Chapter 3

Foundations of Statistical Physics

3.1 Goals and methods of statistical physics

In thermodynamics it is *assumed* that the macroscopically observable state (= "thermodynamic state") of a system comprised of many particles (= "macroscopic system") can be described uniquely by a set of so-called state variables. The properties of thermodynamic states as well as thermodynamic state changes are characterized on very general grounds by the 3 laws of thermodynamics, which are established empirically (only postulates).

However, no attempt is made in thermodynamics

- to calculate the dependence of the macroscopic properties on the state variables for a given system. (e.g. the ideal gas law $p \cdot V = N k_B T$; dependence of p on T for $V = const.$ is only established empirically).
- or even to give expressions for the state variables themselves in terms of the microscopic variables ($\vec{x}_i, \vec{p}_i$ for each particle) of a system. (e.g. pressure p in terms of $\vec{p}_i, \quad i = 1, \ldots, N$).

Only general, but very powerful relations *among* the state variables and among the response functions could be derived.
It is characteristic for thermodynamics that no system-specific information enters.

The goal of statistical physics is to establish the link between the microscopic properties (Hamiltonian) of a system and the macroscopic description of thermodynamics, in detail:

- Definition of the state variables in terms of the microscopic coordinates or quantum numbers (straight forward e.g. for energy, pressure,... but difficult and essential for entropy)
- Justification of the structure of the phenomenological equations (laws of thermodynamics)
- Microscopic derivation of the macroscopic thermodynamical properties of given systems:
  - equations of state
  - phase transitions
  - response functions
- Microscopic calculation of the time-dependent behaviour: dynamics.

Systems in contact with external reservoirs or “heat baths” will be of special interest.

The essential tools of statistical physics are

- the theory of probability, stochastics and
- the microscopic equations of motion.

The entropy will establish the central link between microscopics and macroscopics.

3.2 Essentials of probability theory

We first introduce important definitions

- **(Random) Experiment (Zufallsexperiment):**
  Reproducible measurement procedure, where the result of each individual measurement can be random (i.e. different for each measurement).

  Example: throwing a dice.

- **Set of events (Ereignismenge), "event space":**
  Set of possible results x_i of a measurement, $i = 1, \dots, N_e$

  $$\mathbb{M} = \{\, x_i \,|\, i = 1, \dots, N_e \,\} \tag{3.1}$$

  (Example: Dice: $\mathbb{M} = \{1, 2, 3, 4, 5, 6\}$)

- **Random variable (Zufallsgröße):**
  Physical quantity Y, which depends in a *definite* way on the *random* result of a measurement, i.e. Y is a mapping

  $$Y: \quad x_i \longmapsto Y(x_i) \qquad\qquad i = 1, \dots, N_e. \tag{3.2}$$

  Example: gain of money when throwing dice 6.

- **Relative frequency of occurrence $h_M(x_i)$ (relative Häufigkeit):**
  Perform a random experiment M times. During these M experiments the event x_i occurs M_i times. Then:

  $$\text{relative frequency} \qquad h_M(x_i) = \frac{M_i}{M} \tag{3.3}$$

  Note: $h_M(x_i)$ is not a random variable, since it can be different for each set of M measurements.

- **Probability:**
  For a very large number of repetitions of the measurement, $M \to \infty$, the ratio $h_M(x_i) = \frac{M_i}{M}$ approaches a constant, i.e. reproducible value. It is called probability $W(x_i)$

  $$\boxed{W(x_i) = \lim_{M \to \infty} \frac{M_i}{M}} \tag{3.4}$$

(Follows from empirical law of large numbers, justified by central limit theorem → exercise.)

Simple properties of the probability:

- $W(x_i) \geq 0$ positivity
- $\sum\limits_i W(x_i) = \frac{\sum_i M_i}{M} = 1$ normalization
- $W(x_i) \leq 1$ boundedness

The probability $W(x_i)$ is, hence, a *definite* function ot the x_i for a given experiment. Therefore, $W(x_i)$ *is a random variable.* It is often called *probability distribution.*

- **Conditioned probability (bedingte Wahrscheinlichkeit):**
  In a random experiment, two variables x, y can be measured (note: $x \equiv y$ is included).

$$\begin{aligned} \text{Event spaces} \qquad \mathbb{M}_x &= \{\, x_i \,|\, i = 1, \ldots, N_{e,x} \,\} && (3.5) \\ \mathbb{M}_y &= \{\, y_i \,|\, i = 1, \ldots, N_{e,y} \,\} && (3.6) \end{aligned}$$

Conditioned probability $W(x_i|y_i)$
$W(x_i|y_i)$ = probability that result $x = x_i$ is obtained in one measurement, *if* result $y = y_j$ has already occured for sure:

$$W(x_i|y_i) = \frac{M(x_i, y_j)}{M_{y_j}} \tag{3.7}$$

with M_{y_j}: number of draws for y_j and $M(x_i, y_j)$ = number of events with x_i *and* y_i realized in M experiments.

