Consider a system with a constant number $N$ of identical particles inside a macroscopic finite enclosure with fixed volume $V$. Assume the considered system to be in thermal equilibrium with a very large heat bath (outside world), with which it is in weak energy contact. Together the heat bath and the embedded system form a closed system (isolated system).

**Weak energy contact:** by weak energy contact we mean that the embedded system and heat bath can exchange energy, since only the total energy of the entire isolated system is conserved, but that they do so without having a noticeable influence on each other’s energy spectra. Since the mutual interaction is that weak, both the heat bath and the embedded system can be in a definite energy eigenstate at every instance of time (separation of variables). The system and heat bath merely depend on each other through the weak energy contact, which makes the energy of the system time dependent. This weak energy contact does have a role to play, since it provides the mechanism by which the system can reach thermal equilibrium with the heat bath. A weak energy contact can for instance be achieved by separating the system from the heat bath by means of a macroscopic partition wall. This allows energy to be transferred by means of collisions with the atoms in the wall. In that case only a negligible fraction of the enclosed particles will feel the presence of the partition wall if the average de Broglie wavelength of the particles is much smaller than the dimensions of the enclosure (see §2.5). For instance this applies to systems with sufficiently large (macroscopic) enclosures and/or sufficiently high temperatures.

The heat bath determines the mixture: we will see that in thermal equilibrium all energy eigenstates of a closed system have equal probability, i.e. a closed system is described by a completely random ensemble. For a fixed total energy of the entire closed system the number of energy eigenstates of the heat bath is largest if the energy of the heat bath is highest and therefore the energy of the embedded $N$-particle system is lowest. Subsequently the degrees of freedom of the large heat bath are integrated out, which causes the embedded $N$-particle systems with the lowest energies to automatically have the highest statistical weights. This gives rise to a so-called canonical ensemble, which is sometimes referred to as $(N,V,T)$-ensemble. This is a statistical mixture of $N$-particle systems in specific energy eigenstates. As a result of the weak energy contact with the heat bath, such an $N$-particle system in thermal equilibrium will not have a fixed energy value. However, the ensemble average $\bar{E}$ will remain constant in thermal equilibrium.

**The canonical density operator:** in order to determine the density operator of a canonical ensemble in thermal equilibrium, we have to maximize the entropy under the additional constraints $\text{Tr}(\hat{\rho}) = 1$ and $\text{Tr}(\hat{\rho}\hat{H}) = [\hat{H}] \equiv \bar{E} = \text{constant}$. To this end we employ the Lagrange-multiplier method (see App. C) by varying with respect to the eigenvalues $\rho_k$ as
well as the Lagrange multipliers, i.e.

\[ 0 = \delta \left( \sigma - \beta \left\{ \text{Tr}(\hat{\rho} \hat{H}) - \bar{E} \right\} - \lambda \left( \text{Tr}(\hat{\rho}) - 1 \right) \right) \overset{(164)}{=} \delta \left( \beta \bar{E} + \lambda - \sum_k \rho_k \{ \ln(\rho_k) + \beta E_k + \lambda \} \right) \]

for all variations \( \delta \rho_k, \delta \beta \) and \( \delta \lambda \). Note: there is no need to vary with respect to the energy eigenvalues \( E_k \), as these energy eigenvalues are independent of the statistical mixture in case of a weak energy contact. From the Lagrange-multiplier method it follows automatically that the constraint conditions have to be satisfied as well as the condition

\[ \forall \delta \rho_k \sum_k \delta \rho_k \{ \ln(\rho_k) + 1 + \beta E_k + \lambda \} = 0 \quad \Rightarrow \quad \rho_k = \exp(-1-\lambda) \exp(-\beta E_k) \cdot \]

The Lagrange multiplier \( \lambda \) can now be eliminated by means of the constraint condition

\[ \text{Tr}(\hat{\rho}) = \exp(-1-\lambda) \sum_{k'} \exp(-\beta E_{k'}) = 1 \cdot \]

which implies for \( \rho_k \) that

\[ \rho_k = \frac{\exp(-\beta E_k)}{\sum_{k'} \exp(-\beta E_{k'})} . \]  

(165)

In these sums the summation runs over all fully specified \( N \)-particle energy eigenvalues, including the complete degree of degeneracy of these energy levels. Subsequently we use the Lagrange multiplier \( \beta \) to define the temperature of the considered ensemble:

\[ T \equiv \frac{1}{k_B \beta} \cdot \]

(166)

Out of the complete disorder of the closed system, the contact with the heat bath has created order in the energy distribution of the embedded \( N \)-particle system.

