

Chapter 12

Quantum gases

In classical statistical mechanics, we evaluated thermodynamic relations often for an ideal gas, which approximates a real gas in the highly diluted limit.

An important difference between classical and quantum mechanical many-body systems lies in the *distinguishable* character of their constituent particles, which gives rise to phenomena and concepts that are not present in classical physics. We start with a reminder of the basic notation.

12.1 Microcanonical ensemble

We consider an isolated system in thermodynamical equilibrium, with N particles and energy between E and $E + \Delta$.

Common eigenstates. An isolated ensemble in thermal equilibrium is characterized by a stationary distribution, i.e. by

$$[\hat{\rho}, \hat{H}] = 0 ,$$

which implies that the eigenstates of \hat{H}

$$\hat{H} |E_n\rangle = E_n |E_n\rangle, \quad \langle E_n | E_m \rangle = \delta_{nm}, \quad \langle E_n | \hat{H} | E_m \rangle = E_m \delta_{nm}$$

are also eigenstates of $\hat{\rho}$:

$$\langle E_n | \hat{\rho} | E_m \rangle \sim \delta_{nm} .$$

Principle of uniform a priori probabilities.

For an isolated system, the principle of “a priori” probability, as postulated in Sect. 7.5, states that all possible states of the system have the same probability. Therefore, we can write:

$$\boxed{\hat{\rho}_{micro} = \sum_m P_m |E_m\rangle \langle E_m|} \quad \text{Tr} \hat{\rho} = 1 , \quad (12.1)$$

with

$$P_m = \begin{cases} \text{const.} & E < E_m < E + \Delta \\ 0 & \text{otherwise} \end{cases}$$

where the constant is given by the normalization condition $\text{Tr} \hat{\rho} = 1$.

Energy shell. The operator

$$\hat{P}_\Delta = \sum_{E < E_m < E + \Delta} |E_m\rangle \langle E_m|, \quad \hat{P}_\Delta |\Psi\rangle = \sum_{E < E_m < E + \Delta} |E_m\rangle \langle E_m | \Psi \rangle, \quad (12.2)$$

projects to an arbitrary states to the energy shell. The trace $\Gamma(E)$ of \hat{P}_Δ ,

$$\Gamma(E) = \text{Tr} \left(\hat{P}_\Delta \right) = \sum_{E < E_m < E + \Delta} 1 = \boxed{\text{number of states with energies between } E \text{ and } E + \Delta}, \quad (12.3)$$

is therefore the microcanonical phase-space volume.

Microcanonical density operator. The microcanonical density operator (12.1) is then

$$\hat{\rho}_{micro} = \sum_{E < E_m < E + \Delta} P_m |E_m\rangle \langle E_m|, \quad P_m = \frac{1}{\Gamma(E)}, \quad (12.4)$$

with the expectation value of an operator \hat{B} given in the microcanonical ensemble given by

$$\langle \hat{B} \rangle = \frac{1}{\Gamma(E)} \text{Tr} \left(\sum_{E < E_m < E + \Delta} |E_m\rangle \langle E_m| \hat{B} \right)$$

Internal energy. The internal energy U is simply the expectation value of the energy, $U = \langle H \rangle = E$, which one can show alternatively via

$$\begin{aligned} U &\equiv \frac{1}{\Gamma(E)} \text{Tr} \left(\sum_{E < E_m < E + \Delta} |E_m\rangle \langle E_m| \hat{H} \right) \\ &= \frac{1}{\Gamma(E)} \sum_{E < E_m < E + \Delta} E_m \approx E. \end{aligned}$$

Entropy postulate. One possibility to ground quantum statistics is to postulated that the expression for the microcanonical entropy is within given by

$$\boxed{S = k_B \ln \Gamma(E)}. \quad (12.5)$$

This definition is the quantum mechanical analogum of the postulate (8.5) of the entropy within the classical microcanonical ensemble.

- There is no Gibbs paradox when the the definition (12.3) for the phase space volume $\Gamma(E)$ is used. Quantum mechanics takes the indistinguishability of identical particles correctly into account.

- Instead of postulating (12.5) one can use the information-theoretical expression of the entropy and postulate, in accordance with Sect. 5.5.1, that the entropy is maximal. This point of view will be touched upon Sect. 12.1.1.

Phase space volume. In analogy with classical statistics, we can define the phase space volume $\Phi(E)$ as

$$\Phi(E) = \sum_{E_m \leq E} 1 ,$$

which measures the number of eigenstates of the Hamiltonian operator with energies small or equal to E_m . The relation between the phase space density $\Gamma(E)$, the phase space volume $\Phi(E)$ and the density of states $\Omega(E)$ is

$$\Gamma(E) = \Phi(E + \Delta) - \Phi(E), \quad \Omega(E) = \frac{\delta\Phi}{\delta E} .$$

For small Δ , the entropy (12.5) reduces to $S = k_B \ln(\Omega(E)\Delta)$.

12.1.1 Maximum entropy principle

We may ground quantum statistic on information theoretical principles. One parts from the Shannon entropy $I[P]$,

$$I[P] = - \sum_m P_m \ln P_m , \quad (12.6)$$

introduced in Sect. 5.5.3, demanding in a second step that the dimensionless entropy, S/k_B corresponds to a measure of the disorder present in the system and that this measure is quantified by $I[P]$.

Maximal entropy postulate. In Sect. 5.5.1 we have noted that the second law of thermodynamics implies that maximum entropy principle, which states that irreversible processes may only increase the entropy in isolated systems. Reversing the stance we may use the maximum energy principle as the basic postulate on which to ground quantum statistics.