Normalization:

$$\begin{aligned} \sum_i W(x_i|y_j) &= 1 \qquad \text{and} && (3.8) \\ \sum_j W(x_i|y_j) &= 1. && (3.9) \end{aligned}$$

The probability of finding results x_i *and* y_j in one measurement is

$$\boxed{\begin{aligned} W(x_i, y_j) &= W(x_i|y_j)W(y_j) \\ &= W(y_j|x_i)W(x_i) \end{aligned}} \tag{3.10}$$

(from definition of $W(x_i|y_j)$)

Normalization:

$$\sum_{i,j} W(x_i, y_j) = \underbrace{\left(\sum_i W(x_i|y_j)\right)}_{=1} \cdot \underbrace{\left(\sum_j W(y_j)\right)}_{=1} = 1 \tag{3.11}$$

The two variables x, y are called *statistically independent* if:

$$\boxed{W(x_i|y_j) = W(x_i)} \quad \text{(result } x_i \text{ independent of } y_i\text{)} \tag{3.12}$$

$$\Rightarrow \boxed{W(x_i, y_j) = W(x_i) \cdot W(y_j)} \quad \text{statistical independence} \tag{3.13}$$

3.3 Pure and mixed states: definition of thermodynamic averages and state variables

Intuitively, it is clear :

The macroscopic, thermodynamic state of a system, characterized by definite values of the state variables, can usually be realized by a large number of microscopic states of the system, defined by the microscopic coordinates.

Example: A given amount of gas with particle number N at p,V,T can be realized by realizations of the individual coordinates $\{(\vec{x_i}, \vec{p_i})|i = 1 \dots N\}$ of the particles.

This motivates the definitions:

- **Pure State** or **microstate** $|n\rangle_{\text{QM}}$ or $|(\vec{x_i}, \vec{p_i})\rangle_{\text{class}}$:
  Quantum mechanical (or classical state), defined uniquely by definite values of the set of quantum numbers (or classical coordinates) $\{n\}$.

- **Mixed (or statistical) state** u

  Set of pure states $|n\rangle$, each one occurring with a certain probability $W_u(n)$ in the set u.

  A mixed state is characterized by both:

  - microscopic states $|n\rangle$ and
  - probability $W_u(n)$ with which $|n\rangle$ occurs in the set u.

  Hence, a mixed state does not have a single quantum mechanical wave function, and *cannot* in particular be written as a (coherent) sum of microscopic states $|n\rangle$. It is rather a *set* of microstates.

- **Statistical (or thermodynamic) average**
  The value of a physical observable $\widehat{A}$ ascribed to a mixed state u is calculated as the weighted average of the quantum mechanical expectation values of $\widehat{A}$ in the states $|n\rangle$ which comprise the mixed state u:

$$\bar{A} \equiv \langle A \rangle = \sum_n W_u(n) \langle n|\widehat{A}|n\rangle \tag{3.14}$$

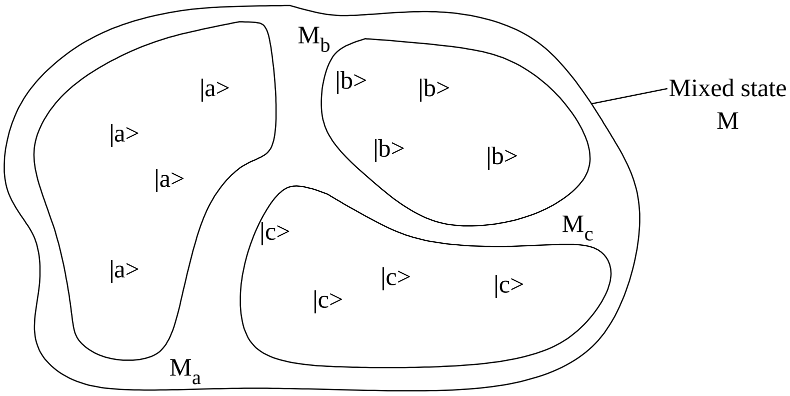

Figure 3.1: Mixed state

Example: $\widehat{A} = \widehat{H}$ =total energy of the system.
Note: $|n\rangle$ need not to be an energy eigenstate.

Of special importance is the case that u corresponds to an *equilibrium state* with certain constrain conditions, e.g. fixed energy, temperature, particle number etc. In this case, $\bar{A} \equiv \langle A \rangle$ is called thermodynamic average.
Below we will derive the probability distribution $W(n)$ corresponding to the equilibrium states. In order to formalize the concept of *equilibrium statistical average*, we first introduce the statistical ensemble.

- **A statistical ensemble (Statistische Gesamtheit)**
  A statistical ensemble is a set of N_G copies of a system, with $N_G \to \infty$, which all satisfy the same constraint conditions, e.g. fixed energy, particle number, etc.
  Among the N_G copies, a number $N_{G,n}$ systems occur in the microstate $|n\rangle$, $\sum_n N_{G,n} = N_G$. The probability that in the ensemble that system is in the state $|n\rangle$ is then

$$W_G(n) = \lim_{N_G \to \infty} \frac{N_{G,n}}{N_G} \tag{3.15}$$

Note: A mixed state can be viewed as a special case of an ensemble. However, the term ”ensemble” is usually used for the case that the constraint conditions correspond to fixing the values of certain but not all (equilibrium) state variables, e.g. energy E and particle number N, but pressure P and Volume V are still undetermined. The mixed state (set of microstates) which is obtained, when all variables are fixed, is called *thermodynamic state*, as defined in thermodynamics.

The ensemble is realized physically in the *thermodynamic limit* (Volume $V \to \infty$) of macroscopic systems, in that the system can be divided into N_G subsystems, where each subsystem is large enough to represent the whole system (in particular that state variables are well-defined for each subsystem) and is thus a copy of the system.

