function. It is defined as follows.

Grand canonical ensemble: The grand canonical ensemble is

$$\rho = \frac{1}{G} e^{-\beta(H-\mu N)} \quad (5.66)$$

and has the partition function

$$G = \text{tr}(e^{-\beta(H-\mu N)}). \quad (5.67)$$

Expectation values of observables A are obtained as

$$\langle A \rangle = \frac{1}{G} \text{tr}(A e^{-\beta(H-\mu N)}). \quad (5.68)$$

The grand canonical ensemble hence goes one step further and considers the particle number not as a fixed number, but one rather holds the expected particle number fixed. In a similar way as the canonical ensemble emerged from a description of a system in contact to a heat bath, we now also have a particle bath. The expected particle number is

$$\langle N \rangle = z \frac{\partial}{\partial z} \log(G). \quad (5.69)$$

Here, we have set

$$\log(z) = \mu\beta. \quad (5.70)$$

z is called the fugacity, and μ the chemical potential. So both take the same role, roughly speaking. In the same way,

$$U = \langle H \rangle. \quad (5.71)$$

Again, we can identify a quantity that can be identified with the respective thermodynamic potential as

$$\tilde{J}(T, V, \mu) = -\frac{1}{\beta} \log G. \quad (5.72)$$

As before, this is not “the same” as the thermodynamic potential J in thermodynamics, but can be identified in the same way as we have done before. One therefore also finds

$$pV = kT \log(G). \quad (5.73)$$

In this way, one gets the following expression for the ideal Bose and Fermi gas:

Grand canonical partition function of the ideal Bose and Fermi gas:

$$\begin{aligned} G &= \sum_{N=0}^{\infty} \sum_{\{n_{\mathbf{p}}: \sum n_{\mathbf{p}}=N\}} z^N e^{-\beta \sum_{\mathbf{p}} E_{\mathbf{p}} n_{\mathbf{p}}} \\ &= \sum_{N=0}^{\infty} \sum_{\{n_{\mathbf{p}}: \sum n_{\mathbf{p}}=N\}} e^{-\beta(\sum_{\mathbf{p}} E_{\mathbf{p}} n_{\mathbf{p}} - \mu N)}. \end{aligned} \quad (5.74)$$

Again, both z and μ take a role of a Lagrange parameter, just in a different disguise. Eq. (5.74) is the same as

$$G = \sum_{N=0}^{\infty} \sum_{\{n_{\mathbf{p}}: \sum n_{\mathbf{p}}=N\}} \prod_{\mathbf{p}} (ze^{-\beta E_{\mathbf{p}}})^{n_{\mathbf{p}}}. \quad (5.75)$$

Again, the occupations are as given for Bose and Fermi gases. This is an easier expression, however: We find that the double summation is equivalent to summing each $n_{\mathbf{p}}$ independently. We therefore find

$$G = \prod_{\mathbf{p}} \left(\sum_n (ze^{-\beta E_{\mathbf{p}}})^n \right) = \prod_{\mathbf{p}} \left(\sum_n (e^{-\beta(E_{\mathbf{p}} - \mu)})^n \right), \quad (5.76)$$

where again the sum extends over $n = 0, 1, 2, \dots$ for the Bose gas and $n = 0, 1$ for the Fermi gas. The result is as follows:

$$G = \prod_{\mathbf{p}} \frac{1}{1 - ze^{-\beta E_{\mathbf{p}}}} = \prod_{\mathbf{p}} \frac{1}{1 - e^{-\beta(E_{\mathbf{p}} - \mu)}} \quad (5.77)$$

for the Bose gas and

$$G = \prod_{\mathbf{p}} (1 + ze^{-\beta E_{\mathbf{p}}}) = \prod_{\mathbf{p}} (1 + e^{-\beta(E_{\mathbf{p}} - \mu)}) \quad (5.78)$$

for the Fermi gas. The equations of state are

$$\frac{pV}{kT} = \log G = - \sum_{\mathbf{p}} \log(1 - ze^{-\beta E_{\mathbf{p}}}) \quad (5.79)$$

for the Bose gas and

$$\frac{pV}{kT} = \log G = \sum_{\mathbf{p}} \log(1 + ze^{-\beta E_{\mathbf{p}}}) \quad (5.80)$$