POSTULATE A statistical ensemble is thermally equilibrated when the Shannon entropy (12.6) is maximal.

This approach comes with the positive side effect that it holds for all three ensembles.

Maximal entropy distributions. In order to put the maximum entropy postulate at work we need to know which are the maximal entropy distributions. For the case of the microcanonical ensemble we need therefore to know which function $p(y)$ maximizes

$$I[p] = \int p(y) \ln (p(y)) dy, \quad \delta I = \int \underbrace{[\ln (p(y)) + 1]}_{\equiv 0} \delta p(y) dy , \quad (12.7)$$

where we have denoted the *variation** of $I[p]$ with δI . With the variation $\delta p(y)$ of the distribution function being arbitrary one has that the bracket on the right-hand-side of δI in (12.7) needs to vanish for $\delta I = 0$. It follows that

$$p(y) = \text{const.} \quad (12.8)$$

Microcanonical entropy. The uniform distribution (12.8) reflects the principle of uniform a priori probabilities entering the formulation of the microcanonical density matrix (12.4). for the entropy,

$$S = -k_B \sum_{E < E_m < E + \Delta} P_m \ln(P_m), \quad P_m = \frac{1}{\Gamma(E)},$$

it then follows

$$S = -\frac{k_B}{\Gamma(E)} \Gamma(E) \ln \left(\frac{1}{\Gamma(E)} \right), \quad \boxed{S = k_B \ln \Gamma(E)}, \quad (12.9)$$

which reproduces the energy postulate (12.5). $\Gamma(E)$ is here the volume of the energy shell.

12.1.2 Third law of thermodynamics

The third law of thermodynamics is of quantum mechanical nature:

“The entropy of a thermodynamical system at $T = 0$ is a universal constant that can be chosen to be zero and this choice is independent of the values taken by the other state variables.”

Ground state degeneracy. For a system with a discrete energy spectrum, there is a lowest energy state, the *ground state*. At $T \rightarrow 0$, the system will go into this state.

If the groundstate is n -times degenerate, the entropy of the system at $T = 0$ is

$$S(T = 0) = k_B \ln n ,$$

n : degeneracy \equiv multiplicity.

For $n = 1$ (no degeneracy), $S = 0$.

Spontaneous symmetry breaking. The entropy S apparently doesn't fulfill the third law of thermodynamics for a finite ground state degeneracy $n > 1$. However, there is no paradox.

* One uses variational calculus to derive Newton's equations of motions,

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}} = \frac{\partial L}{\partial q}, \quad W(L) = \int L(q, \dot{q}) dt,$$

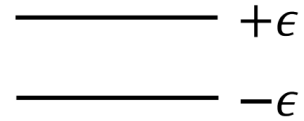
from the action $W(L)$.

When $n > 1$, the groundstate is degenerate due to the existence of internal symmetries of the Hamiltonian (for instance, spin rotational symmetry); at $T = 0$ the symmetry gets broken through a phase transition that lets the entropy go to zero.

Spin rotational symmetry. The magnetization can point in an arbitrary direction for a magnetic compound with spin rotational symmetry. In this case, *one* of the many possible degenerate states is *spontaneously* selected.

12.1.3 Two-level system and the concept of negative temperature

Consider an isolated system of N spin-1/2 particles, which have each two spin orientations, $s = 1/2$ and $s_z = \pm 1/2$. We assume that the two possible energy states $\pm\epsilon$ are occupied by N_{\pm} particles, with



$$N = N_+ + N_-, \quad E = (N_+ - N_-)\epsilon,$$

where E is the total energy. Obviously,

$$N_+ = \frac{1}{2} \left(N + \frac{E}{\epsilon} \right), \quad N_- = \frac{1}{2} \left(N - \frac{E}{\epsilon} \right). \quad (12.10)$$

Volume of the energy shell. The number of possible states with energy E and particle number N is given by the density of states $\Omega(E, N)$:

$$\Gamma(E, N) = \binom{N}{N_+} = \frac{N!}{N_+! N_-!},$$

as there are $\binom{N}{N_+}$ possibilities to select N_+ particles out of a total of N indistinguishable particles.

Microcanonical entropy. The entropy is then

$$\begin{aligned} S(E, N) &= k_B \ln \Gamma(E, N) = k_B \ln \left(\frac{N!}{N_+! N_-!} \right) \\ &= k_B \left[\ln(N!) - \ln(N_+!) - \ln(N_-!) \right] \\ &\approx k_B \left[N \ln N - N_+ \ln N_+ - N_- \ln N_- \right], \quad (12.11) \end{aligned}$$

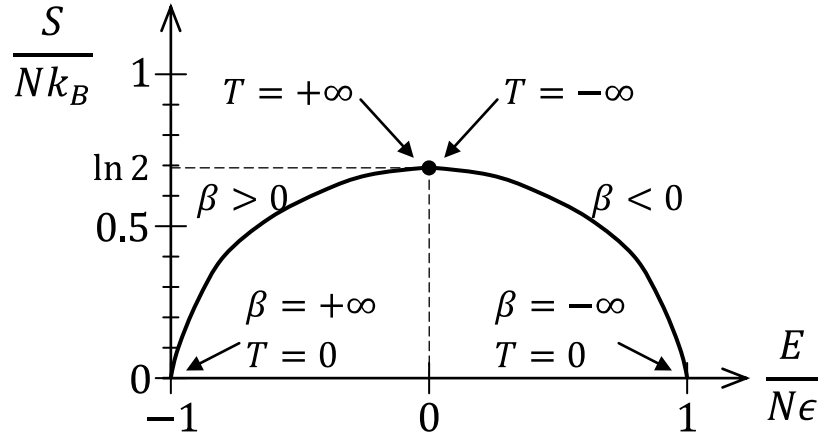
where we have made use of the Stirling formula $\ln(N!) \approx N \ln N$ in the last step.

