H QUANTUM STATISTICS

We have already encountered hints of quantum mechanics in the construction of partitions functions of classical mechanical systems, for instance the factors of $1/h$ that are used to make the phase space volume element $\mathrm{d}p\mathrm{d}q$ dimensionless, or the Gibbs-factor $1/\mathrm{N}!$ which corrects for the fact that the particles are physical identical but indistinguishable. But there are three more points: Any finite system has discrete levels in energy along with a discrete set of states, the two coordinates p and q are not simultaneously defined, as $[p, q] = \mathrm{i}h/(2\pi) \neq 0$, and issues about mutual exclusion in the case of fermions come in. And clearly, phase space functions will be replaced by operators.

H.1 *Averages in classical and quantum physics*

In classical physics, ensemble averages would be defined as

$$\langle \mathrm{A} \rangle = \int\limits_{\mathrm{E}\leq\mathcal{H}\leq\mathrm{E}+\delta\mathrm{E}} \frac{1}{\mathrm{N}!h^{3\mathrm{N}}} \prod_i \mathrm{d}^3p_i \mathrm{d}^3q_i \mathrm{A}(p_i, q_i) \tag{H.308}$$

but in quantum statistics, the average would run over all states ψ

$$\langle \mathrm{A} \rangle = \sum_i \rho_i \langle \psi^{(i)} | \mathrm{A} | \psi^{(i)} \rangle \tag{H.309}$$

with the density of states ρ_i and the expectation value $\langle \psi^{(i)} | \mathrm{A} | \psi^{(i)} \rangle$ of the operator A

$$\langle \psi^{(i)} | \mathrm{A} | \psi^{(i)} \rangle = \int \prod_i \mathrm{d}^3q_i \psi^{(i)}(q_i)^* \mathrm{A}(p_i, q_i) \psi^{(i)}(q_i) \tag{H.310}$$

in position representation.

This, however, is not the most general average. If there is a nonzero overlap of $\mathrm{A}\psi^{(i)}$ with $\psi^{(j)}$ the matrix element $\langle \psi^{(i)} | \mathrm{A} | \psi^{(j)} \rangle$ does not vanish and one should rather write

$$\langle \mathrm{A} \rangle = \sum_{ij} \rho_{ij} \cdot \langle \psi^{(i)} | \mathrm{A} | \psi^{(j)} \rangle \tag{H.311}$$

where ρ_{ij} is called the density matrix, which gives the probability of $\langle \psi^{(i)} | \mathrm{A} | \psi^{(j)} \rangle$, contributing to the average $\langle \mathrm{A} \rangle$. Under a change of basis $\psi^{(i)} = \sum_k a_k^{(i)} \cdot \phi_k$ the expectation value should not change,

$$\langle \mathrm{A} \rangle = \sum_i \rho_i \cdot \sum_{k,k'} \cdot a_k^{(i)*} \cdot a_{k'}^{(i)} \cdot \langle \phi_k | \mathrm{A} | \phi_{k'} \rangle = \sum_{k,k'} \underbrace{\left[\sum_i \rho_i a_k^{(i)*} \cdot a_{k'}^{(i)} \right]}_{\equiv \rho_{k,k'}} \langle \phi_k | \mathrm{A} | \phi_{k'} \rangle \tag{H.312}$$

with the density matrix $\rho_{k,k'}$ (or better, the representation of the density ρ in the basis ϕ_k),

$$\rho_{k,k'} = \langle\phi_{k'}|\rho|\phi_k\rangle \rightarrow \langle A\rangle = \sum_{k,k'}\langle\phi_{k'}|\rho\underbrace{|\phi_k\rangle\cdot\langle\phi_k|}_{=id}A|\phi_k'\rangle = \sum_{k'}\langle\phi_{k'}|\rho A|\phi_{k'}\rangle = \mathrm{tr}(\rho A) \tag{H.313}$$

In general, trace relations have many advantages: They are invariant under orthogonal or unitary transform, they are cyclic, $\mathrm{tr}(ABC) = \mathrm{tr}(BCA) = \mathrm{tr}(CAB)$ in particular $\mathrm{tr}(AB) = \mathrm{tr}(BA)$.

💀 *Please, be very careful: Taking the trace of the canonical commutation relation $[p,q] = i\hbar$ would imply $tr[p,g] = tr(pq - qp) = tr(pq) - tr(qp) = 0 = tr(i\hbar) \neq 0$ right?*

The entries in the density matrix fall into two categories, ρ_{kk} is the probability that the system assumes the state $|\phi_k\rangle$ and $\rho_{kk'}$ is the probability for transitioning between two states $|\phi_k\rangle$ and $|\phi_{k'}\rangle$. While ρ is an abstract object and the elements $\rho_{kk'}$ exist only after assuming a basis set $|\phi_k\rangle$, a change of basis manifests itself as

$$\langle\phi_i|\rho|\phi_j\rangle = \sum_{k,k'}\underbrace{\langle\phi_i|\phi_{k'}\rangle}_{\delta_{ik'}}\rho_{kk'}\underbrace{\langle\phi_k|\phi_j\rangle}_{\delta_{kj}} = \sum_{k,k'}\delta_{ik'}\cdot\rho_{kk'}\cdot\delta_{kj} = \rho_{ij} \tag{H.314}$$

A system is in a pure state if only a single state occurs,$\rho_{ii} = 1$ for a single suitably chosen state $|\psi^{(i)}\rangle$. Writing the corresponding density operator explicitly in matrix form gives

$$\rho^{\mathrm{pure}} = \begin{pmatrix} 0 & \vdots & 0 \\ \cdots & 1 & \cdots_i \\ 0 & \vdots_i & 0 \end{pmatrix} \tag{H.315}$$

in which case it is equal to the projection operator $\rho^{\mathrm{pure}} = |\psi^{(i)}\rangle\langle\psi^{(i)}| = P_{|\psi^i\rangle}$. As projections of linear combinations are equal to linear combinations of projections, they are necessarily linear and can therefore be written as operators. Projections are idempotent, because projecting a wave function after is has been projected onto a state does not change anything. In the language of quantum mechanics this reads

$$P^2_{|\psi^i\rangle} = \left(|\psi^{(i)}\rangle\langle\psi^{(i)}|\right)^2 = |\psi^{(i)}\rangle\underbrace{\langle\psi^{(i)}|\psi^{(i)}\rangle}_{=\,1,\text{ for normalised }|\psi^i\rangle}\langle\psi^{(i)}| = |\psi^{(i)}\rangle\langle\psi^{(i)}| = P_{|\psi^i\rangle} \tag{H.316}$$

for any projection operator $P_{|\psi^i\rangle} = |\psi^{(i)}\rangle\langle\psi^{(i)}|$, which must therefore hold for the density matrix as well, if we are dealing with a pure state.

For mixed states with $\rho_{ii} \neq 1$ it must be the case that

$$\sum_i \rho_{ii} = \mathrm{tr}(\rho) = 1 \tag{H.317}$$

otherwise, the ρ_{ii} would not be probabilities, and Kolmogorov's axioms require that $0 \leq \rho_{ii} \leq 1$.

If the density matrix is known in a single basis, the all expectation values can be computed. The eigenvalue relation determines the possible observations,

$$A|\phi_A\rangle = a|\phi_A\rangle \tag{H.318}$$

and the possible eigenstates of a system, provides the basis set to compute overlaps of a state with the basis functions $\langle\psi_i|$,

$$\left|\langle\psi_i|\phi_A\rangle\right|^2 \tag{H.319}$$

given in terms of particular scalar product, or equally well as projections of any state $|\phi_A\rangle$ onto $\langle\psi_i|$, either in the case of a pure state $\rho^{\mathrm{pure}} = |\psi^{(i)}\rangle\langle\psi^{(i)}|$,

$$\mathrm{tr}\left(\rho^{\mathrm{pure}}P_{|\phi_A\rangle}\right) = \sum_{A'}\langle\phi_{A'}|\rho^{\mathrm{pure}}P_{|\phi_A\rangle}|\phi_{A'}\rangle = \sum_{A'}\langle\phi_{A'}|\psi^{(i)}\rangle\langle\psi^{(i)}|\phi_A\rangle\langle\phi_A|\phi_{A'}\rangle = |\langle\phi_A|\psi^{(i)}\rangle|^2 \tag{H.320}$$

or of a mixed state $P_{|\phi_A\rangle} = |\phi_A\rangle\langle\phi_A|$,

$$\begin{aligned}\mathrm{tr}\left(\rho P_{|\phi_A\rangle}\right) = \sum_{A'}\sum_i\langle\phi_{A'}|\psi^{(i)}\rangle\rho_{ii}\langle\psi^{(i)}|\phi_A\rangle\langle\phi_A|\phi_{A'}\rangle = \\ \sum_i\langle\phi_A|\psi^{(i)}\rangle\rho_{ii}\langle\psi^{(i)}|\phi_A\rangle = \sum_i\rho_{ii}|\langle\phi_A|\psi^{(i)}\rangle|^2\end{aligned} \tag{H.321}$$

Then, when one is using an arbitrary basis $|\phi_k\rangle$ instead of the eigenbasis of the operator A, one obtains for the basis-independent trace

$$\mathrm{tr}(\rho A) = \sum_k\sum_i\langle\phi_k|\psi^{(i)}\rangle\rho_{ii}\langle\psi^{(i)}|A|\phi_k\rangle = \sum_i\sum_{k,k'}\langle\phi_k|\psi^{(i)}\rangle\rho_{ii}\langle\psi^{(i)}|\phi_{k'}\rangle\langle\phi_{k'}|A|\phi_k\rangle \tag{H.322}$$

with the final result

$$\mathrm{tr}(\rho A) = \sum_i\rho_{ii}\sum_{k,k'}\langle\phi_k|\psi^{(i)}\rangle\langle\phi_{k'}|\psi^{(i)}\rangle^*\langle\phi_{k'}|A|\phi_k\rangle \tag{H.323}$$

The time evolution of the density matrix is determined from

$$i\hbar\frac{\partial}{\partial t}\rho = i\hbar\frac{\partial}{\partial t}\sum_i|\psi^{(i)}\rangle\rho_i\langle\psi^{(i)}| = \sum_i H|\psi^{(i)}\rangle\rho_i\langle\psi^{(i)}| - |\psi^{(i)}\rangle\rho_i\langle\psi^{(i)}|H = H\rho - \rho H = [H,\rho] \tag{H.324}$$

after substitution of the Schrödinger-equation $i\hbar\partial_t|\psi\rangle$ and its conjugate $-i\hbar\partial_t\langle\psi| = \langle\psi|H$, as the Hamilton-operator is hermitean, $H^+ = H$. This relation is called the von Neumann-equation and is a bit reminiscent of the Poisson equation of motion,

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho = \frac{\partial}{\partial t}\rho + \{H,\rho\} \tag{H.325}$$

if ρ was a classical phase space function. With the von Neumann-equation, the time evolution of any expectation value is given by

$$i\hbar\frac{\partial}{\partial t}\langle A\rangle = i\hbar\frac{\partial}{\partial t}\mathrm{tr}(\rho A) = \mathrm{tr}\left[i\hbar\frac{\partial}{\partial t}(\rho A)\right] = \mathrm{tr}\left([H,\rho]A\right) = \mathrm{tr}([H,\rho]A) \tag{H.326}$$

if the operator does not depend explicitly on time.

