

# Theoretical Physics IV

## Thermodynamics and Statistical Physics

Prof. Dr. Johann Kroha

University of Bonn

TEXed by

Katinka Ballmann, Sebastian Mai, Anja Marold and Cornelia Monzel



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# Chapter 1

## Introduction and overview

Up to now, during the course of theoretical physics the motion of a single particle (or, at best, a few particles) under the influence of external fields has been considered, first classically, then quantum mechanically. We had seen that, when relativistic motion and quantum mechanics are combined, the sheer concept of single-particle dynamics breaks down, because of the possibility of particle-antiparticle pair generation in an interacting system at sufficiently high energies. The relativistic quantum theory becomes necessarily a theory of many particles (i.e. a field theory). While in relativistic quantum theory the many-particle aspect came, at first glance, as a necessary, but "unwanted" accident, there are many systems in the world around us, which consist naturally of a huge number of Particles.

Examples are

- atoms or molecules in a gas, liquid or solid
- electrons in a metal
- magnetic moments in a ferromagnet
- atomic nuclei and electrons in a plasma (star)
- photons in a laser
- cars on a highway
- individuals in a biological population ...

It is seen that there is a vast variety of many-particle systems with various types of interactions between the particles. Characteristic for all many-particle systems is their huge number of degrees of freedom, typically  $\approx 10^{23}$  (coordinates and momenta of each particle).

It is *neither possible nor desirable* to describe the dynamics of all microscopic degrees of freedom in a many-particle system. The latter holds for two important reasons:

1. Even knowledge of *all microscopic* degrees of freedom would not allow us easily to describe the *macroscopic* behavior of a system, which is observed in experiments and which is relevant for practical applications.

**Example:**

Knowing  $(\vec{x}, \vec{p})$  for all atoms in a gas does not immediately tell us its temperature  $T$  and pressure  $P$ . Calculating  $T$ ,  $P$  would be beyond any computer's memory.

2. Many-particle systems often show *collective behavior ordering phenomena, phase transitions* on the macroscopic level, which could not even principally be deduced from the microscopic coordinates.

**Examples:**

Superconductivity, magnetic and other phase transitions, collective modes (waves in water etc.), fractional quantum Hall effect: fractional excitation.

Thus, the microscopic description breaks down on a more fundamental than merely computational level:

"The whole is more than the sum of its parts."

On the macroscopic level fundamentally new complexity arises, which cannot be seen on the microscopic level.

It is the task of thermodynamics and statistics to develop methods for describing (complex) macroscopic systems consisting of many degrees of freedom. This proceeds in three major logical steps:



- |   |   |                     |
|---|---|---------------------|
| 1. Identify and define relevant macroscopic variables to describe a system:<br>state variables: $T, P, V, N, E, S$  | } | thermodynamics      |
| 2. Provide rules for the dependence of the state variables upon each other  |   |                     |
| 3. Develop methods to calculate the state variables and their mutual dependence from their microscopic Hamiltonian. $\rightarrow$ Statistical methods required, because of vast number of degrees of freedom. | } | statistical physics |
|   |   |                     |

Link between microscopics and macroscopic behavior.

### Thermodynamics

has been developed during the second half of the 19th century and is a closed field of research now. It is a phenomenological theory where the state variables, like temperature  $T$ , entropy  $S$  etc., are defined in an implicit way through their relation to other variables. This often leaves the impression of thermodynamics being incomplete. However, it is the nature of a phenomenological theory, that only implicit definitions are possible. The mathematical structure of thermodynamics is that of the theory of analytical functions of multiple variables. The state variables are defined as derivatives of a given analytical function (potential) and are, thus, related to each other purely on mathematical grounds, not through physical interactions.

Thermodynamics has been the basis for the development of engines like the steam engine etc., which revolutionized industry in the 19th and early 20th century. One of its pioneers was Clausius who was the head of the Bonn physics institute.

### Statistical physics

provides the microscopic basis and methods for the definitions and relations of thermodynamics. It thus allows to calculate macroscopic quantities from a microscopic approach, not only in relation to each other.

Statistical physics is now one of the big active fields of research and is applied to many different systems ranging from many-body quantum systems (superconductivity, laser ...) to biological systems and populations and to the stock market.



# Chapter 2

## Thermodynamics

### 2.1 Description of thermodynamic states and transformations

### 2.2 Introductory remarks and basic definitions

Thermodynamics is a phenomenological theory in contrast to the microscopic theories considered so far, i.e. it does not refer to the microscopic, quantum mechanical behavior of matter, but is based on the observation of the macroscopic properties of "large" systems and the relations among these properties, where "large" requires further specification.

As a result, thermodynamics cannot make absolute statements derived from microscopics, but can only describe the dependence of macroscopic properties on each other. Any definition of a new quantity not known outside of thermodynamics, like temperature  $T$ , entropy  $S$ , must therefore be *implicit* through these dependencies. This leaves some sense of "incompleteness" , like in any phenomenological theory.

On the other hand, because it does not rely on detailed microscopic properties or assumptions, thermodynamics is completely *general* and closed in itself. It is the strength of thermodynamics that it is applicable to a *vast variety of systems*.

### Einstein about thermodynamics

"Eine Theorie ist desto eindrucksvoller, je größer die Einfachheit ihrer Prämissen ist, je verschiedenartigere Dinge sie verknüpft und je weiter ihr Anwendungsbereich ist. Deshalb der tiefe Eindruck, den die klassische Thermodynamik auf mich machte. Es ist die einzige physikalische Theorie allgemeinen Inhalts, von der ich überzeugt bin, dass sie im Rahmen der Anwendbarkeit ihrer Grundbegriffe niemals umgestoßen werden wird."

Thermodynamics has been developed during the 19th century, driven by the need to understand thermodynamic cyclic processes and to develop heat engines that were able to transform heat into mechanical work. Therefore, the central definitions of thermodynamics have an operational character, i.e. are derived from cyclic processes.

Thermodynamics is based on our every-day observation that most macroscopic systems, when left to themselves, reach after a sufficiently long time a steady state, in which the macroscopically observable quantities don't change in time. These states are called "*equilibrium states*". In the present course we will consider only thermodynamic equilibrium states and transitions between them. The statements made above can be quantified by the following basic definitions:

- *Thermodynamic system*: Any macroscopic system consisting of  $N$  equal entities (e.g. particles, magnetic moments (spin)...) with  $\sqrt{N} \gg 1$ . (See statistical mechanics for the relevance of the square root.)
- A *thermodynamical state* is a state of the system which is completely determined by a set of macroscopic *thermodynamic state variables*.
- A *state variable*  $X$  is a physical quantity characterized by the fact that a thermodynamic state is uniquely determined by specifying the value of  $X$  and it *does not depend on the history* by which this state has been reached.

**In other words:** If the thermodynamic state of a system is changed, the amount by which a state variable changes is independent of the path in parameter space taken for this change. For a non-state variable the change will, in general, depend on the the path. This distinguishes state variables from non-state variables.

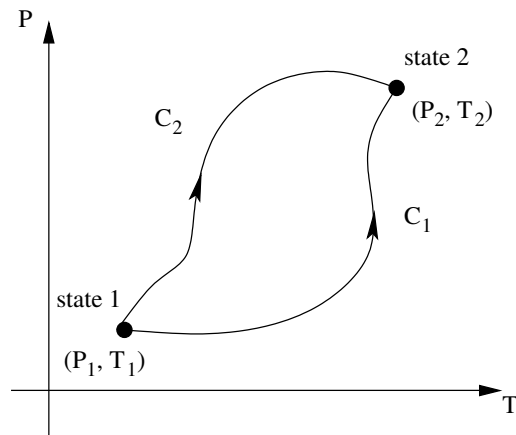


Figure 2.1: A gas undergoing temperature, volume and pressure change

### Examples:

- pressure  $p$
- volume  $V$
- temperature  $T$
- particle number  $N$
- chemical potential  $\mu$  (defined later)
- magnetic field  $\vec{B}$
- magnetization  $\vec{\mu}$
- electric field  $\vec{E}$
- electric polarization  $\vec{P}$

are *state variables*, but "heat"  $Q$  is not a state variable.

- One distinguishes intensive and extensive quantities:

- *intensive*:

volume  $V \rightarrow \alpha V : \quad x(\alpha V) = x(V)$

$x$  is invariant under scaling of the system volume

- *extensive*:

volume  $V \rightarrow \alpha V : \quad x(\alpha V) = \alpha x(V)$

$x$  scales with the system volume

- *Thermodynamic equilibrium:*

State in which the state variables do not change with time.

- The functional relation between all the (relevant) state variables in equilibrium is called *equation of state*:  $f(P, V, N, T) = 0$

E.g. for the ideal gas:

$$\boxed{pV = Nk_B T} \quad (2.1)$$

Equations of state will be considered in more detail later.

### Thermodynamic changes of state:

1. *quasistatic:*

slow change, so that the system remains (nearly) in equilibrium during the change for each momentary set of state variables.

2. *reversible:*

system returns to its initial state upon time reversal (i.e. by running all processes as under reversed time). Entropy change  $\Delta S = 0$ , see below.

3. *irreversible:*

system does not return to its initial state upon time reversal,  $\Delta S > 0$ .

4. *isothermal:*

$$\Delta T = 0 \quad (2.2)$$

5. *adiabatical:*

$$\Delta Q = 0 \quad (2.3)$$

process without heat exchange

6. *isobar:*

$$\Delta P = 0 \quad (2.4)$$

7. *isochor*:

$$\Delta V = 0 \quad (2.5)$$

- A heat bath is a system (heat reservoir) which is large compared to the system under consideration, and which is kept at constant temperature  $T$ .

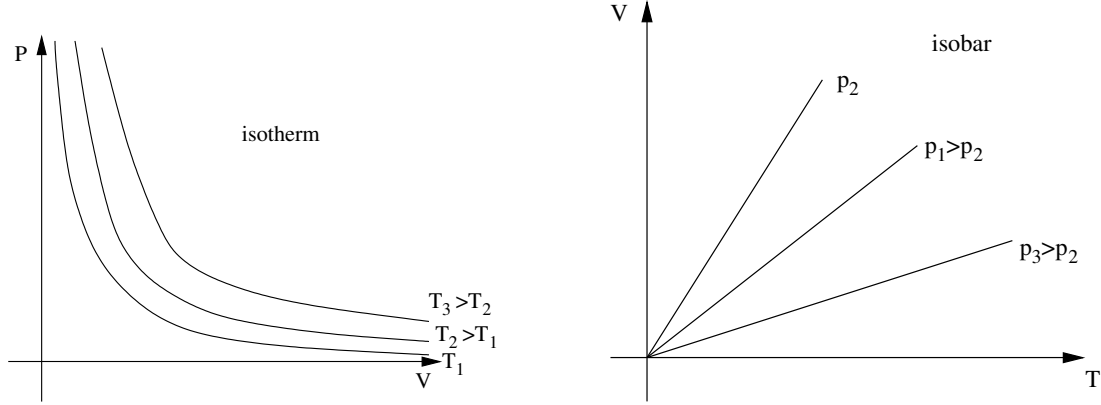


Figure 2.2: Examples for a change of state of an ideal gas

**Note:** These examples preclude the quantity  $T$  which will be defined only below.

## 2.3 State variables and exact differentials

The definition of a state variable (independence of path) can be put in mathematical terms:

Let  $F(x_1, \dots, x_n)$  be a function of the variables  $x_1, \dots, x_n$ . The differential of  $F$  is

$$dF = \sum_{i=1}^n \left( \frac{\partial F}{\partial x_i} \right)_{\{x_j \neq i\}} dx_i \quad (2.6)$$

Partial derivative of  $F$  with respect to  $x_i$ , keeping all  $x_j, j \neq i$ , fixed.

If the  $\{x_i\}$  are state variables, then the partial derivatives commute:

$$\left[ \frac{\partial}{\partial x_k} \left( \frac{\partial F}{\partial x_i} \right)_{\{x_j \neq i\}} \right]_{\{x_l \neq k\}} = \left[ \frac{\partial}{\partial x_i} \left( \frac{\partial F}{\partial x_k} \right)_{\{x_l \neq k\}} \right]_{\{x_j \neq i\}}, \quad i, k = 1, \dots, n \quad (2.7)$$

$$\left[ \text{For 2 variables: } \left[ \frac{\partial}{\partial x_2} \left( \frac{\partial F}{\partial x_1} \right)_{x_2} \right]_{x_1} = \left[ \frac{\partial}{\partial x_1} \left( \frac{\partial F}{\partial x_2} \right)_{x_1} \right]_{x_2} \right]$$

For a non-state variable the partial derivatives do not commute in general.

If the partial derivatives commute 2.7, then  $dF$  (equation 2.6) is called *exact differential*.

**Macroscopic consequence of commuting partial derivatives:**

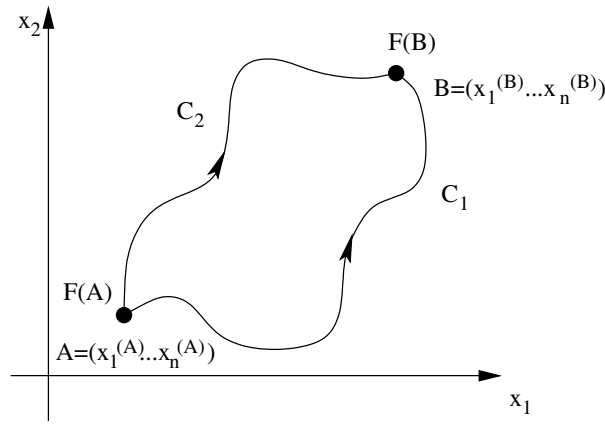


Figure 2.3: Independence of a thermodynamic state change on the path taken

Independence of the path taken:

$$F(B) - F(A) = \int_A^B dF = \int_{C_1} \left[ \sum_{i=1}^n \left( \frac{\partial F}{\partial x_i} \right)_{\{x_j \neq i\}} dx_i \right] \quad (2.8)$$

$$= \int_{C_2} \left[ \sum_{i=1}^n \left( \frac{\partial F}{\partial x_i} \right)_{\{x_i \neq j\}} dx_i \right] \quad (2.9)$$

The property that the differentials of all state variables are *exact* implies interesting relations between the state variables for a path for which  $F(x_1, \dots, x_n) = 0$ , which are purely founded in this mathematical structure, and which are therefore very general.



Let  $x, y, z, w$  be state variables,  $F(x, y, z, w) = 0$ .

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \quad (2.10)$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (2.11)$$

$$\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial w}\right)_z \quad (2.12)$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z \quad (2.13)$$

**Proof of 2.10 and 2.11:**

$$F(x, y, z) = 0 \quad (2.14)$$

$$x = x(y, z), \quad y = y(x, z) \quad (2.15)$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad (*) \quad (2.16)$$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \quad \text{in } (*): \quad (2.17)$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y \right] dz \quad (2.18)$$

varying  $x, z$  independently:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \quad (2.19)$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (2.20)$$

Although these relations follow trivially from any function of multiple variables with exact differential, they imply useful relations between the state variables which can be used in describing state changes.

### Summary of thermodynamic concepts

- Thermodynamical (equilibrium) state:

Stationary state of a system with many degrees of freedom (particles, spins, ...) which is reached after sufficiently long time, if there is no external action on the system. (Only equilibrium states considered here.)

- State variable:

Physical quantity which has a *unique* value for a given thermodynamic state. A complete set of state variables determines a thermodynamic state uniquely.

- State equation:

$$F(p, V, N, T, \dots) = 0 \quad (2.21)$$

Relation between state variables for a given system.

- Mathematical characterization of state variables  $X, Y$

Partial derivatives of  $F$  wrt.  $X, Y$  commute,

$$\left[ \frac{\partial}{\partial Y} \left( \frac{\partial F}{\partial X} \right) \right]_Y = \left[ \frac{\partial}{\partial X} \left( \frac{\partial F}{\partial Y} \right) \right]_X \quad (2.22)$$

for any pair  $X, Y$ , i.e.  $F$  has an *exact* differential wrt.  $X, Y$ :

$$dF = \left( \frac{\partial F}{\partial X} \right)_Y dX + \left( \frac{\partial F}{\partial Y} \right)_X dY \quad (2.23)$$

This implies that the values of  $X, Y$  in a thermodynamic state  $A$  is independent of the path by which  $A$  has been reached.

## 2.4 The fundamental laws of thermodynamics

### 2.4.1 The first law: energy conservation

In any change of state the change of the total energy of a system (=internal energy  $U$ ) is equal to the energy added to the system, minus the energy extracted.

We express the change  $dU$  during an infinitesimal state change in terms of the changes of the *extensive* variables:

- Mechanical work done by the system:

$$-dW = -\vec{F} \cdot d\vec{x} = -\frac{F}{A} \cdot (A dx) = -p dV \quad (2.24)$$

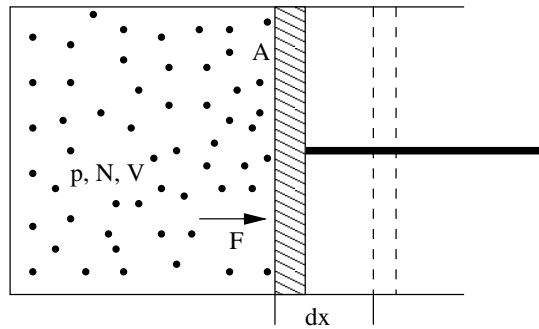


Figure 2.4: Mechanical work

- Change of energy due to increase of particle number:

$$\begin{aligned} \mu dN \quad \mu &= \text{chemical potential} \\ &= \text{change of energy due to adding one particle} \end{aligned} \quad (2.25)$$

- Heat is a form of energy (undirected motion of particles).

$$\begin{aligned} dQ \quad Q &\text{ is extensive, but not a state variable,} \\ &\text{ as will be seen below} \end{aligned} \quad (2.26)$$

The energy conservation is then written in terms of the extensive variables (infinitesimal state change):

$$\boxed{dU = dQ - p dV + \mu dN} + (\text{possibly other variables}) \quad (2.27)$$

For an infinitesimal state change, the law of energy conservation is then written in terms of the *extensive* variables as

$$\boxed{dU = dQ - p dV + \mu dN} \quad (2.28)$$

1st law of thermodynamics.  $U$  is state variable.

### 2.4.2 The second law of thermodynamics: Heat and the state variables temperature $T$ and entropy $S$

We have an intuitive concept of "hot" and "cold", which is a *unique* property of a thermodynamic state, i.e. corresponds to a state variable.

It is clear that "heat", as an amount of energy, is *not* a state variable, because we can add a given amount of heat energy (e.g. by burning a fixed amount of gasoline) to a cold body as well as to a hot body. This means that heat does not characterize the state of a system uniquely.

Therefore, we need to look for a different state variable quantifying the property "hot" or "cold". This leads to the quantity temperature  $T$  and at the same time to the concept of the state variable entropy  $S$ .

The definition of  $T$  is (and has to be !) operational, i.e. through the dependence of other state variables on  $T$ .

#### Basic statement for the definition of temperature:

Two thermodynamic systems which are in heat contract (i.e. can freely exchange heat) are at the same temperature (after sufficiently long time). This means that temperature can be defined for a specific, conveniently chosen system. The temperature of any system can then be determined by comparison (heat contract) with the reference system. This is the basis for any thermometer.

**(a) The ideal gas thermometer (ideal gas  $T$  scale)**

The equation of state for an ideal gas (sufficiently dilute so that atomic interactions are negligible) is known experimentally:

$$p = \frac{\alpha(N, T)}{V} \quad (2.29)$$

where the proportionality constant  $\alpha$  depends on the particle number  $N$  of the gas,

$$\alpha \sim N \quad (2.30)$$

and on the property how "hot" the gas is. The hotter the gas, the bigger  $\alpha$ .

We *define* the temperature  $T$  through the simplest possible, monotonically increasing dependence of  $\alpha$  on  $T$ .

$$\alpha \sim T \quad (2.31)$$

We then have

$$\alpha = Nk_B T \quad (2.32)$$

and the ideal gas law

$$pV = Nk_B T. \quad (2.33)$$

The universal proportionality constant  $k_B$  has units [energy/temperature] and is called Boltzmann constant.

The ideal gas law implies that there is an absolute zero point of  $T$ , since  $pV \geq 0$ .

The numerical value of  $k_B$  depends on the scale chosen for the temperature  $T$ .

**Convention:**

The temperature interval between the freezing and the boiling point of water at atmospheric pressure corresponds to 100 degrees Kelvin, 100K (**Kelvin scale**).

In these units the freezing point of  $H_2O$  is at 273,15K, and  $k_B$  takes the value:

$k_B = 1,38 \cdot 10^{-23} \frac{J}{K}$	Boltzmann constant	(2.34)
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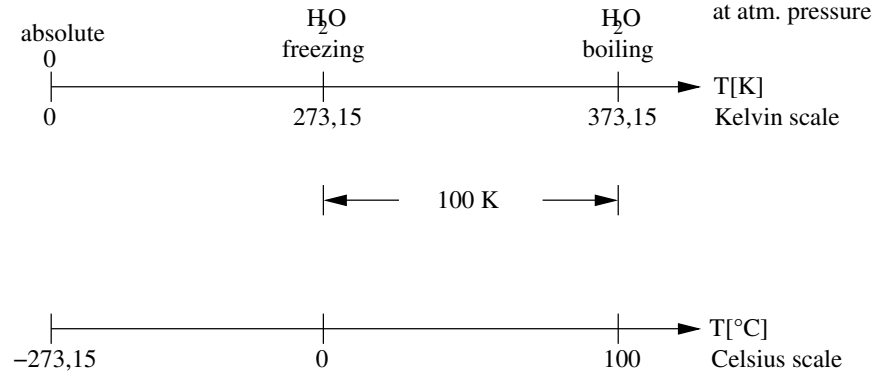


Figure 2.5: Temperature scales

The conventions

$$\left. \begin{array}{l} - \alpha \sim T, \text{ i.e. } T_0 = 0 \text{ and} \\ - T_{\text{boil}} - T_{\text{freeze}} = 100K \end{array} \right\} \text{Kelvin scale}$$

determine the temperature  $T$  uniquely as a state variable and give a prescription how to measure it via the ideal gas law.

**Celsius scale:**

$$T_{\text{boil}}^{\text{Celsius}} - T_{\text{freeze}}^{\text{Celsius}} = 100\,C \quad (2.35)$$

$$T_{\text{freeze}}^{\text{Celsius}} = 0\,C \quad (2.36)$$

$$(T_0^{\text{Celsius}} = -273,15\,C \text{ and } \alpha = T^{\text{Celsius}} + 273.15\,C)$$

For convenience, we will use the Kelvin scale only.

**(b) The second law of thermodynamics**

Through numerous observations of processes in nature it has been established empirically:

There does not exist any thermodynamic change of state, whose *only* consequence is that

- (1) an amount of heat is taken from a heat reservoir and is completely transferred into mechanical work, or
- (2) an amount of heat is taken from a colder heat reservoir and given to a warmer heat reservoir.

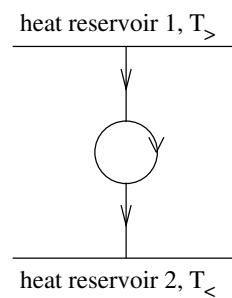


Figure 2.6: A heat engine working between two heat reservoirs 1, 2

For the further considerations we define:

A **Thermodynamic or heat engine** is a cyclic process, where

- (1) a working system takes up an amount of heat  $Q_>$  from a heat reservoir at  $T_>$ ,
- (2) gives an amount of heat  $Q_<$  to another heat reservoir at  $T_<$ , and
- (3) performs the mechanical work  $\Delta W > 0$ .

**(c) The Carnot definition of temperature  $T$  and entropy  $S$** 

Another definition of temperature is given via the so-called Carnot cycle. It is of physical conceptual use, since it involves explicitly the heat transfer, and hence the concept of state variables or non-state variables.

It is also of historical importance, since thermodynamic cycles played an essential role in the development of thermodynamics during the 19th century.

The Carnot cycle allows to transform undirected thermal motion (heat) into directed motion (mechanical work):

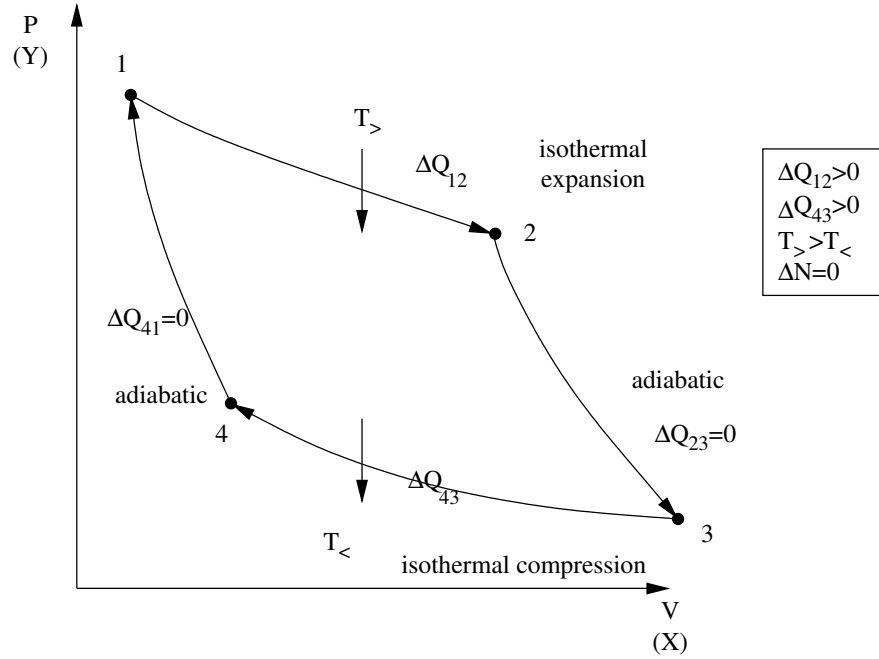


Figure 2.7: Carnot process

<u>1 → 2</u> :	isothermal expansion	contact with heat bath 1
	$T = \text{const.} = T_>$	(slow)
<u>2 → 3</u> :	adiabatic	no contact with heat bath
	$T \searrow \quad \Delta T = T_< - T_> < 0$	(fast)
<u>3 → 4</u> :	isothermal compression	contact with heat bath 2
	$T = \text{const.} = T_<$	(slow)
<u>4 → 1</u> :	adiabatic compression	no contact with heat bath
	$T \nearrow \quad \Delta T = T_> - T_< > 0$	(fast)

**Efficiency of the cycle:**

$$\boxed{\eta = \frac{\text{mechanical work}}{\text{heat injected}} = \frac{\Delta W_{\text{tot}}}{\Delta Q_{12}}} \quad \text{per cycle} \quad (2.37)$$

(heat added *to system* is counted  $> 0$ , work done *by system* is counted  $< 0$ . Energy always counted wrt. the system, not reservoir.)