Temperature. The temperature of the collection of two-level is then

$$\begin{aligned} \frac{1}{T} &= \left. \frac{\partial S}{\partial E} \right|_N = -k_B \left(\ln N_+ + 1 \right) \frac{\partial N_+}{\partial E} - k_B \left(\ln N_- + 1 \right) \frac{\partial N_-}{\partial E} \\ &= -k_B (\ln N_+ - \ln N_-) / 2\epsilon, \end{aligned}$$

where we have used (12.11), namely that $\partial N_{\pm}/\partial E = \pm 1/(2\epsilon)$. We then have

$$\boxed{\frac{1}{T} = \frac{k_B}{2\epsilon} \ln \left(\frac{N_-}{N_+} \right)}, \quad \frac{N_+}{N_-} = e^{-\beta 2\epsilon}, \quad 2N_{\pm} = N \pm E/\epsilon. \quad (12.12)$$



$N_- > N_+$ The normal state is characterized by $E < 0$, i.e. by a situation where there are more particles in the lower energy level $-\epsilon$ than in the higher energy level $\epsilon > 0$. The temperature is then positive, $T > 0$, as usual.

- All particles are in the lower energy level for $N_- = N$, which corresponds to $T = 0$ and $\beta \rightarrow \infty$.
- The slope $1/T = \partial S/\partial E$ diverges at $E = -|\epsilon|$.

$N_- = N_+$ For $T \rightarrow \infty$, the particles distribute equally between the two levels: $N_+ = N_- = N/2$. The total energy is then $E = 0$.

- The entropy (12.11) is then

$$S(E = 0, N) = k_B N [\ln N - \ln(N/2)] = k_B N \ln 2.$$

The entropy per particle is given at $T \rightarrow \infty$ by the logarithm of the number of degrees of freedom (in units of k_B).

- The slope $1/T = \partial S/\partial E$ vanishes at $E = 0$.
- The temperature T jumps from $+\infty$ to $-\infty$ as soon as more particles are in the higher than the lower level.

$N_- < N_+$ Suppose that particles are excited to the higher energy level (for instance, by light irradiation as in a Laser). If the particles remain in the excited state for a certain

period of time (viz if the excited state is metastable), the situation $N_+ > N_-$ is realized. This phenomenon is called *inversion*.

The definition (12.12) of the temperature,

$$\frac{1}{T} = \frac{k_B}{2\epsilon} \ln \left(\frac{N_-}{N_+} \right) ,$$

becomes formally *negative* whenever $N_+ > N_-$.

- The concept of *negative* temperature makes only sense for systems with an upper bound for the energy.
- The inversion of the level occupation needs external pumping. Negative temperatures do therefore not occur for isolated systems. There is no true negative temperature.
- $T \rightarrow 0$ from below when all the particles are in the higher level.

12.2 Canonical ensemble

In order to derive the density matrix $\hat{\rho}$ for the canonical ensemble one follow the route taken in Sect. 9.1 for the classical ensemble. Here we will start, alternatively, from the maximum entropy postulate introduced in Sect. 12.1.1 as a possible grounding principle for statistical mechanics.

Lagrange parameters. We start by determining the probability distribution $p(y)$ maximizing the Shannon information $I[p]$ under the constraint of a given expectation value $\langle y \rangle$. This is done within variational calculus by finding the maximum of

$$I[p] - \lambda \langle y \rangle = - \int \left[\ln(p(y)) + \lambda y \right] p(y) dy , \quad (12.13)$$

where λ is an appropriate *Lagrange parameter*.

Maximum entropy distribution. Variation of (12.13) yields

$$\delta [I[p] - \lambda \langle y \rangle] = - \int \underbrace{\left[1 + \ln(p(y)) + \lambda y \right]}_{\equiv 0} \delta p(y) dy .$$

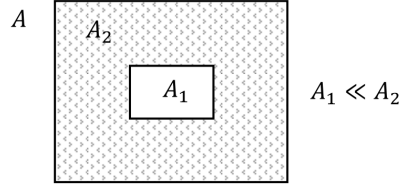
Compare the equivalent expression (12.7) without constraints. We therefore find that

$$p(y) \sim e^{-\lambda y}, \quad p(y) = \frac{e^{-\lambda y}}{Z}, \quad Z = \int dy e^{-\lambda y} , \quad (12.14)$$

with the normalization factor Z .

System in thermal contact with a heat bath.

The energy fluctuates for a system A_1 in thermal equilibrium with a reservoir A_2 , which is the setup of the canonical ensemble. We therefore need to find the distribution function P_m maximizing



$$S - \lambda \langle E \rangle = -k_B \sum_m P_m \ln(P_m) - k_B \lambda \sum_m E_m P_m ,$$

where we rescaled the Lagrange parameter λ by k_B . Our result (12.14) then tells us, that

$$P_m = \frac{e^{-\lambda E_m}}{Z}, \quad Z = \sum_m e^{-\lambda E_m} . \quad (12.15)$$

What remains to be done is to determine the physical significance of the λ .