H.2 *Quantum mechanical partitions*

H.2.1 Construction of phase space densities

As the Boltzmann-factor and suitable quantum mechanical generalisations of it provide a weighting of states with respect to their energy, the basis provided by the energy eigenstates will be the most useful,

$$H|\phi_k\rangle = E_k|\phi_k\rangle \tag{H.327}$$

with is orthogonal with real eigenvalues, as the Hamilton-operator is hermitean $H^+ = H$. The von Neumann-equation then makes sure that if the density matrix is stationary, $\partial_t\rho = 0$, the commutator $[H, \rho]$ would vanish, implying that the eigensystem for the Hamilton-operator and for the density matrix must be identical. In this particular basis $|\phi_k\rangle$ the density matri is diagonal,

$$\rho_{kk'} = \rho_k \cdot \delta_{kk'} \quad \text{with} \quad \rho_k = \langle\phi_k|\rho|\phi_k\rangle \tag{H.328}$$

such that ρ_k is the probability for the system to occupy a state of energy E_k.

H.2.2 Canonical ensemble in quantum statistics

With the density matrix as a statistical weight for expectation values of operators over ensembles of quantum mechanical systems we can define averages and choose the weighting to reflect the ratio between the energy of the state and the thermal energy, in the spirit of a Boltzmann-factor. It is, from a practical point of view, near impossible to do calculations in the microcanonical ensemble in a discrete system typical for quantum mechanics, as the definition of ρ being either 0 or 1 in an energy shell of thickness dE around the energy E is a concept for energy as a continuous quantity.

Instead, the choice of ρ_N for canonical ensembles is straightforward, for instance through

$$\rho = \frac{\exp\left(-\frac{E_N}{k_B T}\right)}{\sum\limits_N \exp\left(-\frac{E_N}{k_B T}\right)} \tag{H.329}$$

with energy eigenvalues E_N. This idea is compatible with the previous definition of a canonical partition function

$$Z(T, V, N) = \sum_N \exp\left(-\frac{E_N}{k_B T}\right) \tag{H.330}$$

as the normalisation for the probabilities, as from the general case of a matrix in any basis (where we can not yet replace H by E)

$$\rho = \frac{\exp\left(-\frac{H}{k_B T}\right)}{\operatorname{tr}\exp\left(-\frac{H}{k_B T}\right)} \tag{H.331}$$

we would compute

$$\mathrm{tr}\exp\left(-\frac{H}{k_BT}\right) = \sum_N \langle \phi_N | e^{-\frac{H}{k_BT}} | \phi_N \rangle = \sum_N \langle \phi_N | e^{-\frac{E_N}{k_BT}} | \phi_N \rangle = \sum_N e^{\frac{-E_N}{k_BT}} \equiv Z(T, V, N) \tag{H.332}$$

H.2.3 Canonical averages of arbitrary observables

Expectation values of arbitrary observables associated with hermitean operators A would result from

$$\langle A \rangle = \mathrm{tr}(\rho A) = \mathrm{tr}\left[A \cdot \frac{\exp\left(-\frac{H}{k_BT}\right)}{\mathrm{tr}\ \exp\left(-\frac{H}{k_BT}\right)}\right] = \frac{\mathrm{tr}\left[A\exp\left(-\frac{H}{k_BT}\right)\right]}{\mathrm{tr}\left[\exp\left(-\frac{H}{k_BT}\right)\right]} \tag{H.333}$$

which again is compatible with the previous definitions: Specifically if $A = H$,

$$E = \langle H \rangle = \frac{\mathrm{tr}\left[H\exp\left(-\frac{H}{k_BT}\right)\right]}{\mathrm{tr}\left[\exp\left(-\frac{H}{k_BT}\right)\right]} = k_BT^2 \frac{\partial}{\partial T} \ln \mathrm{tr}\exp\left(-\frac{H}{k_BT}\right) \tag{H.334}$$

or with the inverse temperature $\beta = \frac{1}{k_BT}$, which is often used for notational compactness in quantum statistics,

💀 *Please be very careful in expressions like* ln *tr* exp(H)*, they're certainly not tr* ln exp(H) = *tr*H*!*

$$E = \langle H \rangle = \frac{\mathrm{tr}\left[H\exp\left(-\beta H\right)\right]}{\mathrm{tr}\left[\exp\left(-\beta H\right)\right]} = -\frac{\partial}{\partial \beta} \ln \underbrace{\mathrm{tr}\exp\left(-\beta H\right)}_{\equiv Z(T,V,N)} = -\frac{\partial}{\partial \beta} \ln Z \tag{H.335}$$

The the logarithm of the canonical ensemble should be linked to the Helmholtz free energy F, i.e.

$$F = E - TS = -k_BT \ln \mathrm{tr}\exp\left(-\frac{H}{k_BT}\right) = -\frac{1}{\beta} \ln \mathrm{tr}\exp(-\beta H) \tag{H.336}$$

With this insight, we can derive an expression for the entropy and see if it is consistent with the previous argument of the expectation value $\langle -k_B \ln \rho \rangle$, but now applied to quantum statistics. Fundamentally from the Helmholtz free energy we obtain

$$TS = E - F = \underbrace{-\frac{\partial}{\partial \beta} \ln \mathrm{tr}\exp(-\beta H)}_{=\langle H \rangle} + \frac{1}{\beta} \ln \mathrm{tr}\exp(-\beta H) \tag{H.337}$$

Being intuitive about the anticipated result, entropy should be related to the averaged logarithmic phase space density

$$\langle \ln \rho \rangle = \mathrm{tr}(\rho \ln \rho) = \mathrm{tr}\left[\frac{\exp(-\beta H)}{\mathrm{tr}\exp(-\beta H)} \cdot \ln \frac{\exp(-\beta H)}{\mathrm{tr}\exp(-\beta H)}\right] = \tag{H.338}$$

continuing we can write decomposing the logarithm of the fraction,

$$\ldots = \mathrm{tr}\left[\frac{\exp(-\beta H)}{\mathrm{tr}\exp(-\beta H)} \cdot (-\beta H)\right] - \mathrm{tr}\left[\frac{\exp(-\beta H)}{\mathrm{tr}\exp(-\beta H)} \cdot \ln \mathrm{tr}\exp(-\beta H)\right] \tag{H.339}$$

While the first term is simply the expectation value of the energy in the canonical ensemble, the second term can be rearranged to have the trace only act on $\exp(-\beta H)$, as all other terms are already traced out and are therefore straightforward numbers, Then, $\mathrm{tr}\exp(-\beta H)$ cancels and one arrives at

$$\langle \ln \rho \rangle = -\beta\langle H\rangle - \ln \mathrm{tr} \exp(-\beta H) \tag{H.340}$$

Comparing this result to the terms in eqn. H.337 lets us write

$$S = \beta\langle H\rangle + \ln \mathrm{tr}\exp(-\beta H) = \langle -k_B \ln \rho\rangle \tag{H.341}$$

H.2.4 Macrocanonical ensembles in quantum statistics

Macrocanonical ensembles allow changes in particle number N controlled by the chemical potential μ: To reach this, the Boltzmann-factor was extended by a second term, the fugacity z, and this extended Boltzmann-term was the weighting function to assemble the partition functions. By analogy, we write

$$\rho_N = \frac{\exp(-\beta(E_N - \mu N))}{\sum\limits_N \sum\limits_N \exp(-\beta(E_N - \mu N))} = \frac{\exp(-\beta E_N - zN)}{\sum\limits_N \sum\limits_N \exp(-\beta E_N - zN)} \tag{H.342}$$

with $z = \mu/(k_B T) = \beta\mu$. Written as an operator, the density matrix becomes

$$\rho = \frac{\exp(-\beta(H - \mu N))}{\mathrm{tr}\exp(-\beta(H - \mu N))} = \frac{\exp(-\beta H - zN)}{\mathrm{tr}\exp(-\beta H - zN)} \tag{H.343}$$

such that one can define a quantum mechanical macrocanonical partition sum

$$\mathcal{Z}(T, V, \mu) = \mathrm{tr}\exp(-\beta(H - \mu N)) = \mathrm{tr}\exp(-\beta H + zN) \tag{H.344}$$

Let's check whether the definition of entropy S, this time as an average of the logarithm of the macrocanonical density, gives a sensible result. Indeed,

$$S = -k_B\langle \ln \rho\rangle = -k_B \mathrm{tr}(\rho \ln \rho) = -k_B \mathrm{tr}[\rho(-\beta H + zN - \ln \mathcal{Z}(T, V, \mu))] \tag{H.345}$$

while the logarithm itself without average is $\ln \rho = -\beta H + zN - \ln \mathrm{tr}\exp(-\beta H + zN) = -\beta H + zN - \mathcal{Z}(T, V, \mu)$ such that the entropy becomes

$$S = \underbrace{k_B\beta}_{=\frac{1}{T}} \underbrace{\mathrm{tr}(\rho H)}_{=\langle H\rangle = E} + \underbrace{k_B\mu\beta}_{=\frac{\mu}{T}} \underbrace{\mathrm{tr}(\rho N)}_{=\langle N\rangle} - \ln \mathcal{Z}(T, V, \mu) \tag{H.346}$$

That implies that the corresponding expression for the macrocanonical potential in consistent with the definition of entropy is the macrocanonical average, as we obtain the macrocanonical potential:

$$J = -k_B T \ln \mathcal{Z} = E - TS - \mu N \tag{H.347}$$

H.3 *Symmetries of wave functions of many particles*

When adding the Gibbs-factor 1/N! to the definition of the phase space volume elements the reasoning was that by composing the system out of N particles, it should not matter which of the particles takes up which of the positions: That would be an indication of the indistinguishability of the particles, and let's dwell on this point a little, because it is a novel concept unknown to classical physics. Clearly, the particles are identical in the sense that they have identical properties like mass or charge and undergo exactly the same interactions. But in classical mechanics we have the idea of a trajectory through phase space for each particle, and these trajectories are non-intersecting, as made sure by Liouville's theorem, such that each particle can be unambiguously tracked from the initial conditions up to the present time. If there were intersecting trajectories, that unambiguity would be lifted and one could mistake particles.

In quantum mechanics this issue is far more involved: A particle would be represented by a wave function, which would necessarily disperse and increase its extension $\propto t$ in both momentum and position space. Then, even for particles that are initially separated, the wave functions would start overlapping after some time and a localisation would yield ambiguous results, as it is impossible to assign the localised particles at the time of the measurement to the particles localised at the initial conditions. That's why one should differentiate between states and particles that might occupy them, a very zen-like thought, which already appeared in the discussion of the Gibbs-factor: There are N! possibilities to distribution N particle among N placeholders.