Since the internal energy is a state variable, its total change around a cycle must be zero:

$$0 = \Delta U_{\text{tot}} = \Delta Q_{\text{tot}} - \Delta W_{\text{tot}} \quad (2.38)$$

$$= \Delta Q_{12} - \Delta Q_{43} - \Delta W_{\text{tot}} \quad (2.39)$$

$$\Delta W_{\text{tot}} = \Delta Q_{12} - \Delta Q_{43} \quad (2.40)$$

$$\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} < 1$$

 since  $\Delta Q_{43} > 0$  (2.41)

The Carnot process is the most efficient heat engine.

**Proof:**

Assume that there is a heat engine  $A$  with  $\eta_A > \eta$ . Then, let engine  $A$  and Carnot engine  $C$  work between the same heat reservoir at  $T_>$  and  $T_<$ .  $A$  can drive  $C$  as a cooling machine:

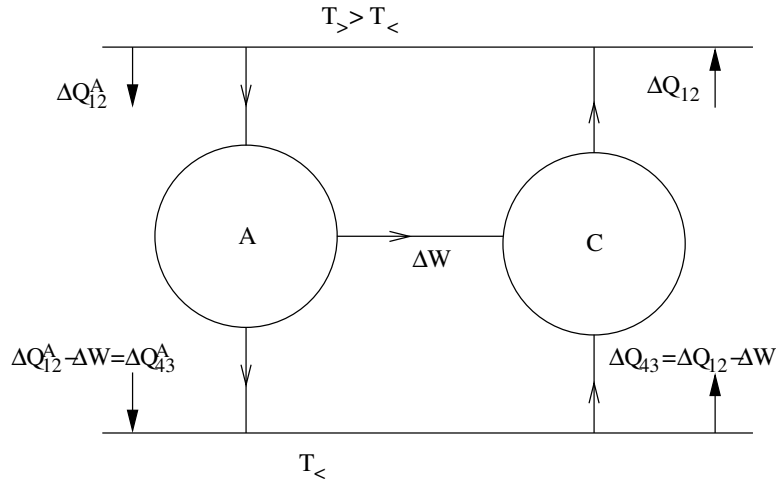


Figure 2.8: Coupled heat engines

Since  $\eta_A > \eta$ ,

$$\frac{\Delta W}{\Delta Q_{12}^A} > \frac{\Delta W}{\Delta Q_{12}} \quad \text{or} \quad \Delta Q_{12} > \Delta Q_{12}^A \quad (2.42)$$

Total heat transfer from  $T_<$  to  $T_>$ :

$$\Delta Q = (\Delta Q_{12} - \Delta W) - (\Delta Q_{12}^A - \Delta W) \quad (2.43)$$

$$= \Delta Q_{12} - \Delta Q_{12}^A > 0 \quad (2.44)$$

Forbidden by 2nd law!  $\nexists$

**Definition of temperature  
using the efficiency of the Carnot cycle:**

It follows from the previous argument that all Carnot engines operating between the same heat reservoirs  $T_>, T_<$  have the same efficiency  $\eta$ . Therefore,  $\eta$  does not depend on the state variables of the system involved in the cycle, but only on the temperatures of the reservoirs  $T_>, T_<$ :

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = f(T_>, T_<) \quad (2.45)$$

Consider now two Carnot engines coupled to each other via heat transfer:

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = \underbrace{f(T_>, T')}_{\text{same function } f} \quad (2.46)$$

$$\frac{\Delta Q_{65}}{\Delta Q_{43}} = f(T', T_<) \quad (2.47)$$

$$\frac{\Delta Q_{65}}{\Delta Q_{12}} = f(T_>, T_<) \quad (2.48)$$

$\Rightarrow$  Functional equation for  $f(T_>, T_<)$ :

$$f(T_>, T_<) = f(T_>, T') f(T', T_<) \quad (2.49)$$

It has the solution

$$f(T_>, T_<) = \frac{g(T_>)}{g(T_<)} \quad (2.50)$$

with a universal function  $g(T)$ , which must be monotonically decreasing, since

$$\frac{\Delta Q_{43}}{\Delta Q_{12}} = \frac{g(T_>)}{g(T_<)} < 1 \quad \text{in order for } \eta > 0. \quad (2.51)$$

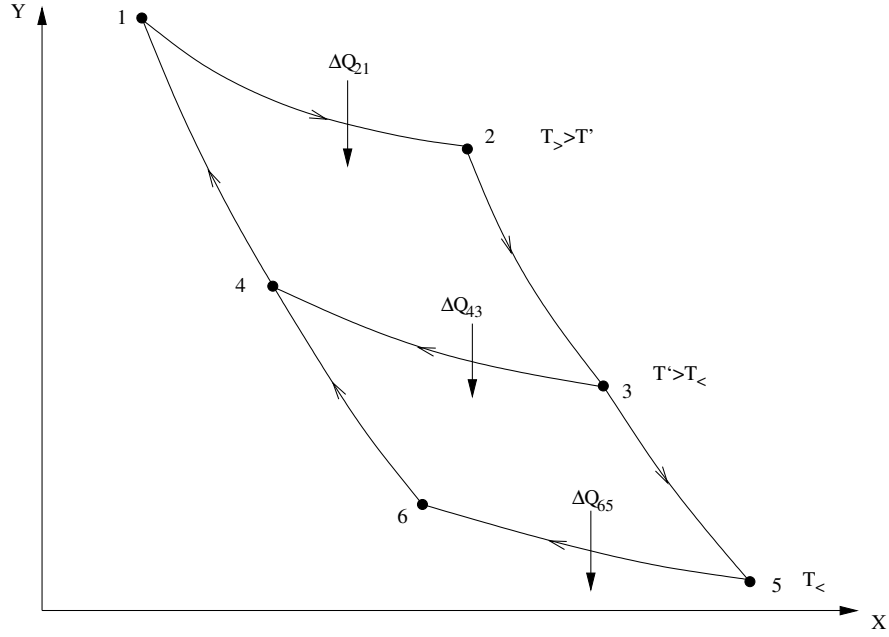


Figure 2.9: Two coupled Carnot processes

The Kelvin temperature scale is defined through the *choice*

$$g(T) = \frac{1}{T} . \quad (2.52)$$

Note the ambiguity in the definition. Hence,

$$\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} = 1 - \frac{T_{<}}{T_{>}} \quad (2.53)$$

It is shown within the microscopic kinetic gas theory that both definitions of the Kelvin scale are equivalent.

### Definition of the state variable entropy

- For any Carnot cycle we have

$$\eta = 1 - \frac{\Delta Q_{43}}{\Delta Q_{12}} = 1 - \frac{T_{<}}{T_{>}} \quad (2.54)$$

and with  $\Delta Q_{34} = -\Delta Q_{43} < 0$

$$\frac{\Delta Q_{12}}{T_{>}} + \frac{\Delta Q_{34}}{T_{<}} = 0 . \quad (2.55)$$

- Any arbitrary *reversible* ( $\rightarrow$  see discussion below) cyclic process can be decomposed into an infinite number of infinitesimal Carnot cycles.

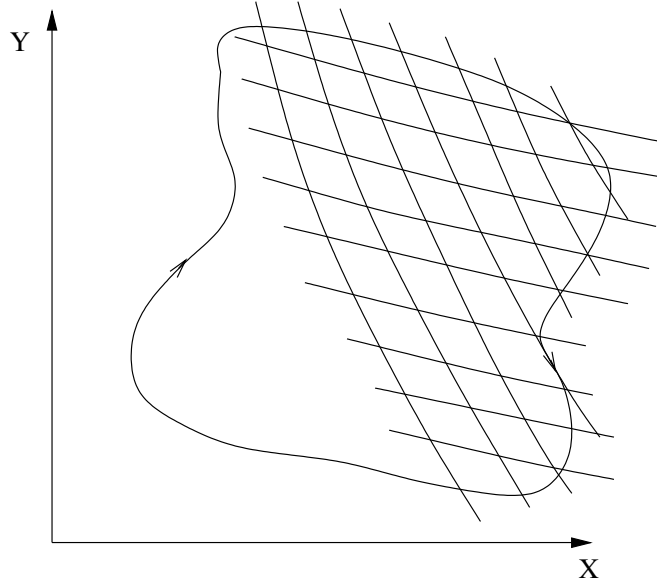


Figure 2.10: Any cyclic process can be decomposed into (infinitesimal) Carnot cycles

The amounts of heat exchanged between neighboring Carnot processes in the interior of the area compensate each other, so that only the contributions from the boundaries remain.

$\Rightarrow$  For a general *reversible* cycle:

$$\oint \frac{\delta Q}{T} = 0 \quad (2.56)$$

(Non-exact variations will be denoted by greek  $\delta Q$ .)

The quantity  $dS = \frac{\delta Q}{T}$  is a complete differential of a state variable. The corresponding *state variable*

$$S = \int \frac{\delta Q}{T} \quad (\text{for a reversible process}) \quad (2.57)$$

is called entropy. It will be related to the "disorder" in the system in statistical mechanics.

**Remark:**

For a *reversible* process the relation  $dS = \frac{\delta Q}{T}$  holds and is an exact (= complete) differential, since it was derived for a collection of reversible Carnot cycles. For *irreversible* processes the relation

$$S = \int \frac{\delta Q}{T}, \quad dS = \frac{\delta Q}{T} \quad (2.58)$$

no longer holds, but the state variable  $S$  can still be defined. The relation  $dS \leftrightarrow \delta Q$  will be discussed next.

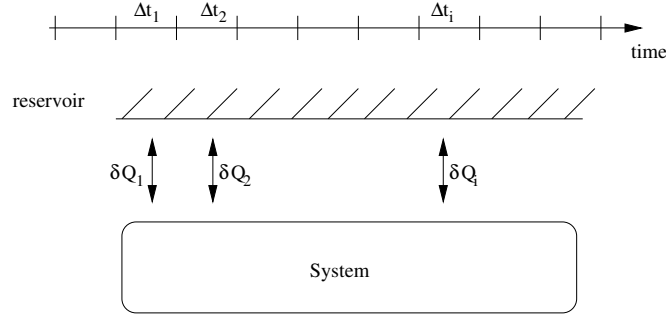
**The behavior of the entropy during thermodynamic changes of state: reversible and irreversible processes**

All the process steps of the Carnot cycle are, by construction, performed in a time reversible way:

- The *isothermal* expansion ( $1 \rightarrow 2$ ) and compression ( $3 \rightarrow 4$ ) are done infinitely slowly, so that the working system is in equilibrium with the reservoir ( $T_>$  and  $T_<$ , respectively) at each instant of time. *Such a process is always reversible.* This is because during each infinitesimal time interval between two *equilibrium* states only an *infinitesimal* amount of heat is transferred between system and reservoir. Therefore, each infinitesimal step is reversible. That the infinite series of infinitesimal steps is still reversible is at the heart of the postulate of the 2nd law and can be understood in a deeper way only from the microscopic concept of entropy as a measure for "disorder" in statistical mechanics. The problem will be re-visited there.
- The *adiabatic* expansion ( $2 \rightarrow 3$ ) or compression ( $4 \rightarrow 1$ ) are done without contact of the system with the reservoir (infinitely fast). Therefore, the internal (potential) energy of the system is completely transformed into mechanical work (since no other form of energy available), i.e. the adiabatic process is reversible.

In practice, however, the processes described above are not ideal:

1. No process can be done infinitely slowly. As a consequence, turbulences (or other disturbances) are generated in the gas (system), are ultimately transformed into additional indirected motion in the gas (i.e. heat) and lead to *irreversible* losses.

Figure 2.11: Reversible infinitesimal heat exchanges  $\delta Q_i$ 

2. Turbulences with the same effect are also generated during the fast, adiabatic processes.
  3. No system can be completely isolated from its surroundings, i.e. the adiabatic process itself is an idealization.
  4. Frictional losses occur in real systems during each of the steps.
- In an *irreversible* cyclic process less than the maximum possible fraction of the heat extracted from reservoir  $T_>$  is transformed into mechanical work.
- I.e. cyclic processes which include *irreversible* processes have a smaller efficiency than the Carnot cycle. Conversely, all *reversible* cyclic processes have the same maximum efficiency  $\eta$ .

Hence, we have

$$\eta_{irrev} = 1 + \frac{\overbrace{Q_{34}}^{=-Q_{43}}}{Q_{12}} < \eta = 1 - \frac{T_<}{T_>} \quad (2.59)$$

$$\text{or } \frac{\Delta Q_{12}}{T_>} + \frac{\Delta Q_{34}}{T_<} < 0, \quad \text{and infinitesimally} \quad (2.60)$$

$$\oint \frac{\delta Q}{T} < 0 \quad (2.61)$$

for irreversible processes.

**Note:**  $T$  is an *equilibrium* concept and may not even be defined in an arbitrary irreversible process.

Or for state change  $1 \rightarrow 2$ :

$$\underbrace{\int_1^2}_{\text{irrev}} \frac{\delta Q}{T} \leq \underbrace{\int_1^2}_{\text{rev}} \frac{\delta Q}{T} \equiv \underbrace{\int_1^2}_{\text{rev}} dS = \Delta S_{1 \rightarrow 2} \quad (2.62)$$

$\Rightarrow$  In a thermally isolated system ( $\delta Q \equiv 0$ ) the entropy  $S$  cannot decrease in any change of state  $1 \rightarrow 2$ :

$$\Delta S_{1 \rightarrow 2} \geq 0 \quad \text{thermally isolated systems} \quad (2.63)$$

This is a mathematical restatement of the 2nd law.

It follows an important, central conclusion of thermodynamics:

Since any system, left to itself (thermally isolated), reaches for time  $t \rightarrow \infty$  the equilibrium state (= definition of equilibrium), and since this final state is reached through a succession of state changes with  $\Delta S \geq 0$  each, the exact statement holds:

In thermodynamic equilibrium, for any set of values of the relevant state variables ( $N, V, \vec{B}, \dots$ ) which can be fixed *externally*, the entropy  $S$  of the system takes the maximum value as a function of the other variables, as illustrated in figure 12.

### 2.4.3 The third law of thermodynamics

The entropy of any closed (no heat, particle,  $\dots$  exchange) thermodynamic system, which has a non-degenerate ground state, vanishes for  $T \rightarrow 0$ :

$$\lim_{T \rightarrow 0} S(T) = 0$$

(2.64)

The requirement "non-degenerate ground state" is the essential condition for the 3rd law. Hence, it is a consequence of quantum mechanics, since in classical mechanics there are many degenerate minimum energy states possible for a many-particle system due to the classical distinguishability of particles. This problem

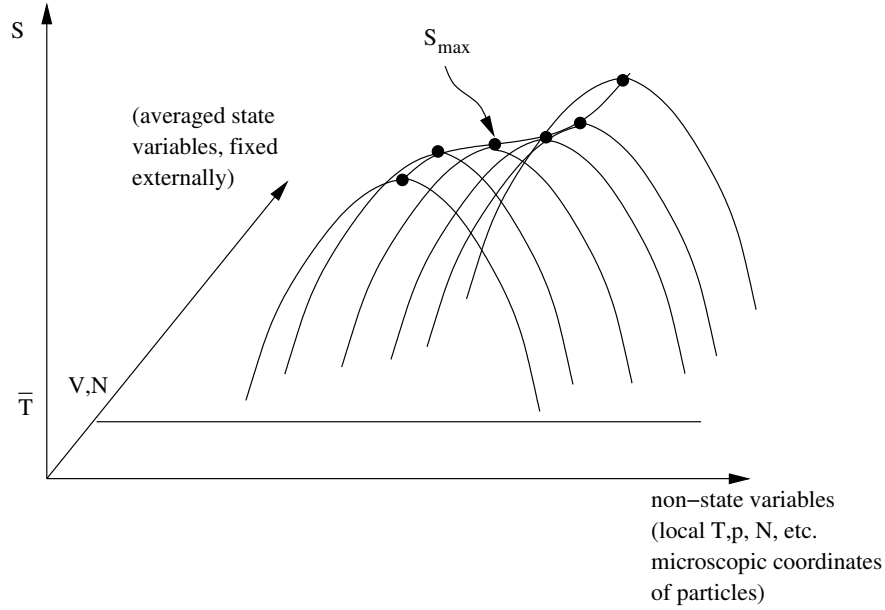


Figure 2.12: In equilibrium the entropy assumes a global maximum as a function of “non-state” variables.

is only lifted by the nondistinguishability of equivalent particles in quantum mechanics. Therefore, quantum mechanics has profound consequences even on the properties of macroscopic systems. This will be discussed further in statistical mechanics.

## 2.5 The fundamental relation of thermodynamics

The relation between the infinitesimal changes of the state variables manifested in the 1st law can be cast into a non-infinitesimal relation using a scaling argument: The 2nd law implies for *reversible* processes:

$$\delta Q = T dS \quad (2.65)$$

i.e. from the 1st law (energy conservation):

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN \quad (2.66)$$



( $S$  is a homogenous function of an external variable.)

Hence, the derivatives of  $S$  wrt.  $U$ ,  $V$ ,  $N$  are

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \quad (2.67)$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T} \quad (2.68)$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T} \quad (2.69)$$

It follows from equation 2.66 that  $S$  is a function of the *extensive* variables  $U$ ,  $V$ ,  $N$  (which are proportional to the system size, "scale" with system size) in such a way that  $S$  scales with  $U$ ,  $V$ ,  $N$ , i.e.  $S$  is also proportional to the system size:

The entropy  $S$  is an extensive quantity.

Then the scaling relation holds,

$$(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) \quad (2.70)$$

which implies by differentiation wrt.  $\lambda$  and  $\lambda \rightarrow 1$ ,

$$\frac{d}{d\lambda}(\lambda S) = S = \frac{\partial S}{\partial U}U + \frac{\partial S}{\partial V}V + \frac{\partial S}{\partial N}N \quad (2.71)$$

and using  $\frac{\partial S}{\partial U}$ ,  $\frac{\partial S}{\partial V}$ ,  $\frac{\partial S}{\partial N}$  above,

$$TS = U + PV - \mu N \quad (2.72)$$

$$\Leftrightarrow U = TS - PV + \mu N .$$

Fundamental relation  
of thermodynamics

(2.73)

$S$  is a homogenous function of  $U$ ,  $V$ ,  $N$ .

It can be seen as a non-infinitesimal form of the 1st law, where now *both* the extensive variables  $S$ ,  $V$ ,  $N$  and the intensive variables  $T$ ,  $P$ ,  $\mu$  can be varied (by changing e.g. external parameters). The *total* differential of the fundamental relation implies another relation between thermodynamic derivatives:

$$TdS + SdT = dU + PdV + VdP - \mu dN - Nd\mu \quad (2.74)$$

and with the 1st law

$$dU = TdS - PdV + \mu dN : \quad (2.75)$$

$$\boxed{d\mu = -\frac{S}{N}dT + \frac{V}{N}dP} \quad \text{Gibbs-Duhem-relation} \quad (2.76)$$

Using particle density  $\rho = \frac{N}{V}$  and entropy density  $s = \frac{S}{V}$  one obtains:

$$\boxed{d\mu = -\frac{1}{\rho}s dT + \frac{1}{\rho}dP} \quad (2.77)$$

The fundamental relation can be used to derive the equations of state for specific state changes from the general equation of state,  $F(P, V, T, \dots) = 0$ .

Equation for an ideal gas:

$$F(P, V, T) = PV - Nk_B T = 0 \quad \text{general EOS} \quad (2.78)$$

$$\underbrace{\Rightarrow}_{F.R.} F_{\delta Q=0}(P, V, T) = 0 \quad \text{adiabatic equation} \quad (2.79)$$

$$F_{dT=0}(P, V, T) = 0 \quad \text{isothermal equation, etc.} \quad (2.80)$$

## 2.6 Thermodynamic potentials

The internal energy  $U$  of a system describes (but is not equivalent to, since  $\eta < 1$ ) the energy stored in the system, i.e. potential energy, that can be transformed into mechanical work. It is, therefore, often called a *thermodynamical potential*.

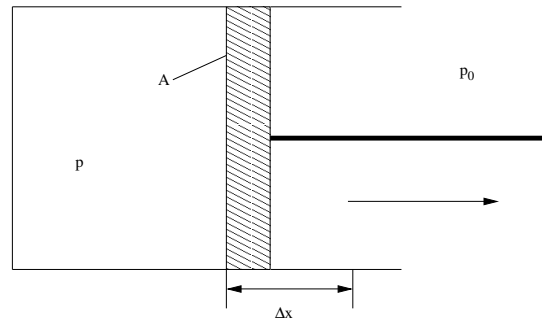
**Example:**

$$\Delta U = \Delta Q - \Delta W \quad (2.81)$$

work done by the gas:

$$\Delta W = -(\Delta U - \Delta Q) > 0 \quad (2.82)$$

$$|\Delta W| < \Delta U \quad (2.83)$$

Figure 2.13: Mechanical work  $\Delta W$  done against external pressure  $P_0$ 

The 2nd law implies a *minimum principle for  $U$* :

For reversible and irreversible processes  $1 \rightarrow 2$  we have

$$\delta Q = T dS \quad \text{for reversible processes} \quad (2.84)$$

$$\delta Q < T dS \quad \text{for irreversible processes} \quad (2.85)$$

$$\Delta U \leq \underbrace{\int_1^2 T dS}_{\Delta Q} - \Delta W_{12} + \int_1^2 \mu dN \quad (2.86)$$

i.e. in a *closed* system with  $S, V, N = \text{const.}$  and  $S$  a fixed variable in  $U$  ( $\rightarrow$  see below):

$(\Delta U)_{S,V,N} \leq 0$

 for any processes in a closed system. (2.87)

The internal energy  $U$  has been written as a function of all the extensive variables of the system,  $S, V, N, \dots$

$U$  is, therefore, useful to describe processes where  $S, V, N, \dots$  are *fixed* from outside, i.e. the minimum of  $U$  as function of  $S, V, N$  ( $dS, dV, dN = 0$ ) is determined for given  $S, V, N$ , and hence the corresponding  $T, P, \mu, \dots$

$\rightarrow$  exercises

$\rightarrow$  examples (below)

In many cases,  $S, V, N$  (especially  $S$ ) are not determined from outside. It is then useful to write the "potential energy" of the system as function of the relevant, externally determined variables, i.e. of intensive or extensive variables, or a combination. For each *extensive* variable there is an *intensive* quantity

which is the derivative of  $U$  wrt. the extensive one; both variables form a pair of canonically conjugated variables:

$$S \rightarrow T = \left( \frac{\partial U}{\partial S} \right)_{V,N} \quad (2.88)$$

$$V \rightarrow P = - \left( \frac{\partial U}{\partial V} \right)_{S,N} \quad (2.89)$$

$$N \rightarrow \mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} \text{ etc.} \quad (2.90)$$

We want to write  $U$  not as a function of  $S$  but as function of  $T$ , the derivative of  $U$  wrt.  $S$ .

The standard way to write a given function  $f(y)$  *locally* in dependence of  $\Pi = \frac{\partial f}{\partial y}$  is the Legendre transformation.

$$f(y) : \quad f = \Pi dy \quad (2.91)$$

$$g(\Pi) = f - \Pi y : \quad dg = \underbrace{df - \Pi dy}_{=0} - y d\Pi = -y d\Pi \quad (2.92)$$

Recipe:  $f \rightarrow g$ : subtract pair of conjugated variables.

**Example:** Classical mechanics

Transformation from Lagrange function  $L(x, \underbrace{\dot{x}}_y)$  to Hamilton function  $H(x, p)$ , where the coordinate  $x$  is an unchanged variable, the velocity  $\dot{x}$  corresponds to  $y$ , and the classical momentum  $p = \frac{\partial L}{\partial \dot{x}}$  corresponds to  $\Pi$ :

$$H = L - x \frac{\partial L}{\partial \dot{x}} \quad (2.93)$$

**Note:**

- It is only necessary to perform a *local* transformation in the vicinity of some given value of the variable  $y$ , since we are looking for the minimum of  $f$ .
- *Locally*, the Legendre transformation is unique.
- If  $f(y)$  has a minimum (extremum) at a given point  $y$  then  $g(\Pi)$  has a minimum (extremum) at the same point, (only expressed by the variable  $\Pi$ ), and vice versa.

**Application to thermodynamics:**

external fixed variables	thermodynamic potential
$S, P, N$	enthalpy $H(S, P, N) = U + PV = ST + \mu N$ $dH = TdS + VdP + \mu dN$
$T, V, N$	free energy (Helmholtz free energy) $F(T, V, N) = U - TS = -PV + \mu N$ $dF = -SdT + PdV + \mu dN$
$T, P, N$	free energy (Gibbs free energy) $G(T, P, N) = U - TS + PV = \mu N$ $dG = -SdT + VdP + \mu dN$
$T, V, \mu$	grand canonical potential $\Omega(T, V, \mu) = U - TS - \mu N = -PV$ $d\Omega = -SdT - PdV - Nd\mu$ (for systems with particle exchange)
$S, V, N$	$U(S, V, N) = TS - PV + \mu N$ $dU = TdS - PdV + \mu dN$

### Relations between thermodynamic derivatives: Maxwell relations

From  $dU = TdS - pdV + \mu dN$  it follows:

$$T = \left( \frac{\partial U}{\partial S} \right)_{V,N} \quad (2.94)$$

$$P = - \left( \frac{\partial U}{\partial V} \right)_{S,N} \quad (2.95)$$

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} \quad (2.96)$$

Taking another derivative and using  $\frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x}$  for state variables, one obtains immediately

$$\begin{aligned} \left( \frac{\partial T}{\partial V} \right)_{S,N} &= - \left( \frac{\partial P}{\partial S} \right)_{V,N} \\ \left( \frac{\partial T}{\partial N} \right)_{S,V} &= \left( \frac{\partial \mu}{\partial S} \right)_{V,N} \\ \left( \frac{\partial P}{\partial N} \right)_{S,V} &= - \left( \frac{\partial \mu}{\partial V} \right)_{S,N} \end{aligned}$$

Maxwell relations (2.97)

and similar relations for other variables.