Temperature as a Lagrange parameter. We will now show that

$$\boxed{\lambda = \frac{1}{k_B T}}, \quad U = \frac{\sum_m E_m e^{-\beta E_m}}{Z}, \quad Z = \sum_m e^{-\beta E_m} , \quad (12.16)$$

which implies that the (inverse) temperature β can be defined as the Lagrange parameter needed to regulate the magnitude of the internal energy $U = \langle E \rangle$.

Free energy. The relation (12.16) is verified by showing that there exist for $\lambda = \beta$ a function F fulfilling with

$$-\frac{\partial F}{\partial T} = S \equiv -k_B \sum_m P_m \ln(P_m), \quad F = U - TS . \quad (12.17)$$

the defining thermodynamic relations of the free energy. We use $\ln(P_m) = -\lambda E_m - \ln Z$, which allows to rewrite the entropy as

$$TS = k_B T \sum_m P_m (\beta E_m + \ln Z) = \underbrace{\lambda \beta}_{=1} \underbrace{\langle E \rangle}_{=U} + \underbrace{k_B T \ln Z}_{=-F} . \quad (12.18)$$

Defining the free energy as $F = -k_B T \ln Z$ is therefore consistent with $F = U - TS$. The first condition of (12.17) is verified by evaluating

$$\begin{aligned} -\frac{\partial F}{\partial T} &= \frac{\partial}{\partial T} [k_B T \ln Z] = k_B \ln Z + \frac{k_B T}{Z} \left(\sum_m e^{-\beta E_m} (-E_m) \right) \frac{-1}{k_B T^2} \\ &= k_B \ln Z + \frac{1}{T} \langle E \rangle \\ &\equiv S , \end{aligned}$$

where we compared with (12.18) in the last step.

Specific heat. With (4.8) and (12.18), namely

$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{C_V}{T}, \quad S = k_B \ln Z + \frac{1}{T} \sum E_m \frac{e^{-\beta E_m}}{Z}$$

we obtain

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_{V,N} &= \frac{k_B}{Z} \sum_m (-E_m) e^{-\beta E_m} \left(\frac{-1}{k_B T^2}\right) + \left(\frac{-1}{T^2}\right) \sum E_m \frac{e^{-\beta E_m}}{Z} \\ &+ \frac{1}{T} \sum (-E_m^2) \frac{e^{-\beta E_m}}{Z} \left(\frac{-1}{k_B T^2}\right) + \frac{\langle E \rangle}{T} \sum_m (-E_m) \frac{e^{-\beta E_m}}{-Z} \left(\frac{-1}{k_B T^2}\right), \end{aligned}$$

which leads to

$$C_V = \frac{1}{k_B T^2} [\langle E^2 \rangle - \langle E \rangle^2]. \quad (12.19)$$

The quantummechanical result (12.19) for the specific heat C_V is hence identical to the classical expression (9.23).

Canonical density matrix. Using that the eigenstates $|E_m\rangle$ of Hamilton operator \hat{H} form a complete basis,

$$\hat{H}|E_m\rangle = E_m|E_m\rangle, \quad \sum_m |E_m\rangle \langle E_m| = \hat{\mathbf{1}},$$

we write the canonical density matrix operator $\hat{\rho}$ as

$$\hat{\rho} = \frac{1}{Z} \sum_m e^{-\beta E_m} |E_m\rangle \langle E_m| = \frac{e^{-\beta \hat{H}}}{Z} \underbrace{\sum_m |E_m\rangle \langle E_m|}_{\hat{\mathbf{1}}},$$

that is as

$$\boxed{\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z}}, \quad Z = \text{Tr}[e^{-\beta \hat{H}}], \quad (12.20)$$

where we have used that the *canonical partition function* as $Z = Z(T, V, N) = \sum_m e^{-\beta E_m}$.

12.2.1 Quantum mechanical harmonic oscillators

As an application we consider N localized independent linear harmonic oscillators with frequency ω in thermal equilibrium at temperature T . Such a system would describe, for instance, the radiation energy of a black body.

Spectrum. A single oscillator is described by

$$\hat{H}\Psi_n = \varepsilon_n \Psi_n, \quad \varepsilon_n = \hbar\omega \left(n + \frac{1}{2}\right),$$

where n is the occupation number. The spectrum ε_n is equally spaced.

Partition function for one oscillator. Then, the partition function in the canonical ensemble for one oscillator is given by

$$\begin{aligned} Z(T, V, N = 1) &= \text{Tr} e^{-\beta \hat{H}} = \sum_n e^{-\beta \varepsilon_n} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n + \frac{1}{2})} \\ &= e^{-\frac{\beta \hbar \omega}{2}} \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega})^n, \end{aligned}$$

which is a geometrical series of the form

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-r}.$$

Therefore,

$$Z(T, V, 1) = \frac{e^{-\frac{\beta \hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}} = \frac{1}{e^{\frac{\beta \hbar \omega}{2}} - e^{-\frac{\beta \hbar \omega}{2}}} = \frac{1}{2 \sinh\left(\frac{\beta \hbar \omega}{2}\right)}.$$

Partition function for N oscillators. For N particles it then follows that

$$Z(T, V, N) = [Z(T, V, 1)]^N = \left[2 \sinh\left(\frac{\beta \hbar \omega}{2}\right) \right]^{-N}.$$

The above expression is valid only because we assumed that the oscillators don't interact with each other and that all eigenfrequencies are identical.