From a conceptual point of view we should therefore always describe the entire system consisting of N particles with a common wave function $\psi(\boldsymbol{r}_1, ..., \boldsymbol{r}_N)$ and ask how such a wave function would behave under the exchange of two particles. To that purpose, one can define an exchange operator $P(i \leftrightarrow j)$

$$P(i \leftrightarrow j)\psi(\boldsymbol{r}_1, ...\boldsymbol{r}_i, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_N) = \psi(\boldsymbol{r}_1, ...\boldsymbol{r}_j, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_N) \tag{H.348}$$

This operator $P(i \leftrightarrow j)$ is clearly idempotent,

$$P(i \leftrightarrow j)^2 = P(i \leftrightarrow j)P(i \leftrightarrow j) = \mathrm{id} \tag{H.349}$$

as a double exchange recovers the initial wave function. Therefore, the eigenvalues of $P(i \leftrightarrow j)$ must be ±1, as

$$P(i \leftrightarrow j)\psi = \lambda\psi \quad \text{so that} \quad P(i \leftrightarrow j)^2\psi = \lambda^2\psi = \psi \tag{H.350}$$

implying $\lambda^2 = 1$ and $\lambda = \pm 1$. Generalising the exchange of two particles to a permutation of particles

$$P\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_N) = \psi(\boldsymbol{r}_{P_1}, \boldsymbol{r}_{P_2}, ..., \boldsymbol{r}_{P_N}) \tag{H.351}$$

lets us define two particular wave functions: A wave function ψ_+ which is fully symmetric under particle exchange,

$$\psi_+(\boldsymbol{r}_1, ..., \boldsymbol{r}_N) \propto \sum_P P\psi(\boldsymbol{r}_1, ..., \boldsymbol{r}_N) \tag{H.352}$$

where one forms a linear combination over all possible permutation with equal weight of +1, as well as a fully antisymmetric wave function,

$$\psi_-(\boldsymbol{r}_1, ..., \boldsymbol{r}_N) \propto \sum_P (-1)^P \cdot P\psi(\boldsymbol{r}_1, ..., \boldsymbol{r}_N) \tag{H.353}$$

with weights depending on the sign of the permutation:

$$(-1)^P = \begin{cases} +1 & \text{even number of particle exchanges} \\ -1 & \text{odd number of particle exchange} \end{cases} \tag{H.354}$$

Nature is very capricious at this point: She only allows fully symmetric wave functions ψ_+ and fully antisymmetric wave functions ψ_- as descriptions of N-particle systems. And she links these two cases to the spin of the particles as internal degrees of freedom of the wave function: Bosons such as photons have integer spin and require symmetric wave functions, whereas fermions such as neutrinos or electrons have half-integer spins and are described by antisymmetric wave functions for them. This is the gist of Pauli's spin-statistics-theorem.

H.4 *Non-interacting systems*

Non-interacting quantum mechanical systems are peculiar, because wave functions factorise into single particle wave functions $\psi_k(\boldsymbol{r}_i) = |k_i\rangle$

$$\psi_{k_1...k_N}(\boldsymbol{r}_1, ..., \boldsymbol{r}_N) = |k_1...k_N\rangle = |k_1\rangle \cdots |k_N\rangle = \prod_i^n \psi_{k_i}(\boldsymbol{r}_i) \tag{H.355}$$

are perfectly compatible with a Hamiltonian operator written as a sum of the individual Hamiltonian operators:

$$H = \sum_i^N H(\boldsymbol{p}_i, \boldsymbol{r}_i) \quad \text{with individual solutions} \quad H(\boldsymbol{p}_i, \boldsymbol{r}_i)\psi_k(\boldsymbol{r}_i) = E_k\psi_k(\boldsymbol{r}_i) \tag{H.356}$$

such that the total energy is given by $E = \sum_k E_k$. The respective (anti)symmetrisation of the N-particle wave function is given by

$$\text{bosons:} \quad |k_1...k_N\rangle^+ = \frac{1}{\sqrt{N! \cdot S}} \cdot \sum_P P|k_1...k_N\rangle$$

$$\text{fermions:} \quad |k_1...k_N\rangle^- = \frac{1}{\sqrt{N!}} \cdot \sum_P (-1)^P \cdot P|k_1...k_N\rangle$$

with the normalisation factor $1/\sqrt{N!}$ for N particles, reflecting the N! possible permutations. While for fermions the wave function vanishes $|k_1...k_N\rangle^- = 0$ if for any two states $|k_i\rangle = |k_j\rangle$ is given, this would not be the case for bosons, making the counting of permutations in the normalisation a bit more difficult, we will brush over this at this moment and absorb this in the factor S.

A very neat trick for antisymmetric wave functions so typical for fermions is the Slater-determinant:

$$|k_1...k_N\rangle^- = \frac{1}{\sqrt{N!}}\det\begin{pmatrix}\phi_{k_1}(\boldsymbol{r}_1) & \cdots & \phi_{k_1}(\boldsymbol{r}_N)\\ \vdots & \ddots & \vdots\\ \phi_{k_N}(\boldsymbol{r}_1) & \cdots & \phi_{k_N}(\boldsymbol{r}_N)\end{pmatrix} \tag{H.357}$$

Because the determinant is the only antisymmetric multilinear form with norm one, it is even uniquely defined.

H.5 *Macrocanonical ensembles in quantum statistics*

As objects like the canonical or macrocanonical partition functions are defined as traces, the actual choice of the representation of the wave function does not matter at all: The trace is invariant under any change of basis. One might lose diagonality, though, making everything technically more difficult. For instance, the canonical partition is given in momentum representation as

$$Z(T,V,N) = \mathrm{tr}\exp(-\beta H) = \frac{1}{N!}\sum_{k_1...k_N} {}^{\pm}\langle k_1...k_N|\exp(-\beta H)|k_1...k_N\rangle^{\pm} \tag{H.358}$$

or, completely equivalently, in terms of energy eigenstates as

$$H|k_1...k_N\rangle^{\pm} = E|k_1...k_N\rangle^{\pm} \quad \text{with} \quad E = \sum_k \epsilon_k \tag{H.359}$$

This particular representation is practical, because the partition separates:

$${}^{\pm}\langle k_1...k_N|\exp(-\beta H)|k_1...k_N\rangle^{\pm} = \langle k_1...k_N|\prod_k \exp(-\beta\epsilon_k)|k_1...k_N\rangle^{\pm} \tag{H.360}$$

such that we finally obtain for classical Maxwell-Boltzmann-statistics (ignoring issues of distinguishability for a second):

$$Z(T,V,N) = \frac{1}{N!}\prod_i^N\sum_{k_i}\langle k_i|\exp(-\beta H_i)|k_i\rangle = \frac{1}{N!}\left(\sum_{k_i}\langle k_i|\exp(-\beta H_i)|k_i\rangle\right)^N = \frac{1}{N!}Z(T,V,1)^N \tag{H.361}$$

with a factorising state $|k_1...k_N\rangle = |k_1\rangle...|k_N\rangle$.

But what about the indistinguishability? What quantum mechanics provides is a way of computing energy levels from the mechanics of the system and *not* the actual energies ϵ_k of particles. Rather, we should pick up the zen-esque idea of asking whether a certain mode $|k\rangle$ of the system is actually excited. The modes $|k\rangle$ provided by quantum mechanics are placeholders in which one (or in the case of bosons more than one) particles may actually reside. With this idea, the occupation number n_k can be

bosons: all values $n_k = 0,\dots,n$

fermions: only $n_k = 0$ or $n_k = 1$ but nothing else such that in both cases the total number of particles is given by $N = \sum_k n_k$ and the total energy by $E = \sum_k \epsilon_k n_k$, which then as well result from the expectation values of H and N. With a characterisation of the state in terms of the set $\{n_k\}$ of occupation numbers we can use as a notation $|n_1 ... n_k\rangle^\pm$ including the information about the symmetry of the wave function encapsulating by ±. In summary, the Hamilton-operator should yield the total energy, $\tilde{H}|n_1, n_2, ...\rangle = E|n_1, n_2, ...\rangle$ with $E = \sum_k^\infty n_k\epsilon_k$, and the particle number operator should return the total number of particles, $\tilde{N}|n_1, n_2, ...\rangle = N|n_1, n_2, ...\rangle$ with $N = \sum_k^\infty n_k$. In the shorthand notation, the particle number operator applied to the N-particle state gives the individual occupation numbers n_k of the states k,

$$|k_1, ..., k_N\rangle^\pm \longrightarrow |n_1, n_2, ...\rangle^\pm \tag{H.362}$$

which can be any number between 0 and N for bosons and just 0 and 1 for fermions.

The occupation number representation of an N-particle state obeys an orthonormality relation

$${}^\pm\langle n_1, n_2, \ldots | n_1', n_2', \ldots\rangle^\pm = \delta_{n_1 n_1'} \delta_{n_2 n_2'} \ldots \tag{H.363}$$

for any of the two fundamental types of particles. In this representation, the density matrix ρ can be expressed as

$${}^\pm\langle n_1, n_2, ... |\rho| n_1, n_2, ...\rangle^\pm = \frac{1}{Z(T, V, N)} {}^\pm\langle n_1 n_2 ... | \underbrace{\exp(-\beta\tilde{H})}_{=\exp\left(-\beta\sum_k n_k\epsilon_k\right)} | n_1 n_2 ...\rangle^\pm \tag{H.364}$$

with the partition function $Z(T, V, N)$

$$Z(T, V, N) = \sum_{\{n_k\} \text{ with } \sum_k n_k = N} \exp\left(-\beta \sum_k n_k\epsilon_k\right) \tag{H.365}$$

which is truly difficult to evaluate: The sum runs over all possible partitions of the total particle number N into sets $\{n_k\}$ fulfilling $\sum_k n_k = N$, so I think that you'll agree that there is a lot of bookkeeping going on!

There is a way out: To use macrocanonical partitions instead. There, the particle number is unconstrained, so one can obtain the density matrix in the macrocanonical ensemble,

$${}^\pm\langle n_1, n_2, ... |\rho| n_1, n_2, ...\rangle^\pm = \frac{1}{\mathcal{Z}} {}^\pm\langle n_1 n_2 ... | \exp(-\beta(\tilde{H} - \mu\tilde{N})) | n_1 n_2 ...\rangle^\pm =$$

$$\frac{1}{\mathcal{Z}} {}^\pm\langle n_1 n_2 ... | \exp\left(-\beta \sum_k n_k(\epsilon_k - \mu)\right) | n_1 n_2 ...\rangle^\pm \tag{H.366}$$

with the normalising macrocanonical partition function

$$\mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = \sum_{\{n_k\}} \exp\left(-\beta \sum_k n_k(\epsilon_k - \mu)\right) \tag{H.367}$$

where there is no restriction in the actual particle number: In fact, the unrestricted sum collects all contributions in the right measure such that the familiar relation between the macrocanonical and canonical partition functions is found:

$$\mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = \underbrace{\sum_{\mathrm{N}=0}^{\infty} \sum_{\{n_k\}\text{ with }\sum_k n_k = \mathrm{N}}}_{=\sum_{\{n_k\}}} \exp\left(-\beta \sum_k n_k(\epsilon_k - \mu)\right) =$$

$$\sum_{\mathrm{N}=0}^{\infty} \sum_{\{n_k\}}{}' \exp\left(-\beta \sum_k n_k \epsilon_k\right) \cdot \underbrace{\exp\left(\beta\mu \sum_k n_k\right)}_{=\exp(\beta\mu)^{\mathrm{N}} = z^{\mathrm{N}}} \tag{H.368}$$

with the definition of fugacity $z = \exp(\beta\mu)$,

$$\mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = \sum_{\mathrm{N}} z^{\mathrm{N}} \sum_{\{n_k\}}{}' \exp(-\beta \sum_k n_k \epsilon_k) = \sum_{\mathrm{N}} z^{\mathrm{N}} \cdot \mathrm{Z}(\mathrm{T},\mathrm{V},\mathrm{N}) \tag{H.369}$$

Effectively, we make the problem easier by making it more complicated! Effectively, the full macrocanonical partition function as an unrestricted sum finally reads:

$$\mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = \sum_{\{n_k\}} g(\{n_k\}) \cdot \exp\left(-\beta \sum_k n_k(\epsilon_k - \mu)\right) \tag{H.370}$$

where the different partitions $\{n_k\}$ are weighed with $g = 1$ for bosons. Fermions are a bit more complicted, for them $g = 1$ for $n_k = 0, 1$, and $g = 0$ in all other cases.