## 2.7 Thermodynamic response functions

The response of a thermodynamic system to the change of external parameters, like temperature  $T$ , magnetic field  $\vec{B}$ , pressure  $p$ , etc., is described by the response functions. If these external functions are time-independent, the response functions can be expressed as derivatives of the thermodynamic potentials.

### 2.7.1 Thermal response functions

The thermal response functions or *specific heats*  $c$  describe the change of the heat content  $\delta Q$  of a system (per volume) due to a change of temperature  $T$  in a

reversible process:

$$c = \frac{\delta Q}{dT} = T \frac{dS}{dT} \quad (2.98)$$

where it must be specified, which other variables are kept constant during that process.

For the  $N - p - V$  system, the particle number  $N$  and either  $V$  or  $p$  are kept constant. Hence, one has

$$c_V = T \left( \frac{\partial S}{\partial T} \right)_{V,N} \quad (2.99)$$

$$\uparrow \quad (2.100)$$

$$dF = SdT - p \underbrace{dV}_{=0} + \mu \underbrace{dN}_{=0} \quad (2.101)$$

$$= -T \left( \frac{\partial^2 F}{\partial T^2} \right)_{V,N} \quad (2.102)$$

$$> 0 \quad (2.103)$$

or equivalently, since  $dU = \delta Q - pdV + \mu dN$ ,

$$c_V = \left( \frac{\partial U}{\partial T} \right)_{V,N} \quad (2.104)$$

$$c_p = T \left( \frac{\partial S}{\partial T} \right)_{p,N} \quad (2.105)$$

$$\uparrow \quad (2.106)$$

$$dG = SdT - V \underbrace{dp}_{=0} + \mu \underbrace{dN}_{=0} \quad (2.107)$$

$$= -T \left( \frac{\partial^2 G}{\partial T^2} \right)_{p,N} \quad (2.108)$$

$$> 0 \quad (2.109)$$

or equivalently, with  $dH = \delta Q - Vdp + \mu dN$ ,

$$c_p = \left( \frac{\partial H}{\partial T} \right)_{p,N} \quad (2.110)$$

It follows from the second law of thermodynamics (formulation (2)) that the specific heat is positive:

$$c_V > 0, \quad c_p > 0 \quad (2.111)$$

### 2.7.2 Mechanical response functions

The *compressibility*  $\kappa$  describes the change of volume of a system due to a pressure change, normalized to its volume:

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{T,N} = -\frac{1}{V} \left( \frac{\partial^2 G}{\partial p^2} \right)_{T,N} \geq 0 \quad (2.112)$$

$$\kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_{S,N} = -\frac{1}{V} \left( \frac{\partial^2 H}{\partial p^2} \right)_{S,N} \geq 0 \quad (2.113)$$

The stability of a physical system requires that the compressibility is not negative (no spontaneous volume collapse).

The compressibility can also be expressed in terms of the density  $n = \frac{N}{V}$ :

$$\frac{1}{n} \left( \frac{\partial n}{\partial p} \right)_N = \frac{V}{N} \left( -\frac{N}{V^2} \right) \frac{\partial V}{\partial p} = \kappa \quad (2.114)$$

The change of volume due to a temperature change is given by the *thermal expansion coefficient*  $\alpha$

$$\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \left\{ \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial p} \right)_T \right\} \gtrless 0 \quad (2.115)$$

The heat expansion  $\alpha$  can be positive or negative.

### 2.7.3 Magnetic response functions

The magnetic susceptibility  $\chi_{T,S}$  is the response of the magnetization  $M$  to a change of the external magnetic field  $B$ :



$$\chi_T = \left( \frac{\partial M}{\partial B} \right)_T = \left( \frac{\partial^2 F_{T,B}}{\partial B^2} \right)_T \quad (2.116)$$

$$\begin{array}{ccc} \uparrow & & \\ dF_{T,B} & = & -SdT - pdV + MdB \\ \chi_S = \left( \frac{\partial M}{\partial B} \right)_S & = & \left( \frac{\partial^2 F_{S,B}}{\partial B^2} \right)_S \end{array} \quad (2.117)$$

$$\uparrow \\ dF_{S,B} = SdT - pdV + MdB$$

where the “free energies” of a magnetic system,  $F_{T,B}$ ,  $F_{S,B}$  are understood as the Legendre transforms of  $U$  with respect to  $T$  and  $B$  and to  $S$  and  $B$ , respectively.

The susceptibility is positive for a para- or ferromagnetic system and negative for a diamagnetic system.

The relations given in 1.6.1-1.6.3 show generally, that the response functions can be expressed in terms of the second derivatives of an appropriate thermodynamic potential.

#### 2.7.4 Relations between thermal and mechanical response functions

The following relations hold:

$$\frac{c_p}{c_V} = \frac{\kappa_T}{\kappa_S} \quad (2.118)$$

$$c_p - c_V = TV \frac{\alpha_p^2}{\kappa_T} \geq 0 \quad (2.119)$$

**Proof:**

- *Relation (1):*

$$\frac{c_p}{c_V} = \frac{\left(\frac{\partial S}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_V} = \frac{\frac{(\partial p/\partial T)_S}{(\partial p/\partial S)_T}}{\frac{(\partial V/\partial T)_S}{(\partial V/\partial S)_T}} = \frac{\frac{(\partial V/\partial S)}{\partial p/\partial S}\Big|_T}{\frac{(\partial V/\partial T)}{(\partial p/\partial T)}\Big|_S} = \frac{\left(\frac{\partial V}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial p}\right)_S} = \frac{\kappa_T}{\kappa_S} \quad (2.120)$$

where we used in the numerator, that the *total* differential of  $p$  vanishes for  $c_p$ :

$$0 = dp = \left(\frac{\partial p}{\partial S}\right)_T dS + \left(\frac{\partial p}{\partial T}\right)_S dT \Rightarrow \left(\frac{\partial S}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_S}{\left(\frac{\partial p}{\partial S}\right)_T} \quad (2.121)$$

and in the denominator, that the total differential of  $V$  vanishes for  $c_V$ :

$$0 = dV = \left(\frac{\partial V}{\partial S}\right)_T dS + \left(\frac{\partial V}{\partial T}\right)_S dT \Rightarrow \left(\frac{\partial S}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_S}{\left(\frac{\partial V}{\partial S}\right)_T} \quad (2.122)$$

- *Relation (2):*

$$c_p - c_V = T \left\{ \left(\frac{\partial S}{\partial T}\right)_p - \left(\frac{\partial S}{\partial T}\right)_V \right\} \quad (2.123)$$

- We use the chain rule to express the  $T$ -derivative at  $p = \text{const.}$  by a  $T$ -derivative at  $V = \text{const.}$  (see also above):

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{\partial}{\partial T} S(T, V(p, T)) \Big|_{p=\text{const.}} \quad (2.124)$$

$$= \left(\frac{\partial S}{\partial T}\right)_V + \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{V \cdot \alpha_p} \left(\frac{\partial V}{\partial T}\right)_p \quad (2.125)$$

- $\left(\frac{\partial S}{\partial V}\right)_T$  is expressed using a Maxwell relation, employing the thermodynamical potential  $F$ :

$$S = - \left( \frac{\partial F}{\partial T} \right)_V \quad (2.126)$$

$$\left( \frac{\partial S}{\partial V} \right)_T = - \left\{ \frac{\partial}{\partial V} \left( \frac{\partial F}{\partial T} \right)_V \right\}_T = \left\{ \frac{\partial}{\partial T} \left( - \frac{\partial F}{\partial V} \right)_T \right\}_V \quad (2.127)$$

$$= \left( \frac{\partial p}{\partial T} \right)_V \quad (2.128)$$

Since in the last expression  $dV = 0$ , we have

$$0 = dV = \left( \frac{\partial V}{\partial p} \right)_T dp + \left( \frac{\partial V}{\partial T} \right)_p dT \quad (2.129)$$

$$\Rightarrow \left( \frac{\partial p}{\partial T} \right)_V = - \frac{\left( \frac{\partial V}{\partial T} \right)_p}{\left( \frac{\partial V}{\partial p} \right)_T} = - \frac{V \alpha_p}{(-V \kappa_T)} = \frac{\alpha_p}{\kappa_T} \quad (2.130)$$

and finally

$$c_p - c_V = T \left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_p = TV \frac{\alpha_p^2}{\kappa_T} \geq 0. \quad (2.131)$$

Physically  $c_p \geq c_V$ , because for  $p = \text{const.}$  part of the heat added is not kept in the system but is transformed to mechanical work. Thus, more heat is necessary to make a given temperature change than in the case  $V = \text{const.}$

Similarly, one can prove the magnetic relations:

$$\begin{aligned} \frac{c_B}{c_M} &= \frac{\chi_T}{\chi_S} \\ c_B - c_M &= T \frac{\alpha_B^2}{\chi_T} \geq 0 \end{aligned}$$

(2.132)



# 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  $p \cdot V = Nk_B T$ ; dependence of  $p$  on  $T$  for  $V = \text{const.}$  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  $\vec{p}_i$ ,  $i = 1, \dots, N$ ).

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,  $i = 1, \dots, N_e$

$$M = \{ x_i \mid i = 1, \dots, N_e \} \quad (3.1)$$

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

- **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

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

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:

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

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,  $M \rightarrow \infty$ , the ratio  $h_M(x_i) = \frac{M_i}{M}$  approaches a constant, i.e. reproducible value. It is called probability  $W(x_i)$

$$W(x_i) = \lim_{M \rightarrow \infty} \frac{M_i}{M}$$

(3.4)

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

**Simple properties of the probability:**

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

The probability  $W(x_i)$  is, hence, a *definite* function of 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).

$$\text{Event spaces} \quad \mathbb{M}_x = \{x_i \mid i = 1, \dots, N_{e,x}\} \quad (3.5)$$

$$\mathbb{M}_y = \{y_i \mid i = 1, \dots, N_{e,y}\} \quad (3.6)$$

**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 occurred for sure:

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

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:**

$$\sum_i W(x_i|y_j) = 1 \quad \text{and} \quad (3.8)$$

$$\sum_j W(x_i|y_j) = 1. \quad (3.9)$$



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

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

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

**Normalization:**

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

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

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

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

### 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  $\hat{A}$  ascribed to a mixed state  $u$  is calculated as the weighted average of the quantum mechanical expectation values of  $\hat{A}$  in the states  $|n\rangle$  which comprise the mixed state  $u$ :

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

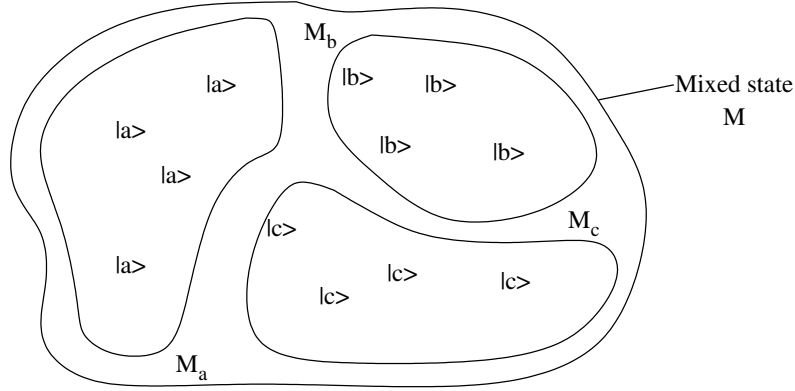


Figure 3.1: Mixed state

**Example:**  $\hat{A} = \hat{H}$  = 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  $N_G \rightarrow \infty$ , which all satisfy the same constrain 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

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

**Note:** An ensemble can be viewed as a special case of a mixed state. 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  $V \rightarrow \infty$ ) 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.

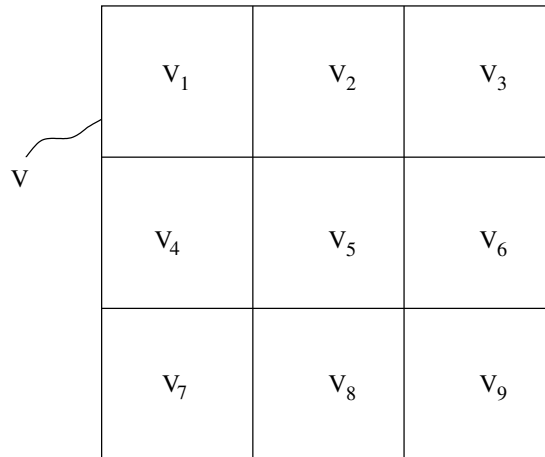


Figure 3.2: Visualization of a statistical ensemble

#### 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  $\hat{A}$  about its average value  $\langle A \rangle$  are small:

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

where

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

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*  $W(n)$ ,

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

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

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

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

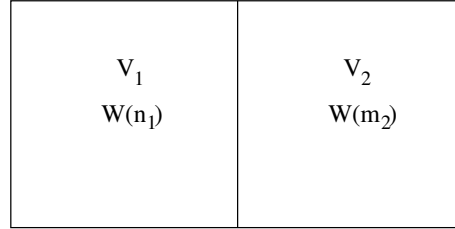


Figure 3.3: Two independent events

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

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

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.

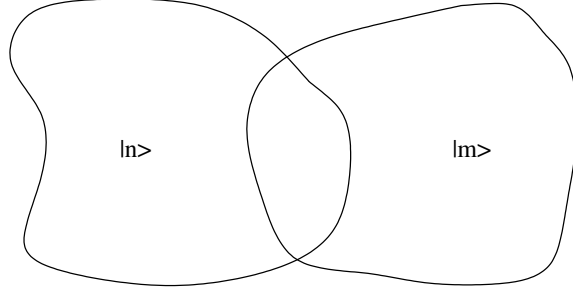


Figure 3.4: Two statistically dependent events

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  $W(n), n = 1, \dots, N_e$  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:

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

Thus, we have using (3.22):

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

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

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

$$\stackrel{\text{symmetry(2)}}{=} \sum_n f(W(n)) \quad (3.23)$$

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

$$\sum_m f(W(1) \cdot W(m|1)) = f(W(1)) + W(1) \sum_m f(W(m|1)) \quad (3.24)$$

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

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

In (3.26):

$$\sum_m g(W(1) \cdot W(m|1)) \cdot \ln(W(1) \cdot W(m|1)) \quad (3.26)$$

$$= g(W(1)) \cdot \ln(W(1)) + W(1) \sum_m g(W(m|1)) \cdot \ln(W(m|1)) \quad (3.27)$$

or

$$\ln(W(1)) \cdot \left[ \sum_m g(W(1) \cdot W(m|1)) - g(W(1)) \right] \quad (3.28)$$

$$+ \sum_m \ln(W(m|1)) \cdot [g(W(1) \cdot W(m|1)) - W(1) \cdot g(W(m|1))] = 0 \quad (3.29)$$

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

$$\underbrace{\sum_m W(1)W(m|1)}_{W(1)} - W(1) = 0 \quad (1st \dots) \quad (3.30)$$

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

It follows the general entropy functional:

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

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*

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



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):

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

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

$$S_{\max} - S = k_B \cdot \ln N_e + k_B \sum_n W(n) \cdot \ln W(n) \quad (3.35)$$

$$\begin{aligned} &= k_B \left[ \underbrace{\sum_n W(n) \cdot \ln N_e}_{=1} + \sum_n W(n) \cdot \ln W(n) \right. \\ &\quad \left. + \underbrace{\sum_n \frac{1}{N_e} - 1}_{=0} \right] \end{aligned} \quad (3.36)$$

$$= k_B \sum_n W(n) \cdot \left[ \ln(N_e \cdot W(n)) + \frac{1}{N_e \cdot W(n)} - 1 \right] \quad (3.37)$$

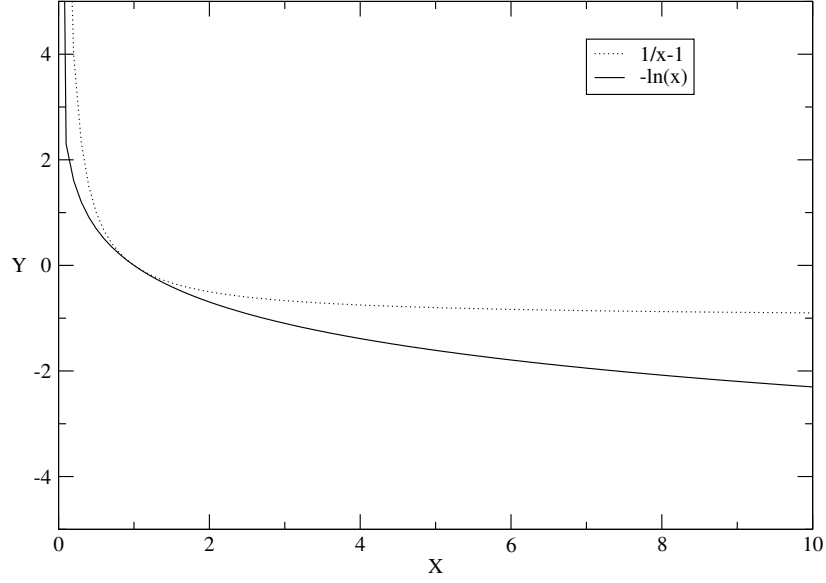
With  $x := N_e \cdot W(n)$ , and  $-\ln x \leq \frac{1}{x} - 1$ ,  $x > 0$  (square bracket) it follows

$$S_{\max} \geq S. \quad (3.38)$$

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

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 equilibrium 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  $W(n)$  is 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  $E_n = E$

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

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

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

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

$$\max_{\sum' W(n)-1=0} [S\{W(n)\}] \quad (3.42)$$

$$= \max \left[ -k_B \sum_n' W(n) \cdot \ln W(n) + \lambda \left( \sum_n' W(n) - 1 \right) \right] \quad (3.43)$$

$$\equiv \max [S\{W(n), \lambda\}] \quad (3.44)$$

The extremum conditions are

$$\frac{\partial S_m}{\partial \lambda} = 0 = \sum_n' W(n) - 1 \quad (3.45)$$

$$\frac{\partial S_m}{\partial W(n)} = 0 = -k_B \cdot \ln W(n) - k_B + \lambda, \quad n = 1, 2, \dots \quad (3.46)$$

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:

$$\sum_n W(n) = 1 \quad (3.49)$$

$$\langle E \rangle = \sum_n E_n \cdot W(n) \quad (3.50)$$

$$= \sum_n \langle n | H | n \rangle \cdot W(n) \quad (3.51)$$

$$(3.52)$$

$$(3.53)$$

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

$$\begin{aligned} \equiv \max & \left[ -k_B \sum_n W(n) \cdot \ln W(n) \right. \\ & + \lambda \left( \sum_n W(n) - 1 \right) \\ & \left. + \eta \left( \sum_n E_n \cdot W(n) - \langle E \rangle \right) \right] \end{aligned} \quad (3.55)$$

The extremum conditions are:

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

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

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

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

The Lagrange multiplier  $\lambda$  is determined by the normalization, which can be written as

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

with

$$Z_c := \sum_n e^{-\frac{\eta}{k_B} E_n}. \quad (3.61)$$

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

We redefine

$$\frac{\eta}{k_B} \equiv \beta \equiv \frac{1}{k_B \tilde{T}}. \quad (3.62)$$

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

### Connection of the statistical treatment with thermodynamics:

Consider a reversible state change with

$$\tilde{T} \rightarrow \tilde{T} + d\tilde{T} \quad (3.63)$$

Change of energy due to change of distribution  $dW_c(n)$ :

$$d\langle E \rangle = \sum_n E_n \cdot dW_c(n) \quad (3.64)$$

Change of entropy:

$$dS = -k_B \sum_n [\ln W_c(n) + 1] \cdot dW_c(n) \quad (3.65)$$

$$= -k_B \sum_n \left[ -\frac{E_n}{k_B \tilde{T}} - \ln Z_c + 1 \right] \cdot dW_c(n) \quad (3.66)$$

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

$$dS = \frac{1}{\tilde{T}} \sum_n E_n \cdot dW_c(n) = \frac{1}{\tilde{T}} d\langle E \rangle \quad (3.67)$$

or

$$d\langle E \rangle = dU = \tilde{T}dS \quad (3.68)$$

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  $\tilde{T}$  with the temperature  $T$ .

We then have the final result for the probability distribution  $W_c(n)$  characterizing the canonical ensemble

$W_c(n) = \frac{1}{Z_c} e^{-\frac{E_n}{k_B T}}$ $Z_c = \sum_n e^{-\frac{E_n}{k_B T}}$	Boltzmann distribution Canonical partition sum	(3.69)
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**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

$$F = U - TS = \langle E \rangle - TS \quad (3.70)$$

$$= \sum_n E_n W_c(n) + k_B T \sum_n W_c(n) \ln \left( \frac{e^{-\frac{E_n}{k_B T}}}{Z_c} \right) \quad (3.71)$$

$$= \sum_n E_n W_c(n) + k_B T \underbrace{\sum_n W_c(n)}_{=1} \left[ - \underbrace{\ln Z_c}_{\text{independent of } n} - \frac{E_n}{k_B T} \right] \quad (3.72)$$

$$= -k_B T \ln Z_c \quad (3.73)$$

$F = -k_B T \ln Z_c$	or	$Z_c = e^{-\frac{F}{k_B T}}$	(3.74)
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These equations, together with the identifications of the thermodynamic temperature  $T \equiv \tilde{T} = \frac{1}{\eta}$ , 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  $Z_c(T, V, N, \dots)$  allows to calculate the complete thermodynamics of a system. Several examples will be considered later. In an exercise it is shown that

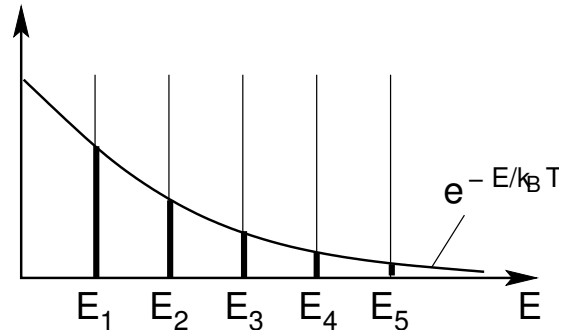


Figure 3.6: Thermal occupation of the energy levels, assuming that the objects (particles, spins etc.) are distinguishable.

in the thermodynamic limit  $N \rightarrow \infty$  the energy fluctuations per particle vanish:  $\langle (E - \langle E \rangle)^2 \rangle / N \rightarrow 0$ . This proves that the microcanonical and the canonical ensemble are equivalent.

### Stability properties of thermodynamic response functions

#### 1. Specific heat: $c_V \geq 0$

(The energy content cannot decrease with increasing temperature.)

**Proof:**

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

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

$$\text{Using } \frac{\partial}{\partial T} \frac{1}{Z_c} = -\frac{1}{Z_c^2} \sum_n \frac{+E_n}{k_B T^2} e^{-\frac{E_n}{k_B T}} \quad (3.77)$$

$$= -\frac{1}{k_B T^2} \frac{\langle E \rangle}{Z_c} \quad (3.78)$$

$$\text{one obtains } c_V = \frac{1}{k_B T^2} (\langle E^2 \rangle - \langle E \rangle^2) \quad (3.79)$$

$$= \frac{1}{k_B T^2} \langle (E - \langle E \rangle)^2 \rangle \geq 0. \quad (3.80)$$

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

**Proof:**

The pressure is calculated microscopically as

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

with  $\langle E \rangle \equiv U$  and  $W_c(n) = e^{-\frac{E_n}{k_B T}} / Z_c$ . 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

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

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

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



### 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:

$$\sum_n W(n) = 1 \quad (3.85)$$

$$\langle E \rangle \equiv U = \sum_n E_n W(n) = \text{const.} \quad (3.86)$$

$$\langle N \rangle = \sum_n N_n W(n) = \text{const.} \quad (3.87)$$

The summation extends over all eigenstates  $|n\rangle$  of the system with arbitrary particle number  $N_n = 1, 2, 3, \dots, \infty$ .

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:

$$S_G\{W(n), \lambda, \eta, \xi\} = \sum_n \left[ -k_B W(n) \ln W(n) + \lambda W(n) - \eta E_n W(n) + \xi N_n W(n) \right] - \lambda + \eta \langle E \rangle - \xi \langle N \rangle \quad (3.88)$$

$$\frac{\partial S_G}{\partial \lambda} = \sum_n W(n) - 1 = 0 \quad (3.89)$$

$$\frac{\partial S_G}{\partial \eta} = \sum_n E_n W(n) - \langle E \rangle = 0 \quad (3.90)$$

$$\frac{\partial S_G}{\partial \xi} = \sum_n N_n W(n) - \langle N \rangle = 0 \quad (3.91)$$

$$\frac{\partial S_G}{\partial W(n)} = -k_B \ln W(n) - k_B + \lambda - \eta E_n + \xi N_n = 0 \quad (3.92)$$

$$\Rightarrow W_G(n) = \frac{1}{Z_G} e^{-\frac{\eta E_n - \xi N_n}{k_B}} \quad (3.93)$$

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

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

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

**Connection of the grand canonical ensemble with thermodynamics:**

Reversible state exchange with  $\tilde{T} \rightarrow \tilde{T} + d\tilde{T}$  and  $\tilde{\mu} \rightarrow \tilde{\mu} + d\tilde{\mu}$ , leaving dynamics, i.e.  $E_n$ , unchanged:

Change of energy:

$$d\langle E \rangle = \sum_n E_n dW_G(n) \quad (3.95)$$

Change of entropy:

$$dS = -k_B \sum_n [\ln W_G(n) + 1] dW_G(n) \quad (3.96)$$

$$= -k_B \sum_n \left[ -\frac{E_n}{k_B \tilde{T}} + \frac{\tilde{\mu}}{k_B \tilde{T}} N_n - \ln Z_G + 1 \right] dW_G(n) \quad (3.97)$$

$$\sum_n dW_G(n) = 0 \quad (3.98)$$

It follows

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

i.e. the identification  $\tilde{T} = T$  the temperature and  $\tilde{\mu} = \mu$  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.