Free energy. The free energy $F = -k_B T \ln(Z)$ is

$$\begin{aligned} F(T, V, N) &= -N k_B T \ln\left(\frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}}\right) \\ &= \underbrace{\frac{N}{2} \hbar \omega}_{\text{zero-point energy of } N \text{ oscillators}} + N k_B T \ln(1 - e^{-\beta \hbar \omega}). \end{aligned}$$

For the derivatives we obtain

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T, V} = \frac{F}{N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T, N} = 0.$$

Note that the pressure P vanishes due to the fact that the oscillators are localized in the sense that the eigenfrequencies ω do not depend on the volume V .

Entropy. The entropy is

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_{V, N} = -N k_B \ln(1 - e^{-\beta \hbar \omega}) - N k_B T \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \left(\frac{-1}{k_B T^2}\right) \\ &= N k_B \left[\frac{\beta \hbar \omega}{e^{\beta \hbar \omega} - 1} - \ln(1 - e^{-\beta \hbar \omega}) \right]. \end{aligned}$$

Internal energy. The internal energy $U = F + TS$ is

$$U = N\hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right], \quad (12.21)$$

which can be written as

$$U = N\hbar\omega \left(\frac{1}{2} + \langle n \rangle \right), \quad \langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1},$$

where $\langle n \rangle$ is the *particle occupation number*. We will see this expression again when we introduce the Bose gas.

- The $T \rightarrow 0$ limit,

$$U \rightarrow \frac{N}{2}\hbar\omega,$$

gives the ground-state energy of a system of N quantum oscillators (vacuum fluctuations).

- For $T \rightarrow \infty$ one recovers with

$$U \rightarrow Nk_B T$$

the expression for the energy N classical oscillators.

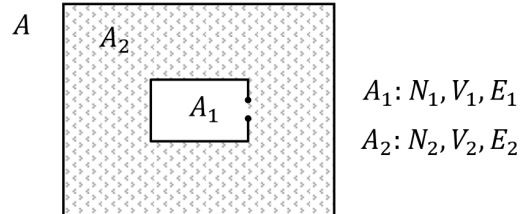
12.3 Grand canonical ensemble

A grand canonical ensemble may exchange both energy and particles with a reservoir. The eigenstates depend therefore on the number N of particles present:

$$\hat{H}|E_m(N)\rangle = E_m(N)|E_m(N)\rangle,$$

$$\hat{N}|E_m(N)\rangle = N|E_m(N)\rangle,$$

$$\hat{\mathbf{1}} = \sum_{N,m} |E_m(N)\rangle \langle E_m(N)|,$$



where \hat{N} is the particle number operator.

Maximum entropy postulate. In order to apply the maximum entropy principle to the grand canonical ensemble we have therefore to find the distribution function $P_m(N)$ maximizing the Shannon entropy under the constraints that the expectation values of the energy and of the particle number,

$$E = \langle \hat{H} \rangle, \quad N = \langle \hat{N} \rangle,$$

are given. Following the calculation performed in Sect. 12.2 for the canonical ensemble we look for the distribution $P_m(N)$ maximizing

$$k_B [I[P] - \lambda_E \langle \hat{H} \rangle - \lambda_N \langle \hat{N} \rangle] = -k_B \sum_{N,m} P_m(N) \left[\ln P_m(N) + \lambda_E E_m(N) + \lambda_N N \right],$$

where $I[P]$ is the Shannon entropy. The solution is, in analogy to (12.15),

$$P_m(N) = \frac{e^{-\lambda_E E_m - \lambda_N N}}{\mathcal{Z}}, \quad \mathcal{Z} = \sum_{N,m} e^{-\lambda_E E_m - \lambda_N N}. \quad (12.22)$$

The chemical potential as an Lagrange parameter. The physical significance of the two Lagrange parameters involved are given by

$$\lambda_E \equiv \beta, \quad \lambda_N \equiv -\beta\mu. \quad (12.23)$$

The first equivalence was shown in Sect. 12.2. The second term in (12.23) implies that the chemical potential μ may be defined, modulo a factor $(-\beta)$, as the Lagrange parameter regulating the particle number.

Density matrix. Using (12.23) we find

$$\hat{\rho} = \frac{e^{-\beta(\hat{H} - \mu\hat{N})}}{\mathcal{Z}}, \quad \mathcal{Z} = \text{Tr}[e^{-\beta(\hat{H} - \mu\hat{N})}] \quad (12.24)$$

for the grand canonical density matrix $\hat{\rho}$ and

$$\Omega(T, V, \mu) = -k_B T \ln \mathcal{Z}(T, V, \mu) \quad (12.25)$$

respectively for the grand canonical potential Ω .

Particle number. In order to verify (12.23) we confirm that

$$N = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V} = k_B T \underbrace{\frac{\partial}{\partial \mu} \ln \left(\sum_{N,m} e^{-\beta(E_m(N) - \mu N)} \right)}_{\beta(\sum_{N,m} N e^{-\beta(E_m(N) - \mu N)}) / \mathcal{Z} = \beta \langle \hat{N} \rangle}$$

holds.

12.3.1 Entropy and the density matrix operator

We showed in Sect. 12.1.1 that the entropy S can be written within the microcanonical ensemble in terms of the density matrix operator $\hat{\rho}$ as

$$S = -k_B \text{Tr}(\hat{\rho} \ln \hat{\rho}) = -k_B \langle \ln \hat{\rho} \rangle, \quad (12.26)$$

i.e., the entropy is given by the expectation value of the negative logarithm of the density matrix operator $\hat{\rho}$.