Let's carry out these summations to obtain a closed expression for $\mathcal{Z}(\mathrm{T},\mathrm{V},\mu)$. For bosons this would mean

$$\mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = \sum_{n_1,n_2,\ldots}^{\infty} \exp(-\beta(\epsilon_1 - \mu))^{n_1} \cdot \exp(-\beta(\epsilon_2 - \mu))^{n_2} \ldots = \prod_k^{\infty} \sum_{n_k=0}^{\infty} \exp(-\beta(\epsilon_k - \mu))^{n_k} \tag{H.371}$$

where one can continue with the geometric series,

$$\sum_j^n q^j = \frac{1 - q^n}{1 - q} \tag{H.372}$$

applied to the n_k-summation, such that the partition becomes

$$\mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = \prod_k \frac{1}{1 - \exp(-\beta(\epsilon_k - \mu))} = \prod_k \frac{1}{1 - z \cdot \exp(-\beta\epsilon_k)} \tag{H.373}$$

with the fugacity $z = \exp(\beta\mu)$. Analogously, fermions would yield

$$\mathcal{Z}(T, V, \mu) = \sum_{n_1, n_2, \ldots}^{1} \exp(-\beta(\epsilon_1 - \mu))^{n_1} \cdot \exp(-\beta(\epsilon_2 - \mu))^{n_2} \ldots = \prod_k^{\infty} \sum_{n_k=0}^{1} \exp(-\beta(\epsilon_k - \mu))^{n_k} \tag{H.374}$$

and as the occupation numbers can really only be 0 or 1,

$$\mathcal{Z}(T, V, \mu) = \prod_k [1 + \exp(-\beta(\epsilon_k - \mu))] = \prod_k [1 + z \cdot \exp(-\beta\epsilon_k)] \tag{H.375}$$

with the final results just differing in their signs. The macrocanonical potential $J(T, V, \mu)$ derived from the bosonic or fermionic macrocanonical partition function is given by

$$J(T, V, \mu) = -k_B T \ln \mathcal{Z}(T, V, \mu) = -pV \tag{H.376}$$

with derivatives $S = -\frac{\partial J}{\partial T}$, $p = -\frac{\partial J}{\partial V}$ and $N = -\frac{\partial J}{\partial \mu}$. Specifically, for the two particle species the macrocanonical potential becomes

$$\text{bosons:} \quad J(T, V, \mu) = +k_B T \cdot \sum_{k=1}^{\infty} \ln[1 - z \cdot \exp(-\beta\epsilon_k)]$$

$$\text{fermions:} \quad J(T, V, \mu) = -k_B T \cdot \sum_{k=1}^{\infty} \ln[1 + z \cdot \exp(-\beta\epsilon_k)]$$

Finally, particle number of the two species are given as derivatives with respect to μ of the logarithm of the macrocanonical partition function $\mathcal{Z}$:

$$N(T, V, \mu) = k_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z} = \begin{cases} \sum_{k=1}^{\infty} \underbrace{\frac{1}{z^{-1}\exp(\beta\epsilon_k) - 1}}_{=n_k, \text{ because } N=\sum_k n_k} & \text{for bosons} \\ \sum_{k=1}^{\infty} \frac{1}{z^{-1}\exp(\beta\epsilon_k) + 1} & \text{for fermions} \end{cases} \tag{H.377}$$

as well as through a differentiation with respect to β

$$E(T, V, \mu) = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} = \begin{cases} \sum_{k=1}^{\infty} \underbrace{\frac{\epsilon_k}{z^{-1}\exp(\beta\epsilon_k) - 1}}_{=n_k\epsilon_k, \text{ because } E=\sum_k n_k\epsilon_k} & \text{for bosons} \\ \sum_{k=1}^{\infty} \frac{\epsilon_k}{z^{-1}\exp(\beta\epsilon_k) + 1} & \text{for fermions} \end{cases} \tag{H.378}$$

As examples for quantum macrocanonical ensembles we should discuss a couple of applications: Firstly the Planck-spectrum as the first application of quantum statistics, where we do not have to worry about the ground state occupation and because chemical potential is particularly simple to deal with. Then, we should discuss fermionic statistics and the exclusion principle for a degenerate fermonic gas, as the ground state is easy to treat as it can be at most occupied by a single particle.

Both statistical systems have profound implications for the statistics of the particle number and its fluctuations. Thirdly, we should go through the case of non-relativistic bosons which show condensation phenomena at low temperature.

H.5.1 Ultrarelativistic ideal Bose-gas

The statistical perspective of an electromagnetic field in thermal equilibrium is that of an ultra-relativistic gas of photons at a given temperature. The dispersion relation of photons is

$$\epsilon = cp = \hbar ck \tag{H.379}$$

with the modulus $p^2 = \boldsymbol{p}^2$ of the momentum and the energy ϵ. The discrete summation over all momentum eigenstates becomes in the continuum limit an integration, if the volume is large,

$$\sum_k \rightarrow \frac{1}{h^3}\int \mathrm{d}^3p \int \mathrm{d}^3x = 4\pi \mathrm{V}\int k^2 \mathrm{d}k = \frac{4\pi \mathrm{V}}{h^3c^3}\int_0^\infty \epsilon^2 \mathrm{d}\epsilon \tag{H.380}$$

where the volume element is reduced to a radial integration to to spherical symmetry. Photons are particles with spin 1 with two polarisation state sypical for a massless vector particle, and the masslessness implies that the system can change the number of particles easily (while conserving energy), because there is no rest mass. But physically, the change of number of particles would mean to have interactions between the photons (for instance, fusing two photons into a single one or vice versa), which can not be achieved by linear Maxwell-electrodynamics. This is why Max Planck was so adamant to always include a grain of coal into his considerations, where groups photons can get absorbed and emitted at different particle number but same total energy. The missing rest mass of the photons is reflected by $\mu = 0$ as for example a process of a photon splitting into multiple photons through interaction with matter can proceed at arbitrary low energies without the need to come up with the rest mass, possibly impeding the process.

As always in quantum statistics, we formulate the macrocanonical partition function

$$\ln \mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = -\frac{4\pi \mathrm{V}}{(hc)^3}\int_0^\infty \epsilon^2 \mathrm{d}\epsilon \ln[1-\exp(\beta\epsilon)] = \frac{4\pi \mathrm{V}}{(hc)^3}\frac{\beta}{3}\int_0^\infty \mathrm{d}\epsilon \frac{\epsilon^3}{\exp(\beta\epsilon)-1} \tag{H.381}$$

in the continuum limit and after an integration by parts (where the integrand vanishes at both $\epsilon = 0$ and at $\epsilon \to \infty$), which can be compared the value of the macrocanonical potential (through $\mathrm{J} = -k_\mathrm{B}\mathrm{T}\ln \mathcal{Z} = -p\mathrm{V}$)

$$\ln \mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = \frac{p\mathrm{V}}{k_\mathrm{B}\mathrm{T}} \tag{H.382}$$

from which we conclude that the pressure is equal to a third of the energy density. In equation eqn. H.381 the fugacity $z = \exp(\beta\mu)$ is already set to one as a consequence of $\mu = 0$.

The type of integral as in eqn. H.381 is typical for calculations around bosonic systems.

$$\zeta(s) \cdot \Gamma(s) = \zeta(s) \cdot (s-1)! = \int_0^\infty \mathrm{d}x \frac{x^{s-1}}{\exp(x) - 1} \tag{H.383}$$

which follows from this argument:

$$\int_0^\infty \mathrm{d}x \frac{x^{s-1}}{\exp(x) - 1} = \int_0^\infty \mathrm{d}x\, x^{s-1} \frac{\exp(-x)}{1 - \exp(-x)} =$$

$$\int_0^\infty \mathrm{d}x\, x^{s-1} \sum_{m=1}^\infty \exp(-mx) = \sum_{m=1}^\infty \int_0^\infty \mathrm{d}x\, x^{s-1} \cdot \exp(-mx) \tag{H.384}$$

with a geometric series

$$\frac{q}{1-q} = q \sum_{m=0}^\infty q^m = \sum_{m=1}^\infty q^m \tag{H.385}$$

on $q = \exp(-x) \leq 1$ for positive x. Substitution $y = mx$ with $\mathrm{d}x = \mathrm{d}y/m$ and $x = y/m$ yields

$$\int_0^\infty \mathrm{d}x \frac{x^{s-1}}{\exp(x) - 1} == \underbrace{\sum_{m=1}^\infty \frac{1}{m^s}}_{=\zeta(s)} \cdot \underbrace{\int_0^\infty \mathrm{d}y\, y^{s-1} \cdot \exp(-y)}_{=\Gamma(s)=(s-1)!} \tag{H.386}$$

with the Riemann-ζ-function and the Γ-function as a generalisation to the factorial. Then, the result for the logarithmic macrocanonical partition function is

$$\ln \mathcal{Z}(T, V, \mu) = \frac{4\pi V}{(hc)^3} \cdot \frac{\beta}{3} \int_0^\infty \mathrm{d}\epsilon \frac{\epsilon^3}{\exp(\beta\epsilon) - 1} \tag{H.387}$$

with the substitution $x = \beta\epsilon$ with the differential $\mathrm{d}x = \beta \mathrm{d}\epsilon$ yields a form which is compatible with relation H.386 making evaluation of a closed form possible

$$\ln \mathcal{Z}(T, V, \mu) = \frac{4\pi V}{3(hc)^3} \frac{1}{\beta^3} \underbrace{\int_0^\infty \mathrm{d}x \frac{x^3}{\exp(x) - 1}}_{=\zeta(4)\cdot 3!} = \frac{4\pi^5 V}{90(hc)^3} (k_B T)^3 \tag{H.388}$$

where the actual value for $\zeta(4)$ is given by $\zeta(4) = \frac{\pi^4}{90}$. Continuing with the macrocanonical potential

$$J(T, V, \mu) = -k_B T \ln \mathcal{Z} = -\frac{8\pi^5 V}{90(hc)^3} (k_B T)^4 \tag{H.389}$$

one can derive the state variables by differentiation and substitute back into the thermodynamical potentials

$$\text{entropy:}\quad S = -\frac{\partial J}{\partial T} = \frac{32\pi^5 V}{90(hc)^3}(k_B T)^3 k_B$$

$$\text{pressure:}\quad p = -\frac{\partial J}{\partial V} = \frac{8\pi^5}{90(hc)^3}(k_B T)^4$$

$$\text{Euler-relation:}\quad E = TS - pV = \frac{24\pi^5 V}{90(hc)^3}(k_B T)^4$$

$$\text{free energy:}\quad F = E - TS = -pV = -\frac{8\pi^5 V}{90(hc)^3}(k_B T)^4$$

$$\text{Gibbs enthalpy:}\quad G = E + pV - TS = F + pV = 0 \quad (= \mu N)$$

where we recognise the Stefan-Boltzmann-law $E \propto T^4$, the relation $E = 3p$ for the radiation pressure and the consistency of the Gibbs-enthalpy with the chemical potential being zero. Of course, the formal derivation through the partition sum has to be consistent with a direct, intuitive evaluation of the expectation values of energy and particle number:

$$E = \sum_k \frac{\epsilon_k}{\exp(\beta\epsilon_k) - 1} \rightarrow E = \frac{4\pi V}{(hc)^3}\int_0^\infty d\epsilon \frac{\epsilon^3}{\exp(\beta\epsilon) - 1} = \frac{24\pi V}{(hc)^3}(k_B T)^4 \zeta(4)$$

$$N = \sum_k \frac{1}{\exp(\beta\epsilon_k) - 1} \rightarrow N = \frac{4\pi V}{(hc)^3}\int_0^\infty d\epsilon \frac{\epsilon^2}{\exp(\beta\epsilon) - 1} = \frac{8\pi V}{(hc)^3}(k_B T)^3 \zeta(3)$$

confirming the result on E, and giving some insight into the entropy S, which comes out as being proportional to the particle number as both scale with T^3. In some sense, the entropy carried by the electromagnetic field in thermal equilibrium is just the number of photons. Of course, exactly the same results on particle number would have been obtained if μ had been included in the definition of the macrocanonical partition such that $-\partial J/\partial\mu$ could have been computed and evaluated at $\mu = 0$ to yield N. The scaling $VT^3 = \text{const}$ along with $pT^{-4} = \text{const}$ imply $pV^{4/3} = \text{const}$, such that the adiabatic index κ of the photon gas needs to be $\kappa = 4/3$.