Note: if the \( N \)-particle ground state is not degenerate, then the canonical ensemble will change in the low-temperature limit \( T \to 0 \) (\( \beta \to \infty \)) into a pure ensemble where all \( N \)-particle systems will be in the ground state.

Finally we introduce the canonical partition function (normalization factor)

\[ Z_N(T) \equiv \sum_{k'} \exp(-\beta E_{k'}) = \sum_{k'} \langle k' | exp(-\beta \hat{H}) | k' \rangle = \text{Tr}(\exp(-\beta \hat{H})) \cdot \]

(167)

In spectral decomposition the density operator of a canonical ensemble then reads

\[ \hat{\rho} \overset{(164)}{=} \sum_k \rho_k |k\rangle\langle k| \overset{(165)}{=} \sum_k \frac{\exp(-\beta E_k)}{Z_N(T)} |k\rangle\langle k| = \frac{1}{Z_N(T)} \exp(-\beta \hat{H}) \sum_k |k\rangle\langle k| \]

\[ = \overset{\text{compl.}}{\Rightarrow} \quad \hat{\rho}(\hat{H}) = \frac{1}{Z_N(T)} \exp(-\beta \hat{H}) = \frac{\exp(-\beta \hat{H})}{\text{Tr}(\exp(-\beta \hat{H}))} . \]

(168)
The label $N$ in $Z_N(T)$ refers to the number of particles of the considered type of embedded system. An arbitrary averaged physical quantity of the embedded system is then given by the ensemble average

$$\left[ \hat{A} \right] = \frac{1}{Z_N(T)} \text{Tr}(\hat{A} \exp(-\beta \hat{H})),$$

allowing us to derive the average system energy from the partition function:

$$\overline{E} = [\hat{H}] = \frac{\text{Tr}(\hat{H} \exp(-\beta \hat{H}))}{Z_N(T)} = -\frac{\partial Z_N(T)/\partial \beta}{Z_N(T)} = -\frac{\partial}{\partial \beta} \ln(Z_N(T)).$$

(169)

(170)

**Number of particles and the canonical-ensemble concept:** the embedded systems of a canonical ensemble can just as well consist of a single particle as of a macroscopic number of particles (such as a gas). A popular way to link up with the classical thermodynamics of ideal gases is to single out one particle in a larger gas system and consider the corresponding (single-particle) canonical ensemble. This approach of treating the rest of the gas as part of the heat bath has its limitations, though. The canonical-ensemble concept implies that the influence exerted by the particles of the heat bath on the particle of the embedded system is exclusively limited to a weak energy contact. This obviously breaks down if the particle density is too high, causing the quantum mechanical overlap between the identical particles in embedded system and heat bath to become relevant. In that case also the effective quantum mechanical interaction induced by the (anti)symmetrization procedure should be taken into account. These quantum mechanical effects will become more pronounced with increasing particle densities (see §2.5–2.7). In the two examples given below we will nevertheless consider two canonical ensembles of systems that consist of a single particle. The reason to do so is to first link up with classical statistical physics before zooming in on the quantum mechanical aspects. In order to study these many-particle aspects, the grand-canonical ensemble approach will turn out to be more handy.

**Equipartition of energy:** as a standard example we consider a canonical ensemble of systems that each consist of a single free spin-0 particle with mass $m$ that is contained in a macroscopic enclosure (box). Since quantum mechanical many-particle aspects evidently do not play a role in a 1-particle system, we expect the average energy per particle in that case to obey the classical principle of equipartition of energy for an ideal gas. This states that each kinetic and elastic degree of freedom of the considered type of system (i.e. a position/momentum degree of freedom that contributes quadratically to the Hamiltonian) will contribute $k_B T/2$ to the average energy. This is indeed confirmed by the quantum mechanical calculation (see exercise 13), which tells us that the quantum mechanical definitions of entropy, temperature and Boltzmann constant are consistent with their classical thermodynamic counterparts.
Example: magnetization. Consider a canonical ensemble of systems that each consist of a single free electron that is experiencing a constant homogeneous magnetic field in the \( z \)-direction, \( \vec{B} = B \vec{e}_z \). In spin space this corresponds to an interaction