$\begin{aligned} W_G(n) &= \frac{1}{Z_G} e^{-\frac{E_n - \mu N_n}{k_B T}} \\ Z_G &= \sum_n e^{-\frac{E_n - \mu N_n}{k_B T}} \end{aligned}$	<div style="display: flex; justify-content: space-between;"> <div> <p>grand canonical distribution</p> <p>grand canonical partition sum</p> </div> <div style="text-align: right;">(3.100)</div> </div>
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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:

$$\Omega = \langle E \rangle - TS - \mu N \quad (3.101)$$

$$= \sum_n W_G(n) [E_n - \mu N_n + k_B T \underbrace{\ln W_G(n)}_{-\ln Z_G - \frac{E_n}{k_B T} + \frac{\mu N_n}{k_B T}}] \quad (3.102)$$

$$= -k_B T \ln Z_G \quad (3.103)$$

$\begin{aligned} \Omega &= -k_B T \ln Z_G \\ Z_G &= e^{-\frac{\Omega}{k_B T}} \end{aligned}$	<div style="display: flex; justify-content: space-between;"> <div> <p>grand canonical potential</p> <p>grand canonical partition sum</p> </div> <div style="text-align: right;">(3.104)</div> </div>
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The grand canonical ensemble automatically includes the thermodynamical limit  $N \rightarrow \infty$ , since infinite summation over  $n$ . As in the canonical case, it can be shown that in the thermodynamical limit the fluctuations vanish:

$$\frac{\sqrt{\langle (N - \langle N \rangle)^2 \rangle}}{\langle N \rangle} \xrightarrow{N \rightarrow \infty} 0 \quad (3.105)$$

$$\frac{\sqrt{\langle (E - \langle E \rangle)^2 \rangle}}{\langle N \rangle} \xrightarrow{N \rightarrow \infty} 0 \quad (3.106)$$

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

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

# Chapter 4

## Ideal Systems: Some Examples

In this chapter we consider some examples which visualize the statistical physics approach of chapter 2 to describing many-particle systems. This will also demonstrate characteristic thermodynamical and statistical properties of such systems.

### 4.1 2-level systems

A 2-level system is a quantum mechanical system whose Hilbert space consists of exactly 2 states, e.g. a spin  $\frac{1}{2}$  in a magnetic field  $\vec{B} = (0, 0, B)$ .

$$H_i = -g\mu_0\vec{\sigma}_i \cdot \vec{B} = -2\mu_0\sigma_{z,i}B \quad (4.1)$$

with the Landé factor  $g = 2$  and the spin components along the z-axis  $s_i = \pm\frac{1}{2}$ . We consider a system of  $N \gg 1$  such non-interacting spins,

$$H = \sum_{i=1}^N H_i \quad (4.2)$$

which has the energy eigenvalues

$$E(\{m_i\}) = -\sum_{i=1}^N 2\mu_0 s_i B, \quad s_i = \pm\frac{1}{2}. \quad (4.3)$$

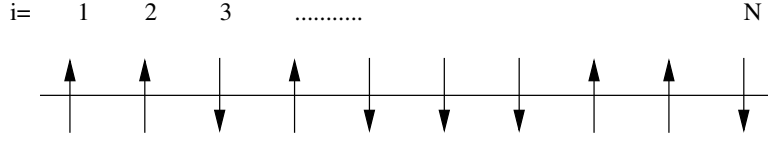


Figure 4.1: System of many independent spins

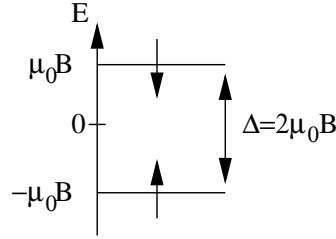


Figure 4.2: Two-level system

The possible energy eigenvalues of the system with  $N$  independent spins are

$$E_n = -n\mu_0 B \quad (4.4)$$

$$n = -N, -N+2, \dots, N \quad (4.5)$$

$$\begin{aligned} n &= n_{\uparrow} - n_{\downarrow} \\ &= \text{number of up-spins} - \text{number of down-spins} \end{aligned} \quad (4.6)$$

#### 4.1.1 Microcanonical treatment (isolated system)

The energy has a fixed value. To calculate the equilibrium distribution of the isolated system, the number of microstates with a given energy  $E_n$  must be enumerated:

$$n_{\uparrow} + n_{\downarrow} = N \quad (4.7)$$

$$n_{\uparrow} - n_{\downarrow} = n \quad (4.8)$$

For given  $N, n$ , there are

$$n_{\uparrow} = \frac{1}{2}(N + n) \quad \text{spins } \uparrow \quad (4.9)$$

$$n_{\downarrow} = \frac{1}{2}(N - n) \quad \text{spins } \downarrow \quad (4.10)$$

**Note:**  $n_\uparrow, n_\downarrow \in \mathbb{N}_0$  for  $N$  even or odd.

Thus,

$$\Omega(E_n) \equiv \Omega(N, n) = \left( \begin{array}{c} \text{number of possibilities to} \\ \text{select } n_\uparrow = \frac{1}{2}(N+n) \text{ spins } \uparrow \\ \text{from } N \text{ spins without ordering} \end{array} \right) \quad (4.11)$$

$$= \frac{N \cdot (N-1) \cdot \dots \cdot (N - n_\uparrow + 1)}{n_\uparrow!} \quad (4.12)$$

$$= \frac{N!}{n_\uparrow!(N - n_\uparrow)!} \quad (4.13)$$

$$= \frac{N!}{\left(\frac{N+n}{2}\right)! \left(\frac{N-n}{2}\right)!} \quad (4.14)$$

and

$$W_M(N, n) = \frac{1}{\Omega(N, n)}. \quad (4.15)$$

The average value of one spin (e.g.  $s_1$ ) in the system with energy  $E_n$  is

$$\langle s_1 \rangle = \frac{1}{2} \frac{1}{\Omega(N, n)} \left[ N \left( s_1 = \frac{1}{2} \right) - N \left( s_1 = -\frac{1}{2} \right) \right] \quad (4.16)$$

with

$$N \left( s_1 = \pm \frac{1}{2} \right) = \text{number of spin configurations with } s_1 = \pm \frac{1}{2} \quad (4.17)$$

and total energy  $E_n$

$$= \Omega(N-1, n \mp 1) \quad (4.18)$$

$$= \begin{cases} \frac{(N-1)!}{\left(\frac{N+n-2}{2}\right)! \left(\frac{N-n}{2}\right)!} \\ \frac{(N-1)!}{\left(\frac{N+n}{2}\right)! \left(\frac{N-n-2}{2}\right)!} \end{cases} . \quad (4.19)$$

Thus,

$$\langle s_1 \rangle = \frac{1}{2} \frac{1}{N} \left[ \frac{(N+n)}{2} - \frac{(N-n)}{2} \right] = \frac{1}{2} \frac{n}{N} = \frac{1}{2} \frac{(n_\uparrow - n_\downarrow)}{(n_\uparrow + n_\downarrow)}. \quad (4.20)$$

The average fluctuations (variance) about this mean value are

$$\langle (s_1 - \langle s_1 \rangle)^2 \rangle = \langle s_1^2 \rangle - \langle s_1 \rangle^2 = \frac{1}{4} \left( 1 - \frac{n^2}{N^2} \right), \quad (4.21)$$

where we have used

$$\langle s_1^2 \rangle = \frac{1}{4} \frac{1}{\Omega(N, n)} \left[ N \left( s_1 = \frac{1}{2} \right) + N \left( s_1 = -\frac{1}{2} \right) \right] = \frac{1}{4}. \quad (4.22)$$

The fluctuations never vanish for  $N \rightarrow \infty$ , unless  $E_n$  has its maximum absolute value, i.e. all spins point in the same direction,  $n = \pm N$ . This is clear, because any energy  $|E_n| < |E_{\max}| = N\mu_0 B$  can be realized by several spin configurations with  $s_1 = +\frac{1}{2}$  or  $s_1 = -\frac{1}{2}$ .

### Entropy and temperature

The entropy of the microcanonical ensemble is

$$S(E) = k_B \ln \Omega(N, n) \quad (4.23)$$

$$\stackrel{N! \approx \left(\frac{N}{e}\right)^N}{\approx} -k_B \left[ \frac{N+n}{2} \ln \left( \frac{N+n}{2} \right) + \frac{N-n}{2} \ln \left( \frac{N-n}{2} \right) \right]. \quad (4.24)$$

With  $E = -n\mu_0 B$ ,  $n = -N, -N+2, \dots, N$  as above and  $dE \equiv dU = T dS$  we can calculate the temperature

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{1}{-\mu_0 B} \frac{\partial S}{\partial n} = \frac{k_B}{2\mu_0 B} \ln \left( \frac{1 - \frac{n}{N}}{1 + \frac{n}{N}} \right) = \frac{k_B}{\Delta} \ln \left( \frac{1 - \frac{2E}{\Delta}}{1 + \frac{2E}{\Delta}} \right) \quad (4.25)$$

or

$$E = -N \frac{\Delta}{2} \tanh \left( \frac{\Delta/2}{k_B T} \right). \quad (4.26)$$

Hence we have

$$T \begin{cases} > 0 & \text{for } E < 0 \\ < 0 & \text{for } E > 0 \end{cases} \quad (4.27)$$

It is a general feature of systems whose energy spectrum is bounded from above, that their entropy is zero both for the minimum and the maximum energy value, since these two microstates are non-degenerate. Therefore,  $S$  must have a maximum for an intermediate energy, as shown in figure 22, and  $T = \left( \frac{\partial S}{\partial E} \right)^{-1}$  can be  $> 0$  or  $< 0$ .

The physical meaning of negative temperatures will become more evident in the canonical ensemble.



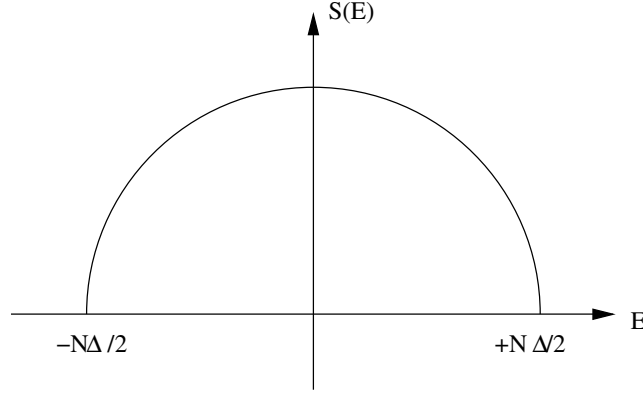


Figure 4.3: Entropy of an ideal spin system in the microcanonical ensemble

We see from the above calculations that for the microcanonical treatment the enumeration of the states  $\Omega(N, n)$  is crucial. This can be a cumbersome task, because the counting is constrained by the fact that the energy is fixed, i.e. that  $n = n_{\uparrow} - n_{\downarrow}$  has a fixed value. Therefore, in most cases it is more efficient to calculate in the canonical ensemble, where the summation in  $Z_c$  runs over all microstates, irrespective of their energy.

#### 4.1.2 Canonical treatment and thermodynamic properties of a 2-level system

The canonical partition function is

$$Z_c = \sum_{s_1=\pm\frac{1}{2}} \sum_{s_2=\pm\frac{1}{2}} \cdots \sum_{s_N=\pm\frac{1}{2}} e^{-\frac{E(s_1, \dots, s_N)}{k_B T}}, \quad (4.28)$$

where the total energy of the  $N$ -spin system is

$$E_n = E(s_1, \dots, s_N) = \sum_{i=1}^N E^1(s_i) = \sum_{i=1}^N (-2s_i \mu_0 B). \quad (4.29)$$

$$Z_c = \sum_{s_1=\pm\frac{1}{2}} \dots \sum_{s_N=\pm\frac{1}{2}} e^{-\frac{E_1(s_1)}{k_B T}} e^{-\frac{E_1(s_2)}{k_B T}} \dots e^{-\frac{E_1(s_N)}{k_B T}} \quad (4.30)$$

$$= \left( \sum_{s=\pm\frac{1}{2}} e^{-\frac{E_1(s)}{k_B T}} \right)^N = (Z_{c,1})^N, \quad (4.31)$$

where

$$Z_{c,1} = \sum_{s=\pm\frac{1}{2}} e^{-\frac{-2s\mu_0 B}{k_B T}} = 2 \cosh \left( \frac{\mu_0 B}{k_B T} \right) = 2 \cosh \left( \frac{\Delta/2}{k_B T} \right). \quad (4.32)$$

It is generally true:

**Note:** For a system of  $N$  *independent* subsystems (i.e. not interacting with each other) the canonical partition sum  $Z_c$  factorizes into the product of the canonical partition sums of each subsystem,  $Z_{c,1}$ .

This is because for non-interacting subsystems the total energy is simply the sum of the energies of the subsystems.

The Boltzmann distribution function is then

$$W_c(n) = \frac{1}{Z_c} e^{-\frac{E_n}{k_B T}} \prod_{i=1}^N \frac{1}{Z_{c,1}} e^{\frac{\Delta}{k_B T} s_i} = \prod_{i=1}^N W_{c,1}(s_i). \quad (4.33)$$

The average value of the spin  $s_i$  is

$$\langle s_i \rangle = \sum_{s_1=\pm\frac{1}{2}} \dots \sum_{s_i=\pm\frac{1}{2}} \dots \sum_{s_N=\pm\frac{1}{2}} s_i W_{c,1}(s_1) \dots W_{c,1}(s_i) \dots W_{c,1}(s_N) \quad (4.34)$$

$$= \sum_{s_i=\pm\frac{1}{2}} s_i W_{c,1}(s_i) \quad (4.35)$$

$$= \frac{1}{Z_{c,1}} \frac{1}{2} \left[ e^{\frac{\Delta/2}{k_B T}} - e^{-\frac{\Delta/2}{k_B T}} \right] \quad (4.36)$$

$$= \frac{1}{2} \tanh \left( \frac{\Delta/2}{k_B T} \right). \quad (4.37)$$

It is seen that the average spin  $\langle s_i \rangle$  is independent of the other spins in the canonical ensemble, since the total energy is not fixed.

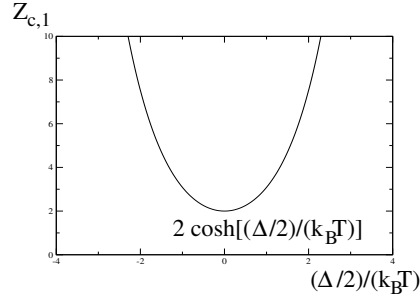


Figure 4.4: Canonical partition sum of a two-level system

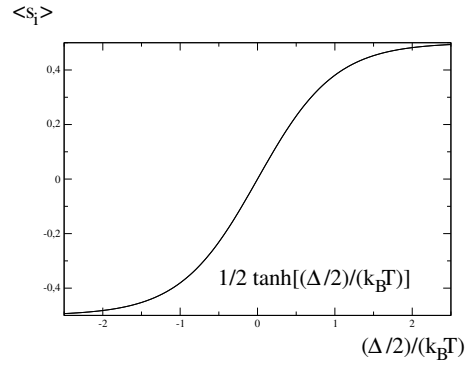


Figure 4.5: Average spin per site

The magnetization of the system is

$$M = Ng\mu_0 \langle s_i \rangle = Ng\mu_0 \frac{1}{2} \tanh \left( \frac{\Delta/2}{k_B T} \right) = N\mu_0 \tanh \left( \frac{\mu_0 B}{k_B T} \right). \quad (4.38)$$

### Thermodynamics of spin systems (2-level systems)

The **free energy** can be calculated microscopically from the canonical partition sum:

$$F(T) = -k_B T \ln Z_c = -Nk_B T \ln \left( 2 \cosh \left( \frac{\Delta/2}{k_B T} \right) \right) \quad (4.39)$$

The **entropy** is

$$S(T) = -\frac{\partial F}{\partial T} = Nk_B \left[ \ln \left( 2 \cosh \left( \frac{\Delta/2}{k_B T} \right) \right) - \frac{\Delta/2}{k_B T} \tanh \left( \frac{\Delta/2}{k_B T} \right) \right] \quad (4.40)$$

and the **specific heat** for  $B = \text{const.}$ ,

$$C_B(T) = \left( \frac{\delta Q}{\delta T} \right)_B = T \left( \frac{\partial S}{\partial T} \right)_B = N k_B \left( \frac{\Delta/2}{k_B T} \right)^2 \frac{1}{\cosh^2 \left( \frac{\Delta/2}{k_B T} \right)}. \quad (4.41)$$

**Discussion of the  $T$ -dependence of  $c_B$ :**

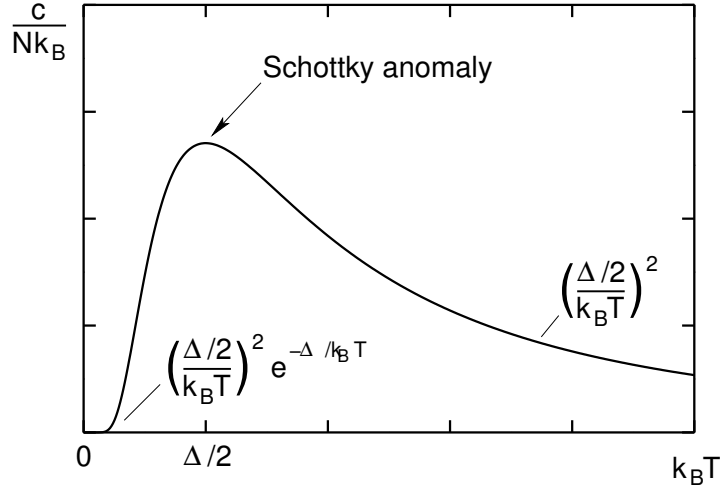


Figure 4.6: Specific heat of an ideal two-level system

- (1) For  $k_B T \ll \Delta/2$ ,  $c_B \sim \left(\frac{\Delta/2}{k_B T}\right)^2 e^{-\frac{\Delta}{k_B T}}$  vanishes exponentially in a nonanalytical way (all derivatives are zero). This is typical for systems with an excitation gap  $\Delta$  between the ground state and the first excited state:

At low  $T$ , the occupation of the excited state(s) is exponentially small due to the Boltzmann distribution, making the  $T$ -dependence of the internal energy  $U$  and of the specific heat  $c_B = \left(\frac{\partial U}{\partial T}\right)_B$  exponential.

- (2) For  $k_B T \gg \Delta/2$ ,  $c_B \sim \frac{1}{T^2} \xrightarrow{T \rightarrow \infty} 0$ .

This is typical for systems whose energy spectrum is bounded from above: For  $k_B T \gg E_{\max} = \Delta/2$  ground state and excited state(s) are equally occupied, and increasing  $T$  does not increase  $U$  anymore.  $\rightarrow c_B = \left(\frac{\partial U}{\partial T}\right)_B \rightarrow 0$ .

- (3) From (1) and (2) it follows  $c_B(T)$  must have a maximum. This maximum is called *Schottky anomaly* and is characteristic for a discrete 2-level system. It is therefore often used to detect 2-level systems in experiments.

The **internal energy** is calculated from the above expressions as,

$$U = F + TS = -N\mu_0 \tanh\left(\frac{\mu_0 B}{k_B T}\right) = -MB \quad (4.42)$$

or equivalently

$$U = \sum_i (-2\mu_0 B) \langle s_i \rangle = -\underbrace{2N\mu_0 \langle s_i \rangle}_M B. \quad (4.43)$$

The **magnetization** can also be calculated by thermodynamic derivative:

$$M = -\left(\frac{\partial F}{\partial B}\right)_T \quad (4.44)$$

$$= -\frac{\partial}{\partial B} (k_B T \ln Z_c) \quad (4.45)$$

$$= -\frac{\partial}{\partial B} (Nk_B T \ln Z_{c,1}) \quad (4.46)$$

$$= -Nk_B T \frac{1}{Z_{c,1}} \frac{\partial Z_{c,1}}{\partial B} \quad (4.47)$$

$$\stackrel{(*)}{=} 2N\mu_0 \sum_{s=\pm\frac{1}{2}} s e^{-\frac{2s\mu_0 B}{k_B T}} \quad (4.48)$$

$$= 2N\mu_0 \langle s \rangle \quad (4.49)$$

$$= N\mu_0 \tanh\left(\frac{\mu_0 B}{k_B T}\right) \quad (4.50)$$

$$(*) \quad Z_{c,1} = \sum_{s=\pm\frac{1}{2}} e^{-\frac{2s\mu_0 B}{k_B T}}, \quad (4.51)$$

as in the direct calculation, Eqs. (4.34)–(4.38).

This shows how statistical averages are generated by thermodynamic derivatives of  $F$ .

The **magnetic susceptibility**  $\chi$  of a system of *distinguishable* (e.g. localized) spins is

$$\chi = \left(\frac{\partial M}{\partial B}\right)_{S,V,N} = N \frac{\mu_0^2}{k_B T} \frac{1}{\cosh^2\left(\frac{\mu_0 B}{k_B T}\right)}. \quad (4.52)$$

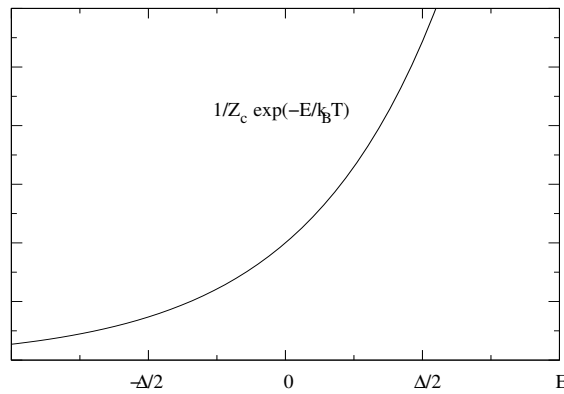
Hence, for vanishing B-field the susceptibility is

$$\chi = \left( \frac{\partial M}{\partial B} \right)_{S,V,N;B=0} = N \frac{\mu_0^2}{k_B T} . \quad (4.53)$$

This so-called Curie behavior,  $\chi_{B=0} \sim 1/T$ , is characteristic for localized spins and is used experimentally to detect local magnetic moments in solids, as compared to the  $T$  – *independent* low-temperature susceptibility of the mobile spins of electrons in a metal (see section 5.2.2).

**Negative “temperature”:**

$T < 0$  leads to nondiverging occupation probabilities, if the spectrum is bounded from above, and corresponds to an occupation inversion, as shown in figure 26, i.e. to a nonequilibrium state. In the case  $T < 0$ ,  $T$  should, therefore, be understood as a mere parameter to describe a special (non-equilibrium) distribution rather than an actual temperature. The latter is defined only in thermodynamic equilibrium and must be positive semidefinite. The inversion can be realized ex-

Figure 4.7: Occupation probability for  $T < 0$ 

perimentally by adiabatically (i.e. quickly) inverting the magnetic field  $B \rightarrow -B$ , so that no relaxation of the average occupation numbers  $W_C(E)$  is possible:

$$E \left( s_i = +\frac{1}{2} \right) = -\mu_0 B \rightarrow +\mu_0 B \quad (4.54)$$

$$E \left( s_i = -\frac{1}{2} \right) = +\mu_0 B \rightarrow -\mu_0 B \quad (4.55)$$

**Adiabatic demagnetization:**

By quickly (adiabatically) reducing the external magnetic field  $B \rightarrow B' < B$ , such that no change of the occupation probabilities  $W_C(E)$  occurs during this process, the temperature  $T$  is reduced by the factor  $B'/B$ . This is because in  $W_C(E)$  the quantities  $B$  and  $T$  appear as the ratio  $B/T$  only, and because  $W_C(E)$ , and hence  $B/T$  remains unchanged. This method is called *adiabatic demagnetization*.

The lowest, technically reachable temperatures ( $T \approx 1\mu K$ ) are realized in spin systems by using this method.

## 4.2 A system of independent harmonic oscillators

We consider a system of  $N$  identical, uncoupled harmonic oscillators with eigenfrequency  $\omega$ :

$$H = \sum_{i=1}^N \hbar\omega \left( a_i^\dagger a_i + \frac{1}{2} \right) \quad (4.56)$$

with possible energy eigenvalues of a microstate

$$|n\rangle = |n_1, n_2, \dots, n_N\rangle \quad (4.57)$$

are

$$E_n = \sum_{i=1}^N \hbar\omega \left( n_i + \frac{1}{2} \right) = \sum_{i=1}^N E_{n_i}^{(1)}, \quad (4.58)$$

where  $n_i$  is the number of excitation quanta ("phonons") of the  $i$ -th oscillator,  $i = 1, \dots, N$ .

The canonical partition sum factorizes like for any system of non-interacting subsystems:

$$Z_c = Z_{c,1}^N = \left( \sum_{n=0}^{\infty} e^{-\frac{E_{n_i}^{(1)}}{k_B T}} \right)^N \quad (4.59)$$

$$= \left( e^{-\frac{\hbar\omega}{2k_B T}} \frac{1}{1 - e^{-\frac{\hbar\omega}{k_B T}}} \right)^N \quad (4.60)$$

$$= \left( \frac{1}{2 \sinh \left( \frac{\hbar\omega}{2k_B T} \right)} \right)^N \quad (4.61)$$

It is seen that in the canonical ensemble the summation over all microstates is easily performed, because one can sum over all eigenstates of the individual oscillators independently, without the restriction that the total energy of the  $N$ -oscillator system is constant, which would be there in the microcanonical ensemble.