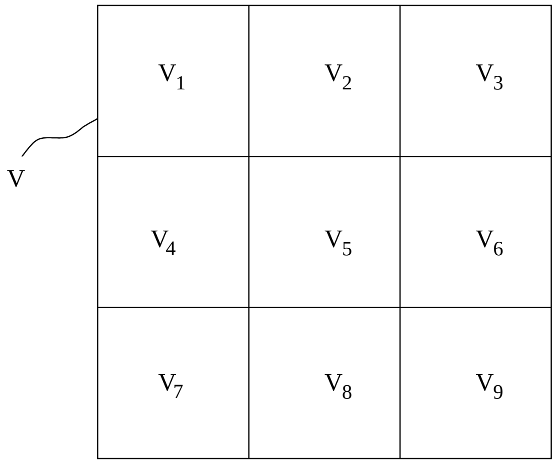

Figure 3.2: Visualization of a statistical ensemble

Deviations from the average values:

It will be shown explicitly that in a statistical ensemble in the thermodynamic limit the quadratic variations of a physical quantity $\widehat{A}$ about its average value $\langle A \rangle$ are small:

$$\langle (A - \langle A \rangle)^2 \rangle \ll \langle A \rangle^2 \quad , \tag{3.16}$$

where

$$\langle A \rangle = \sum_n W_G(n) \langle n | \widehat{A} | n \rangle. \tag{3.17}$$

Only if this condition is fulfilled it is meaningful to represent a physical quantity by its thermal average.

3.4 The entropy in Statistical Physics

In thermodynamics the entropy was introduced as a state variable associated with reversible heat exchange. The 2nd law of thermodynamics gave us an intuitive understanding that entropy is a measure of how "undetermined/disordered" a state is.

This concept will now be formulated mathematically. It will be shown that it is equivalent to the thermodynamic definition of entropy.

Observable quantities like energy, particle number, etc. are well defined for each microstate in an ensemble and therefore their values in a thermodynamic state (= state variables) can be calculated as the thermal averages defined above.

In contrast, the entropy is a measure of how undetermined a thermodynamic state is by fixing its macroscopic state variables, i.e. a measure of how many microstates realize one and the same thermodynamic macrostate. Thus, entropy cannot be defined for a single microstate (like energy) but must be a *functional* of the probability distribution $W(n)$ of microstates $|n\rangle$ in a macrostate u. In the following the subscript u is dropped.

Definition and basic properties of entropy:

The entropy S is a (real) *functional* of the probability *distribution* $W(n)$,

$$\begin{aligned} S: \quad & [0,1]^{N_e} \longrightarrow \mathbb{R} \\ & W(n) \longmapsto S\{W(n)\} \in \mathbb{R} \end{aligned} \tag{3.18}$$

which satisfies the following properties:

1. $S \geq 0$ and $S = 0$ for $W(n) = \delta_{n,n_0}$ ($\equiv$ 3rd law of thermodynamics)

2. S can be seen as a function of the N_e variables $W(1), \dots W(N_e)$: $S = S(W(1), \dots W(N_e))$. S is symmetrical in the $W(n)$.

3. S is an extensive variable.

For statistical independent events (i.e. microstates) e.g. microstates $|n_1\rangle, |n_2\rangle$ in different independent subvolumes V_1, V_2 of the complete system this means

$$S\{W(n_1, m_2)\} = S\{W(n_1)\} + S\{W(m_2)\}, \tag{3.19}$$

where $|n_1\rangle$ *and* $|n_2\rangle$ are realized and $W(n_1, m_2) = W(n_1) \cdot W(m_2)$.

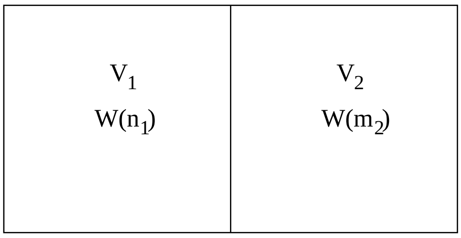

Figure 3.3: Two independent events

For the microstates which are not statistically independent we demand the more general relation

$$S\{W(n, m)\} = S\{W(n)\} + \sum_n W(n) \cdot S\{W(m|n)\} \tag{3.20}$$

where $S\{W(n)\}$ is the measure of probability for state $|n\rangle$, $\sum_n W(n)$ the weighted sum over all the measures $S\{W(m|n)\}$ for which $|m\rangle$ is realized and $S\{W(m|n)\}$ is the measure probability for state $|m\rangle$ under the condition that $|n\rangle$ is realized.

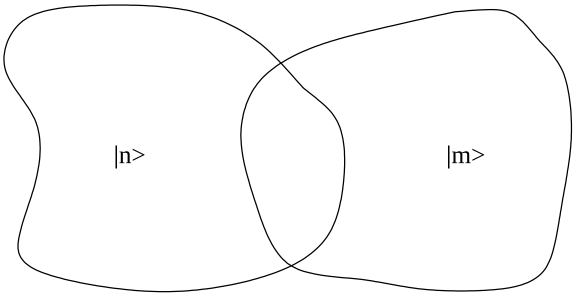

Figure 3.4: Two statistically dependent events

Condition (3.22) includes (3.21) trivially, since for independent states $W(m|n) = W(m)$ and $\sum_n W(n) = 1$. The conditions 1., 2. and equation (3.21) determine the functional $S\{W(n)\}$ essentially uniquely, as will be derived now.