\[
\hat{H}^{\text{spin}}_B = -\hat{S} \cdot \vec{B} = \frac{2\mu_B B}{\hbar} \hat{S}_z ,
\]

in terms of the Bohr magneton \( \mu_B \). The full Hamilton operator \( \hat{H} = \hat{H}^{\text{spatial}} + \hat{H}^{\text{spin}}_B \) of the electron commutes with \( \hat{S}_z \) and therefore the same should hold for \( \hat{\rho}(\hat{H}) \). Hence, the density matrix is diagonal in spin space if we use a basis of eigenvectors of \( \hat{S}_z \) to describe it. For a given spatial energy level the density operator has the following form in spin space:

\[
\rho^{\text{spin}} = \frac{1}{\exp(-\beta \mu_B B) + \exp(\beta \mu_B B)} \begin{pmatrix}
\exp(-\beta \mu_B B) & 0 \\
0 & \exp(\beta \mu_B B)
\end{pmatrix} .
\]

This ensemble corresponds to the following polarization vector:

\[
\rho^{\text{spin}} = \frac{\cosh(\beta \mu_B B) I_2 - \sinh(\beta \mu_B B) \sigma_z}{2 \cosh(\beta \mu_B B)} = \frac{1}{2} \left( I_2 - \tanh(\beta \mu_B B) \sigma_z \right)
\]

\[\Rightarrow \quad \vec{P} = -\tanh(\beta \mu_B B) \vec{e}_z = \frac{2}{\hbar} [\hat{S}_z] \vec{e}_z .
\]

From this we can derive the magnetization, i.e. the average magnetic moment per electron in the direction of the magnetic field:

\[
\overline{M}_S \equiv \frac{1}{B} \langle \hat{S} \cdot \vec{B} \rangle = \frac{2 \mu_B}{\hbar} [\hat{S}_z] = \mu_B \tanh(\beta \mu_B B) .
\]

If \( \beta \mu_B B \ll 1 \), for instance when the magnetic field is weak or the temperature high, then we obtain Curie’s law:

\[
\overline{M}_S \approx \mu_B (\beta \mu_B B) \Rightarrow \chi_S(T) \equiv \left( \frac{d\overline{M}_S}{dB} \right)_{B=0} = \frac{\mu_B^2}{k_B T} \propto T^{-1} ,
\]

where \( \chi_S(T) \) is called the paramagnetic susceptibility of the spin ensemble.

2.4.3 Microcanonical ensembles

If we do not impose the constraint \( \text{Tr}(\hat{\rho}\hat{H}) = \bar{E} \) in the previous derivation, then we will obtain the ensemble with maximum disorder once we maximize the entropy. After all, there is no heat bath to integrate out and create any order in the ensemble. We speak in that case of a microcanonical ensemble or \((N, V, E)\)-ensemble, which determines the thermodynamical properties of a closed system in thermal equilibrium. Because of the absence of energy contact, the system energy is constant and not just the average value of
the system energy. If we take the density matrix $\rho$ to have dimensionality $D$, then we find by employing the Lagrange-multiplier method that

$$
\delta \left( \sigma - \lambda \{ \text{Tr}(\hat{\rho}) - 1 \} \right) \overset{(164)}{=} \delta \left( \lambda - \sum_{k=1}^{D} \rho_k \{ \ln(\rho_k) + \lambda \} \right) = 0
$$

for all variations $\delta \rho_k$ and $\delta \lambda$. From this it follows that $\text{Tr}(\hat{\rho}) = 1$ and $\ln(\rho_k) + 1 + \lambda = 0$. By combining the two conditions $\rho_k = \exp(-1 - \lambda)$ and $\text{Tr}(\hat{\rho}) = D \exp(-1 - \lambda) = 1$, we arrive at the typical diagonal form $\rho_k = 1/D$ as given in §2.4 for a completely random ensemble. This also proves the conjecture that the density matrix of a completely random ensemble gives rise to the absolute maximum of entropy. Note also that from equation (168) it can be read off that a microcanonical ensemble coincides with the high-temperature limit $T \to \infty$ ($\beta \to 0$) of a canonical ensemble.