for the Fermi gas. From this, we can eliminate the Lagrange parameter z with the help of the equations

$$\langle N \rangle = z \frac{\partial}{\partial z} \log G = \sum_{\mathbf{p}} \frac{ze^{-\beta E_{\mathbf{p}}}}{1 - ze^{-\beta E_{\mathbf{p}}}} \quad (5.81)$$

for bosons and

$$\langle N \rangle = z \frac{\partial}{\partial z} \log G = \sum_{\mathbf{p}} \frac{ze^{-\beta E_{\mathbf{p}}}}{1 + ze^{-\beta E_{\mathbf{p}}}} \quad (5.82)$$

for fermions. The average occupation numbers are

$$\langle n_{\mathbf{p}} \rangle = - \frac{1}{\beta} \frac{\partial}{\partial E_{\mathbf{p}}} \log G = \frac{ze^{-\beta E_{\mathbf{p}}}}{1 \mp ze^{-\beta E_{\mathbf{p}}}} = \frac{e^{-\beta(E_{\mathbf{p}} - \mu)}}{1 \mp e^{-\beta(E_{\mathbf{p}} - \mu)}}, \quad (5.83)$$

where the minus sign is for bosons and the plus sign for fermions. We hence get

$$N = \sum_{\mathbf{p}} \langle n_{\mathbf{p}} \rangle. \quad (5.84)$$

We now progress, hopefully in a not too elliptic style, by looking at the limit of large V and performing the continuum limit. Hence, sums become integrals, as explained above. The value $z \geq 0$, the fugacity is non-negative. Again, it is related to the chemical potential as $\log(z) = \mu/(kT)$.

Performing the continuum limit, we get for ideal fermions the following equation of state.

$$\frac{pV}{kT} = \frac{4\pi}{h^3} \int_0^{\infty} dp p^2 \log(1 + ze^{-\beta p^2/(2m)}), \quad (5.85)$$

$$\frac{1}{v} = \frac{4\pi}{h^3} \int_0^{\infty} dp p^2 \left(z^{-1} e^{\beta p^2/(2m)} + 1 \right)^{-1}, \quad (5.86)$$

where $v = V/N$. This can also be written as

$$\frac{pV}{kT} = \frac{1}{\lambda^3} f_{5/2}(z), \quad (5.87)$$

$$\frac{1}{v} = \frac{1}{\lambda^3} f_{3/2}(z), \quad (5.88)$$

where

$$\lambda = (2\pi\hbar^2)^{1/2} \quad (5.89)$$

is the thermal wavelength and

$$f_{5/2} = \frac{4}{\sqrt{\pi}} \int_0^\infty dx x^2 \log(1 + ze^{-x^2}), \quad (5.90)$$

$$f_{3/2} = z \frac{\partial}{\partial z} f_{5/2}(z). \quad (5.91)$$

The thermal wavelength is called like that since it is of the order of the de Broglie wavelength of a particle with mass m and energy kT .

For the ideal Bose gas, things are slightly messier, as the sums over \mathbf{p} in the equations of state diverge as $z \rightarrow 1$, since the single term corresponding to $\mathbf{p} = 0$ diverges. Thus, the term corresponding to $\mathbf{p} = 0$ may be as important as the entire sum. We split off the terms reflecting $\mathbf{p} = 0$, therefore, when we compute the equation of state. This gives

$$\frac{pV}{kT} = \frac{4\pi}{h^3} \int_0^\infty dp p^2 \log(1 - ze^{-\beta p^2/(2m)}) - \frac{1}{V} \log(1 - z), \quad (5.92)$$

$$\frac{1}{v} = \frac{4\pi}{h^3} \int_0^\infty dp p^2 \left(z^{-1} e^{\beta p^2/(2m)} - 1 \right)^{-1} + \frac{1}{V} \frac{z}{1 - z}, \quad (5.93)$$

where again $v = V/N$. This can again be written as

$$\frac{pV}{kT} = \frac{1}{\lambda^3} g_{5/2}(z) - \frac{1}{V} \log(1 - z), \quad (5.94)$$

$$\frac{1}{v} = \frac{1}{\lambda^3} g_{2/3}(z) + \frac{1}{V} \frac{z}{1 - z}. \quad (5.95)$$