We consider S as a function of the N_e variables $W(n), n = 1, ..., N_e$ and keep all the $W(n)$ with $n \geq 2$ fixed (without loss of generality).
The event $n = 1$ can be comprised of several subevents:

$$n = 1 \left\{ \begin{array}{llll} n = 1 & m = a & \text{with condition probability} & W(1) \cdot W(a|1) \\ n = 1 & m = b & \text{with condition probability} & W(1) \cdot W(b|1) \\ \vdots & \vdots & \vdots & \vdots \end{array} \right.$$

Thus, we have using (3.22):

$$\begin{aligned} S(\{W(1) \cdot W(m|1)\}, W(2), ..., W(N_e)) &= S(W(1), W(2), ..., W(N_e)) \\ &\quad + W(1) \cdot S\{W(m|1)\} \end{aligned} \tag{3.21}$$

Since the dependence holds for any of the variables $W(1), W(2), ...$, it is natural to assume

$$S\{W(n)\} = S(W(1), W(2), ...) = \sum_n f_n(W(n)) \tag{3.22}$$

$$\underset{\text{symmetry(2)}}{=} \sum_n f(W(n)) \tag{3.23}$$

where f is a universal function. This implies the functional equation for f:

$$\sum_m f(W(1) \cdot W(m|1)) = f(W(1)) + W(1) \sum_m f(W(m|1)) \tag{3.24}$$

Because of the dependence on the product in the argument of f we make the Ansatz:

$$f(x) = g(x) \cdot \ln(x) \quad \text{with } g(x) \text{ to be determined} \tag{3.25}$$

In (3.26):

$$\begin{aligned} & \sum_m g(W(1) \cdot W(m|1)) \cdot \ln(W(1) \cdot W(m|1)) & (3.26) \\ = \; & g(W(1)) \cdot \ln(W(1)) + W(1) \sum_m g(W(m|1)) \cdot \ln(W(m|1)) & (3.27) \end{aligned}$$

or

$$\begin{aligned} & \ln(W(1)) \cdot [\sum_m g(W(1) \cdot W(m|1)) - g(W(1))] & (3.28) \\ + \; & \sum_m \ln(W(m|1)) \cdot [g(W(1) \cdot W(m|1)) - W(1) \cdot g(W(m|1))] = 0 & (3.29) \end{aligned}$$

This is fulfilled for $g(x) \sim x$, since:

$$\underbrace{\sum_m W(1)W(m|1)}_{W(1)} - W(1) = 0 \qquad (1st\ [...]) \tag{3.30}$$

$$\sum_m \ln(W(m|1)) \cdot [W(1) \cdot W(m|1) - W(1) \cdot W(m|1)] = 0 \quad (2nd\ [...]) \tag{3.31}$$

It follows the general entropy functional:

$$\boxed{S\{W(n)\} = -k \sum_n W(n) \cdot \ln(W(n))} \tag{3.32}$$

Since $0 \leq W(n) \leq 1$, $\ln(W(n)) < 0$, the constant k must be $k > 0$.
As seen below in equilibrium, this definition is equivalent to the thermodynamic one, i.e. S has units $\left[\frac{E}{T}\right] = \frac{J}{K}$. Therefore we *choose*

$$\boxed{k = k_B = \text{Boltzmann constant} = 1{,}38 \cdot 10^{-23} \frac{J}{K}} \tag{3.33}$$

the value known from the ideal gas law.

Maximum of the entropy S:

For N_e different events n, S assumes its absolute maximum for the equidistribution (Gleichverteilung):

$$W_{max}(n) = \frac{1}{N_e} = \text{const.}(n) \quad \text{and hence} \quad S_{max} = k_B \cdot \ln N_e \tag{3.34}$$

Proof: Consider the difference, for any $S = S(W(n))$

$$\begin{aligned} S_{\text{max}} - S &= k_B \cdot \ln N_e + k_B \sum_n W(n) \cdot \ln W(n) && (3.35) \\ &= k_B \Big[\underbrace{\sum_n W(n)}_{=1} \cdot \ln N_e + \sum_n W(n) \cdot \ln W(n) && (3.36) \\ &\quad \underbrace{+ \sum_n \frac{1}{N_e} - 1}_{=0} \Big] \\ &= k_B \sum_n W(n) \cdot \left[\ln(N_e \cdot W(n)) + \frac{1}{N_e \cdot W(n)} - 1 \right] && (3.37) \end{aligned}$$

With $x := N_e \cdot W(n)$, and $-\ln x \leq \frac{1}{x} - 1, \; x > 0$ (square bracket) it follows

$$S_{\text{max}} \geq S. \tag{3.38}$$

$$S\{W(n) = \delta_{n,n_0}\} = 0 \tag{3.39}$$

Since S is a measure of the “undeterminedness” of a thermodynamic state, i.e. S increases with the number of microstates realizing a thermodynamic state, it is intuitively clear that on average a system (without external forces applied) makes transitions only from one thermodynamic state with fewer micro-realizations to a thermodynamic state with more or equal micro-realizations, since the latter is more probable. In the thermodynamic limit, variations around this behaviour vanish. Hence, the entropy does not decrease in any thermodynamical state change (2nd law).