All physical quantities can be computed from  $Z_c$ :

• **Internal energy  $U$ :**

$$U = \langle E \rangle = \frac{1}{Z_c} \sum_n E_n e^{-\frac{E_n}{k_B T}} \quad (4.62)$$

$$= \sum_{\substack{n_i=0 \\ i=1,\dots,N}}^{\infty} (E_{n_1} + E_{n_2} + \dots + E_{n_N}) \prod_{j=1}^N \frac{e^{-\frac{E_{n_j}^{(1)}}{k_B T}}}{Z_{c,1}} \quad (4.63)$$

$$= N \left( \sum_{n_1=0}^{\infty} E_{n_1}^{(1)} \frac{e^{-\frac{E_{n_1}^{(1)}}{k_B T}}}{Z_{c,1}} \right) = N \langle E^{(1)} \rangle, \quad (4.64)$$

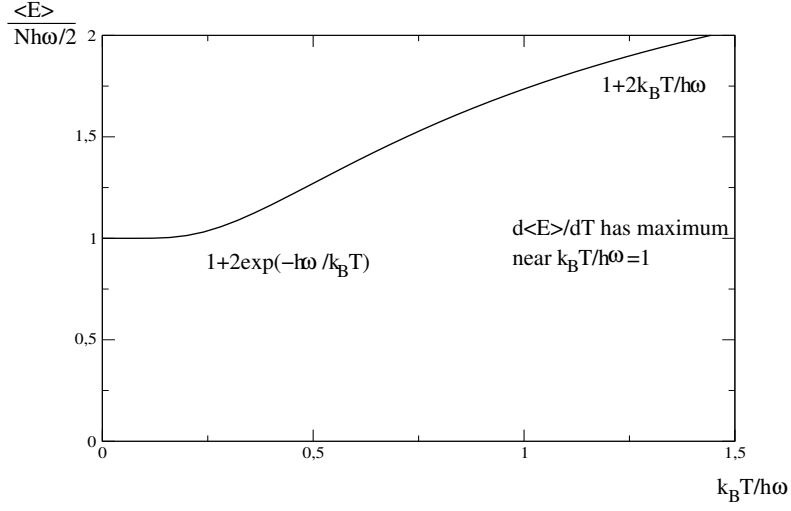
where the expression in brackets in the last line is the internal energy of a single oscillator. It can be calculated directly from the partition sum as a derivative, as seen from:

$$\langle E^{(1)} \rangle = -\frac{\partial}{\partial \beta} \ln Z_c^{(1)} \quad (4.65)$$

$$= 2 \sinh \left( \frac{\hbar \omega}{2k_B T} \right) \frac{\cosh \left( \frac{\hbar \omega}{2k_B T} \right)}{2 \sinh^2 \left( \frac{\hbar \omega}{2k_B T} \right)} \frac{\hbar \omega}{2} \quad (4.66)$$

$$\text{with } \beta = \frac{1}{k_B T} \quad (4.67)$$

$$\langle E^{(1)} \rangle = \frac{\hbar \omega}{2} \coth \left( \frac{\hbar \omega}{2k_B T} \right). \quad (4.68)$$

Figure 4.8: Internal energy of a system of  $N$  harmonic oscillators

- The internal energy has for  $T \rightarrow 0$  a finite value  $N \frac{\hbar\omega}{2}$  because of the zero-point energy of the harmonic oscillator.
- The  $T$ -dependence for  $k_B T < \hbar\omega/2$  is *exponential* because there is an excitation gap to the next excited state.
- For  $k_B T \gg \hbar\omega/2$   $\langle E \rangle \sim T$

This can be understood by calculating the average number of oscillator quanta per oscillator:

$$\langle n \rangle = \sum_{n_1=0}^{\infty} n_1 \frac{e^{-\frac{\hbar\omega(n_1 + \frac{1}{2})}{k_B T}}}{Z_{c,1}} \quad (4.69)$$

$$= -\frac{\partial}{\partial(\beta\hbar\omega)} \ln Z_{c,1} - \frac{1}{2} \quad (4.70)$$

$$= \frac{1}{2} \left[ \coth \left( \frac{\hbar\omega}{2k_B T} \right) - 1 \right] \quad (4.71)$$

$$\langle n \rangle = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (4.72)$$

Thus,

$$\langle E^{(1)} \rangle = \hbar\omega \left( \langle n \rangle + \frac{1}{2} \right). \quad (4.73)$$

The average number of quanta at a given temperature  $T$  is proportional to  $T$  for  $k_B T \gg \hbar\omega/2$ , where each quantum has a fixed  $T$ -independent energy  $\hbar\omega$ . Hence,  $\langle E^{(1)} \rangle \sim T, k_B T \gg \frac{\hbar\omega}{2}$ .

• **Free energy  $F$ :**

$$F = -k_B T \ln Z_c \quad (4.74)$$

$$= -N k_B T \ln Z_{c,1} \quad (4.75)$$

$$= N k_B T \ln \left( 2 \sinh \left( \frac{\hbar\omega}{2k_B T} \right) \right) \quad (4.76)$$

$$= N \left[ k_B T \ln \left( 1 - e^{-\frac{\hbar\omega}{k_B T}} \right) + \frac{\hbar\omega}{2} \right] \quad (4.77)$$

• **Entropy  $S$ :**

$$S = -\frac{\partial F}{\partial T} \quad (4.78)$$

$$= -N k_B \left[ \ln \left( 1 - e^{-\frac{\hbar\omega}{k_B T}} \right) - \frac{\hbar\omega/k_B T}{e^{\frac{\hbar\omega}{k_B T}} - 1} \right] \quad (4.79)$$

$$= \begin{cases} N k_B \frac{\hbar\omega}{k_B T} e^{-\frac{\hbar\omega}{k_B T}}, & k_B T \ll \hbar\omega \\ N k_B \left( \ln \left( \frac{k_B T}{\hbar\omega} \right) + 1 \right), & k_B T \gg \hbar\omega \end{cases} \quad (4.80)$$

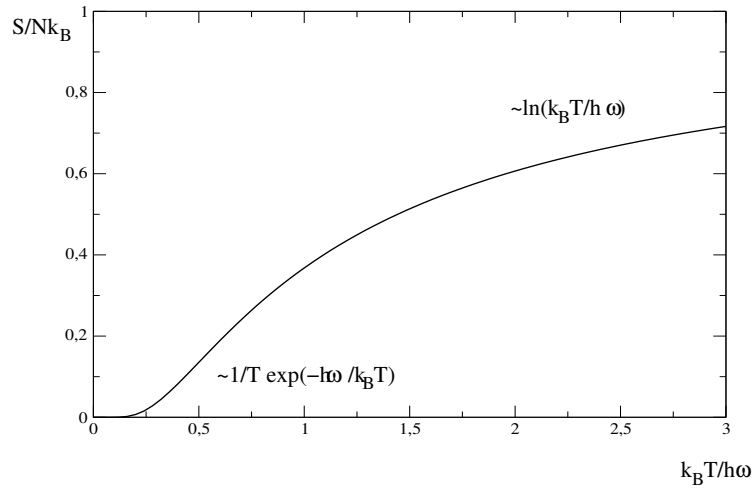
The internal energy can be calculated from the thermodynamic relation,

$$U = F + TS \quad (4.81)$$

$$= N \left[ \frac{\hbar\omega}{2} + \hbar\omega \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \right] \quad (4.82)$$

$$= N \hbar\omega \left[ \langle n \rangle + \frac{1}{2} \right] \quad (4.83)$$

in agreement with the above direct calculation.

Figure 4.9: Entropy of a system of  $N$  independent harmonic oscillators

- **Specific heat:**

$$c = \frac{\partial U}{\partial T} \quad (4.84)$$

$$= N\hbar\omega \frac{\partial \langle n \rangle}{\partial T} \quad (4.85)$$

$$= Nk_B \frac{\left(\frac{\hbar\omega}{2k_B T}\right)^2}{\sinh^2\left(\frac{\hbar\omega}{2k_B T}\right)} \quad (4.86)$$

$$= \begin{cases} Nk_B, & k_B T \gg \hbar\omega \\ Nk_B \left(\frac{\hbar\omega}{2k_B T}\right)^2 e^{-\frac{\hbar\omega}{k_B T}}, & k_B T \ll \hbar\omega \end{cases} \quad (4.87)$$

or equivalently,

$$c = T \frac{\partial S}{\partial T}. \quad (4.88)$$

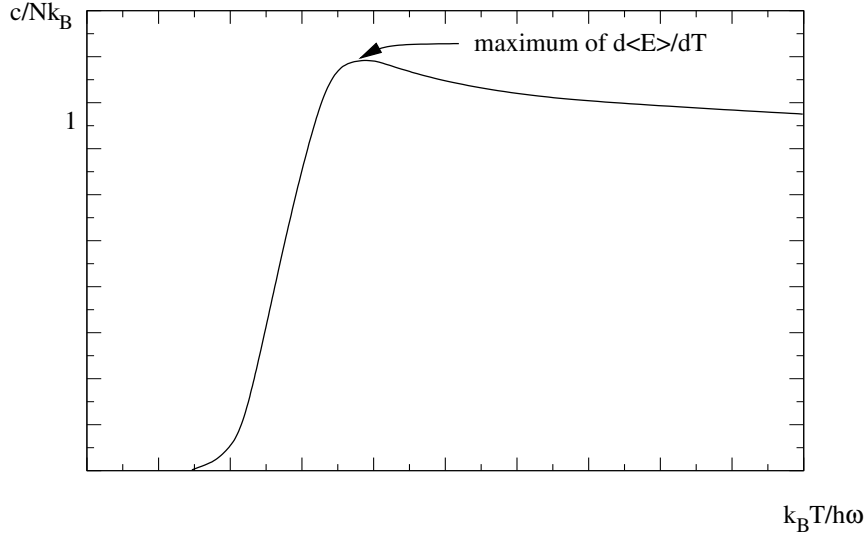


Figure 4.10: Specific heat of a system of  $N$  harmonic oscillators

The result for  $T \rightarrow \infty$  is in agreement with the virial and the equipartition theorems (see Chapter 5.5).

The high-temperature behavior  $c(T) = \text{const.}$  is characteristic for systems with a spectrum unbounded from above and is in agreement with the equipartition theorem.

"In the classical limit ( $T, \langle E \rangle \gg \hbar\omega$ ) each degree of freedom which appears quadratically in the Hamiltonian, contributes  $\frac{1}{2}k_B$  to the specific heat  $c$ ."

(Here the degrees of freedom are  $p_i$  and  $x_i, i = 1, \dots, N$ .)

The general equipartition theorem will be discussed later.

From the above calculation one can learn that

- thermodynamic expectation values, like  $\langle E \rangle, \langle n \rangle$  etc. can often be calculated directly as derivatives of  $Z_c$  with respect to appropriate variables.
- for non-interacting systems which do not share the same volume, derivatives of  $\ln Z_c$  wrt. an intensive variable (e.g.  $T$ ) are extensive, trivially. This will be different for a classical ideal gas.

### 4.3 The ideal Boltzmann gas and the Gibbs paradox

As the third important example we consider a system of  $N$  non-interacting particles in a large cubic box of length  $L$  and volume  $V = L^d$ , where  $d$  is the spatial dimension. This example will serve two purposes:

- (1) The fact that these particles share the same volume  $V$  means that they are indistinguishable in the quantum mechanical sense - in contrast to the spins or harmonic oscillators of the previous sections, which are not mobile and therefore distinguishable. The treatment as distinguishable particles familiar from classical mechanics will lead to an unresolvable inconsistency, which will motivate the treatment as a quantum gas, introducing *quantum statistics*.
- (2) By deriving the ideal gas law from a *microscopic* statistical basis, we will be able to make the identification of the Boltzmann constant  $k_B$  of statistical physics with the proportionality factor  $k_B$  of the gas law.

#### 4.3.1 Statistics of the ideal gas

As usual, we define first the Hamiltonian  $H$ , the energy eigenstates  $|n\rangle$ , and the possible total energy eigenvalues  $E_n$  of the  $N$ -particle system:

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} = \sum_{i=1}^N \frac{1}{2m} (p_{ix}^2 + p_{iy}^2 + p_{iz}^2) \quad (4.89)$$

$$\psi_{\vec{k}_i}(\vec{x}_i) = \frac{1}{\sqrt{V}} e^{i\vec{k}_i \cdot \vec{x}_i} \quad (4.90)$$

with quantization

$$\vec{k}_i = \frac{2\pi}{L} (n_{ix}\hat{e}_x + n_{iy}\hat{e}_y + n_{iz}\hat{e}_z) \quad (4.91)$$

$$n_{ix}, n_{iy}, n_{iz} = -\infty, \dots, \infty \quad (4.92)$$

and in position representation

$$\langle \{\vec{x}\} | n \rangle = \psi_{\vec{k}_1}(\vec{x}_1) \psi_{\vec{k}_2}(\vec{x}_2) \dots \psi_{\vec{k}_N}(\vec{x}_N) \quad (4.93)$$

$$E_n = \frac{1}{2m} \left( \frac{2\pi\hbar}{L} \right)^2 \left[ \sum_{i=1}^N (n_{ix}^2 + n_{iy}^2 + n_{iz}^2) \right], \quad (4.94)$$

with

$$\Delta := \frac{2\pi^2\hbar^2}{mL^2} \quad (4.95)$$

**Note:** This corresponds to the treatment of *classical distinguishable* particles, since in the many-body wave function  $\langle \{\vec{x}\} | n \rangle$  the particles are distinguishable, particle 1 (with coordinate  $\vec{x}_1$ ) being in state  $\vec{k}_1$ , etc. The representation of the states in terms of wave functions is chosen here only make the  $\vec{k}$ -states discrete and, thus, to make it easy to enumerate the states. Otherwise the treatment is classical.

In the canonical ensemble the partition function factorizes, because the particles and their momentum components are independent,

$$Z_c = (Z_1)^{N \cdot d} \quad (4.96)$$

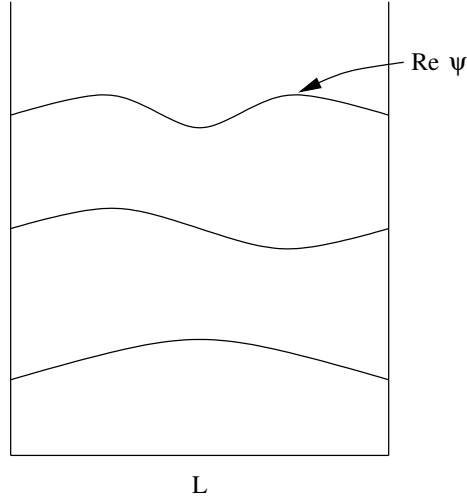
$$\text{with } Z_1 = \sum_{n=-\infty}^{+\infty} e^{-\frac{2\pi^2\hbar^2}{mL^2 k_B T} n^2} = \sum_{n=-\infty}^{+\infty} e^{-\frac{\lambda_T^2}{L^2} n^2} \quad (4.97)$$

being the canonical partition function per particle and spatial direction. The "thermal de Broglie wavelength"  $\lambda_T$  is defined through the relation

$$k_B T = \frac{1}{2m} \left( \frac{2\pi\hbar}{\lambda_T} \right)^2 \quad (4.98)$$

$$\lambda_T = \frac{2\pi\hbar}{\sqrt{2mk_B T}} = \sqrt{\frac{\Delta}{k_B T}} \cdot L$$

thermal wavelength (4.99)

Figure 4.11: Wave functions of free particles in a box of length  $L$ 

In the thermodynamic limit,  $L \gg \lambda_T$ , where we must have  $T > 0$ , the sum in  $Z_1$  can be replaced by an integral and can be evaluated,

$$\lim_{L \rightarrow \infty} Z_1 = \int_{-\infty}^{+\infty} dn e^{-\left(\frac{\lambda_T}{L}\right)^2 n^2} = \frac{L}{\lambda_T} \sqrt{\pi} \quad (4.100)$$

and

$$Z_c = \left( \sqrt{\pi} \frac{L}{\lambda_T} \right)^{Nd} \quad (4.101)$$

In the limit  $T \rightarrow 0$  the evaluation as an integral breaks down, and a quantum mechanical treatment in terms of discrete states is required.

The thermodynamic quantities of the ideal Boltzmann gas follow in a straightforward way:

(1) *Free energy:*

$$F = -Nk_B T \ln \left( \sqrt{\pi}^d \frac{V}{\lambda_T^d} \right) \quad (4.102)$$

$$= -\frac{d}{2} Nk_B T \ln \left( \pi \frac{k_B T}{\Delta} \right) \quad (4.103)$$



(2) *Entropy:*

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N} \quad (4.104)$$

$$= \frac{d}{2} N k_B \ln \left( \pi \frac{k_B T}{\Delta} \right) + \frac{d}{2} N k_B \quad (4.105)$$

(3) *Internal energy:*

$$U = F + TS = \frac{d}{2} N k_B T$$

(4.106)

(4) *Specific heat:*

$$c_V = \left( \frac{\partial U}{\partial T} \right)_{V,N} = T \left( \frac{\partial S}{\partial T} \right)_{V,N} = \frac{d}{2} N k_B$$

(4.107)

equipartition rule (see above)

(5) *Pressure:*

$$p = - \left( \frac{\partial F}{\partial V} \right)_T = \frac{N k_B T}{V} \quad (4.108)$$

$$pV = N k_B T$$

Ideal gas law (4.109)

Note that the proportionality constant  $k_B$  in this equation is the (still arbitrary) Boltzmann constant  $k = k_B$  as defined in the context of the statistical entropy. By comparison this statistical law with the thermodynamic definition of the temperature through the gas law (see chapter 1), the value of  $k_B$  is now fixed.

(The Maxwell distribution of the velocities in an ideal gas will be computed as an exercise.)

### 4.3.2 The Gibbs paradox

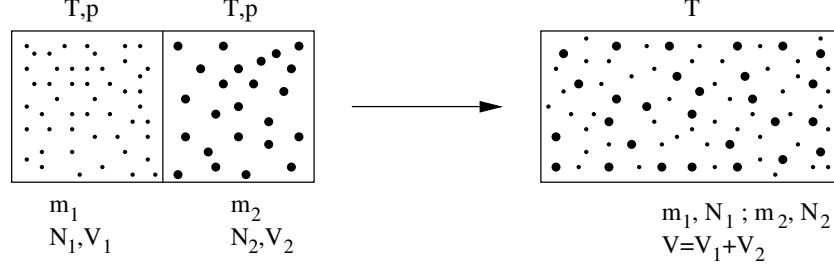


Figure 4.12: Mixing of two gases

We consider two ideal Boltzmann gases  $(m_1, N_1, V_1)$ ,  $(m_2, N_2, V_2)$  with particle mass  $m_1$  and  $m_2$ , respectively, in volumina  $V_1$  and  $V_2$ , separated by a wall, at the same temperature  $T = T_1 = T_2$  and pressure  $p = p_1 = p_2$ . At a time  $t = 0$  the wall is removed, and the two gases mix;  $T = \text{const.}$

Before the mixing the total entropy is ( $d = 3$ )

$$S = S_1 + S_2 \quad (4.110)$$

$$= \frac{3}{2}k_B \left[ 2N_1 \ln \left( \sqrt{\pi} \frac{V_1^{1/3}}{\lambda_{T_1}} \right) + 2N_2 \ln \left( \sqrt{\pi} \frac{V_2^{1/3}}{\lambda_{T_2}} \right) + N_1 + N_2 \right]. \quad (4.111)$$

After the mixing the entropy is

$$S' = S'_1 + S'_2 \quad (4.112)$$

$$= \frac{3}{2}k_B \left[ 2N_1 \ln \left( \sqrt{\pi} \frac{V^{1/3}}{\lambda_{T_1}} \right) + 2N_2 \ln \left( \sqrt{\pi} \frac{V^{1/3}}{\lambda_{T_2}} \right) + N_1 + N_2 \right]. \quad (4.113)$$

i.e. the entropy changes by

$$\Delta S = S' - S = \frac{3}{2}k_B \left[ 2N_1 \ln \left( \frac{V_1 + V_2}{V_1} \right)^{1/3} + 2N_2 \ln \left( \frac{V_1 + V_2}{V_2} \right)^{1/3} \right] > 0. \quad (4.114)$$

The increase of entropy is expected, *if the gases are different* ( $m_1 \neq m_2$ ), because the mixing process is *irreversible* in this case (entropy of mixing).

However, if the two gases consist of the same kind of particles ( $m_1 = m_2$ ), the mixing process is *reversible*, since it actually constitutes no change of state at

all. Therefore, we must have  $\Delta S = 0$  for  $m_1 = m_2, T_1 = T_2, p_1 = p_2$ . But in our classical treatment the entropy change would still be given by (4.116),  $\Delta S > 0$ . This is called *Gibbs paradox* of classical statistics. It shows that it is incorrect to consider the identical particles ( $m_1 = m_2$ ) as distinguishable.

The paradox is resolved by quantum statistics:

The states of a many-particle system comprised of particles of the same kind (identical particles) are counted such that the particles are indistinguishable.



## Chapter 5

# Quantum Statistical Mechanics: Systems of Identical Particles

### 5.1 The correct enumeration of states

In the previous chapter we had seen that unphysical results can arise, if in counting the states, the particles are treated as classically distinguishable.

In a system of  $N$  *localized* spins (which have no motional degree of freedom) the individual spins are *distinguishable* since each one can be thought of as sitting on a different, distinguishable site of the lattice. This gives each spin its own identity. The lattice site can be identified in principle, e.g. by absorbing a  $\gamma$  quantum and thereby going to an excited state which distinguishes that site from the others.

By contrast, particles of the same kind in a gas or liquid sharing the same volume cannot be distinguished: Suppose the particles number 1 and number 2,  $p_1$ ,  $p_2$ , are of the same kind, i.e. they have no internal quantum number(s) which would allow to distinguish them. Then there is no experiment - not even in principle - which would allow to distinguish the two-particle state  $|a, b\rangle$  with  $p_1$  in the single-particle state  $|a\rangle$  and  $p_2$  in the single-particle state  $|b\rangle$  from the state  $|b, a\rangle$  where  $p_1$  is in the state  $|b\rangle$  and  $p_2$  is in the state  $|a\rangle$ . Hence the particles  $p_1$ ,  $p_2$  are indistinguishable. The states  $|a, b\rangle$  and  $|b, a\rangle$  can differ only by a “ $-$ ” sign (in

3 spatial dimensions), as discussed in many-particle quantum mechanics.

As a first step, we will consider only non-interacting particles (ideal systems). The general case will be discussed in succeeding chapters.

In the correct enumeration of states for indistinguishable particles, states which “differ” only by a permutation (interchange) of particles *must not be counted as being different*. The correct counting is conveniently done not in the coordinate representation (where the coordinates and other quantum numbers are specified for each particle) but rather in the occupation number representation (where first a complete basis of single-particle states  $\{|\alpha\rangle\}$  is chosen and then the number  $n_\alpha$  of particles in each single-particle state  $|\alpha\rangle$  is specified):

$$|\Phi\rangle = |n_{\alpha_1}, n_{\alpha_2}, \dots\rangle \quad (5.1)$$

In this representation the double counting of identical states is automatically avoided.

Enumerating the states by the occupation numbers  $n_\alpha$  is, however, difficult in the canonical ensemble, because here the total number of particles is fixed;

$$N = n_{\alpha_1} + n_{\alpha_2} + n_{\alpha_3} + \dots, \quad (5.2)$$

and thus the summations over the occupation numbers  $n_{\alpha_i}$  cannot be done independently of each other. Therefore, in quantum statistics, it is convenient to calculate in the grand canonical ensemble, which is equivalent in the thermodynamic limit. Since the grand canonical ensemble contains all the states with arbitrary total particle numbers,  $N = 0, 1, 2, 3, \dots, \infty$ , the sums over the occupation numbers  $n_{\alpha_i}$  are independent of each other.

## 5.2 The ideal Fermi gas

### 5.2.1 General expressions

Because of the antisymmetry of the total wave function with respect to particle exchange the occupation numbers of a single-particle state are restricted to

$n_{\alpha_i} = 0, 1$  with  $i = 1, 2, \dots$

The total energy eigenvalues of the many-particle system are

$$E(n_{\alpha_1}, n_{\alpha_2}, \dots) = \sum_{i=1}^{\infty} n_{\alpha_i} E_{\alpha_i} \quad (5.3)$$

where  $E_{\alpha_i}$  = energy of the single-particle state  $|\alpha_i\rangle$ .

The grand canonical partition function is

$$Z_{\text{GC}} = \sum_{\substack{n_{\alpha_i}=0,1 \\ i=1,2,3,\dots}} e^{-\frac{E(\{n_{\alpha_i}\}) - \mu N}{k_B T}} \quad (5.4)$$

$$= \prod_{i=1}^{\infty} \left( \sum_{n_{\alpha_i}=0,1} e^{-\frac{n_{\alpha_i}(E_{\alpha_i} - \mu)}{k_B T}} \right) \quad (5.5)$$

$$\equiv \prod_{i=1}^{\infty} Z_{\text{GC},1}(\alpha_i, \mu, T) \quad (5.6)$$

$$= \prod_{i=1}^{\infty} \left( 1 + e^{-\frac{E_{\alpha_i} - \mu}{k_B T}} \right) \quad (5.7)$$

where  $N = \sum_{i=1}^{\infty} n_{\alpha_i}$ .