Here now

$$g_{5/2} = -\frac{4}{\sqrt{\pi}} \int_0^\infty dx x^2 \log(1 - ze^{-x^2}), \quad (5.96)$$

$$g_{2/3} = z \frac{\partial}{\partial z} g_{5/2}(z). \quad (5.97)$$

We have that the quantity $z/(1 - z)$ is the average occupation number $\langle n_0 \rangle$ for the single particle level,

$$\langle n_0 \rangle = \frac{z}{1 - z}. \quad (5.98)$$

This term contributes if $\langle n_0 \rangle/V$ is a non-negligible number, so if a non-zero fraction of the particles occupy a level with $\mathbf{p} = 0$. Such a macroscopic occupation of the ground state is called Bose-Einstein-condensation. We now compute the inner energy from this:

$$U = -\frac{\partial}{\partial \beta} \log G, \quad (5.99)$$

and since $\log G = pV/(kT)$, we get

$$\frac{U}{V} = \frac{3}{2} \frac{kT}{\lambda^3} f_{5/2}(z), \quad (5.100)$$

for fermions and

$$\frac{U}{V} = \frac{3}{2} \frac{kT}{\lambda^3} g_{5/2}(z), \quad (5.101)$$

for bosons. Eliminating z gives

$$U = \frac{3}{2} pV. \quad (5.102)$$

5.2.4 Fermi gases at high temperatures and low densities

Let us have a slightly more detailed look at the equation

$$\frac{\lambda^3}{v} = f_{3/2}(z), \quad (5.103)$$

where again $v = V/N$. The function $f_{3/2} : \mathbb{R}^+ \rightarrow \mathbb{R}$ is a monotone increasing function of z . For small z , one finds a power series expansion

$$f_{3/2}(z) = z - \frac{z^2}{2^{3/2}} + O(z^3). \quad (5.104)$$

For large z , one finds with slightly heavier machinery that

$$f_{3/2}(z) = \frac{4}{3\sqrt{\pi}} \left((\log(z))^{3/2} + \frac{\pi^2}{8} (\log(z))^{-1/2} + O(z^{-1}) \right) \quad (5.105)$$

For high temperatures and low densities, one should expect

$$\lambda^3/v \ll 1 \quad (5.106)$$

to be true. Then quantum effects should be rather negligible. We find

$$\frac{\lambda^3}{v} \approx z - \frac{z^2}{2^{3/2}}. \quad (5.107)$$

The equation of state then becomes

$$\frac{pv}{kT} = \frac{v}{\lambda^3} \left(z - \frac{z^2}{2^{5/2}} + O(z^3) \right) = 1 + \frac{1}{2^{5/2}} \frac{\lambda^3}{v} + o(v^{-1}). \quad (5.108)$$

This has the form of a virial expansion. Again, we find a correction to the expression for the classical ideal gas. But this time, the correction is not due to molecular interactions, but rather due to quantum effects. The additional pressure is sometimes also referred to as Fermi pressure.

5.2.5 Low temperatures and high densities

For

$$\lambda^3/v \gg 1, \quad (5.109)$$

one finds that the de Broglie wavelength of a particle is much greater than the average particle separation. Thus quantum effects will become most important. This holds true in particular for the Pauli principle. Close to zero temperature, we have

$$\frac{1}{v} \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} \approx \frac{4}{3\sqrt{\pi}} (\log(z))^{3/2}, \quad (5.110)$$

so

$$z \approx e^{\beta E_F}, \quad (5.111)$$

where

$$E_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{v} \right)^{2/3} \quad (5.112)$$

is the Fermi energy. In order to assess its physical significance, let us have a look at $\langle n_{\mathbf{p}} \rangle$ near zero temperature. We have

$$\langle n_{\mathbf{p}} \rangle \approx \frac{1}{e^{\beta(E_{\mathbf{p}} - E_F)} + 1}. \quad (5.113)$$

If now $E_{\mathbf{p}} < E_F$, then the exponential in the denominator vanishes as $T \rightarrow 0$ or as $\beta \rightarrow \infty$. Then

$$\langle n_{\mathbf{p}} \rangle \approx 1. \quad (5.114)$$

Otherwise, $\langle n_{\mathbf{p}} \rangle \approx 0$. In fact, at exactly zero temperature, one has

$$\langle n_{\mathbf{p}} \rangle = \begin{cases} 1, & E_{\mathbf{p}} \leq E_F, \\ 0, & E_{\mathbf{p}} > E_F. \end{cases} \quad (5.115)$$

The interpretation of this should be rather obvious: The fermions try to occupy the levels with the lowest energy. Due to the Pauli principle, they cannot all occupy the same, so they fill up the levels up to the Fermi energy. This “jump” is also called the Fermi surface. So E_F is the single particle energy below which there are exactly N levels. In momentum space, one obtains a sphere, the Fermi sphere.