However, a rigorous proof is still missing to date.

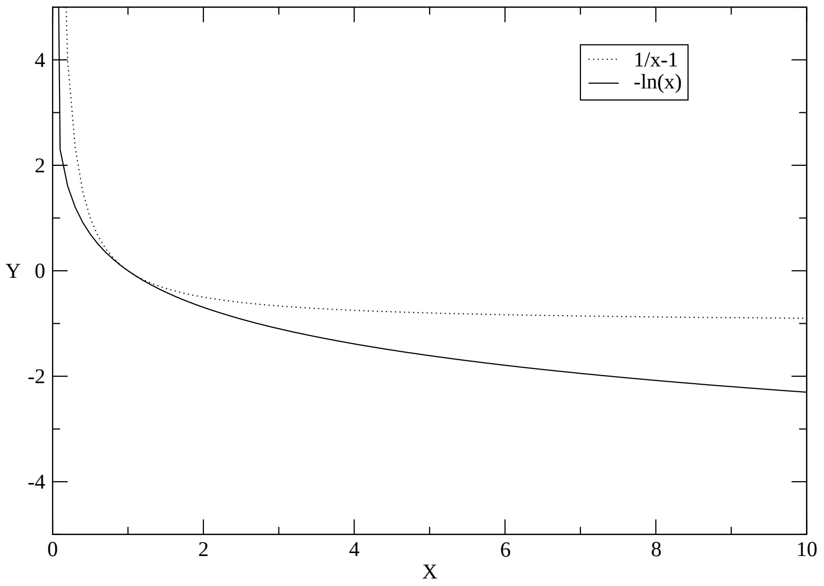

Figure 3.5: Maximum of the entropy S

3.4.1 Thermodynamic equilibrium for an isolated system: microcanonical ensemble

We now want to find the statistical ensembles for thermodynamic equlilibrium states. From the preceding consideration, this amounts to finding the probability distribution characterizing the ensemble, for which the entropy functional $S\{W(n)\}$ is maximal.

The maximization must be done under the constraint conditions applied from outside. If $W(n)$ in known, all thermodynamic quantities can be calculated from microscopics. We first consider an ensemble of completely isolated systems, i.e. all systems in the ensemble have exactly the same energy E.

The ensemble is called

Microcanonical ensemble:

Energy fixed exactly to $E_n = E$

$$W(n) = 0 \quad \text{for} \quad E_n \neq E \tag{3.40}$$

Hence, $S\{W(n)\}$ must be maximized with the constraint

$$\sum_n W(n) = \sum_n{}' W(n) = 1 \quad \text{where } E_n = E. \tag{3.41}$$

This task is performed by means of the method of the Lagrange multiplier (see appendix A):

$$\begin{aligned}
& \max\big[S\{W(n)\}\big]_{\sum' W(n)-1=0} && (3.42)\\
= & \max\left[-k_B{\sum_n}' W(n)\cdot\ln W(n)+\lambda\left({\sum_n}' W(n)-1\right)\right] && (3.43)\\
\equiv & \max\left[S\{W(n),\lambda\}\right] && (3.44)
\end{aligned}$$

The extremum conditions are

$$\begin{aligned}
\frac{\partial S_m}{\partial\lambda} = & \ 0 \ = {\sum_n}' W(n)-1 && (3.45)\\
\frac{\partial S_m}{\partial W(n)} = & \ 0 \ = -k_B\cdot\ln W(n)-k_B+\lambda, \quad n=1,2,... && (3.46)
\end{aligned}$$

The second set of equations determines the number $W(n)$ for each n and is independent of n. Therefore $W(n)$ is an equidistribution for $|n\rangle$ with $E_n = E$ and because of normalization

$$\boxed{W(n)=\begin{cases}\frac{1}{\Omega(E)}=\text{const.} & ,E_n=E\\ 0 & ,E_n\neq E\end{cases}} \quad \text{microcanonical ensemble} \quad (3.47)$$

where $\Omega(E)$ is the number of microstates $|n\rangle$ with energy E.
The entropy is then

$$\boxed{S_m(E)=k\cdot\ln\Omega(E)} \quad \begin{array}{l}\text{equilibrium entropy for}\\ \text{microcanonical ensemble}\end{array} \quad (3.48)$$

and depends only on the fixed energy.

3.4.2 Thermodynamical equilibrium for open systems with energy exchange

We now consider the ensemble of systems which are in contact with a heat bath, i.e. the temperature is fixed but there is energy exchange possible between the system and the bath. This fixes the average value of the energy of the system. This ensemble is called *canonical ensemble:* $\langle E\rangle$ fixed.

Note: In the statistical treatment we don't have defined the temperature T yet. This will be achieved below. For the following treatment we only need the condition $\langle E\rangle$ fixed.