- Note that since the eigenvalues of $\hat{\rho}$ are probabilities, i.e., they are between 0 and 1, the logarithm in Eq. (12.26) will therefore be *negative* and S *positive*.

- For the canonical ensemble we used (12.2) as the starting point for the maximum energy principle and showed that the resulting free energy $F = F(T, V, N)$ is consistent with the requirement that $F = U - TS$ and $S = -\partial F/\partial T$.

An analogous consistency check as done for the canonical ensemble can be performed also for the grand canonical ensemble.

Consistency check. For the grand canonical ensemble we have $\Omega(T, V, \mu) = -k_B T \ln \mathcal{Z}$ and hence

$$\hat{\rho} = \frac{1}{\mathcal{Z}} e^{-\beta(\hat{H} - \mu\hat{N})} = e^{\beta\Omega} e^{-\beta(\hat{H} - \mu\hat{N})} \quad \mathcal{Z} = e^{-\beta\Omega} .$$

With $F = U - TS$ and $\Omega = F - \mu N$ we then have

$$\begin{aligned} -k_B \langle \ln \hat{\rho} \rangle &= -\frac{1}{T} \left(\Omega - \langle \hat{H} \rangle + \mu \langle \hat{N} \rangle \right) \\ &= -\frac{1}{T} (F - U) = S . \end{aligned}$$

Q.e.d.

12.4 Partition function of ideal quantum gases

The adequate ensemble to deal with quantum gases is the grand canonical ensemble:

$$\mathcal{Z}(T, V, \mu) = \text{Tr} e^{-\beta(\hat{H} - \mu\hat{N})} . \quad (12.27)$$

Particle number operator. The particle number operator \hat{N} entering (12.27) is given by

$$\hat{N} = \sum_{\mathbf{k}} c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}}, \quad \underbrace{\langle c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} \rangle}_{\text{fermions}} \in [0, 1], \quad \underbrace{\langle a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} \rangle}_{\text{bosons}} = 0, 1, 2, \dots \quad (12.28)$$

where $c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}}$ is the operator measuring the occupancy of a plane wave with momentum $\hbar\mathbf{k}$. Two fermions may never occupy the same orbital.

Hamiltonian. The Hamilton operator \hat{H} is

$$\hat{H} = \sum_{\mathbf{k}} \epsilon_k c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}}, \quad \epsilon_k = \frac{(\hbar k)^2}{2m}, \quad k = |\mathbf{k}| \quad (12.29)$$

for a gas of a non-interacting gas. ϵ_k is the *dispersion relation*.

Additive Hamilton operators. The particle number operator \hat{N} is always additive. The exponential in the partition function (12.27) factorizes,

$$e^{-\beta(\hat{H} - \mu\hat{N})} = \prod_{\mathbf{k}} e^{-\beta(\epsilon_k - \mu)c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}}} \quad (12.30)$$

when the Hamilton operators is also additive. This holds because particle number operators for different orbitals commute for both fermions and bosons,

$$[c_{\mathbf{k}_1}^{\dagger} c_{\mathbf{k}_1}, c_{\mathbf{k}_2}^{\dagger} c_{\mathbf{k}_2}] = 0, \quad [a_{\mathbf{k}_1}^{\dagger} a_{\mathbf{k}_1}, a_{\mathbf{k}_2}^{\dagger} a_{\mathbf{k}_2}] = 0 ,$$

where $\mathbf{k}_1 \neq \mathbf{k}_2$.

Partition function. We define

$$n_k = \begin{cases} \langle c_{\mathbf{k}}^\dagger c_{\mathbf{k}} \rangle & \text{fermions} \\ \langle a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \rangle & \text{bosons} \end{cases} \quad (12.31)$$

and find with (12.30) that

$$\begin{aligned} \mathcal{Z}(T, V, \mu) &= \left(\sum_{n_{\mathbf{k}_1}} e^{-\beta n_{\mathbf{k}_1} (\epsilon_{\mathbf{k}_1} - \mu)} \right) \left(\sum_{n_{\mathbf{k}_2}} e^{-\beta n_{\mathbf{k}_2} (\epsilon_{\mathbf{k}_2} - \mu)} \right) \dots \\ &= \prod_{\mathbf{k}} \left(\sum_{n_{\mathbf{k}}} e^{-\beta n_{\mathbf{k}} (\epsilon_{\mathbf{k}} - \mu)} \right) \end{aligned} \quad (12.32)$$

holds for the partition function $\mathcal{Z}(T, V, \mu)$ of non-interaction particles. Note that the partition function factorizes only for the grand canonical partition function.

Bosons. The occupation numbers n_r runs over all non-negative integers for a system of bosons, so that the parenthesis of (12.32) reduces to a geometrical series[†]:

$$\boxed{\mathcal{Z}(T, V, \mu) = \prod_r \left[\frac{1}{1 - e^{-\beta(\epsilon_r - \mu)}} \right]} \quad \text{bosons} \quad (12.33)$$

We have used here an index r for the sum over orbitals characterized by an energy ϵ_r . One may identify r with the wavevector \mathbf{k} whenever needed. Note that (12.33) implies that $\epsilon_r - \mu > 0$. The chemical potential μ must hence be small than any eigenenergy ϵ_r .

Fermions. The orbital occupations number n_r takes only the values $n_r = 0$ and $n_r = 1$ for a system of fermions. This implies that

$$\boxed{\mathcal{Z}(T, V, \mu) = \prod_r [1 + e^{-\beta(\epsilon_r - \mu)}]} \quad \text{fermions} \quad (12.34)$$

Once \mathcal{Z} has been determined one can obtain the remaining thermodynamic properties of ideal quantum gases.