H.5.2 Planck-spectrum

The differential flux per energy $\epsilon = \hbar\omega$ or angular frequency ω observed from the electromagnetic field in thermal equilibrium is given by the Planck-spectrum,

$$S(\omega) = \frac{\hbar}{4\pi^2 c^2} \cdot \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \tag{H.390}$$

from which we recover the Rayleigh-Jeans limit for $\hbar\omega \ll k_B T$

$$S(\omega) = \frac{1}{4\pi^2 c^2} \cdot \omega^2 \cdot k_B T \tag{H.391}$$

showing that there is a parabolic increase of the spectrum, with a infinite amount of total energy, if integrated over all frequencies ω: This is known as the ultraviolet catastrophe. For high energies $\hbar\omega \gg k_B T$ one obtains the Wien-limit

$$(\omega) = \frac{\hbar}{4\pi^2 c^2} \cdot \omega^3 \cdot \exp\left(-\frac{\hbar\omega}{k_B T}\right) \tag{H.392}$$

which would result for a system of ultrarelativistic particles following classical statistics instead of quantum staticstics, markedly being different at low frequencies. Weirdly enough, all scaling properties of the Wien-spectrum come out in exactly the same way as for the proper Planck-spectrum, only the numerical prefactors are off by a tiny bit: The absence of the −1 in the distribution lead to simple factorials in Bose-type integrals and miss the ζ-function.

Wien's displacement law states that one is going to observe more highly energetic radiation for higher temperatures; the maximum frequency is determined to be

$$\frac{dS}{d\omega} = 0 \quad \rightarrow \quad 3 - \frac{\hbar\omega}{k_B T} \cdot \frac{\exp\left(\frac{\hbar\omega}{k_B T}\right)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} = 0 \tag{H.393}$$

which (only) has a numerical solution, $\hbar\omega \simeq 2.821 k_B T$. Again, the Wien-prediction is but a tiny bit off, as $\hbar\omega$ results in 3 instead of $\simeq 2.081$. The Wien-displacement law suggests that it is possible to assign a length scale to a temperature as we did before, but this time for a relativistic particle,

☠ *These numbers are all impossible to guess and must have puzzled Wilhelm Wien profoundly.*

$$\epsilon = cp = c\hbar k = \frac{ch}{\lambda_{th}} = k_B T \quad \rightarrow \quad \lambda_{th} = \frac{ch}{k_B T}, \tag{H.394}$$

as the de Broglie-wavelength of an ultrarelativistic particle carrying the thermal energy, and therefore it is justified to call it thermal wavelength λ_{th}, as it is derived from equipartition, $k_B T = \hbar\omega$. That means, that one can measure temperature spectroscopically!

☠ *It is a curious property of the Planck-spectrum that* $S(\omega)$ *for different temperatures never cross. So any measurement of* $S(\omega)$ *at an arbitrary frequency* ω *determines* T.

There is a very neat derivation of the Planck-specktrum full of physical intuition, naturally by Einstein himself: The Bose-factor $1/(\exp(\hbar\omega/(k_B T)) - 1)$ leads to an overabundance of photons at low energies relative to a Boltzmann-factor $\exp(-\hbar\omega/(k_B T))$ (which of course vanishes at high energies as $\exp(\hbar\omega/(k_B T)) \gg 1$), and this overabundance introduces all the weird numbers into the scaling relations that Wien couldn't make sense of. So somehow Einstein needed to engineer a solution to make low-energetic photons more abundant relative to the Wien-prediction, and his idea was that of induced emission as the mechanism to generate Bose-distributions.

Imagine two quantum mechanical levels for Planck's grain of coal (bringing the photon gas into thermal equilibrium as discussed before) with occupation numbers n_1 and n_2: The occupation numbers can change due to absorption in the lower level n_1 and inducing a transition into n_2. That process must scale with the intensity S of the radiation field. Then, there can be spontaneous emission, decreasing n_2 and increasing n_1, which is independent of S, as the process takes place spontaneously. Induced emission is a transition from n_2 to n_1 which actually depends on S, as postulated by Einstein. The rate equations with suitable transition coefficents then read

$$\dot{n}_1 = -SBn_1 + A_i S n_2 + A_s n_2$$

$$\dot{n}_2 = +SBn_2 - A_i S n_1 - A_s n_1$$

with coefficients A_i, A_s and B: B determines the rate that the atoms in the lower state are able to absorb a photon from the radiation field, and the two As determine the rate at which atoms in the upper state are doing transitions, either spontaneous or induced. They are characteristics of how easily an atom in that particular state reacts to the radiation field (for instance, how strong dipole moments are). As there is no spontaneous transition to a state of higher energy (that would be in violation of energy conservation) it is unnecessary to introduce two Bs.

In equilibrium $\dot{n}_1 = \dot{n}_2 = 0$ must hold (which is called detailed balance condition), as there is not any net change in the occupation numbers, leading to

$$n_2(SA_i + A_s) = SBn_1 \tag{H.395}$$

for instance from $\dot{n}_1 = 0$. Applying Boltzmann-statistics to the occupation number ratio,

$$\frac{n_2}{n_1} = \exp\left(-\frac{\hbar\omega}{k_B T}\right) \tag{H.396}$$

yields an expression reminiscent of the Bose-factor,

$$S \propto \frac{A_s}{B\exp\left(\frac{\hbar\omega}{k_B T}\right) - A_i} \tag{H.397}$$

If we had neglected the term $A_i S n_2$ in the rate equation describing induced emission, a conventional Wien-like spectrum would have come out:

$$S \propto \frac{A_s}{B}\exp\left(-\frac{\hbar\omega}{k_B T}\right) \tag{H.398}$$

To be very specific, what the derivation is doing is to assume standard Boltzmann-statistics for the occupation number statistics of the atomic levels in the coal, and transfer that with the radiative processes discussed (absorption, induced and spontaneous emission) to the photon gas. The inclusion of induced emission clearly generates Bose-distributions instead of Boltzmann-distributions.

The constants can be fixed to be in accordance with the known Wien and Rayleigh-Jeans radiation laws: At very high energies $\hbar\omega \gg k_B T$ one needs to recover $S \sim \omega^3 \exp\left(-\frac{\hbar\omega}{k_B T}\right)$. In this limit, A_i should be negligible, and the ratio A_s/B should become proportional to ω^3. The Rayleigh-Jeans limit $\hbar\omega \ll k_B T$ is a bit more tricky. Taylor-expanding S for small $\hbar\omega/(k_B T)$ yields

$$S \propto \frac{1}{\frac{B}{A_s} + \frac{B}{A_s}\frac{\hbar\omega}{k_B T} - \frac{A_i}{A_s}} \tag{H.399}$$

such that there is a term $B/A_s\,\hbar\omega/(k_B T)$, which generates the Rayleigh-Jeans scaling $\propto \omega^2$ if B/A_s and A_i/A_s were equal. That implies that $B = A_i$ and therefore

$$S \propto \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \tag{H.400}$$

and voilà, the Bose-factor appears. Fig. 3 gives an impression of the Planck-spectrum

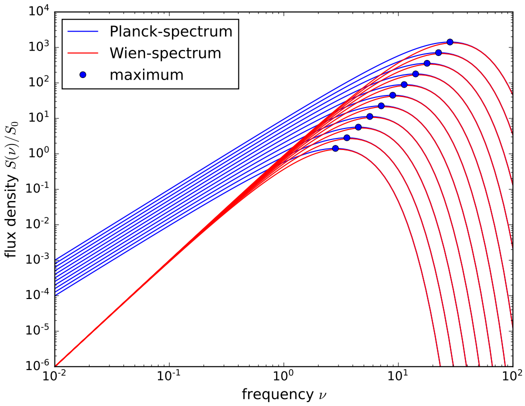

Figure 3: Planck-spectrum for ultrarelativistic bosons, in comparison to the Wien-approximation using classical instead of quantum statistics, both for a range of temperatures T. *The maxima in frequency for different temperatures clearly follow a linear Wien-displacement law.*

for a range of temperatures T, along with the Wien-approximation, where the Bose-factor is replaced by a plain Boltzmann-factor: Clearly, there is an overabundance of photons at low energies in proper quantum statistics, underlining their bosonic nature.

H.6 *Fluctuations in quantum and classical statistics*

The bottom line of the spectral distribution of photons and the Planck-spectrum is an overabundance of photons at low energies compared to the classical prediction, encapsulated by the difference between the Bose- and Boltzmann-factors. It is not only the case that there are just more photons at low energies but also that these photons are correlated: The observation of one photon makes it more likely to observe a second one, as first discovered by Hanburry-Brown and Twiss. One might think that photons from a thermal source are necessarily uncorrelated, but the mechanism of induced emission or, equivalently, the symmetry requirement on the wave functions in the macrocanonical expectation values and the resulting photon bunching introduce correlations between the photons. Therefore, when observing photons from a thermal source, the variance $\langle n^2\rangle$ of photon counts has a variance which is super-Poissonian and not just $\langle n\rangle$. Conversely, fermions from a thermal source are anti-correlated with a sub-Poissonian counting statistic.