At non-zero temperature, this Fermi surface is “melting”, and is no longer discontinuous. To obtain a correction, let us perform an expansion in kT/E_F . Let us define the Fermi temperature by $kT_F = E_F$. Then low temperatures and high densities mean $T \ll T_F$. In this domain, the gas is called degenerate, as the particles try to occupy the lowest levels. The average occupation number is

$$\langle n_{\mathbf{p}} \rangle = \frac{1}{e^{\beta(E_{\mathbf{p}} - \log(z))} + 1} = \frac{1}{e^{\beta(E_{\mathbf{p}} - \mu)} + 1}. \quad (5.116)$$

From this point on, one can derive all thermodynamic properties, although we will not go too much into detail here. For example one gets the expansion

$$p = \frac{2}{5} \frac{E_F}{v} \left(1 + \frac{5\pi^2}{12} \left(\frac{kT}{E_F} \right)^2 + o(T^2) \right). \quad (5.117)$$

A lot of interesting physics emerges from the statistical physics of non-interacting fermions. For example, the theory of white dwarf stars can be pushed quite far with only the tools that we have just encountered. To go too much into detail would be beyond the scope of our course, but feel invited to have a look in the literature on that.

5.2.6 Bose-Einstein condensation

We finally have a brief look at the situation of bosons at low temperatures. Again, we already know the equation of state for an ideal Bose gas of N particles of mass m contained in a volume V . In order to render this expression useful, we must identify the fugacity as a function of the temperature and the specific volume by solving the above equation of state, i.e.,

$$\frac{1}{v} = \frac{1}{\lambda^3} g_{2/3}(z) + \frac{1}{V} \frac{z}{1-z}, \quad (5.118)$$

where again $v = V/N$ and $\lambda = (2\pi\hbar^2/(mkT))^{1/2}$. In order to accomplish this task, we have to have a close look at the function $g_{2/3} : [0, 1] \rightarrow \mathbb{R}$. For real values between 0 and 1, $g_{2/3}(z)$ is bounded, and a positive, monotone increasing function of z . For small z , a power series expansion delivers

$$g_{2/3}(z) = z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + o(z^3). \quad (5.119)$$

At $z = 1$ the derivative diverges, but its value is finite,

$$g_{2/3}(1) = \zeta(3/2) = 2.612\dots, \quad (5.120)$$

where ζ is the Riemann zeta function. Therefore, for all values $z \in [0, 1]$, we have that

$$g_{2/3}(z) \leq \zeta(3/2). \quad (5.121)$$

Now let us rewrite the above equation of state as

$$\lambda^3 \frac{\langle n_0 \rangle}{V} = \frac{\lambda^3}{v} - g_{2/3}(z). \quad (5.122)$$

This means that

$$\frac{\langle n_0 \rangle}{v} > 0 \quad (5.123)$$

whenever the temperature and the specific volume are such that

$$\frac{\lambda^3}{v} > g_{2/3}(1). \quad (5.124)$$

Bose-Einstein condensation: For $\lambda^3/v > g_{2/3}(1)$, a finite fraction $\langle n_0 \rangle/v$ occupies the level with

$$\mathbf{p} = 0. \quad (5.125)$$

This phenomenon is called Bose-Einstein condensation.

So for low temperatures and if the densities are right, a macroscopic fraction of all bosons accumulate in the lowest energy level. This is a quite intriguing phenomenon. In order to study it experimentally, one of the problems is to cool down the bosonic gases sufficiently, and to understand the impact of interactions, which will be weak, but cannot be truly neglected at such small temperatures. Of course, the study of cold atomic bosonic gases has in the meantime become a big field of research in its own right, and interest has exploded since the Nobel prize was given to protagonists who were involved in experimentally generating the first Bose-Einstein condensate. If there is time, we will say more about this at the end of the course.