The grand canonical potential is:

$$\Omega = -k_B T \ln Z_{\text{GC}} = -k_B T \sum_{i=1}^{\infty} \ln Z_{\text{GC},1}(\alpha_i, \mu, T). \quad (5.8)$$

The average occupation number of the single particle state  $|\alpha_i\rangle$  is computed as,

$$\langle n_{\alpha_i} \rangle = \sum_{\substack{n_{\alpha_j}=0,1 \\ j=1,2,\dots}} n_{\alpha_i} W_{\text{GC}}(\{\alpha_j\}) = \sum_{n_{\alpha_i}=0,1} n_{\alpha_i} \frac{e^{-\frac{n_{\alpha_i}(E_{\alpha_i} - \mu)}{k_B T}}}{Z_{\text{GC},1}(\alpha_i, \mu, T)} \quad (5.9)$$

$$= -k_B T \frac{\partial}{\partial E_{\alpha_i}} \ln Z_{\text{GC},1}(\alpha_i, \mu, T) \quad (5.10)$$

$$= \frac{e^{-\frac{E_{\alpha_i} - \mu}{k_B T}}}{1 + e^{-\frac{E_{\alpha_i} - \mu}{k_B T}}} = \frac{1}{e^{\frac{E_{\alpha_i} - \mu}{k_B T}} + 1} \quad (5.11)$$

$$\langle n_{\alpha_i} \rangle = \frac{1}{e^{\beta(E_{\alpha_i} - \mu)} + 1} \equiv f(E_{\alpha_i}), \quad \beta = \frac{1}{k_B T}$$

Fermi distribution function

(5.12)

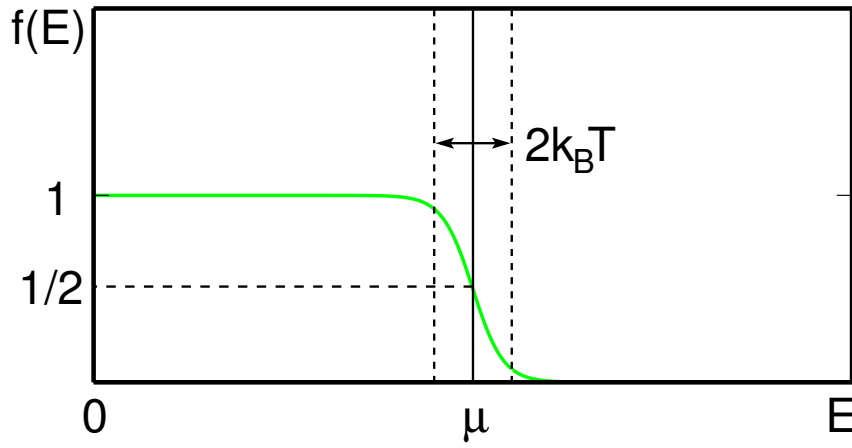


Figure 5.1: Fermi-Dirac distribution function

$$\langle n_{\alpha_i} \rangle = \frac{1}{2} \left\{ 1 - \tanh \left( \frac{1}{2} \beta (E_{\alpha_i} - \mu) \right) \right\} \quad (5.13)$$

$$\langle n_{\alpha_i} \rangle \xrightarrow{T \rightarrow 0} \theta(\mu - E_{\alpha_i}) \quad (5.14)$$

**Note the difference:**

The Boltzmann distribution  $\frac{1}{Z_{GC}} e^{\frac{E - \mu N}{k_B T}}$  is the probability that a *many-particle state* with energy  $E$  and average total particle number  $N$  is realized in the grand canonical ensemble.

The Fermi distribution  $f_{\mu}(E_{\alpha_i})$  is the average occupation number  $\langle n_{\alpha_i} \rangle$  (or occupation probability) of a *single-particle state*  $|\alpha_i\rangle$  within a many-particle state.



The correct counting of indistinguishable particles and the restriction  $n_{\alpha_i} = 0, 1$  induces the non-trivial form of  $f(E_{\alpha_i})$ .

In the limit  $T \rightarrow 0$   $\mu$  is called Fermi energy:

$$\mu(T = 0) \equiv \varepsilon_F. \quad (5.15)$$

According to Equation (5.15) it is the energy up to which the single-particle states are occupied in a Fermi gas with total particle number  $N$  at  $T = 0$ . The Fermi momentum  $p_F$  is the momentum of the highest occupied single-particle state, i.e. defined by  $\varepsilon_F = p_F^2/2m$ .

The chemical potential  $\mu$  is determined so as to fix the average total particle number:

$$\langle N \rangle = \sum_{i=1}^{\infty} f_{\mu}(E_{\alpha_i}) = \int dE \rho(E) f_{\mu}(E), \quad (5.16)$$

where  $\rho(E) = \sum_{i=1}^{\infty} \delta(E - E_{\alpha_i})$  is the density of states (DOS).

This is an implicit equation for  $\mu$ .

The occupation number fluctuations in state  $\alpha$  are (with  $n_{\alpha}^2 = n_{\alpha}$  for fermions),

$$\langle (n_{\alpha} - \langle n_{\alpha} \rangle)^2 \rangle = \langle n_{\alpha}^2 \rangle - \langle n_{\alpha} \rangle^2 \quad (5.17)$$

$$= \langle n_{\alpha} \rangle - \langle n_{\alpha} \rangle^2 \quad (5.18)$$

$$= f(E_{\alpha}) (1 - f(E_{\alpha})) \quad (5.19)$$

The relative fluctuations of the total particle number are, thus,

$$\frac{\sqrt{\langle \Delta N^2 \rangle}}{\langle N \rangle} = \frac{[\int dE \rho(E) f(E) (1 - f(E))]^{1/2}}{\int dE \rho(E) f(E)} \sim \frac{1}{\sqrt{V}} \xrightarrow{V \rightarrow \infty} 0 \quad (5.20)$$

since  $\rho(E) \sim V$ .

This shows that grand canonical and canonical ensembles are equivalent in the thermodynamic limit  $V \rightarrow \infty$ : Although the formulas for physical quantities may look different in the canonical and in the grand canonical treatment, their numerical values are the same in both treatments.

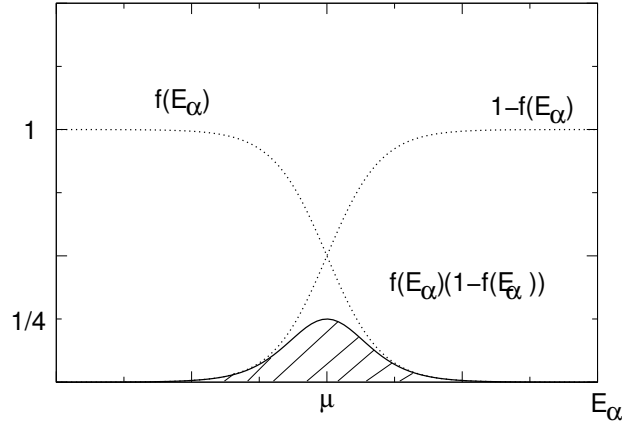


Figure 5.2: Occupation number fluctuations in a Fermi gas

### Thermodynamic properties of the free electron gas

To be specific, we will consider the free electron gas with single-particle energies

$$E_{\vec{p},\sigma} = \frac{\vec{p}^2}{2m} \quad (5.21)$$

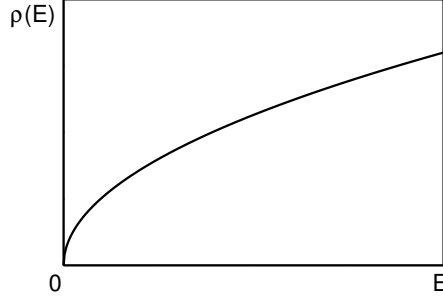
$$\vec{p} = \frac{2\pi\hbar}{L}[m_x\hat{e}_x + m_y\hat{e}_y + m_z\hat{e}_z] \quad (5.22)$$

$$L = \text{system length.} \quad (5.23)$$

The DOS per spin orientation is

$$\rho_\sigma(E)dE = \frac{4\pi p^2 dp}{\frac{(2\pi\hbar)^3}{V}} = \frac{4\pi p^2 \left(\frac{dE_{\vec{p},\sigma}}{dp}\right)^{-1}}{(2\pi\hbar)^3} V dE \quad (5.24)$$

$$\rho_\sigma(E) = \frac{mp(E)}{2\pi^2\hbar^3} V = V \frac{m^{3/2}}{\sqrt{2}\pi^2\hbar^3} \sqrt{E} = V c_3 \sqrt{E}. \quad (5.25)$$

Figure 5.3: Density of states (DOS) of the free electron gas in  $d_3$  dimensions

For the free electron gas (spin 1/2) in  $d = 3$  dimensions the Fermi energy  $\varepsilon_F$  is determined by

$$N = 2Vc_3 \int_0^{\varepsilon_F} dE \sqrt{E} = 2Vc_3 \frac{2}{3} \varepsilon_F^{3/2} \quad (5.26)$$

$$\varepsilon_F = \left( \frac{3n}{4c_3} \right)^{2/3} = (3\pi^2 n)^{2/3} \frac{\hbar^2}{2m} \quad (5.27)$$

with the particle density  $n = N/V$ .

The density of states per spin orientation and volume is then, expressing  $c_3$  in Eq. (5.25) using Eq. (5.27),

$$\frac{\rho_\sigma(E)}{V} = \frac{3}{4} n \frac{1}{\varepsilon_F} \sqrt{\frac{E}{\varepsilon_F}} \quad (5.28)$$

It can be expressed in units of the Fermi energy  $\varepsilon_F$ , the only characteristic energy scale of the free Fermi gas, and in terms of the particle density  $n$  only.

- **Extensivity in the grand canonical ensemble:**

Since  $\rho_\sigma(E) \sim V$  and quantities like the grand potential  $\Omega$  involving a sum over all single-particle eigenstates can be written as  $\sum_\alpha(\dots) = \sum_\sigma \int dE \rho_\sigma(E)$ , these quantities are explicitly extensive.

- **Entropy, internal energy and specific heat:**

Using the grand potential

$$\Omega = -k_B T \ln Z_{GC} = -k_B T \sum_{\alpha} \ln \left( 1 + e^{-\frac{E_{\alpha} - \mu}{k_B T}} \right) \quad (5.29)$$

the entropy of the Fermi gas is obtained as ( with  $\alpha$  =single-particle eigen-state)

$$S = - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} \quad (5.30)$$

$$= k_B \sum_{\alpha} \left[ \ln \left( 1 + e^{-\frac{E_{\alpha} - \mu}{k_B T}} \right) + \frac{E_{\alpha} - \mu}{k_B T} \frac{e^{-\frac{E_{\alpha} - \mu}{k_B T}}}{1 + e^{-\frac{E_{\alpha} - \mu}{k_B T}}} \right] \quad (5.31)$$

$$= -k_B \sum_{\alpha} \left[ \frac{E_{\alpha} - \mu}{k_B T} [1 - f(E_{\alpha})] + \ln(f(E_{\alpha})) \right] \geq 0 \quad (5.32)$$

$$S = -\frac{\Omega}{T} + k_B \sum_{\alpha} \frac{E_{\alpha} - \mu}{k_B T} f(E_{\alpha}) \quad (5.33)$$

The internal energy (for a fixed volume  $V$ ) is then using  $N = \langle N \rangle = \sum_{\alpha} f(E_{\alpha})$  in the thermodynamic limit,

$$U = \Omega + TS + \mu N \quad (5.34)$$

$$= \sum_{\alpha} (E_{\alpha} - \mu) f(E_{\alpha}) + \mu N = \sum_{\alpha} E_{\alpha} f(E_{\alpha}) = \langle E \rangle \quad (5.35)$$

This agrees with the expression used for calculating  $\langle E \rangle$  from the average occupation numbers  $f(E_{\alpha})$ .

The specific heat (for constant volume) is:

$$c_V = \left( \frac{\delta Q}{dT} \right)_{V, \mu} = -T \left( \frac{\partial S}{\partial T} \right)_{V, \mu} \quad (5.36)$$

$$= T \left\{ \frac{\Omega}{T^2} - k_B \sum_{\alpha} \frac{E_{\alpha} - \mu}{k_B T^2} f(E_{\alpha}) - \frac{1}{T} \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} \right. \quad (5.37)$$

$$\left. + k_B \sum_{\alpha} \frac{E_{\alpha} - \mu}{k_B T} \left( \frac{\partial f(E_{\alpha})}{\partial T} \right)_{V, \mu} \right\}$$

$$= -S - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} + \sum_{\alpha} (E_{\alpha} - \mu) \frac{\partial f(E_{\alpha})}{\partial T}. \quad (5.38)$$

where we made in equation (5.36) use of equation (5.32).

Note that in this development  $\mu$  is kept constant according to the grand canonical treatment, i.e. the  $T$ -dependence of  $\mu$  is *not* taken into account in taking the  $T$  derivative.

Using the general expression for the entropy,  $(\frac{\partial \Omega}{\partial T})_{V,\mu} = -S$  we have

$$c_V = \sum_{\alpha} (E_{\alpha} - \mu) \frac{\partial f(E_{\alpha})}{\partial T} = \left( \frac{\partial}{\partial T} \langle E - \mu \rangle \right)_{V,\mu=\text{const.}} \quad (5.39)$$

$$= \frac{\partial}{\partial T} \langle E \rangle = \left( \frac{\partial U}{\partial T} \right)_{V,\mu} \quad (5.40)$$

The specific heat for constant volume is the  $T$ -derivative of the ( internal) energy of the system, measured relative to the ( constant) chemical potential  $\mu$ . Since  $\langle \mu \rangle = \text{const.}(T)$ , this shows that the grand canonical and the canonical calculation of  $c_V$  are equivalent.

$c_V$  obeys the following properties:

1.  $c_V \geq 0$  :

$$\frac{\partial f(E)}{T} = \left( - \left( \frac{\partial f(E)}{\partial E} \right) k_B T \cdot \frac{E - \mu}{k_B T^2} \right) \quad (5.41)$$

$$= \underbrace{\left( - \frac{\partial f(E)}{\partial E} \right)}_{>0} \frac{E - \mu}{T} \quad (5.42)$$

$$\Rightarrow c_V = \frac{1}{T} \sum_{\alpha} (E_{\alpha} - \mu)^2 \left( - \frac{\partial f(E)}{\partial E} \right) \geq 0. \quad (5.43)$$

2.  $T = 0$  limit:

$$\left( - \frac{\partial f(E)}{\partial E} \right)_{T=0} = - \frac{d}{dE} \theta(\mu - E) = \delta(E - \mu) \quad (5.44)$$

$$\Rightarrow c_V(T=0) = 0. \quad (5.45)$$

- **Pressure:**

In calculating the pressure  $p = -(\partial\Omega/\partial V)_{T,\mu}$  from the grand potential  $\Omega$ ,

$$\Omega = -k_B T \sum_{\alpha} \ln \left( 1 + e^{-\frac{E_{\alpha} - \mu}{k_B T}} \right) \quad (5.46)$$

$$= -k_B T \sum_{\sigma} \int dE_{\alpha} \rho_{\sigma}(E_{\alpha}) \ln \left( 1 + e^{-\frac{E_{\alpha} - \mu}{k_B T}} \right), \quad (5.47)$$

one can either use the first expression, taking into account the dependence of the eigenenergies on the volume  $V$ ,

$$E_{\alpha} = \frac{1}{2m} \frac{(2\pi\hbar)^2}{V^{2/3}} (n_x^2 + n_y^2 + n_z^2) \quad (5.48)$$

$$\text{with } \alpha = (n_x, n_y, n_z) \quad (5.49)$$

$$L = V^{1/3}, \quad (5.50)$$

or the second expression, where  $E$  is a volume independent integration variable and  $\rho_{\sigma}(E)$  is explicitly proportional to  $V$ .

Hence, one obtains:

$$p = - \left( \frac{\partial\Omega}{\partial V} \right)_{T,\mu} = - \frac{\Omega}{V} > 0 \quad (5.51)$$

This should be compared to the pressure of the ideal Boltzmann gas:

$$p = \frac{Nk_B T}{V} = \frac{\frac{2}{3}U^{\text{classical}}}{V} \quad (5.52)$$

with  $U^{\text{classical}} = \frac{3}{2}Nk_B T$ .

- **The spin susceptibility of the electron gas ( $s = \frac{1}{2}$ ):**  
is defined as,

$$\chi = \left( \frac{\partial M}{\partial B} \right)_{T,\mu} \quad (5.53)$$

with the spin magnetization,

$$M = 2\mu_0 \sum_{\alpha} \sigma f(E_{\alpha}) \quad (5.54)$$

$$= \mu_0 \sum_{\vec{k}} \left[ f(E_{\vec{k}\uparrow}) - f(E_{\vec{k}\downarrow}) \right] \quad (5.55)$$

and

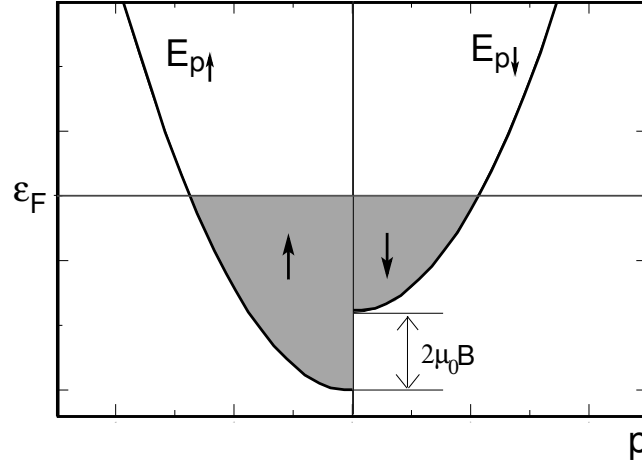


Figure 5.4: Spin magnetization of a free electron gas

$$\alpha = (\vec{k}, \sigma) : \quad \text{single-particle quantum number} \quad (5.56)$$

$$\sigma = \pm \frac{1}{2} : \quad \text{spin orientation of one electron} \quad (5.57)$$

$$E_{\vec{k}\sigma} = E_{\vec{k}}(B=0) - 2\sigma\mu_0 B = E_{\vec{k}}(0) \mp \mu_0 B \quad (5.58)$$

$E_{\vec{k}\sigma}$  is the energy of an electron in the magnetic field  $B$  with Zeeman splitting  $\Delta = 2\mu_0 B$

Note that orbital effects (“Lorentz force”, Landau levels) have been neglected in  $E_{\vec{k}\sigma}$ . These would lead to diamagnetism and are not considered

here.

For small magnetic field ( $B \ll \varepsilon_F, k_B T$ ) we have:

$$M = 2\mu_0^2 B \sum_{\vec{k}} \left( -\frac{\partial f(E_{\vec{k}}(B=0))}{\partial E_{\vec{k}}} \right) + \mathcal{O}(B^3) \quad (5.59)$$

$$\chi = 2\mu_0^2 \sum_{\vec{k}} \left( -\frac{\partial f(E_{\vec{k}})}{\partial E_{\vec{k}}} \right) \Big|_{B=0} = 2\mu_0^2 \int dE \rho(E) \left( -\frac{\partial f}{\partial E} \right) \Big|_{B=0} \quad (5.60)$$

↗  
DOS per spin orientation



### 5.2.2 The low-temperature region $k_B T \ll \varepsilon_F$

From the expressions derived in section 4.2.1 it is clear that physical quantities of Fermi systems usually involve integrals over the Fermi distribution or its derivative (e.g.  $\langle E \rangle$  or  $M$ ).

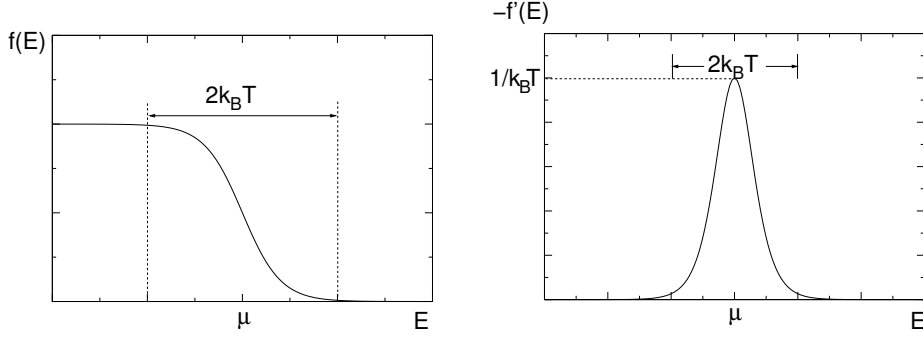


Figure 5.5: Fermi distribution and its derivative

Knowing that for  $k_B T \ll \varepsilon_F$   $f(E)$  is essentially a constant function except near the Fermi edge  $E = \mu \approx \varepsilon_F$ , we see that partial integration transforms the integrand from  $f(E)$  to  $\frac{\partial f(E)}{\partial E}$  which is strongly peaked near  $E = \mu$ .

Therefore, the integrals are effectively limited to the region of width  $2k_B T$  around  $\varepsilon_F$ . This demonstrates that for Fermi systems all physical properties are dominated by contributions from the Fermi edge only.

This observation can be formalized to develop a low-temperature expansion in the width  $2k_B T$ , the so-called *Sommerfeld expansion*.

We perform the Sommerfeld expansion for the grand potential  $\Omega$  and then derive the low- $T$  behaviour of physical quantities from it.

The expression

$$\Omega = -k_B T \sum_{\sigma} \int_{-\infty}^{+\infty} dE \rho_{\sigma}(E) \ln \left[ 1 + e^{-\frac{E-\mu}{k_B T}} \right] \quad (5.61)$$

requires one partial integration to bring out  $f(E)$ :

$$\Omega = - \sum_{\sigma} \int_{-\infty}^{+\infty} dE a_{\sigma}(E) f(E) \quad (5.62)$$

$$\text{where} \quad a_{\sigma}(E) = \int_{-\infty}^E d\varepsilon \rho_{\sigma}(\varepsilon) \quad (5.63)$$

$$\frac{\partial}{\partial E} \ln \left[ 1 + e^{-\frac{E-\mu}{k_B T}} \right] = -\frac{1}{k_B T} f(E) \quad (5.64)$$

and the boundary terms vanish because  $a(E) = 0$  for  $E < 0$  (lower band edge) and  $\ln \left( 1 + e^{-\frac{E-\mu}{k_B T}} \right) \rightarrow 0$  for  $E \rightarrow \infty$ .

One more partial integration yields

$$\Omega = - \sum_{\sigma} \int_{-\infty}^{+\infty} dE b(E) \left( -\frac{\partial f(E)}{\partial E} \right) \quad (5.65)$$

$$\text{with} \quad b_{\sigma}(E) = \int_{-\infty}^E d\varepsilon' a_{\sigma}(\varepsilon') = \int_{-\infty}^E d\varepsilon' \int_{-\infty}^{\varepsilon'} d\varepsilon \rho_{\sigma}(\varepsilon). \quad (5.66)$$

The double integral  $b(E)$  is a weakly varying function compared to  $\frac{\partial f}{\partial E}$  for  $k_B T \ll \varepsilon_F$  and can therefore be expanded with respect to  $E = \mu \approx \varepsilon_F$ :

$$b_{\sigma}(E) = b_{\sigma}(\mu) + b'_{\sigma}(\mu)(E - \mu) + \frac{1}{2} b''_{\sigma}(\mu)(E - \mu)^2 + \dots \quad (5.67)$$

$$= b_{\sigma}(\mu) + a_{\sigma}(\mu)(E - \mu) + \frac{1}{2} \rho_{\sigma}(\mu)(E - \mu)^2 \quad (5.68)$$

Using the *Fermi integrals* (derived using function theory):

$$I_n = \int_{-\infty}^{+\infty} dE (E - \mu)^n \left( -\frac{\partial f(E)}{\partial E} \right) \quad (5.69)$$

$$= \begin{cases} 1 & , \quad n = 0 \\ \frac{\pi^2}{3} (k_B T)^2 & , \quad n = 2 \\ \frac{7\pi^4}{15} (k_B T)^4 & , \quad n = 4 \\ 0 & , \quad n = 1, 3, 5, \dots \end{cases} \quad (5.70)$$

We can write the Sommerfeld expansion of  $\Omega$  as:

$$\begin{aligned}
\Omega &= \sum_{\sigma} \left\{ -b_{\sigma(\mu)} - \frac{\pi^2}{6} \rho_{\sigma}(\mu) (k_B T)^2 + \mathcal{O}[(k_B T)^4] \right\} \\
&= -pV
\end{aligned} \tag{5.71}$$

The chemical potential  $\mu(T)$  is  $T$ -dependent as well ( see below). However, when taking thermodynamic derivatives of  $\Omega$ ,  $\mu$  is kept constant. Therefore one can put  $\mu = \mu(0) = \varepsilon_F$  in the above expression for  $\Omega$ .