☠ *A laser is, despite induced emission, a perfect example of a Poissonian light source: that's because the photon avalanches are effectively a classical process and there is no thermal equilibrium at all.*

Therefore, we should analyse fluctuations and counting statistics of Bose-Einstein, Fermi-Dirac and Maxwell-Boltzmann distributions: The macrocanonical potentials including a chemical potential μ are given by

$$J_{\mathrm{MB}}(T, V, \mu) = -k_B T \sum_k \exp(-\beta(\epsilon_k - \mu))$$

$$J_{\mathrm{BE}}(T, V, \mu) = +k_B T \sum_k \ln[1 - \exp(-\beta(\epsilon_k - \mu))]$$

$$J_{\mathrm{FD}}(T, V, \mu) = -k_B T \sum_k \ln[1 + \exp(-\beta(\epsilon_k - \mu))]$$

which all coincide at high energies $-\beta\epsilon_k \gg 1$, because $\ln(1 \pm x) = \pm x$ for $x = \exp(-\beta\epsilon)$, which then becomes small. All three cases can be summed into a single expression,

$$\ln \mathcal{Z}(T, V, \mu) = \frac{1}{a} \sum_k \ln[1 - a \exp(-\beta(\epsilon_k - \mu))] \tag{H.401}$$

where they only differ by the value of the parameter a,

$$a = \begin{cases} -1 & \text{Fermi-Dirac} \\ 0 & \text{Maxwell-Boltzmann} \\ +1 & \text{Bose-Einstein} \end{cases} \tag{H.402}$$

Maxwell-Boltzmann-statistics follows in the limit $a \to 1$ as an application of the de l'Hôpital-rule. The particle number follows from the macrocanonical potential directly through differentiation,

$$N = \frac{\partial}{\partial\mu} k_B T \ln \mathcal{Z}(T, V, \mu) = -\frac{\partial}{\partial\mu} J \tag{H.403}$$

or through the expectation value of the occupation number operator,

$$\langle N \rangle = \frac{1}{\mathcal{Z}} \sum_{\{n_k\}} \exp(-\beta \sum_k n_k(\epsilon_k - \mu)) \cdot \underbrace{\langle n_1, \dots | N | n_1, \dots \rangle}_{=\sum_k \langle n_k \rangle = N} =$$

$$\frac{1}{\mathcal{Z}} \frac{1}{\beta} \frac{\partial}{\partial\mu} \sum_{\{n_k\}} \exp(-\beta \sum_{n_k} n_k(\epsilon_k - \mu)) = \frac{1}{\mathcal{Z}} (k_B T) \frac{\partial}{\partial\mu} \mathcal{Z} = k_B T \frac{\partial}{\partial\mu} \ln \mathcal{Z} \tag{H.404}$$

This implies for the three distributions that

$$\langle n_k \rangle = \frac{1}{\exp(\beta(\epsilon_k - \mu)) - a} \tag{H.405}$$

because each occupation number can be isolated through differentiation by ϵ_k

$$\langle n_k\rangle = \frac{1}{\mathcal{Z}}\sum_{\{n_k\}}\exp(-\beta\sum_k n_k(\epsilon_k-\mu))\cdot n_k = \frac{1}{\mathcal{Z}}\frac{-1}{\beta}\frac{\partial}{\partial\epsilon_k}\sum_{\{n_k\}}\exp(-\beta\sum_k n_k(\epsilon_k-\mu)) =$$

$$\frac{1}{\mathcal{Z}}\left(-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k}\mathcal{Z}\right) = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k}\ln\mathcal{Z}(\mathrm{T},\mathrm{V},\mu) \quad \text{(H.406)}$$

The variance of the expectation value $\langle n_k\rangle$

$$\sigma_k^2 = \langle n_k^2\rangle - \langle n_k\rangle^2 = \frac{1}{\mathcal{Z}}\left(-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k}\right)^2\mathcal{Z} - \left[\frac{1}{\mathcal{Z}}\left(-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k}\right)\right]^2 \quad \text{(H.407)}$$

can likewise be computed through successive derivatives with respect to μ. Trying out

$$\frac{\partial^2}{\partial\epsilon_k^2}\ln\mathcal{Z} = \frac{\partial}{\partial\epsilon_k}\left(\frac{1}{\mathcal{Z}}\frac{\partial}{\partial\epsilon_k}\mathcal{Z}\right) = \frac{1}{\mathcal{Z}}\frac{\partial^2}{\partial\epsilon_k^2}\mathcal{Z} - \frac{1}{\mathcal{Z}^2}\left(\frac{\partial}{\partial\epsilon_k}\mathcal{Z}\right)^2 = \frac{1}{\mathcal{Z}}\frac{\partial^2}{\partial\epsilon_k^2}\mathcal{Z} - \left(\frac{1}{\mathcal{Z}}\frac{\partial}{\partial\epsilon_k}\mathcal{Z}\right)^2 \quad \text{(H.408)}$$

suggest for the variance

$$\sigma_k^2 = \left(-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k}\right)^2\ln\mathcal{Z} = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k}\left[-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k}\ln\mathcal{Z}\right] = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_k}\langle n_k\rangle \quad \text{(H.409)}$$

The specific calculation for the three distributions in question then gives for the variance

$$\sigma_k^2 = \frac{\exp(\beta(\epsilon_k-\mu))}{[\exp(\beta(\epsilon-\mu))-a]^2} = \exp(\beta(\epsilon_k-\mu))\cdot\langle n_k\rangle^2 \quad \text{(H.410)}$$

as well as for the expectation value

$$\langle n_k\rangle = \frac{1}{\exp(\beta(\epsilon_k-\mu))-a} \quad\rightarrow\quad \exp(\beta(\epsilon_k-\mu)) = \frac{1}{\langle n_k\rangle}+a \quad \text{(H.411)}$$

such that the final result becomes

$$\sigma_k^2 = \langle n_k\rangle^2\cdot\left(\frac{1}{\langle n_k\rangle}-a\right) = \begin{cases}\langle n_k\rangle & \text{Maxwell-Boltzmann}\\ \langle n_k\rangle+\langle n_k\rangle^2 & \text{Bose-Einstein}\\ \langle n_k\rangle-\langle n_k\rangle^2 & \text{Fermi-Dirac}\end{cases} \quad \text{(H.412)}$$

such that there is an increased variance for bosonic systems as opposed to a reduced variance for fermionic systems in perfect agreement with the results from the Hanburry-Brown and Twiss experiment. Classical particles reproduces a perfectly Poissonian behaviour as variance and expectation value are identical, $\sigma_k^2 = \langle n_k\rangle$. And actually, there is no problem subtracting $\langle n_k\rangle^2$ from $\langle n_k\rangle$ for the fermionic case, as n_k can only range between 0 and 1, the square is certainly smaller.

Fig. 4 shows the Bose-Einstein distribution for bosons, the Fermi-Dirac distribution for fermions and the Boltzmann-distribution for classical particles. Clearly, there is an overabundance of bosons relative to the classical prediction, and an under-

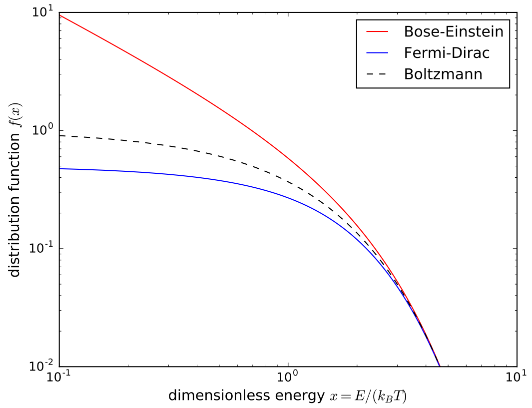

Figure 4: Bose-Einstein and Fermi-Dirac distribution in comparison to the Boltzmann-distribution, as a function of energy E*, expressed in terms of thermal energy* $k_B T$.

abundance of fermions, most prominently for small energies, while the differences disappear towards higher energies.

☠ *In the scifi-novel* His master's voice *by S. Lem humankind receives an alien message modulated on a NASER, i.e. on a coherent neutrino beam: Would this be possible?*

H.7 *Third law of thermodynamics and entropy at absolute zero*

The obscure third law of thermodynamics ensures that the entropy approaches a constant value (which can be set to zero, as it only appears differentially in thermodynamics) for very low temperatures in the limit $T \to 0$. Let's see whether this result is predicted by statistical mechanics for an ideal, classical gas. In the canonical ensemble one gets

$$Z(T, V, N) = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \tag{H.413}$$

such that one derives the Helmholtz free energy F from the canonical partition function,

$$F(T, V, N) = -k_B T \ln Z(T, V, N) = -N k_B T\left[1 + \ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right)\right] \tag{H.414}$$

and the entropy S through differentiation,

$$S(T, V, N) = -\frac{\partial F}{\partial T} = N k_B\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\right)\right] \tag{H.415}$$

On the other hand, the entropy S should follow directly as an expectation value of $\ln\rho$:

$$\begin{aligned}
S &= -k_B\langle\ln\rho\rangle = -k_B \mathrm{tr}(\rho\ln\rho)\\
&= -k_B \mathrm{tr}\left[\frac{\exp(-\beta H)}{\mathrm{tr}\exp(-\beta H)}\cdot\ln\frac{\exp(-\beta H)}{\mathrm{tr}\exp(-\beta H)}\right]\\
&= -k_B\frac{1}{\mathrm{tr}\exp(-\beta H)}\mathrm{tr}[\exp(-\beta H)\cdot\ln(\exp(-\beta H)) - \ln\mathrm{tr}\exp(-\beta H)]\\
&= -k_B\frac{1}{\sum_N\exp(-\beta E_N)}\sum_N\exp(-\beta E_N)\left[\ln\exp(-\beta E_N) - \ln\sum_M\exp(-\beta E_M)\right]\\
&= -k_B\frac{1}{\sum_N\exp(-\beta E_N)}\sum_N\exp(-\beta E_N)\left[-\beta E_N - \ln\sum_M\exp(-\beta E_M)\right]
\end{aligned}$$

specifically in an energy-eigenbasis for the traces, and introducing a second index for the nested sums. Introducing a ground state $\bar{E}$ such that all energies are measured relative to it, $E_N - \bar{E} = \Delta$ then implies:

$$S = -k_B\frac{1}{\sum_N\exp(-\beta\Delta)}\sum_N\exp(-\beta\Delta)\left[-\beta\Delta - \ln\sum_m\exp(-\beta\Delta)\right]\to 0 \qquad \text{(H.416)}$$

with the limit of $S\to 0$ as $T\to 0$ or equivalently, $\beta\to\infty$.

$$\lim_{T\to 0}\exp(-\beta\Delta) = \begin{cases}1 & \text{for}\quad \Delta = 0, E = \mathcal{E}\\ 0 & \text{for}\quad \Delta\neq 0, E > \mathcal{E}\end{cases} \qquad \text{(H.417)}$$

This is actually a very surprising result: Finite volumes V and vanishing energies $E = 0$ for the ground state are not compatible with each other. In the light of quantum mechanics this makes perfect sense, as a finite size of the system Δx restricts the momentum to be $\Delta p \geq \hbar/2/\Delta x$, which limits the kinetic energy $\Delta E \geq \hbar^2/(8m)/(\Delta x)^2$ as a consequence of the uncertainty relation.

H.8 *Fermionic statistics and the exclusion principle*

Fermions are particles with half-integer spin and according to Pauli's spin-statistics-theorem, they have to obey Fermi-Dirac-statistics. Examples of fermions in statistical systems are electrons in a metal or neutrinos in the cosmic neutrino background. The logarithmic macrocanonical parition is given by

$$q(T,V,\mu) = \ln\mathcal{Z}(T,V,\mu) = \sum_k\ln[1 + z\exp(-\beta\epsilon_k)] \qquad \text{(H.418)}$$

with the fugacity $z = \exp(\beta\mu)$ in general being nonzero: Adding new particles to a system has to be done in accordance with the exclusion principle, so it might not be possible to put particles in the ground state when it's already occupied. In general, μ (or z) increases with N, so the effective chemical potential can be determined with

$$N(T,V,\mu) = \sum_k \langle n_k \rangle = \sum_k \frac{1}{z^{-1}\exp(\beta\epsilon_k)+1} \tag{H.419}$$

for non-interacting, ideal fermions. The sum over the discrete states transitions into an integral in the continuum limit

$$\sum_k \longrightarrow V \cdot \int \frac{d^3p}{h^3} = V \cdot \int d\epsilon\, g(\epsilon) \tag{H.420}$$

with a corresponding density of states $g(\epsilon)$, using energy ϵ rather than momentum $\boldsymbol{p}$ for the phase space integration. Then, the expressions for the macrocanonical partition function and the particle number become

$$q(T,V,\mu) = \int_0^\infty d\epsilon\, g(\epsilon) \ln[1 + z\exp(-\beta\epsilon)]$$

$$N(T,V,\mu) = \int_0^\infty d\epsilon\, g(\epsilon) \frac{1}{z^{-1}\exp(\beta\epsilon)+1}$$

In particular for a system of N classical fermions in thermal equilibrium (like a gas of electrons in a metal, for instance), the total number N would be fixed, so you might wonder why we're using macrocanonical partitions anyway. The answer is that macrocanonical partitions make counting so much easier, since we can simply sum over all states, not the states that are compatible with a total particle number. One employs macrocanonical partitions while reverse-engineering the chemical potential μ so that N is fixed, and using the same μ for $q(T,V,\mu)$ as well, making everything consistent.