$\langle E\rangle = U$ is identified with the internal energy of thermodynamics. We now maximize the entropy $S\{W(n)\}$ under the constraints normalization and fixed average value of energy:

$$\sum_n W(n) = 1 \tag{3.49}$$

$$\langle E\rangle = \sum_n E_n \cdot W(n) \tag{3.50}$$

$$= \sum_n \langle n|H|n\rangle \cdot W(n) \tag{3.51}$$

$$\tag{3.52}$$

$$\tag{3.53}$$

$$\max[S\{W(n)\}]\Big|_{\sum_n E_n\cdot W(n)=1} \equiv \max[S_c\{W(n),\lambda,\eta\}] \tag{3.54}$$

$$\equiv \max\Bigg[-k_B\sum_n W(n)\cdot\ln W(n) \tag{3.55}$$

$$+\lambda\left(\sum_n W(n)-1\right)$$

$$+\eta\left(\sum_n E_n\cdot W(n)-\langle E\rangle\right)\Bigg]$$

The extremum conditions are:

$$\frac{\partial S_c}{\partial\lambda} = 0 = \sum_n W(n)-1 \tag{3.56}$$

$$\frac{\partial S_c}{\partial\eta} = 0 = \sum_n E_n\cdot W(n)-\langle E\rangle \tag{3.57}$$

$$\frac{\partial S_c}{\partial W(n)} = 0 = -k_B\cdot\ln W(n)-k_B+\lambda-\eta E_n \tag{3.58}$$

$$\Rightarrow W(n) = e^{-1+\frac{\lambda}{k_B}-\frac{\eta E_n}{k_B}} = e^{-1+\frac{\lambda}{k_B}}\cdot e^{-\frac{\eta E_n}{k_B}} \tag{3.59}$$

The Lagrange multiplier λ is determined by the normalization, which can be written as

$$W_c(n) = \frac{1}{Z_c}\, e^{-\frac{\eta}{k_B}\, E_n} \tag{3.60}$$

with

$$Z_c := \sum_n e^{-\frac{\eta}{k_B}\, E_n}. \tag{3.61}$$

The parameter η is determined by $\sum_n E_n \cdot W(n) = \langle E \rangle$.
We redefine

$$\frac{\eta}{k_B} \equiv \beta \equiv \frac{1}{k_B \widetilde{T}}. \tag{3.62}$$

The new parameter $\widetilde{T}$ will now be identified with the temperature as defined in thermodynamics:

Connection of the statistical treatment with thermodynamics:
Consider a reversible state change with

$$\widetilde{T} \to \widetilde{T} + d\,\widetilde{T} \tag{3.63}$$

Change of energy due to change of distribution $d\,W_c(n)$:

$$d\langle E \rangle = \sum_n E_n \cdot d\,W_c(n) \tag{3.64}$$

Change of entropy:

$$dS = -k_B \sum_n \; [\ln W_c(n) + 1] \cdot d\,W_c(n) \tag{3.65}$$

$$= -k_B \sum_n \; \left[-\frac{E_n}{k_B \widetilde{T}} - \ln Z_c + 1 \right] \cdot d\,W_c(n) \tag{3.66}$$

From normalization of $W_c(n)$ before and after the state change it follows $\sum_n d\,W_c(n) = 0$, i.e.

$$dS = \frac{1}{\widetilde{\widetilde{T}}} \sum_n E_n \cdot d\,W_c(n) = \frac{1}{T}\, d\langle E \rangle \tag{3.67}$$

or

$$d\langle E\rangle = dU = \widetilde{T}dS \tag{3.68}$$

This relation is identical to the thermodynamic one if we identify the statistical equilibrium entropy of the canonical ensemble with the thermodynamic one and the parameter $\widetilde{T}$ with the temperature T.
We then have the final result for the probability distribution $W_c(n)$ characterizing the canonical ensemble

$$\boxed{\begin{array}{c} W_c(n) = \frac{1}{Z_c}\, e^{-\frac{E_n}{k_BT}} \\ Z_c = \sum_n e^{-\frac{E_n}{k_BT}} \end{array}} \quad \begin{array}{l} \text{Boltzmann distribution} \\ \text{Canonical partition sum} \end{array} \tag{3.69}$$

Remarks:

1. $W_c(n)$ is the probability that in the canonical ensemble ($\langle E\rangle$ fixed from outside) the microstate $|n\rangle$ is realized.
2. $W_c(n)$ depends only on the energy $|n\rangle$ for given temperature.
3. In the partition sum, the summation runs over all microscopic quantum states (not over the energy) with a fixed particle number N, but arbitrary energy.

Using the Boltzmann distribution, the free energy evaluated as

$$\begin{aligned} F &= U - TS = \langle E\rangle - TS && (3.70)\\ &= \sum_n E_n W_c(n) + k_BT \sum_n W_c(n) \ln\left(\frac{e^{-\frac{E_n}{k_BT}}}{Z_c}\right) && (3.71)\\ &= \sum_n E_n W_c(n) + k_BT \underbrace{\sum_n W_c(n)}_{=1}[-\underbrace{\ln Z_c}_{\text{independent of n}} - \frac{E_n}{k_BT}] && (3.72)\\ &= -k_BT \ln Z_c && (3.73) \end{aligned}$$

$$\boxed{F = -k_BT\ln Z_c} \quad \text{or} \quad \boxed{Z_c = e^{-\frac{F}{k_BT}}} \tag{3.74}$$

These equations, together with the identifications of the thermodynamic temperature $T \equiv \widetilde{T} = \frac{1}{\eta}$, constitute the connection between the microscopic theory and the macroscopic thermodynamic theory, because the partition sum Z_c can be calculated, if the energy eigenvalues E_n are known from a microscopic theory, and the equilibrium free energy F allows to calculate any thermodynamic quantity as a thermodynamic derivative.
Z_c depends explicitly on T through the Boltzmann factor (T-dependent average occupation of the eigenstates with energies E_n) and depends on other thermodynamic variables like volume V, particle number N etc. through the dependence of E_n on V, N. For this reason, Z_c is often called "partition function". Knowledge of $Z_c(T, V, N, \ldots)$ allows to calculate the complete thermodynamics of a system. Several examples will be considered later. In an exercise it is shown that in the thermodynamic limit $N \to \infty$ the energy fluctuations per particle vanish: $\langle (E - \langle E \rangle)^2 \rangle / N \to 0$. This proves that the microcanonical and the canonical ensemble are equivalent.