2.4.4 Grand canonical ensembles (J.W. Gibbs, 1902)

Finally, we consider a quantum mechanical ensemble that satisfies the same criteria as for a canonical ensemble with the exception that the embedded system is allowed to exchange both energy and particles with a reservoir. The (open) many-particle systems described by the ensemble have a variable number of particles. However, the total many-particle Hamilton operator $\hat{H}_{\text{tot}}$ of such a many-particle system satisfies certain particle-number conservation laws.\footnote{For particles that are not constrained by conservation laws, such as thermal photons, only a canonical-ensemble approach is formally applicable. This will be explained in chapter 4 during the discussion of photon-gas systems.} We know that the density operator has to be a constant of motion and that any order in the ensemble is imparted by the contact with the reservoir. As such, we expect the density operator to depend exclusively on observables that belong to conserved quantities that can be exchanged between reservoir and open system. In the considered case that would be the total many-particle Hamilton operator and the conserved...
combinations of total number operators. Let’s for convenience assume that the open system consists of one type of particle, i.e. we exclude the possibility of particle mixtures, and that no reactions can occur that affect the number of particles (such as particle decays). In that case $\hat{H}_{\text{tot}}$ has to be additive, i.e. $[\hat{H}_{\text{tot}}, \hat{N}] = 0$, to guarantee that $\hat{N}$ is a constant of motion. In this way the number of particles plays the same role as energy did in the canonical case, simply because the open system has no fixed number of particles but the complete closed system including the reservoir does. In thermal and diffusive equilibrium, the resulting type of ensemble is called a grand canonical ensemble, $(\alpha, V, T)$-ensemble, or $(\mu, V, T)$-ensemble.

Apart from the average energy we now also have to impose a constraint on the average number of particles of the open system while maximizing the entropy. For this purpose we use the total number operator $\hat{N}$ that counts the total number of particles in the open system, which has eigenvalues $0, 1, 2, \cdots$. Apart from the Hamilton operator also the density operator is additive, in order to guarantee that the entropy is additive. Hence, the total number operator commutes with both the Hamilton operator and the density operator. Bear in mind, though, that these two operators will depend on the precise number of particles present in the open system. This gives rise to the following set of mutually commuting observables $\hat{N}, \hat{H}_{\text{tot}}(\hat{N})$ and $\hat{\rho}(\hat{N})$, with corresponding orthonormal basis $\{|k, N\rangle\}$:

$$\begin{align*}
\hat{N}|k, N\rangle &= N|k, N\rangle, \quad \hat{H}_{\text{tot}}(\hat{N})|k, N\rangle = E_k(N)|k, N\rangle \\
\text{and} \quad \hat{\rho}(\hat{N})|k, N\rangle &= \rho_k(N)|k, N\rangle. \quad (176)
\end{align*}$$

The grand canonical density operator: in order to determine the density operator of a grand canonical ensemble in thermal and diffusive equilibrium we have to maximize the entropy under the additional constraints $\text{Tr}(\hat{\rho}) = 1$, $[\hat{H}_{\text{tot}}(\hat{N})] \equiv \hat{E}_{\text{tot}} = \text{constant}$ and $[\hat{N}] \equiv \bar{N} = \text{constant}$. By means of the Lagrange-multiplier method we find

$$0 = \delta \left( \sigma - \alpha \left\{ [\hat{N}] - \bar{N} \right\} - \beta \left\{ [\hat{H}_{\text{tot}}(\hat{N})] - \bar{E}_{\text{tot}} \right\} - \lambda \left\{ \text{Tr}(\hat{\rho}) - 1 \right\} \right)$$

$$\overset{(176)}{=} \delta \left( \alpha \bar{N} + \beta \bar{E}_{\text{tot}} + \lambda - \sum_N \sum_k \rho_k(N) \left\{ \ln(\rho_k(N)) + \alpha N + \beta E_k(N) + \lambda \right\} \right) \quad (177)$$

for all variations $\delta \rho_k(N), \delta \alpha, \delta \beta$ and $\delta \lambda$. From this it follows automatically that the constraint conditions have to be satisfied as well as the condition

$$\forall \delta \rho_k(N) \sum_N \sum_k \delta \rho_k(N) \left\{ \ln(\rho_k(N)) + 1 + \alpha N + \beta E_k(N) + \lambda \right\} = 0. \quad (178)$$
Combined with the constraint $\text{Tr}(\rho) = 1$ this results in

$$\rho_k(N) = \frac{\exp(-\beta E_k(N) - \alpha N)}{\sum_{N'} \sum_{k'} \exp(-\beta E_{k'}(N') - \alpha N')} .$$

(178)

As in equation (166), the temperature $T$ of the ensemble is defined through $T \equiv 1/k_B \beta$.