12.5 Thermodynamic properties of ideal quantum gases

Using the index (+) and (-) for bosons and fermions respectively we find with (12.33)

$$\boxed{\Omega^{(+)}(T, V, \mu) = k_B T \sum_r \ln [1 - e^{-\beta(\epsilon_r - \mu)}]} \quad \text{bosons} \quad (12.35)$$

[†] The sum of a geometrical series is $\sum_{n=0}^{\infty} x^n = 1/(1-x)$.

for the bosonic grand canonical potential $\Omega^{(+)} = -k_B T \ln \mathcal{Z}^{(+)}$ and

$$\boxed{\Omega^{(-)}(T, V, \mu) = -k_B T \sum_r \ln [1 + e^{-\beta(\epsilon_r - \mu)}]} \quad \text{fermions} \quad (12.36)$$

for the case of fermions. The volume dependence results from the sum \sum_r over orbitals.

Bose-Einstein distribution. The expectation value of the particle number operator \hat{N} is

$$\langle \hat{N} \rangle^{(+)} = -\frac{\partial}{\partial \mu} \Omega^{(+)}(T, V, \mu) = \sum_r \frac{1}{e^{\beta(\epsilon_r - \mu)} - 1},$$

which allows to define the *Bose-Einstein distribution*

$$\boxed{\langle \hat{n}_r \rangle^{(+)} = \frac{1}{e^{\beta(\epsilon_r - \mu)} - 1}} \quad \text{Bose-Einstein} \quad (12.37)$$

where $\hat{n}_r = a_{\mathbf{k}}^\dagger a_{\mathbf{k}}$ denotes the number operator for the orbital r .

Fermi-Dirac distribution. For Fermions one finds correspondingly

$$\langle \hat{N} \rangle^{(-)} = -\frac{\partial}{\partial \mu} \ln \Omega^{(-)}(T, V, \mu) = \sum_r \frac{1}{e^{\beta(\epsilon_r - \mu)} + 1}.$$

The expectation value of the orbital occupation,

$$\boxed{\langle \hat{n}_r \rangle^{(-)} = \frac{1}{e^{\beta(\epsilon_r - \mu)} + 1}} \quad \text{Fermi-Dirac} \quad (12.38)$$

is the *Fermi-Dirac distribution function*.

Thermal equation of state. The *Thermal equation of state* is

$$PV = -\Omega, \quad PV = k_B T \ln \mathcal{Z}^{(\pm)}(T, V, \mu).$$

according to Sect. 5.4, which holds also for ideal quantum gases.

Internal energy. The internal energy $U = U^{(\pm)}$ is given with (5.21) by

$$U - \mu N = \frac{\partial}{\partial \beta} (\beta \Omega), \quad U^{(\pm)} = \sum_r \epsilon_r \langle \hat{n}_r \rangle^{(\pm)},$$

where the orbital occupation number $\langle \hat{n}_r \rangle^{(\pm)}$ is given by (12.37) and (12.38) for bosons and respectively for fermions. The internal energy reduces hence to the sum over the mean orbital energies, For the derivation of this intuitive results we consider the case of bosons:

$$U^{(+)} - \mu \langle \hat{N} \rangle^{(+)} = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}^{(+)}(T, V, \mu) = \sum_r \frac{\epsilon_r - \mu}{e^{\beta(\epsilon_r - \mu)} - 1} = \sum_r n_r^{(+)} (\epsilon_r - \mu).$$

12.5.1 Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac distribution

The three distributions

$$n^{MB}(\epsilon_r) = e^{-\beta(\epsilon_r - \mu)}, \quad n^{BE}(\epsilon_r) = \frac{1}{e^{\beta(\epsilon_r - \mu)} - 1}, \quad n^{FD}(\epsilon_r) = \frac{1}{e^{\beta(\epsilon_r - \mu)} + 1}$$

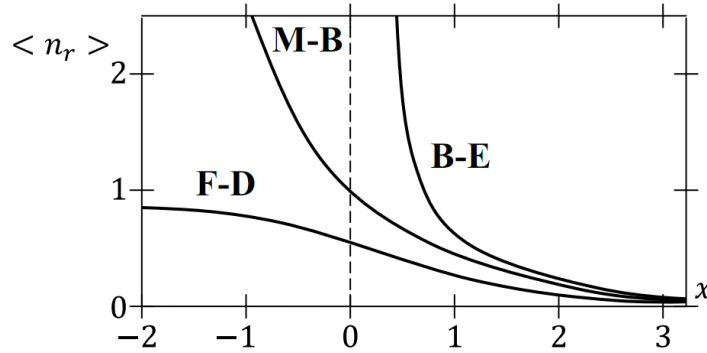
quantify the occupation of an energy level for a non-interacting gas.

n^{MB} : Maxwell-Boltzmann (classical grand canonical ensemble)

n^{BE} : Bose-Einstein (quantum)

n^{FD} : Fermi-Dirac (quantum)

For large one-particle energies, i.e., for $\epsilon_r - \mu \gg k_B T$, both the Bose-Einstein and the Fermi-Dirac distribution functions converge to the Maxwell-Boltzmann distribution function.



All three distribution functions are function only of $x = \beta(\epsilon_r - \mu)$.