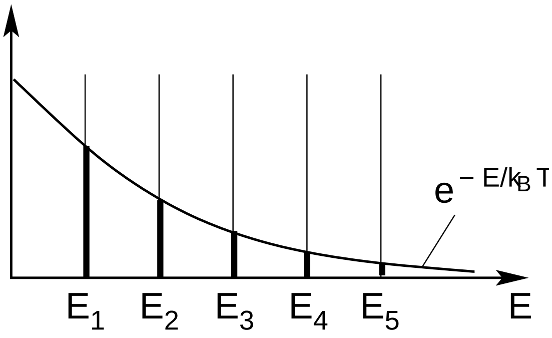

Figure 3.6: Thermal occupation of the energy levels, assuming that the objects (particles, spins etc.) are distinguishable.

Stability properties of thermodynamic response functions

1. **Specific heat:** $c_V \geq 0$
   (The energy content cannot decrease with increasing temperature.)

Proof:

$$c_V = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_V = \frac{\partial}{\partial T}\sum_n E_n \frac{e^{-\frac{E_n}{k_BT}}}{Z_c} \tag{3.75}$$

$$= \frac{1}{k_BT^2}\sum_n (E_n^2 - E_n\langle E\rangle)\frac{e^{-\frac{E_n}{k_BT}}}{Z_c} \tag{3.76}$$

Using

$$\frac{\partial}{\partial T}\frac{1}{Z_c} = -\frac{1}{Z_c^2}\sum_n \frac{+E_n}{k_BT^2}e^{-\frac{E_n}{k_BT}} \tag{3.77}$$

$$= -\frac{1}{k_BT^2}\frac{\langle E\rangle}{Z_c} \tag{3.78}$$

one obtains

$$c_V = \frac{1}{k_BT^2}(\langle E^2\rangle - \langle E\rangle^2) \tag{3.79}$$

$$= \frac{1}{k_BT^2}\langle (E-\langle E\rangle)^2\rangle \geq 0. \tag{3.80}$$

2. **Compressibility:** $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left[\left(\frac{\partial p}{\partial V}\right)^{-1}\right]_T \geq 0$

Proof:
The pressure is calculated microscopically as

$$p = -\left(\frac{\partial\langle E\rangle}{\partial V}\right)_{T,N} = -\frac{\partial}{\partial V}\sum_n E_n W_c(n) \tag{3.81}$$

with $\langle E\rangle \equiv U$ and $W_c(n) = e^{-\frac{E_n}{k_BT}}/Z_c$. I.e. the pressure arises because of the volume dependence of the energy eigenvalues of the system: $E_n \sim \frac{1}{V}$; assume $E_n \geq 0$ without loss of generality. Then

$$p = -\sum_n \left[\underbrace{\frac{\partial E_n}{\partial V}}_{\sim -\frac{1}{V^2}<0} W_c(n) + E_n \underbrace{\frac{\partial W_c(n)}{\partial V}}_{<0}\right] \geq 0 \tag{3.82}$$

$$\kappa_T = \frac{1}{V}\sum_n \frac{\partial^2 E_n}{\partial V^2}W_c(n) + 2\left(\frac{\partial E_n}{\partial V}\right)\frac{\partial W_c(n)}{\partial V} \tag{3.83}$$

$$+E_n\frac{\partial^2 W_c(n)}{\partial V^2} \geq 0 \tag{3.84}$$

3.4.3 Thermodynamical equilibrium for open systems with energy and particle exchange

Often, a system is in contact with a reservoir with energy and particle exchange.

Example: Electrons in a wire connected to a battery.

In this case, only the average energy and the average particle number are fixed:

$$\begin{aligned} \sum_n W(n) &= 1 && (3.85)\\ \langle E\rangle &\equiv U = \sum_n E_n W(n) = const. && (3.86)\\ \langle N\rangle &= \sum_n N_n W(n) = const. && (3.87) \end{aligned}$$