Finally, we introduce the grand canonical partition function

$$Z(\alpha, T) \equiv \sum_{N'} \sum_{k'} \exp(-\beta E_{k'}(N') - \alpha N') = \sum_{N'} \exp(-\alpha N') Z_{N'}(T)$$

(167)

and rewrite the grand-canonical density operator as

$$\hat{\rho} = \frac{1}{Z(\alpha, T)} \exp(-\beta \hat{H}_{\text{tot}}(\hat{N}) - \alpha \hat{N}) = \hat{\rho}(\hat{H}_{\text{tot}}(\hat{N}), \hat{N}) .$$

(180)

The quantity $\exp(-\alpha)$ can be regarded as the fugacity of the ensemble, which describes how easy it is to move a particle from the reservoir to the open system:

- if $\exp(-\alpha)$ is small, than contributions from small $N$ values dominate and quantum mechanical many-particle aspects are not important;
- if $\exp(-\alpha)$ is not small, than particle exchange is easier and quantum mechanical many-particle aspects are relevant.

Often the fugacity is written as $\exp(\beta \mu)$, with $\mu = -\alpha/\beta$ known as the chemical potential. The average total energy and the average number of particles of the open system can be extracted directly from the grand canonical partition function:

$$\bar{E}_{\text{tot}} = -\frac{\partial}{\partial \beta} \ln(Z(\alpha, T)) \quad \text{and} \quad \bar{N} = -\frac{\partial}{\partial \alpha} \ln(Z(\alpha, T)) .$$

(181)

Remark: in scenarios that do either involve chemical reactions, particle decays or relativistic energies, we have to abandon conservation laws for individual types of particles. However, in those cases certain combinations of particle numbers often will be conserved. While maximizing the entropy, these generalized conservation laws will have to be imposed as constraints on the corresponding ensemble averages. As before this can be implemented by means of the Lagrange-multiplier method, assigning to each conservation law a specific Lagrange multiplier and a related chemical potential. For instance, for relativistic energies particle–antiparticle pair creation can occur, so that only the difference between the number of particles and antiparticles remains conserved (which is equivalent to charge conservation). Another example is provided by a statistical mixture of $A$-, $B$- and $C$-particles for which the reversible reaction $A \rightleftharpoons B + C$ is in chemical equilibrium. In that case the particle-number combination $2N_A + N_B + N_C$ is conserved.
**Possible realization:** if we are dealing with a very large number of particles inside a macroscopic volume, then the grand canonical ensemble can be realized straightforwardly by partitioning the macroscopic volume in very many identical cells. The inherent condition is that the cells themselves are again sufficiently macroscopic to guarantee that the energy contact with the reservoir (read: the other cells) can be regarded as weak. Repeated measurements can be performed on such an ensemble by simply measuring locally. The internal structure of a star can, for instance, be determined along these lines by partitioning the star in macroscopic volume elements that are of negligible size compared to the dimensions of the star itself (see exercise 18). The relevant “measurable” quantities are in that case the local particle densities and the local total energy density.

### 2.4.5 Summary

The differences between the three types of ensembles reside in the increasing degree of order that is imparted on the embedded systems by the contact with the reservoir. In the microcanonical case this contact is extremely weak. It is that weak that we could effectively speak of the absence of any contact, causing $E$ and $N$ to be effectively fixed. Thermal equilibrium is in that case equivalent with the absence of any order. In the canonical case energy transfer occurs between reservoir and embedded system, with the total energy being conserved. Since the reservoir has so many more degrees of freedom than the embedded system, in thermal equilibrium order is generated in the energy mix of the embedded system with a preference for lower energies (i.e. higher reservoir energies). In the grand canonical case we add to this the possibility of particle exchange, with the corresponding particle conservation law translating into extra order in the particle mix of the embedded open system. The three different types of ensembles give rise to identical physical results if the relative fluctuations around the equilibrium values $\bar{E}_{\text{tot}}$ and $\bar{N}$ are very small, causing the energy and number of particles of the embedded system to be effectively fixed. It is then a matter of choice which type of ensemble is more suitable for performing calculations (which in most cases will be the grand canonical ensemble). For instance this applies to systems consisting of a very large number of particles, in view of the extra factors $1/\sqrt{\bar{N}}$ that in general occur in the average relative fluctuations on the measurements.