H.8.1 Density of states for non-relativistic fermions

The definition of density of states depends crucially on the dispersion relation, as momentum $\boldsymbol{p}$ is exchanged in favour of energy ϵ as the integration variable for the partition function, with an implicit assumption on homogeneity in configuration space as well as isotropy in momentum space. With a non-relativistic dispersion $\epsilon = p^2/(2m)$ and the differential $d\epsilon = p\,dp/m$ one can reformulate the integration as

$$\int d^3x \int d^3p = V4\pi \int dp\, p^2 = V4\pi \int d\epsilon\, 2m\epsilon \frac{m}{p} = V2\pi(2m)^{\frac{3}{2}} \int d\epsilon\, \sqrt{\epsilon} \tag{H.421}$$

By integrating over the density of states with ϵ as the integration variable one obtains for the logarithm of the canonical partition

$$q(T,V,\mu) = \frac{2\pi V}{h^3}(2m)^{\frac{3}{2}} \int_0^\infty d\epsilon \sqrt{\epsilon}\, \ln[1 + z\exp(-\beta\epsilon)] =$$

$$\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}} \frac{2\beta}{3} \int_0^\infty d\epsilon \frac{\epsilon^{\frac{3}{2}}}{z^{-1}\exp(\beta\epsilon)+1} \tag{H.422}$$

and similarly for the particle number

$$N(T,V,\mu) = \frac{2\pi V}{h^3}(2m)^{\frac{3}{2}} \int\limits_0^\infty d\epsilon \frac{\epsilon^{\frac{1}{2}}}{z^{-1}\exp(\beta\epsilon)+1} \tag{H.423}$$

Similar to the bosonic case one encounters a particular type of integral for fermions

$$f_s(z) = \frac{1}{\Gamma(s)} \cdot \int\limits_0^\infty dx \frac{x^{s-1}}{z^{-1}\exp(x)+1} \tag{H.424}$$

with the substitution $x = \beta\epsilon$. With the definition of thermal wavelength for non-relativistic particles

$$\frac{1}{\lambda} = \sqrt{\frac{2\pi m k_B T}{h^2}} \tag{H.425}$$

one can write for the logarithmic macrocanonical parition and the particle number

$$q(T,V,\mu) = \frac{V}{\lambda^3} \cdot f_{\frac{5}{2}}(z) \quad \text{and} \quad N(T,V,\mu) = \frac{V}{\lambda^3} \cdot f_{\frac{3}{2}}(z) \tag{H.426}$$

The Fermi-Dirac distribution can be reformulated as

$$\frac{1}{z^{-1}\exp(x)+1} = z\exp(-x)\frac{1}{1+z\exp(-x)} = \\ z\exp(-x)\sum_{k=0}^{\infty}[-z\exp(-x)]^k = \sum_{k=1}^{\infty}(-1)^{k-1} \cdot z^k \cdot \exp(-kx) \tag{H.427}$$

where in the last step the lower summation boundary has been increase by one to accommodate the prefactor $z\exp(-x)$, leading to an alternating geometric series. The integral eqn. H.424 can then be addressed by substitution $y = kx$, and differentially $dy = kdx$, such that

$$f_s(z) = \frac{1}{\Gamma(s)} \cdot \sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^s} \cdot \int\limits_0^\infty dy y^{s-1} \cdot \exp(-y) = \sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^s} \tag{H.428}$$

and for the special case $s = 0$

$$f_0(z) = \sum_{k=1}^{\infty}(-1)^{k-1}z^k = -1 + 1 - \sum_{k=1}^{\infty}(-1)^k z^k = \\ 1 - \sum_{k=0}^{\infty}(-z)^k = 1 - \frac{1}{1+z} = \frac{1+z-1}{1+z} = \frac{z}{1+z} \simeq z \tag{H.429}$$

where the last approximation is valid for small $z \ll 1$. There is a practical recursion formula

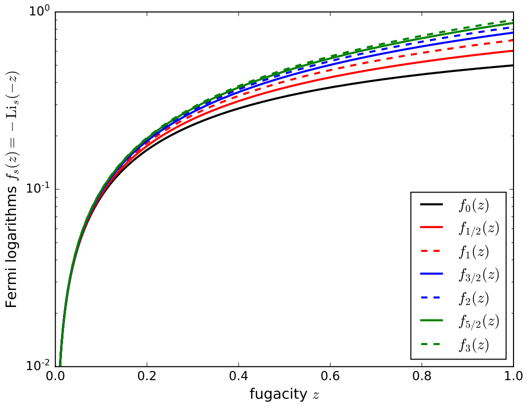

Figure 5: Fermi logarithms $f_s(z) = -\mathrm{Li}_s(-z)$ *as a function of fugacity* z*.*

$$\frac{\partial}{\partial z} f_s(z) = \frac{1}{z} f_{s-1}(z) \tag{H.430}$$

the validity of which can bee seen from this argument: Having the differentiation act on f_N in its integral representation gives

$$z\frac{\partial}{\partial z} f_s(z) = \frac{1}{\Gamma(s)} \int_0^\infty \mathrm{d}x \frac{x^{s-1} z^{-1}\exp(x)}{(z^{-1}\exp(x)+1)^2} \tag{H.431}$$

which can be integrated by parts to yield

$$\ldots = \frac{1}{\Gamma(s)}\Bigg(\underbrace{-\left.\frac{x^{s-1}}{z^{-1}\exp(x)+1}\right|_0^\infty}_{=0,\text{ for } s>1} + (s-1)\int_0^\infty \frac{x^{s-2}}{z^{-1}\exp(x)+1}\Bigg) =$$

$$\frac{s-1}{\Gamma(s)}\int_0^\infty \mathrm{d}x \frac{x^{s-2}}{z^{-1}\exp(x)+1} = f_{s-1}(z) \tag{H.432}$$

It is actually true for all values of s that $f_s(z) \sim z$ for $z \ll 1$, i.e. for small chemical potentials. Fig. 5 illustrates polylogarithms for different values of s as a function of fugacity.

H.8.2 Fermi-gases

Non-relativistic gases made out of fermions in thermal equilibrium would follow exactly the partition function $\mathcal{Z}(\mathrm{T}, \mathrm{V}, \mu)$ in eqn. H.422, so the energy is given as

$$\mathrm{E} = -\frac{\partial}{\partial\beta}\ln\mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = k_\mathrm{B}\mathrm{T}^2\frac{\partial}{\partial \mathrm{T}}\ln\mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = \frac{3}{2}k_\mathrm{B}\mathrm{T}\frac{\mathrm{V}}{\lambda^3}\cdot f_{\frac{5}{2}}(z) \tag{H.433}$$

implying

$$E = \frac{3}{2} N k_B T \frac{f_{\frac{5}{2}(z)}}{f_{\frac{3}{2}(z)}} \tag{H.434}$$

where the last result is obtained through substitution of N. The ratio $f_{5/2}(z)/f_{3/2}(z)$ approaches one for fugacities $z \to 1$ or for chemical potentials $\mu \to 0$, so the result for a classical gas is recovered. Similarly, the pressure is given by

$$p = +k_B T \frac{\partial}{\partial V} \ln \mathcal{Z}(T, V, \mu) = \frac{1}{\lambda^3} k_B T \cdot f_{\frac{5}{2}}(z) = \frac{2}{3}\frac{E}{V} \tag{H.435}$$

which is typical for non-relativistic systems.

H.8.3 Degenerate Fermi-gases in the limit T → 0

A surprising application in many physical systems is that of a fully degenerate Fermi-gas, alluding to the fact that all level up to the Fermi-energy are fully occupied and empty for higher energies. Effectively, this means

$$k_B T \ll \mu \quad \to \quad z \sim 0 \tag{H.436}$$

and the occupation number $\langle n_k \rangle$ becomes the Heaviside-function $\Theta(\mu - \epsilon)$. In this limit, the chemical potential μ is identical to the Fermi energy ϵ_F, which can be interpreted as the energy of the highest occupied state: Clearly, adding a new fermion to the system would require exactly this energy to be invested. The integrals for energy and particle number simplify tremendously due to the simple form of the Heaviside-function:

$$E = \int_0^\mu d\epsilon \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} \epsilon^{\frac{3}{2}} = V \cdot \left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}} \frac{4}{5} \frac{\mu^{\frac{5}{2}}}{\sqrt{\pi}} \tag{H.437}$$

as well as

$$N = \int_0^\mu d\epsilon \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} = V \cdot \left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}} \frac{4}{3} \frac{\mu^{\frac{3}{2}}}{\sqrt{\pi}} \tag{H.438}$$

such that the energy per particle becomes

$$\frac{E}{N} = \frac{3}{5} \mu \tag{H.439}$$

Interpreting μ as the Fermi-energy shows that the energy per particle is simply 3/5 of the energy of the highest occupied state.

☠ *Perhaps this result reminds you of the moment of inertia of a sphere with radius $\epsilon_F = \mu$!*

We've see that computations in relation to Fermi-Dirac-statistics are always a bit trickier than the bosonic case, but there is a very neat trick motivated by the addition theorem of the hyperbolic tangent,

$$\frac{1}{\exp(x) + 1} = \frac{1}{\exp(x) - 1} - 2 \cdot \frac{1}{\exp(2x) - 1} \tag{H.440}$$

that allows to write the Fermi-Dirac-distribution as a difference between two Bose-Einstein-distributions at temperatures T and 2T, which maps every possible computation onto the simpler bosonic case.

☠ *The opposite (writing a BE-distribution in terms of two FD-distributions) is sadly not possible.*

H.9 *Ideal non-relativistic Bose-gas*

The discussion an ideal non-relativistic thermal system of bosons concludes our discussion: From a technical and conceptual point of view it is the most complicated case, as one needs to deal explicitly with the ground state and its occupation. As before, we are using macrocanonical partitions functions because they're so practical for quantum statistics despite the fact that the particle number N is fixed and despite the absence of a particle reservoir: Instead, from the explicit computation of particle number we determine fugacity z and therefore the chemical potential μ to use it in the partition itself. Specifically, the logarithmic macrocanonical partition function is given by

$$q(\mathrm{T},\mathrm{V},\mu(\mathrm{N})) = \ln\mathcal{Z}(\mathrm{T},\mathrm{V},\mu) = -\sum_k \ln[1 - z\cdot\exp(-\beta\epsilon_k)] \tag{H.441}$$

and the particle number is computed by summing over the individual occupation numbers

$$\mathrm{N}(\mathrm{T},\mathrm{V},\mu) = \sum_k \langle n_k\rangle = \sum_k \frac{1}{z^{-1}\cdot\exp(\beta\epsilon_k) - 1} \tag{H.442}$$

From the range of possible values of $\langle n_k\rangle : 0 \leq \langle n_k\rangle \leq \mathrm{N}$ which may be unrestricted between zero and full occupation one can see that

$$z^{-1}\exp(\beta\epsilon_k) = \exp(\beta(\epsilon_k - \mu)) > 1 \tag{H.443}$$

which implies that $\epsilon_k > \mu$ for all states, otherwise the high occupation numbers could not be reached; or one would get a divergence as $\exp(\beta(\epsilon_k - \mu)) \to 1$ for $\epsilon_k = \mu$. Because the lowest possible energy is $\epsilon = 0$ one can conclude that the chemical potential is in fact negative $\mu < 0$, as $\mu < \epsilon_k \leq 0$ for all states, meaning that $0 \geq z \geq 1$: This relation might seem a bit surprising, but this is exactly what one needs to engineer a μ that is consistent with N.