• **Chemical potential (for fixed particle number  $N$ ):**

It is evident from figure 37 that  $\mu(T)$  is a decreasing function if the DOS  $\rho_{\sigma}(E)$  is a monotonically increasing function of energy  $E$ :

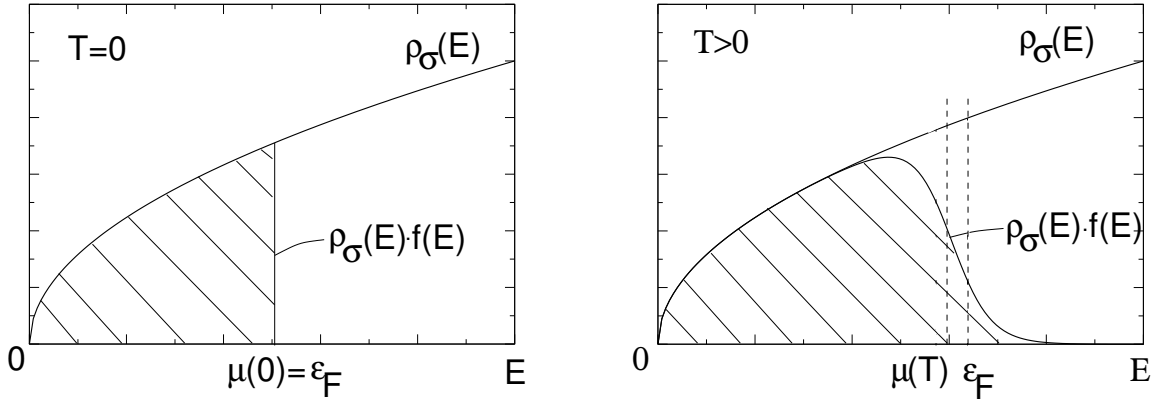


Figure 5.6: The temperature dependence of the chemical potential in a Fermi gas

The shaded area represents the particle number

$$N = \sum_{\sigma} \int dE \rho_{\sigma}(E) f(E) \tag{5.72}$$

and must stay constant as function of  $T$ .

$$\Rightarrow \quad \mu(T > 0) < \mu(T = 0). \tag{5.73}$$

The low- $T$  expansion of  $\mu(T)$  follows as

$$N = \text{const.} = -\frac{\partial \Omega}{\partial \mu} = 2 \left[ \frac{\partial b(\mu)}{\partial \mu} + \frac{\pi^2}{6} \frac{\partial \rho(\mu)}{\partial \mu} (k_B T)^2 + \dots \right] \quad (5.74)$$

where we have assumed spin degeneracy,

$$b_\sigma(\mu) \equiv b(\mu), \quad (5.75)$$

$$\rho_\sigma(\mu) \equiv \rho(\mu), \quad (5.76)$$

$$\sum_\sigma (\dots) = 2(\dots). \quad (5.77)$$

$$\frac{\partial b}{\partial \mu} = a(\mu) \quad (5.78)$$

$$= a(\varepsilon_F) + a'(\varepsilon_F)(\mu(T) - \varepsilon_F) \quad (5.79)$$

$$= a(\varepsilon_F) + \rho(\varepsilon_F)(\mu(T) - \varepsilon_F), \quad (5.80)$$

where

$$a'(\varepsilon_F) = \frac{\partial}{\partial E} \int_{-\infty}^E d\varepsilon \rho(\varepsilon) \Big|_{\varepsilon_F}, \quad a(\varepsilon_F) = \frac{1}{2} N \quad (5.81)$$

$\uparrow$   
 spin!

Inserting this into  $N$  and solving for  $\mu$  we obtain:

$$0 = 2\rho(\varepsilon_F)(\mu(T) - \varepsilon_F) + \frac{\pi^2}{3} \frac{\partial \rho(\varepsilon_F)}{\partial \varepsilon_F} (k_B T)^2 + \mathcal{O}((k_B T)^4) \quad (5.82)$$

$$\mu(T) = \varepsilon_F - \frac{\pi^2}{6} \frac{1}{\rho(\varepsilon_F)} \frac{\partial \rho(\varepsilon_F)}{\partial \varepsilon_F} (k_B T)^2 + \mathcal{O}((k_B T)^4)$$

(5.83)

- **Entropy:**

$$S = - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} = 2 \frac{\pi^2}{3} \rho(\varepsilon_F) k_B^2 T \quad (5.84)$$

explicitly extensive  $\rightarrow$  Gibbs paradox resolved

- **Specific heat:**

$$\begin{aligned} c_V &= T \left( \frac{\partial S}{\partial T} \right)_{V, \mu} \equiv S \\ &= 2 \frac{\pi^2}{3} \rho(\varepsilon_F) k_B^2 T \\ &= \gamma T + \mathcal{O}(T^2) \end{aligned} \quad (5.85)$$

The linear temperature coefficient of  $c_V$  is a measure of the DOS at the Fermi energy in a Fermi gas.

Physically:  $U(t) \sim E(\text{ex. state}) \cdot n(\text{ex. states}) \sim T \cdot T \Rightarrow c_V \sim T$

- **Magnetization and spin susceptibility:**

$$M = 2\mu_0^2 B \int dE \rho(E) \left( -\frac{\partial f}{\partial E} \right) \quad (5.86)$$

$$\rho(E) = \rho(\mu) + \rho'(\mu)(E - \mu) + \frac{1}{2} \rho''(\mu)(E - \mu)^2 + \dots \quad (5.87)$$

$$M = 2\mu_0^2 B \left[ \rho(\mu) + \rho''(\mu) \cdot \frac{\pi^2}{6} (k_B T)^2 + \mathcal{O}(T^4) \right] \quad (5.88)$$

$$\begin{aligned} &= 2\mu_0^2 B \left[ \rho(\varepsilon_F) - \frac{\pi^2}{6} \frac{1}{\rho(\varepsilon_F)} \left[ \rho'(\varepsilon_F) \right]^2 (k_B T)^2 \right. \\ &\quad \left. + \frac{\pi^2}{6} \rho''(\varepsilon_F) (k_B T)^2 + \mathcal{O}(T^4) \right] \end{aligned} \quad (5.89)$$

$$= 2\mu_0^2 B \left[ \rho(\varepsilon_F) - \frac{\pi^2}{6} \underbrace{\left[ \frac{1}{\rho(\varepsilon_F)} \left[ \rho'(\varepsilon_F) \right]^2 - \rho''(\varepsilon_F) \right]}_{>0} (k_B T)^2 \right] \quad (5.90)$$

$$\begin{aligned}
\chi &= \left( \frac{\partial M}{\partial B} \right)_{T, \mu} \\
&= 2\mu_0^2 \rho(\varepsilon_F) - \frac{\pi^2}{3} \left[ \frac{1}{\rho(\varepsilon_F)} \left[ \rho'(\varepsilon_F) \right]^2 - \rho''(\varepsilon_F) \right] (k_B T)^2 \\
&= \chi(T=0) - \mathcal{O}(T^2).
\end{aligned} \tag{5.91}$$

Pauli susceptibility

For indistinguishable (mobile) fermionic spins the susceptibility is  $\chi(0) = \text{const.}$  for  $T \rightarrow 0$  (Pauli behaviour).

For distinguishable (localized) spins the susceptibility diverges  $\chi(T) \sim \frac{1}{T}$  for  $T \rightarrow 0$  (Curie behaviour)

### 5.2.3 The high-temperature region $k_B T \gg \varepsilon_F$ (Classical or Boltzmann limit)

In the limit  $T \rightarrow \infty$  the Fermi distribution

$$f(E) = \frac{1}{\exp((E - \mu)/k_B T) + 1} \rightarrow \frac{1}{2} \quad \text{for all energies } E \tag{5.92}$$

which differ from  $\mu$  by a *finite* amount (less than  $k_B T$ ). In order to keep the average particle number finite, the chemical potential  $\mu$  must therefore approach  $-\infty$  faster than  $-T$ . This means that for any possible single-particle energy  $E \geq 0$ , the average occupation number of a single-particle state becomes a Boltzmann factor:

$$f(E) = \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1} \xrightarrow{T \rightarrow \infty} e^{-\frac{E-\mu}{k_B T}} \tag{5.93}$$

with  $E \geq 0$   $T \gg \varepsilon_F$  or  $\lambda_T \ll a_0$ .

Anticipating this limiting behaviour of  $f(E)$ , the  $T$ -dependence of  $\mu$  can be given explicitly.

$$N = \sum_{\sigma} \int dE \rho_{\sigma}(E) f(E) \rightarrow 2 \int dE \rho_{\sigma}(E) e^{-\frac{E-\mu}{k_B T}} \quad (5.94)$$

With  $\rho_{\sigma}(E) = V \frac{m^{\frac{3}{2}}}{\sqrt{2\pi^2} \hbar^3} \sqrt{E} = V \frac{3}{4} \frac{n}{\varepsilon_F} \sqrt{\frac{\varepsilon}{\varepsilon_F}}$  in d=3 dimensions we obtain ( $x = \frac{E}{k_B T}$ ),

$$N = 2e^{\frac{\mu}{k_B T}} (k_B T)^{\frac{3}{2}} \frac{3}{4} \frac{Vn}{\varepsilon_F^{\frac{3}{2}}} \int_0^{\infty} dx \sqrt{x} e^{-x} \quad (5.95)$$

$$= N \frac{3}{2} \frac{\sqrt{\pi}}{2} e^{\frac{\mu}{k_B T}} \left( \frac{k_B T}{\varepsilon_F} \right)^{\frac{3}{2}} \quad (5.96)$$

and:

$$\mu(T) = -\frac{3}{2} k_B T \ln \left( \left( \frac{3\sqrt{\pi}}{4} \right)^{\frac{2}{3}} \frac{k_B T}{\varepsilon_F} \right), \quad k_B T \gg \varepsilon_F \quad (5.97)$$

It is seen that  $\mu(T) \rightarrow -\infty$  faster than  $-T$ , in agreement with the argument above.

In the high- $T$  limit all other quantities cross over to the behaviour of the classical Boltzmann gas, using  $f(E) \rightarrow e^{-\frac{E-\mu}{k_B T}} \ll 1$  for  $E \geq 0$ .

The grand potential  $\Omega$  is:

$$\Omega = -k_B T \cdot 2 \int dE \rho_{\sigma}(E) \ln \left( 1 + e^{-\frac{E-\mu}{k_B T}} \right) \quad (5.98)$$

$$\approx -k_B T \cdot 2 \int dE \rho_{\sigma}(E) e^{-\frac{E-\mu}{k_B T}} + \mathcal{O} \left( e^{-\frac{E-\mu}{k_B T}} \right)^2 \quad (5.99)$$

$$\approx -k_B T \cdot 2 \int dE \rho_{\sigma}(E) f(E) = -N k_B T \quad (5.100)$$

Using the thermodynamic relation

$$\Omega = U - TS - \mu N \equiv -pV \quad (5.101)$$

the ideal gas follows:

$$pV = N k_B T \quad (5.102)$$

- **Internal energy in d=1,2,3 dimensions**

$$U \approx 2 \int dE \rho_{d,\sigma}(E) E \cdot e^{-\frac{E-\mu}{k_B T}} \quad (5.103)$$

with

$$\rho_{d\sigma}(E) = c_d E^{\frac{d}{2}-1} \left\{ \begin{array}{ll} \sim \sqrt{E}, & d = 3 \\ \sim 0, & d = 2 \\ \sim \frac{1}{\sqrt{E}}, & d = 1 \end{array} \right\}. \quad (5.104)$$

Using the substitution  $x = \frac{E}{k_B T}$  and the partial integration

$$\int_0^\infty dx x^{\alpha-1} e^{-x} = \frac{1}{\alpha} \int_0^\infty dx \frac{d}{dx} x^\alpha e^{-x} \quad (5.105)$$

$$= \frac{1}{\alpha} \int_0^\infty dx x^\alpha e^{-x} \quad (5.106)$$

U can be reduced to the integral of the particle number (with  $\alpha = \frac{d}{2}$ )

$$\boxed{U = (k_B T) \frac{d}{2} 2 \int dE c_d E^{\frac{d}{2}-1} e^{-\frac{E-\mu}{k_B T}} = \frac{d}{2} N k_B T} \quad (5.107)$$

in agreement with expression for classical gas.

- **Entropy**

Since in the grand canonical ensemble the particle number N is not a fixed quantity, its  $T$ -dependence for fixed  $\mu$  must be taken into account when taking the  $T$ -derivative

$$S = - \left( \frac{\partial \Omega}{\partial T} \right)_{V,\mu} = \frac{d}{dT} (N k_B T) = N k_B + k_B T \left( \frac{\partial N}{\partial T} \right)_{V,\mu} \quad (5.108)$$

$$= N k_B + k_B T \int dE \rho_\sigma(E) \frac{\partial}{\partial T} \left( e^{\frac{E-\mu}{k_B T}} \right)_{V,\mu} \quad (5.109)$$

$$= N k_B + \int dE \rho_\sigma(E) \frac{E - \mu}{T} e^{-\frac{E-\mu}{k_B T}} \quad (5.110)$$

$$= N k_B + \frac{U}{T} - \frac{\mu}{T} N \quad (5.111)$$

$$\boxed{S = N k_B \left[ \frac{d}{2} + 1 - \frac{\mu}{k_B T} \right] \equiv \frac{d}{2} N k_B \ln \left( \frac{k_B T}{\varepsilon F} \right) + const.} \quad (5.112)$$



where the first term is the grand canonical expression with  $N = N(T, V, \mu)$  and the second term is the canonical expression with  $N = \text{const.}$

• **Specific heat**

(a) *Grand canonical evaluation* (process with changing  $N, \mu = \text{const.}$ )

$$c_V = T \left( \frac{\partial S}{\partial T} \right)_{V, \mu} = T \left( \frac{\partial N}{\partial T} \right)_{V, \mu} k_B \left[ \frac{d}{2} + 1 - \frac{\mu}{k_B T} \right] + N k_B \frac{\mu}{k_B T} \quad (5.113)$$

**Note** concerning thermodynamic derivatives:

In  $\frac{\partial}{\partial T}$   $\mu$  is kept const. according to the grand canonical ensemble.

With  $\left( \frac{\partial N}{\partial T} \right)_{V, \mu}$  as above:

$$c_V = \left( \frac{U}{T} - \frac{\mu}{T} N \right) \left[ \frac{d}{2} + 1 - \frac{\mu}{k_B T} \right] + N k_B \frac{\mu}{k_B T} \quad (5.114)$$

$$= N k_B \left[ \frac{d}{2} \left( \frac{d}{2} + 1 \right) - d \frac{\mu}{k_B T} + \frac{\mu^2}{(k_B T)^2} \right] \quad (5.115)$$

$$c_V = \frac{d}{2} \left( \frac{d}{2} + 1 \right) N k_B + \mathcal{O} \left( \frac{1}{T} \right)$$

(5.116)

By increasing  $T$  the Fermi gas takes up additional energy, if there is particle exchange with  $\mu = \text{const.}$

(b) **Canonical evaluation**

Alternatively, we can conceive the expression for  $S$  as obtained in the canonical ensemble, i.e. we keep  $N$  fixed, but take the  $T$ -dependence of  $\mu(T)$  into account in  $\frac{\partial}{\partial T}$ . Then we have

$$c_V = T \left( \frac{\partial S}{\partial T} \right)_{V, N} = T \frac{\partial}{\partial T} \left( \frac{d}{2} N k_B \ln \frac{k_B T}{\varepsilon_F} \right) = \frac{d}{2} N k_B \equiv \left( \frac{\partial U}{\partial T} \right)_{V, N} \quad (5.117)$$

in explicit agreement with the classical result.

- Spin susceptibility and magnetization

$$M = 2\mu_0^2 B \int dE \rho_\sigma(E) \left( -\frac{\partial f}{\partial E} \right) \quad (5.118)$$

$$\approx 2\mu_0^2 B \int dE \rho_\sigma(E) \frac{1}{k_B T} e^{-\frac{E-\mu}{k_B T}} \quad (5.119)$$

$$= 2N\mu_0^2 B \frac{1}{k_B T} \quad (5.120)$$

$$X(B=0) = \left( \frac{\partial M}{\partial B} \right)_{B=0} = 2N \frac{\mu_0^2}{k_B T} \quad (5.121)$$

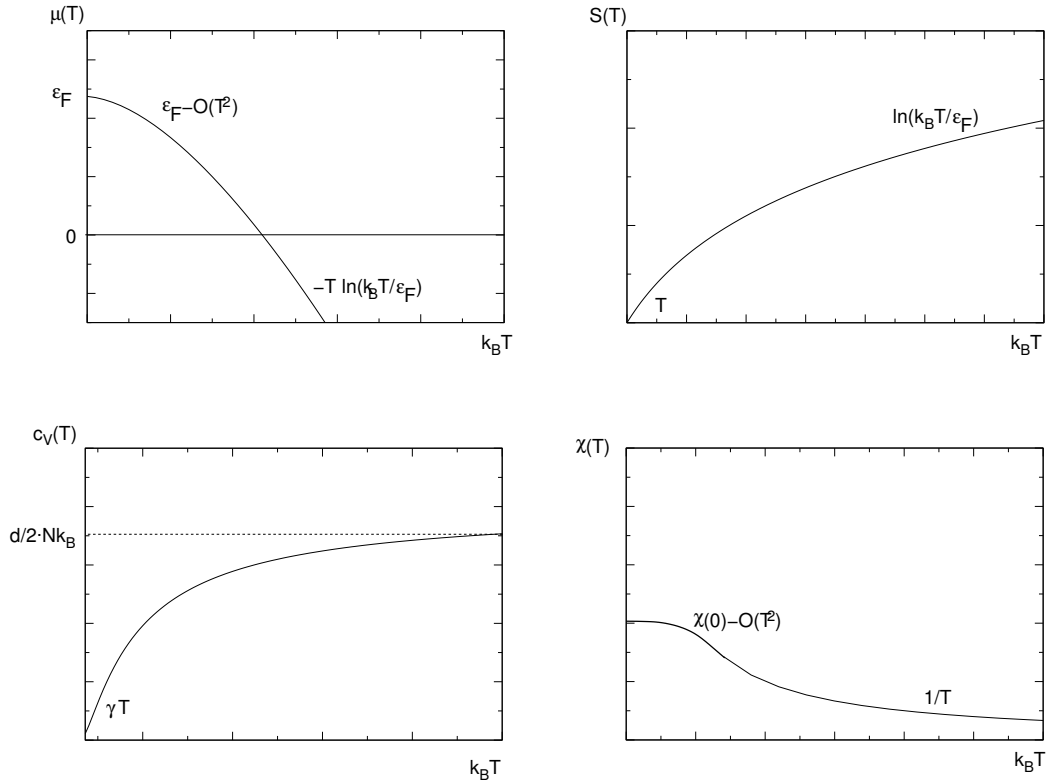


Figure 5.7:  $T$ -dependence of  $\mu(T)$ ,  $S(T)$ ,  $c_V(T)$ , and  $\chi(T)$

## 5.3 The ideal Bose gas

### Fermion number conservation and Boson number non-conservation:

In any closed system there does not exist any interaction process which would only create or destroy a single fermion, because this would change the total angular momentum  $J$  of the system by a half-integer value, while  $J$  is a conserved quantity (Fermion number conservation). Therefore, in an isolated system the fermion number  $N$  is fixed (canonical ensemble) and in a system with particle number  $\langle N \rangle$  is fixed by means of the Lagrange multiplier  $\mu$  (grand canonical ensemble). This has been naturally assumed in section 4.2.

By contrast, creating or destroying a boson changes the total angular momentum  $J=L+S$  by an integer value. This can be compensated by a corresponding integer change of the orbital angular momentum  $\vec{L}$  of the system. Hence, it is not forbidden that a bosonic particle is destroyed or created, e.g. absorbed or emitted by the wall of the container. The (integer) spin of the boson is then taken up as an orbital angular momentum of the container.

Indeed, there exists two types of bosonic particles, (1) those with conserved particle number  $N$ , whose average number  $\langle N \rangle$  is fixed by a chemical potential  $\mu$  in the grand canonical ensemble, and (2) those whose particle number is not conserved and which, therefore, do not have a chemical potential, i.e.  $\mu = 0$  in the grand canonical ensemble. These different constraints lead to different thermodynamical behaviour.

### Statistical behaviour of particles:

#### 1. *Fermions* (half integer spin):

$n_\alpha = 0, 1$  occupation number of single-particle state

$N$  conserved implied by angular momentum conservation

$\rightarrow \mu(T)$

**Examples:** Electrons, atoms with half-integer total spin,  $^3\text{He}$ , neutrons

#### 2. *Bosons* (integer spin)

$n_\alpha = 0, 1, 2, \dots$

(a)  $N$  conserved in a physical process

$\rightarrow \mu(T)$

**Example:** Atoms,  $^4\text{He}$

(b) N not conserved

$$\mu \equiv 0$$

**Example:** Photons, oscillator quanta of a h.o. (phonons), quantized collective excitations in a solid (magnons etc.)

### 5.3.1 Bosons with conserved particle number: Bose-Einstein condensation

We calculate the grand canonical partition sum with arbitrary occupation number  $n_{\alpha_i}$  of the single-particle states  $|\alpha_i\rangle$  with energies  $E_{\alpha_i}$

$$Z_{GC} = \sum_{n_{\alpha_i}=0,1,2,\dots} e^{-\frac{\sum_{j=1}^{\infty} (E_{\alpha_j} - \mu) n_{\alpha_j}}{k_B T}} \quad (5.122)$$

$$= \prod_{i=1}^{\infty} \sum_{n=0}^{\infty} e^{-\frac{(E_{\alpha_i} - \mu)n}{k_B T}} \quad (5.123)$$

$$= \prod_{i=1}^{\infty} \frac{1}{1 - e^{-\frac{E_{\alpha_i} - \mu}{k_B T}}} \equiv \prod_{i=1}^{\infty} Z_{GC,1}(\alpha_i) \quad (5.124)$$

i.e.  $Z_{GC}$  factorizes again into a product of the single-particle partition sums

$$\boxed{Z_{GC,1}(\alpha_i) = \sum_{n=0}^{\infty} e^{-\frac{(E_{\alpha_i} - \mu)n}{k_B T}} = \frac{1}{1 - e^{-\frac{E_{\alpha_i} - \mu}{k_B T}}} \quad (5.125)}$$

In order for this geometrical series to converge, one must have

$$E_{\alpha_i} - \mu \geq 0 \quad \forall |\alpha_i\rangle \quad (5.126)$$

which means for  $E_{\alpha_i} \in [0, \infty[$ :

$$\boxed{\mu(T) \leq 0} \quad \text{for bosonic systems} \quad (5.127)$$

The grand potential is

$$\Omega = -k_B T \ln Z_{GC} = -k_B T \ln \left( \frac{1}{1 - e^{-\frac{E_\alpha - \mu}{k_B T}}} \right) \quad (5.128)$$

$$\boxed{\Omega = k_B T \sum_{\alpha} \ln \left( 1 - e^{-\frac{E_\alpha - \mu}{k_B T}} \right)} \quad (5.129)$$

The sum runs over all single-particle states.

The average occupation number of the single-particle state  $|\alpha_i\rangle$  is

$$\langle n_{\alpha_i} \rangle = \sum_{\substack{n_{\alpha_j}=0 \\ j=0,1,2,\dots}}^{\infty} n_{\alpha_i} \underbrace{\prod_{k=0}^{\infty} \frac{e^{-\frac{E_{\alpha_k} - \mu}{k_B T} n_{\alpha_k}}}{Z_{GC,1}(\alpha_k)}}_{W_{GC}(\{n_{\alpha_k}\})} \quad (5.130)$$

$$= \sum_{n_{\alpha_i}=0}^{\infty} n_{\alpha_i} \frac{e^{-\frac{E_{\alpha_i} - \mu}{k_B T} n_{\alpha_i}}}{Z_{GC,1}(\alpha_i)} \quad (5.131)$$

$$= -\frac{\partial}{\partial(\beta(E_{\alpha_i} - \mu))} \ln Z_{GC,1}(\alpha_i) \quad (5.132)$$

$$\boxed{\langle n_{\alpha_i} \rangle = \frac{1}{e^{\frac{E_{\alpha_i} - \mu}{k_B T}} - 1} \equiv b(E_{\alpha_i})} \quad \text{Bose-Einstein distribution} \quad (5.133)$$

The *entropy* and the *internal energy* are

$$S = -\left( \frac{\partial \Omega}{\partial T} \right)_{V,\mu} = -\frac{\Omega}{T} + \sum_{\alpha} \frac{E_{\alpha} - \mu}{T} b(E_{\alpha}) \quad (5.134)$$

$$U = \Omega + TS + \mu N = \sum_{\alpha} (E_{\alpha} - \mu) b(E_{\alpha}) = \sum_{\alpha} E_{\alpha} b(E_{\alpha}) \quad (5.135)$$

with

$$N = \sum_{\alpha} b(E_{\alpha}). \quad (5.136)$$

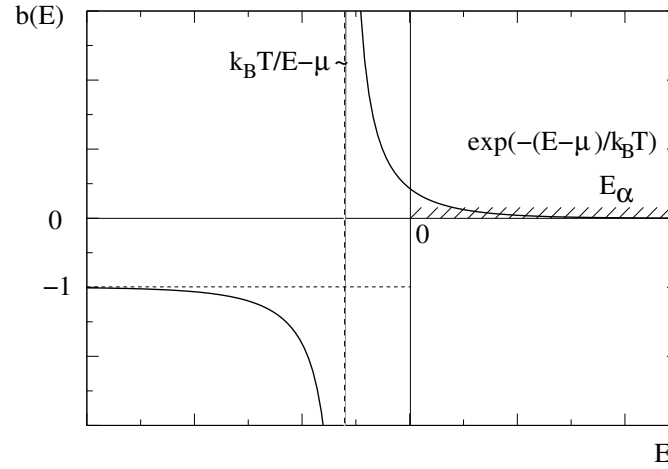


Figure 5.8: Bose-Einstein distribution function

### T-dependence of the chemical potential $\mu(T)$ and Bose-Einstein condensation

We expect generally that quantum effects due to indistinguishability become important when the wavelength  $\lambda_T = \frac{2\pi}{k}$  of a particle with typical thermal excitation energy  $E_k = \frac{(\hbar k)^2}{2m} = k_B T$  becomes longer than the average spacing  $a_0$  between the particles, i.e. when the thermal wavelength

$$\lambda_T = \frac{2\pi\hbar}{\sqrt{2mk_B T}} \gtrsim a_0 = \left(\frac{V}{N}\right)^{\frac{1}{3}} = n^{-\frac{1}{3}} \quad (*) \quad (5.137)$$

the condition for quantum behaviour.

This is because the length scale within which a particle can be localized in principle by a scattering experiment is at best its wavelength  $\lambda_T$ .

If  $\lambda_T < a_0$  the particles can be identified in space (by a scattering experiment), i.e. they behave classically as distinguishable particles.