Chemical potential – bosons. For bosons the lowest energy state ϵ_0 sets an upper limit for the chemical potential. The occupation

$$n_0^{BE}(\epsilon_0) = \frac{1}{e^{\beta(\epsilon_0 - \mu)} - 1}, \quad \epsilon_0 \leq \epsilon_r$$

of the lowest energy state would be otherwise negative, i.e. if μ would be larger than ϵ_0 .

Bose-Einstein condensation. There are cases when the chemical potential μ approaches the lowest energy level ϵ_0 from below. The occupation of the lowest energy level then diverges:

$$\lim_{\mu \rightarrow \epsilon_0} n_0^{BE}(\epsilon_0) = \lim_{\mu \rightarrow \epsilon_0} \frac{1}{e^{\beta(\epsilon_0 - \mu)} - 1} \rightarrow \infty. \quad (12.39)$$

This phenomenon is called *Bose-Einstein condensation*.

- A finite fraction αN , with $0 \leq \alpha \leq 1$, of all particles occupy the identical state, namely ϵ_0 when (12.39) occurs. The remaining fraction $(1 - \alpha)N$ of particles occupy the higher level.
- ^4He is a famous example of a real gas undergoing a Bose-Einstein condensation. The residual interactions between the Helium atoms are however substantial.

Chemical potential – fermions.

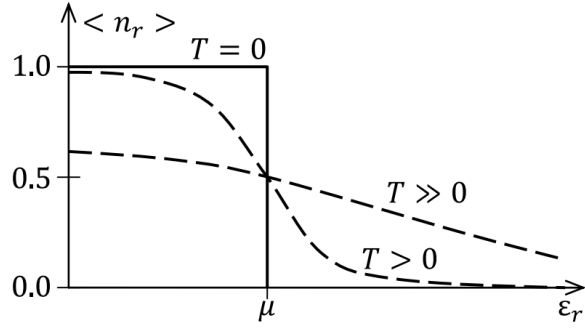
The chemical potential regulates the number of particles,

$$0 \leq n^{FD} \leq 1 \quad (\text{Pauli principle}).$$

μ can have any value. The $T \rightarrow 0$ limit of n^{FD} is a step function:

$$\lim_{T \rightarrow 0} \frac{1}{e^{\beta(\epsilon_r - \mu)} + 1} = \begin{cases} 1 & \epsilon_r < \mu \\ 0 & \epsilon_r > \mu \end{cases}$$

$\epsilon_F = \lim_{T \rightarrow 0} \mu(T)$ is the *Fermi energy*.

**12.5.2 Particle number fluctuations**

We restrict ourselves to a single orbital with orbital energy ϵ_r and write the expectation value of the particle number as

$$\langle \hat{n}_r \rangle = \frac{1}{\mathcal{Z}} \sum_{n_r} n_r e^{-n_r x_r}, \quad \mathcal{Z} = \sum_{n_r} e^{-n_r x_r}, \quad x_r = \beta(\epsilon_r - \mu).$$

We leave the allowed values of n_r , which depend on the statistics, open. We have

$$\langle \hat{n}_r \rangle = -\frac{\partial}{\partial x_r} \ln \mathcal{Z}, \quad \langle \hat{n}_r^2 \rangle = \frac{1}{\mathcal{Z}} \sum_{n_r} n_r^2 e^{-n_r x_r},$$

where the second relation defines the second moment $\langle \hat{n}_r^2 \rangle$ of the particle number operator \hat{n}_r . We evaluate

$$\begin{aligned} \frac{\partial}{\partial x_r} \langle \hat{n}_r \rangle &= \frac{\partial}{\partial x_r} \frac{1}{\mathcal{Z}} \sum_{n_r} n_r e^{-n_r x_r} \\ &= \left(\frac{1}{\mathcal{Z}} \sum_{n_r} n_r e^{-n_r x_r} \right) \left(\frac{1}{\mathcal{Z}} \sum_{n_r} n_r e^{-n_r x_r} \right) - \frac{1}{\mathcal{Z}} \sum_{n_r} n_r^2 e^{-n_r x_r}. \end{aligned}$$

Particle number fluctuations. Using above expressions we find that the relation

$$\boxed{\langle \hat{n}_r^2 \rangle - \langle \hat{n}_r \rangle^2 = -\frac{\partial}{\partial x_r} \langle \hat{n}_r \rangle} \quad (12.40)$$

holds independently of the statistics considered. The variance of the particle number operator is proportional to the (negative) derivative of its expectation value.

Relative particle number fluctuations. Carrying the derivation on the right-hand side of (12.40) out for the our three statistics (MB, BE, FD), we obtain

$$\frac{\langle \hat{n}_r^2 \rangle - \langle \hat{n}_r \rangle^2}{\langle \hat{n}_r \rangle^2} = e^{\beta(\epsilon_r - \mu)}, \quad \boxed{\frac{\langle \hat{n}_r^2 \rangle - \langle \hat{n}_r \rangle^2}{\langle \hat{n}_r \rangle^2} = \frac{1}{\langle \hat{n}_r \rangle} - c}$$

for the relative particle number fluctuations .

$$\begin{array}{lll} c^{MB} = 0 & \text{for classical particles} & \text{(Maxwell-Boltzmann)} \\ c^{BE} = -1 & \text{for bosons} & \text{(Bose-Einstein)} \\ c^{FD} = +1 & \text{for fermions} & \text{(Fermi-Dirac)} \end{array}$$

The particle fluctuations for bosons are larger than those for classical particles while for fermions they are smaller. This result reflect the intuition that The reason for that is that the Pauli principle hinders the change of a particle state for the case of fermions but not for bosons.