The summation extends over all eigenstates $|n\rangle$ of the system with arbitrary particle number $N_n = 1, 2, 3, \ldots, \infty$.
The ensemble of systems with fixed $\langle E\rangle$ and $\langle N\rangle$ is called *grand canonical ensemble.* To find the probability distribution of the grand canonical ensemble, we maximize the entropy with these constraints:

$$\begin{aligned} S_G\{W(n), \lambda, \eta, \xi\} &= \sum_n \big[-k_B W(n) \ln W(n) + \lambda W(n) && (3.88)\\ &\quad -\eta E_N W(n) + \xi N_n W(n)\big] - \lambda + \eta\langle E\rangle - \xi\langle N\rangle \\ \frac{\partial S_G}{\partial \lambda} &= \sum_n W(n) - 1 = 0 && (3.89)\\ \frac{\partial S_G}{\partial \eta} &= \sum_n E_n W(n) - \langle E\rangle = 0 && (3.90)\\ \frac{\partial S_G}{\partial \xi} &= \sum_n N_n W(n) - \langle N\rangle = 0 && (3.91)\\ \frac{\partial S_G}{\partial W(n)} &= -k_B \ln W(n) - k_B + \lambda - \eta E_n + \xi N_n = 0 && (3.92)\\ \Rightarrow\ W_G(n) &= \frac{1}{Z_G} e^{-\frac{\eta E_n - \xi N_n}{k_B}} && (3.93) \end{aligned}$$

where the prefactor $\exp\left(1-\frac{\lambda}{k_B}\right)$ is fixed such that $W_G(n)$ is normalized, i.e.:

$$\boxed{Z_G = \sum_n e^{-\frac{\eta E_n - \xi N_n}{k_B}}} \quad \text{grand canonical partition sum} \tag{3.94}$$

The parameters $\frac{\eta}{k_B} \equiv \beta \equiv \frac{1}{k_B\widetilde{T}}$ and $\frac{\xi}{k_B} \equiv \frac{\widetilde{\mu}}{k_B\widetilde{T}}$ are determined in analogy to the canonical case:

Connection of the grand canonical ensemble with thermodynamics:
Reversible state exchange with $\widetilde{T} \to \widetilde{T} + d\widetilde{T}$ and $\widetilde{\mu} \to \widetilde{\mu} + d\widetilde{\mu}$, leaving dynamics, i.e. E_n, unchanged:

Change of energy:

$$d\langle E\rangle = \sum_n E_n dW_G(n) \tag{3.95}$$

Change of entropy:

$$\begin{aligned} dS &= -k_B \sum_n [\ln W_G(n) + 1] dW_G(n) && (3.96)\\ &= -k_B \sum_n [-\frac{E_n}{k_B\widetilde{T}} + \frac{\widetilde{\mu}}{k_B\widetilde{T}} N_n - \ln Z_G + 1] dW_G(n) && (3.97)\\ \sum_n dW_G(n) &= 0 && (3.98) \end{aligned}$$

It follows

$$\sum_n E_n dW_G(n) \equiv d\langle E\rangle = \widetilde{T} dS + \widetilde{\mu} d\langle N\rangle \tag{3.99}$$

i.e. the identification $\widetilde{T} = T$ the temperature and $\widetilde{\mu} = \mu$ the chemical potential.

Note: The prefactor k_B of $S\{W\}$ is up to now still arbitrary. It will be fixed later when calculating S for the ideal classical gas, which was used to define the temperature scale, and in the course of this the value of the Boltzmann constant.

$$\boxed{\begin{array}{lcl} W_G(n) & = & \frac{1}{Z_G} e^{-\frac{E_n - \mu N_n}{k_B T}} \\ Z_G & = & \sum_n e^{-\frac{E_n - \mu N_n}{k_B T}} \end{array}} \quad \begin{array}{l} \text{grand canonical distribution} \\ \text{grand canonical partition sum} \end{array} \tag{3.100}$$

The sum runs over all particle numbers N and all eigenstates $|n\rangle$ for given particle number N.
The grand canonical potential is given as follows:

$$\begin{aligned} \Omega &= \langle E \rangle - TS - \mu N && (3.101) \\ &= \sum_n W_G(n)[E_n - \mu N_n + k_B T \underbrace{\ln W_G(n)}_{-\ln Z_G - \frac{E_n}{k_B T} + \frac{\mu N_n}{k_B T}}] && (3.102) \\ &= -k_B T \ln Z_G && (3.103) \end{aligned}$$

$$\boxed{\begin{array}{lcl} \Omega & = & -k_B T \ln Z_G \\ Z_G & = & e^{-\frac{\Omega}{k_B T}} \end{array}} \quad \begin{array}{l} \text{grand canonical potential} \\ \text{grand canonical partition sum} \end{array} \tag{3.104}$$

The grand canonical ensemble automatically includes the thermodynamical limit $N \to \infty$, since infinite summation over n. As in the canonical case, it can be shown that in the thermodynamical limit the fluctuations vanish:

$$\frac{\sqrt{\langle (N - \langle N \rangle)^2 \rangle}}{\langle N \rangle} \overset{N\to\infty}{\longrightarrow} 0 \tag{3.105}$$

$$\frac{\sqrt{\langle (E - \langle E \rangle)^2 \rangle}}{\langle N \rangle} \overset{N\to\infty}{\longrightarrow} 0 \tag{3.106}$$

i.e. the microcanonical, canonical and grand canonical ensembles are equivalent. We have the correspondence:

ensemble	thermodyn. potential	externally fixed variable
microcanonical	$U = E = const.$	S, N
canonical	$F = \langle E \rangle - TS$	T, N and E fixed on average only
grand canonical	$\Omega = \langle E \rangle - TS - \mu N$	T, μ and E, N fixed on average only

Remark: It is often useful for calculated many-particle systems to calculate in the grand canonical ensemble, since the states are more easily enumerated without fixing the total number of particles. This will be seen explicitly for fermions and bosons, where the statistics imposes restrictions on the occupation of single particle states.