The continuum for large systems would be given by

$$\sum_k \to \frac{\int \mathrm{d}^3x \int \mathrm{d}^3p}{h^3} = \frac{2\pi\mathrm{V}}{h^3}(2m)^{\frac{3}{2}}\int \mathrm{d}\epsilon\sqrt{\epsilon} \tag{H.444}$$

and allows for a definition of a density of states $g(\epsilon)$ resulting from a classical dispersion relation $\epsilon = p^2/(2m)$, together with an isotropic momentum distribution. Then, the logarithmic partition function is written as

$$q(\mathrm{T},\mathrm{V},\mu) = -\frac{2\pi\mathrm{V}}{h^3}(2m)^{\frac{3}{2}}\int \mathrm{d}\epsilon\sqrt{\epsilon}\ln[1 - z^{-1}\exp(\beta\epsilon)] \tag{H.445}$$

along with particle number, which is needed to engineer μ (or z) from N,

$$N(T, V, \mu) = \frac{2\pi V}{h^3}(2m)^{\frac{3}{2}} \int d\epsilon \frac{\sqrt{\epsilon}}{z^{-1}\exp(\beta\epsilon) - 1} \tag{H.446}$$

The last expression neglects the ground state, though: $\epsilon = 0$ implies $g(\epsilon) = 0$, so the integral does not collect any contribution from the ground state. With fermions, we did not have this problem as there can only be a single fermion in the ground state, so for a typical system with many fermions (think of Avogadro's number 10^{23}) the mistake is truly neglible. Taking the occupation number into the limit $\epsilon \to 0$ yields

$$\ln[1 - z\exp(-\beta\epsilon)]|_{\epsilon=0} = \ln(1 - z) \tag{H.447}$$

for the logarithmic macrocanonical partition and

$$\left.\frac{1}{z^{-1}\exp(\beta\epsilon) - 1}\right|_{\epsilon=0} = \frac{1}{z^{-1} - 1} = \frac{1}{\frac{1}{z} - 1} = \frac{z}{1 - z} \tag{H.448}$$

for the particle number, and therefore, we should enhance the expressions for $q(T, V, \mu)$ and $N(T, V, \mu)$ with these expressions, as the $d\epsilon$-integration would not cover them: First for the partition,

$$q(T, V, \mu) = \frac{2\pi V}{h^3}(2m)^{\frac{3}{2}} \frac{2}{3}\beta \cdot \int_0^\infty d\epsilon \frac{\epsilon^{\frac{3}{2}}}{z^{-1}\exp(\beta\epsilon) - 1} - \underbrace{\ln(1 - z)}_{\text{for the } \epsilon = 0 \text{ state}} \tag{H.449}$$

after an integration by parts, and then for the particle number

$$N(T, V, \mu) = \frac{2\pi V}{h^3}(2m)^{\frac{3}{2}} \cdot \int_0^\infty d\epsilon \frac{\epsilon^{\frac{1}{2}}}{z^{-1}\exp(\beta\epsilon) - 1} + \underbrace{\frac{z}{1 - z}}_{\text{for the } \epsilon = 0 \text{ state}} \tag{H.450}$$

Around bosonic partition functions, typical integrals of the form appear,

$$\mathrm{Li}_s(z) = g_s(z) = \frac{1}{\Gamma(s)} \int_0^\infty dx \frac{x^{s-1}}{z^{-1}\exp(x) - 1} \tag{H.451}$$

called polylogarithms, similar to the function $f_s(z)$ which had a plus sign in the denominator instead of a minus. With the definition of thermal wavelength

$$\frac{1}{\lambda} = \sqrt{\frac{2\pi m k_B T}{h^2}} \tag{H.452}$$

for non-relativistic particles and the help of the function $g_N(z)$ one quickly obtains these two compact expressions for the logarithmic partition function and the particle

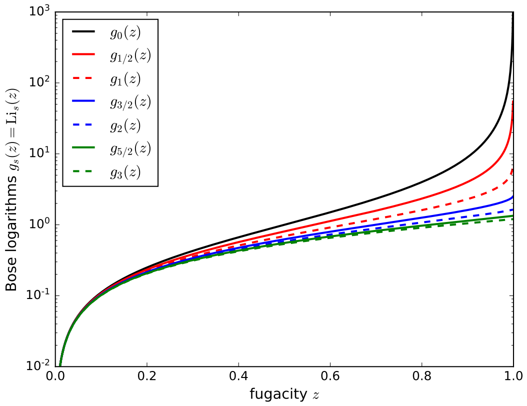

Figure 6: Bose logarithms $g_s(z) = \mathrm{Li}_s(z)$ *as a function of fugacity* z*.*

number,

$$q(\mathrm{T}, \mathrm{V}, \mu) = \frac{\mathrm{V}}{\lambda^3} g_{\frac{5}{2}}(z) - \ln(1-z)$$

$$\mathrm{N}(\mathrm{T}, \mathrm{V}, \mu) = \frac{\mathrm{V}}{\lambda^3} g_{\frac{3}{2}}(z) + \frac{z}{1-z}$$

with the last terms explicitly taking care of the ground state. In the general case one would need to use the relation $\partial \mathrm{J}/\partial\mu = -\mathrm{N}$ to supply the $\mu(\mathrm{N})$-relation to any other derivative, for instance $\partial \mathrm{J}/\partial \mathrm{V} = -p$ as both depend naturally on T, V and μ, just as the macrocanonical potential J itself. The invertibility of $\mathrm{N}(\mu)$ to $\mu(\mathrm{N})$ in made sure because of the monotonicity of the polylogarithms. But please keep in mind that there is no analytical inverse $z = \mathrm{Li}_s^{-1}$, rather, one needs to find the correct value for z numerically. Fig. 6 illustrates polylogarithms for different values of s as a function of fugacity.

The properties of the function $g_s(z)$ are related to the Riemann-ζ that we encountered for the case $\mu = 0$, i.e. for the ideal photon gas. Including $z \neq 1$ changes the calculation slightly, but the general procedure to go through the geometric series is the same, hence

$$\frac{1}{z^{-1}\exp(x) - 1} = z\exp(-x)\frac{1}{1 - z\exp(-x)} =$$
$$z\exp(-x) \cdot \sum_{k=0}^{\infty}(z\exp(-x))^k = \sum_{k=1}^{\infty}(z\exp(-x))^k = \sum_{k=1}^{\infty} z^k \exp(-kx) \quad \text{(H.453)}$$

where one obtains almost miraculously two Γ-functions which cancel each other

$$g_s(z) = \frac{1}{\Gamma(s)}\sum_{k=1}^{\infty} z^k \int \mathrm{d}x x^{s-1}\exp(-kx) = \frac{1}{\Gamma(s)}\sum_{k=1}^{\infty}\frac{z^k}{k^s}\underbrace{\int \mathrm{d}y y^{s-1}\exp(-y)}_{=\Gamma(s)} = \sum_{k=1}^{\infty}\frac{z^k}{k^s} \quad \text{(H.454)}$$

with the substitution $y = kx$ and $\mathrm{d}y = k\mathrm{d}x$. Please keep in mind that here the fugacity ranges between 0 and 1. For $z = 1$ (or $\mu = 0$), though, one recovers the Riemann-ζ function

$$g_s(1) = \sum_{k=1}^{\infty} \frac{1}{k^s} = \zeta(s) \tag{H.455}$$

Let's separate the particle number into the occupation of excited states N_ϵ and of the ground state N_0

$$N = \underbrace{\frac{V}{\lambda^3} g_{\frac{3}{2}}(z)}_{N_\epsilon} + \underbrace{\frac{z}{1-z}}_{N_0} = N_\epsilon + N_0 \tag{H.456}$$

to see what happens at low temperatures. The range of possible values for the bosonic function $g_{\frac{3}{2}}(z)$ is

$$0 \leq g_{\frac{3}{2}}(z) \leq \zeta(3/2) \simeq 2.612 \tag{H.457}$$

with a bound given by the ζ-function, which can be numerically evaluated to be $\zeta(3/2) \simeq 2.612$. This provides a mean of estimating the maximum occupancy of the excited states,

$$N_\epsilon^{\max} = \frac{V}{\lambda^3}\zeta(3/2) = V \cdot \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} \zeta(3/2) \sim V \cdot T^{\frac{3}{2}} \tag{H.458}$$

which is a finite number and can be controlled by temperature T. The surplus of particles $N - N_\epsilon^{\max}$ can be accommodated in the ground state, which can encompass basically all particles if T is only low enough and V is only small enough. Can the ground state accommodate these particles? Yes! The ground state occupation is given by

$$N_0 = \frac{z}{1-z} = z + z^2 + z^3 + \ldots \simeq N \quad \rightarrow \quad z = \frac{N}{N+1} \rightarrow 1 \tag{H.459}$$

which can be solved for the chemical potential or the fugacity, which need to come out as $\mu = 0$ and $z = 1$, respectively. In the thermodynamic limit where $N \rightarrow \infty$ and $V \rightarrow \infty$ while $\frac{N}{V}$ is kept constant we get

$$\frac{N_\epsilon}{N} + \frac{N_0}{N} = 1, \quad \text{with} \quad N_\epsilon = \frac{V}{\lambda^3} g_{\frac{3}{2}}(z), \quad N_0 = \frac{z}{1-z} \tag{H.460}$$

such that one immediately recognises the two cases

$$\text{for } z = 1: \quad \frac{N_\epsilon^{\max}}{N} + \frac{N_0}{N} = 1 \quad \text{Bose-Einstein-condensation}$$

$$\text{for } z < 1: \quad \frac{N_\epsilon}{N} = 1, \quad \frac{N_0}{N} = 0 \quad \text{dilute gas}$$

where condensation would set in by the choice of low T and small V. Clearly,

$$N_\epsilon^{\max} = \frac{V}{\lambda^3} \cdot \zeta(3/2) \quad \rightarrow \quad \frac{N\lambda^3}{V} < \zeta(3/2) \tag{H.461}$$

which suggests that there is a comparison between the total volume of the system and N times the volume λ^3 associated with each wave packet is going on: If the particle separation is smaller than the thermal wavelength, quantum mechanical effects can play a role and the bosonic nature of the wave functions comes to bear. Then, $N > N_\epsilon^{max}$, and condensation sets in.

Interestingly enough, through this construction, one implicitly controls the fugacity or, equivalently, the chemical potential. From an experimental point of view, the fugacity z is implicitly determined by

$$N = \frac{V}{\lambda^3} g_{\frac{3}{2}}(z) \tag{H.462}$$

as particle number N and volume V (for instance through the design of the atom trap) are controllable, with temperature then as well the chemical potential μ. In my personal experience (or lack thereof) I find chemical potential to be a difficult concept, and in this script we approached it in three different systems: The relativistic Bose-gas asserts the interpretation of a vanishing particle mass, and the degenerate Fermi-gas that of the energy of the lowest unoccupied state. The non-relativistic Bose-gas suggests that μ is determined by the combination of N and V, and enables the usage of macrocanonical statistics for a quantum system with fixed particle number, therefore it is perhaps the least physical interpretation of μ.