If  $\lambda_T \geq a_0$  the regions in which a particle can be localized necessarily overlap, the particles become indistinguishable and quantum statistical effects become important.

$$\left[ \begin{array}{ll} \text{Fermi system:} & \lambda_T \gg a_0 \quad \text{degenerate Fermi gas} \\ \text{Bose system:} & \lambda_T \gg a_0 \quad \text{Bose condensation} \end{array} \right]$$

**Note:** The wave functions still penetrate each other for  $\lambda_T < a_0$ , since they are

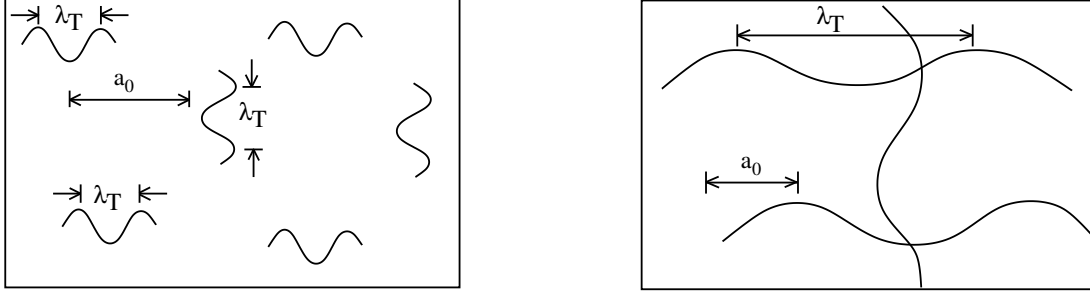


Figure 5.9: Classical regime  $\lambda_T < a_0$  and quantum regime  $\lambda_T > a_0$  of a gas

extended over the whole system, but a scattering experiment can localize them.

For low temperatures, deep in the quantum regime of a Bose gas (spin 0) we have

$$\lambda_T \gg a_0 \quad \text{or} \quad k_B T \ll \frac{2\pi\hbar^2}{2ma_0^2} \quad (5.138)$$

and the particle density is

$$n = \frac{N}{V} = \frac{1}{V} \sum_k \frac{1}{e^{\frac{E_k - \mu}{k_B T}} - 1} \quad (5.139)$$

$$\stackrel{V \rightarrow \infty}{=} \frac{N_0(T)}{V} + \frac{1}{V} \int_0^\infty dE \rho(E) \frac{1}{e^{\frac{E - \mu}{k_B T}} - 1} \quad (5.140)$$

where  $N_0(T) = \langle n_{k=0} \rangle$  is the occupation number of the lowest single-particle state ( $\vec{k} = 0, \vec{E}_k = 0$  for a free Bose gas).

In going over to the thermodynamic limit,  $V \rightarrow \infty$ , the energies  $E_{\vec{k}}$  become continuous and the sum  $\sum_k$  can be replaced by the integral  $\int_0^\infty dE \rho(E) (\dots)^n$ , if the spacing of successive energy levels  $\Delta E_k \ll E_k$ . In the thermodynamic limit this is always achieved for  $E_k > 0$ , since  $\Delta E_k \sim \frac{1}{V}$ .

However, it can never be achieved for the lowest state  $E_0 = 0$ . Therefore, the occupation number  $n$  of the  $E_0 = 0$  state must be counted separately in the above expression. For massive bosons ( $m > 0$ ) in  $d=3$  dimensions  $\rho(E) = V c_3 \sqrt{E}$  (as for

electrons), and one can estimate the number of particles in the *excited* states as

$$N_{ex} = \int dE \rho(E) \frac{1}{e^{\frac{E-\mu}{k_B T}} - 1} \leq \int dE \rho(E) \frac{1}{e^{\frac{E}{k_B T}} - 1} \quad (5.141)$$

$$= V c_3 (k_B T)^{\frac{3}{2}} \int_0^\infty dx \underbrace{\frac{\sqrt{x}}{e^x - 1}}_{\sqrt{x}e^{-x}(1+e^{-x}+..)} \left( \text{using } \lambda_T^3 = \frac{2\pi}{c_3^3} \right) \quad (5.142)$$

$$= \frac{2\pi V}{\lambda_T^3} \zeta\left(\frac{3}{2}\right) \approx 2,612 \frac{2\pi V}{\lambda_T^3} \sim T^{\frac{3}{2}} \xrightarrow{T \rightarrow 0} 0! \quad (5.143)$$

For high T ( $\lambda_T \ll a_0$ ) the total number of particles in excited states is  $N_{ex} \gg n_0$ ,

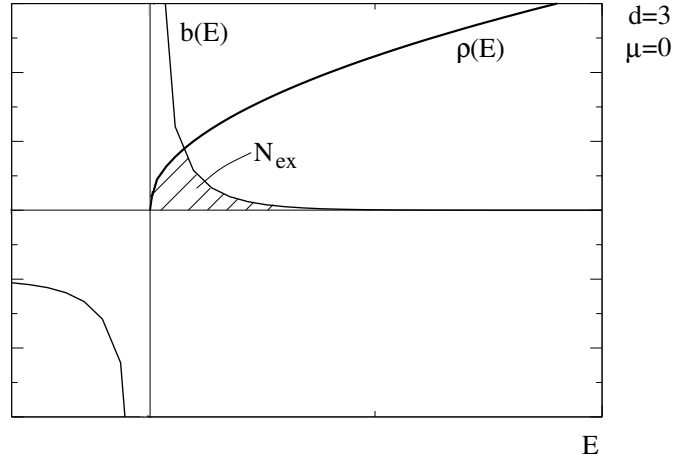


Figure 5.10: Number of particles  $N_{ex}$  in the excited single-particle states of a free Bose gas

i.e.  $n_0 \approx 1 \approx V$  (non-extensive) and can be neglected for  $V \rightarrow \infty$ .

Then  $N = N_{ex}$  for  $V \rightarrow \infty$ . However, below a critical temperature  $T < T_0$  the fixed  $N$  particles of the system cannot all be fit into the excited states, and  $n_0$  must become an extensive quantity  $N_0 \sim V$ , i.e. the lowest single-particle state (single-particle ground state) becomes macroscopically occupied.

$$n = \frac{N_0}{V} + \frac{2\pi}{\lambda_T^3} \zeta\left(\frac{3}{2}\right) = \frac{N}{V} \equiv \frac{1}{a_0^3} \quad (5.144)$$



Thus, one obtains for the ground state occupation

$$n_0 \equiv \frac{N_0}{V} = n \left[ 1 - 2\pi\zeta\left(\frac{3}{2}\right) \frac{a_0^3}{\lambda_T^3} \right] = n \left[ 1 - \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \right] \quad (5.145)$$

with  $\lambda_T = \frac{2\pi\hbar}{\sqrt{2mk_BT}}$  and  $T < T_0$ .

Hence, the critical temperature  $T_0$  below which  $n_0 = \frac{N_0}{V} \Big|_{V \rightarrow \infty} > 0$  is

$$\left(\frac{T}{T_0}\right)^{\frac{3}{2}} = 2\pi\zeta\left(\frac{3}{2}\right) \left(\frac{a_0}{\lambda_T}\right)^3 \quad (5.146)$$

$$k_B T_0 = \frac{1}{\left[2\pi\zeta\left(\frac{3}{2}\right)\right]^{\frac{2}{3}}} \frac{\hbar^2 \left(\frac{2\pi}{a_0}\right)^2}{2m} \quad \text{Bose-Einstein condensation temperature} \quad (5.147)$$

The state in which the single-particle ground state is macroscopically occupied, i.e. its occupation number scales with the system volume,  $n_0 = \frac{N_0}{V} > 0$ , is called *Bose-Einstein-condensate*. The  $T$ -dependence of the chemical potential for  $T \geq T_0$  is extracted from the condition

$$N = \int d\varepsilon \rho(\varepsilon) b(\varepsilon) = \text{const.} \quad (5.148)$$

by implicit differentiation:

$$0 = \int d\varepsilon \rho(\varepsilon) \frac{db}{dT} = \int d\varepsilon \rho(\varepsilon) \frac{-e^{\frac{\varepsilon-\mu}{k_B T}}}{\left(e^{\frac{\varepsilon-\mu}{k_B T}} - 1\right)^2} \left[ -\frac{\varepsilon - \mu}{k_B T^2} - \frac{\frac{d\mu}{dT}}{k_B T} \right] \quad (5.149)$$

$$\frac{d\mu}{dT} = -\frac{1}{T} \frac{\int d\varepsilon \rho(\varepsilon) \frac{\varepsilon - \mu}{4 \sinh^2\left(\frac{\varepsilon - \mu}{2k_B T}\right)}}{\int d\varepsilon \rho(\varepsilon) \frac{1}{4 \sinh^2\left(\frac{\varepsilon - \mu}{2k_B T}\right)}} \quad (\text{for } T \rightarrow T_c + 0, \mu \rightarrow 0 - 0) \quad (5.150)$$

$$\rightarrow -\frac{1}{T} \frac{\int_0^\infty d\varepsilon \varepsilon^{\frac{3}{2}} \frac{1}{\sinh^2\left(\frac{\varepsilon}{2k_B T_c}\right)}}{\int_0^\infty d\varepsilon \varepsilon^{\frac{1}{2}} \frac{1}{\sinh^2\left(\frac{\varepsilon}{2k_B T_c}\right)}} = 0 \quad (5.151)$$

2nd implicit differentiation yields a finite value of  $\frac{d^2\mu}{dT^2} < 0$  at  $T = T_c$ . For  $T \rightarrow +\infty$   $b(\varepsilon) \rightarrow e^{-\frac{\varepsilon - \mu(T)}{k_B T}}$  for the same reason as for fermions, and  $\mu(T) \rightarrow -T \ln T$  takes on the same classical behavior.

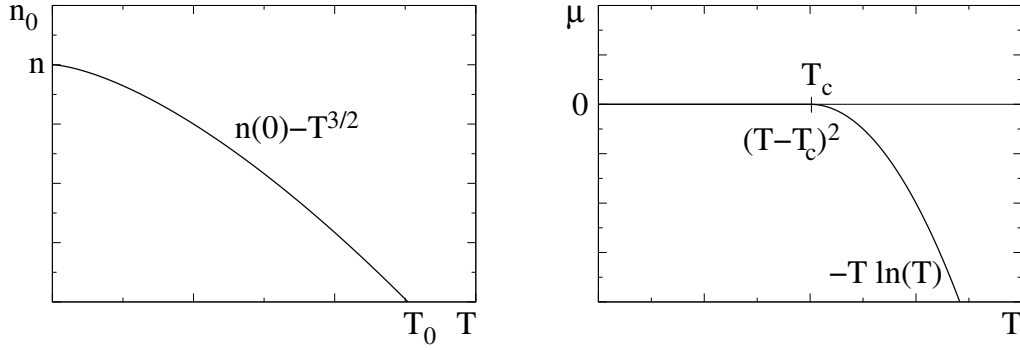


Figure 5.11: Verlauf  $\mu$  gegen  $T$

### Properties of the Bose-Einstein-condensate

1. The Bose condensation transition occurs when  $\lambda_T \approx a_0$ , i.e. when the bosons become indistinguishable in space. This can be seen from equation (\*\*).
2. The Bose condensate is described by a *macroscopic wave function*  $\psi_0(\vec{x})$  with a *single*, macroscopic phase  $\phi$ :

In position representation, the condensate state  $|n_0\rangle$  is a simple product wave function

$$\psi_0(x_1, \dots, x_{N_0}) = \langle x_1 \dots x_{N_0} | n_0 \rangle \quad (5.152)$$

$$= \prod_{i=1}^{N_0} \varphi_0(x_i) e^{i\phi_i} \quad (5.153)$$

$$= e^{i \sum_{i=1}^{N_0} \phi_i} \prod_{i=1}^{N_0} \varphi_0(x_i) \quad (5.154)$$

where  $\varphi_0(x_i) e^{i\phi_i}$  is the ground state wave function of particle  $i$  with

- an arbitrary phase  $\phi_i$
- $\varphi_0(x)$  the same wave function for all particles and
- $\phi = \sum_{i=1}^{N_0} \varphi_i$  the macroscopic phase.

The expectation value of any single-particle operator  $\hat{F}(x_1, \dots, x_{N_0}) = \sum_{i=1}^{N_0} \hat{f}(x_i)$  in the condensate is

$$\langle \psi_0\{x_i\} | \sum_i \hat{f}(x_i) | \psi_0\{x_i\} \rangle = N_0 \langle \varphi_0(x) | \hat{f}(x) | \varphi_0(x) \rangle. \quad (5.155)$$

Therefore,  $\psi_0\{x_i\}$  can be written as

$$\boxed{\psi_0(x) = \sqrt{N_0} e^{i\phi} \varphi_0(x)} \quad (5.156)$$

with a single, macroscopic coordinate  $x$  and a macroscopic phase  $\phi$ .

$\psi_0(x)$  is normalized to  $N_0$ , the occupation number of the condensate. It leads to the same expectation values of single-particle operators as the many-particle wave function of the condensate.<sup>1</sup>

3. The Bose condensation depends on the spatial dimension. For massive particles,  $E_p = \frac{p^2}{2m}$ , there is no condensation transition in  $d = 1, 2$  for  $T > 0$ :

In dimensions  $d = 1, 2$  the integral

$$N_{ex} = V c_d \int_0^\infty d\varepsilon \varepsilon^{\frac{d}{2}-1} \frac{1}{e^{\frac{\varepsilon}{k_B T}} - 1} \quad (5.157)$$

diverges, i.e. an arbitrary number of particles can be put into the excited states, and the ground state is not macroscopically occupied for any finite temperature  $T > 0$ .

4. The place wherence of all particles in the condensate implies that there is no scattering in the condensate; the condensate has viscosity 0.

### Entropy and specific heat of the Bose gas

Grand canonical potential:

$$\Omega = k_B T \int dE \rho(E) \ln \left( 1 - e^{-\frac{E-\mu}{k_B T}} \right) \quad (5.158)$$

---

<sup>1</sup>For a free Bose gas  $\varphi_0(x)$  is the  $\vec{k} = 0$  wave function,  $\varphi_0(x) = \text{const.}$ , and  $\psi_0(x) \equiv \psi_0$  is a single complex number.

Entropy:

$$S = - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} \quad (5.159)$$

$$= -k_B \int dE \rho(E) \ln \left( 1 - e^{\frac{E-\mu}{k_B T}} \right) \quad (5.160)$$

$$-k_B T \int dE \rho(E) (-b(E)) \left( \frac{E-\mu}{k_B T^2} \right) \quad (5.161)$$

$$= -\frac{\Omega}{T} + \frac{\langle E \rangle}{T} - \frac{\mu}{T} N \quad (5.162)$$

in agreement with the general thermodynamic relation  $\Omega = U - TS - \mu N$ .

For  $T < T_0$  only the excited states contribute to the entropy, since the condensate state  $\psi_0$  is unique and, thus, has entropy  $S_0 = 0$ . Therefore, the summation over states in the above expression can be written as an integral, neglecting the ground state. One can show for massive particles with dispersion  $E_p = \frac{p^2}{2m}$  in  $d = 3$  dimensions ( $\rho(E) \sim \sqrt{E}$ ):

$$S(T) \sim T^{\frac{3}{2}} \quad \text{for } T \rightarrow 0. \quad (5.163)$$

The specific heat for fixed volume  $V$  and particle number  $N$  is

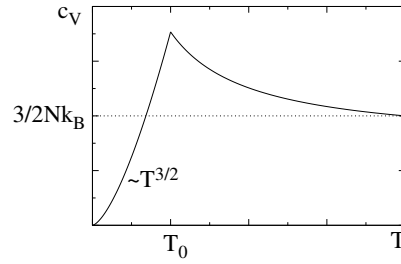
$$c_V = T \left( \frac{\partial S}{\partial T} \right)_{V, N} \quad (5.164)$$

**Remark:**

In calculating  $S$  from the grand canonical potential  $\Omega$ ,  $\mu$  is kept fixed (i.e. not differentiation wrt.  $T$ ), since  $\Omega$  is a function of  $\mu$  by definition (thermodynamic derivative).  $S$  is a general function of  $T$ , both through the explicit dependence and through the implicit dependence of  $\mu(T)$  on  $T$ . In calculating  $c_V$  one can, therefore choose to keep  $N$  fixed (as is usually done) and differentiate  $\frac{\partial \mu}{\partial T}$ . Since

$$\frac{\partial^2 \mu}{\partial T^2} = \begin{cases} 0 & , \quad T < T_0 \\ < 0 & , \quad T > T_0 \end{cases} \quad \text{discontinuous at } T = T_0, \text{ the } T\text{-derivative of } c_V \text{ has a}$$

discontinuity at the condensation transition:

Figure 5.12: Verlauf  $c_V$  gegen  $T$ 

### 5.3.2 Bosons without particle number conservation: Black body radiation

Photons are an example of bosons (spin 1) which can be absorbed or emitted e.g. by the walls of a container, i.e. whose particle number is not conserved:  $\mu = 0$ . A body which can absorb or emit photons with equal probability for *all frequencies* is called *black body*. We consider a system of photons (the electromagnetic field) in thermodynamic equilibrium with a black body at temperature  $T$  and calculate its spectral energy density  $\frac{dE_\omega}{d\omega}|_\omega$ , i.e. the energy content  $dE_\omega$  in a given photon frequency interval  $d\omega$  at frequency  $\omega$ :

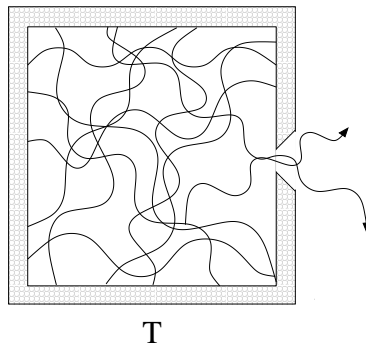


Figure 5.13: Black body radiation

For  $d = 3$  and  $\omega = ck$  the photon density of states is

$$\rho(\omega)d\omega = \underbrace{2}_{\text{Polarization}} \frac{4\pi k^2}{(2\pi)^3} \cdot dk = V \frac{\omega^2}{\pi^2 c^3} d\omega \quad (5.165)$$

and with  $x = \frac{\hbar\omega}{k_B T}$

$$\Omega = V \frac{(k_B T)^4}{\pi^2 (\hbar c)^3} \underbrace{\int_0^\infty dx x^2 \ln[1 - e^{-x}]}_{-\frac{\pi^4}{45}} = -\gamma V T^4 \quad (5.166)$$

with  $\gamma = \frac{\pi^2 k_B^4}{45(\hbar c)^3}$ . The pressure of the photon gas (radiation pressure) is

$$P_{ph} = - \left( \frac{\partial \Omega}{\partial V} \right)_{T, \mu} = -\gamma T^4, \quad (5.167)$$

and the spectral energy density

$$\boxed{\frac{dE_\omega}{d\omega} = \rho(\omega) \hbar\omega b(\hbar\omega) = V \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\frac{\hbar\omega}{k_B T}} - 1}} \quad (5.168)$$

The radiation law has been historically one of the first signatures of the quantum

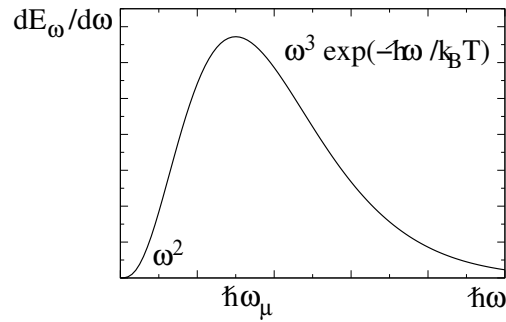


Figure 5.14: Planck's radiation law with maximum at  $\hbar\omega_M = 2.822 k_B T$

nature of light. It lead Planck to postulate the light quantum with energy  $\hbar\omega$  for light of frequency  $\omega$ .

Measuring the Planck radiation law of e.g. light from a distant star, one can measure the star's surface temperature.

# Chapter 6

## General Formulation of Statistical Mechanics

### 6.1 The density matrix

#### 6.1.1 Definition

Up to now we have assumed that

- the energy eigenvalues  $E_n$  and eigenstates  $|n\rangle$  of the many-particle system are known, i.e. the many-particle problem has been solved;
- the system is in thermodynamic equilibrium, where the distribution probability  $W(n)$  for an eigenstate  $|n\rangle$  to be realized depends on its energy  $E_n$  only and is, in particular, time dependent.

In realistic situations neither the energy eigenvalues  $E_n$  are known in general nor is the system in equilibrium, i.e. in general the thermodynamic (mixed) state cannot simply be represented in terms of energy eigenstates. In such situations it is useful to have a basis independent formulation of the statistical formalism. We consider a general mixed state  $M$  of a system, represented by a statistical ensemble in which the many-particle states  $|\psi_i\rangle$  of the system (not necessarily energy eigenstates!) occur with the relative frequencies  $h_i$ ,  $i = 1, 2, 3, \dots$

The thermodynamic average of an observable quantity  $A$  in this mixed state is

$$\langle A \rangle = \sum_i h_i \langle \psi_i | \hat{A} | \psi_i \rangle, \quad (6.1)$$

where  $\hat{A}$  is the quantum mechanic operator representing  $A$ . Using an *arbitrary*, complete many-body basis set  $\{|n\rangle\}$  of the system one can write

$$\langle A \rangle = \sum_i h_i \sum_{n,m} \langle \psi_i | n \rangle \langle n | \hat{A} | m \rangle \langle m | \psi_i \rangle \quad (6.2)$$

$$= \sum_i h_i \sum_{n,m} \langle n | \hat{A} | m \rangle \langle m | \psi_i \rangle \langle \psi_i | m \rangle \quad (6.3)$$

$$= \sum_i h_i \sum_n \langle n | \hat{A} \hat{P}_i | n \rangle \quad (6.4)$$

$$= \sum_n \left\langle n \left| \hat{A} \left( \sum_i h_i \hat{P}_i \right) \right| n \right\rangle \quad (6.5)$$

where we have defined the operator  $\hat{P}_i = |\psi_i\rangle\langle\psi_i|$ .  $\hat{P}_i$  is the projector in Hilbert space onto the (arbitrary, normalized) state  $|\psi_i\rangle$ :

1.

$$\hat{P}_i |\phi\rangle = |\psi_i\rangle\langle\psi_i|\phi\rangle \quad \text{for arbitrary } |\phi\rangle, \text{ and} \quad (6.6)$$

2.

$$\hat{P}_i^2 = |\psi_i\rangle \underbrace{\langle\psi_i|\psi_i\rangle}_{=1 \text{ (normalization)}} = |\psi_i\rangle\langle\psi_i| = \hat{P}_i \quad (6.7)$$

We define the operator

$$\hat{W} = \sum_i h_i |\psi_i\rangle\langle\psi_i|$$

(6.8)

as the *density matrix* or density operator of the mixed state  $M$  and one has from equation (\*) above

$$\langle A \rangle = \sum_n \langle n | \hat{A} \hat{W} | n \rangle = \text{tr}(\hat{A} \hat{W})$$

(6.9)



**Remarks:**

1. The density operator is the sum of the projectors  $\widehat{P}_i$  onto the states  $|\psi_i\rangle$  in the mixed state  $M$ , weighted with the relative frequencies (probabilities)  $h$ , with which these states occur in  $M$ .
2. The above expression for  $\langle A \rangle$  is independent of the chosen basis set  $\{|n\rangle\}$  because of the basis independent of the trace  $tr$ .
3. If  $\{|\psi_i\rangle\}$  is chosen to be an (orthonormal) energy eigenbasis of the system and  $|\psi_i\rangle \equiv |i\rangle$  and the mixed state  $M$  is an equilibrium state, then the formalism reduces to the one used previously, with

$$h_i = \frac{e^{-\frac{E_i}{k_B T}}}{Z_c}, \quad Z_c = \sum_i e^{-\frac{E_i}{k_B T}} \quad (6.10)$$

in the canonical ensemble, and

$$\langle A \rangle = \sum_{n,i} \frac{e^{-\frac{E_i}{k_B T}}}{Z_c} \langle n | \widehat{A} | \psi_i \rangle \underbrace{\langle \psi_i | n \rangle}_{\delta_{in}} \quad (6.11)$$

$$= \sum_i \frac{e^{-\frac{E_i}{k_B T}}}{Z_c} \langle i | \widehat{A} | i \rangle. \quad (6.12)$$

### 6.1.2 The time dependence of the density matrix

The time dependence of  $\widehat{W}$  is derived from the Schrödinger equation for the states  $|\psi_i\rangle$ :

$$i\hbar \frac{d}{dt} |\psi_i\rangle = \widehat{H} |\psi_i\rangle \quad (6.13)$$

$$-i\hbar \frac{d}{dt} \langle \psi_i | = \langle \psi_i | \widehat{H} \quad (6.14)$$

$$i\hbar \frac{d}{dt} |\psi_i\rangle \langle \psi_i| = \widehat{H} |\psi_i\rangle \langle \psi_i| - |\psi_i\rangle \langle \psi_i| \widehat{H} \quad (6.15)$$

$$= [\widehat{H}, \widehat{P}_i]. \quad (6.16)$$

It follows

$$i\hbar \frac{d}{dt} \widehat{W}(t) = i\hbar \frac{d}{dt} \sum_i h_i |\psi_i\rangle \langle \psi_i| \quad (6.17)$$

$$= \sum_i h_i [\widehat{H}, \widehat{P}_i] \quad (6.18)$$

$$= [\widehat{H}, \widehat{W}(t)] \quad (6.19)$$

**Note:**

The values  $h_i$  are chosen as initial conditions at  $t = 0$ , i.e. they are time independent.

$$\boxed{i\hbar \frac{\partial}{\partial t} \widehat{W}(t) = [\widehat{H}, \widehat{W}(t)]} \quad \text{von Neumann equation} \quad (6.20)$$

The von Neumann equation is analogous to the Heisenberg equation of motion of an operator in the Heisenberg picture, however with a relative "−" sign.

Using the formal solution of the time dependent Schrödinger equation

$$|\psi_i(t)\rangle = e^{-\frac{i}{\hbar} \widehat{H}t} |\psi_i(0)\rangle \quad (6.21)$$

we obtain

$$\widehat{W}(t) = e^{-\frac{i}{\hbar} \widehat{H}t} \widehat{W}(0) e^{+\frac{i}{\hbar} \widehat{H}t} . \quad (6.22)$$

By preparing a system in a given (non-equilibrium) mixed state,  $\widehat{W}(0)$  (i.e.  $h_i$ ) is given, and

## 6.2 The reduced density matrix

In many situations one is only interested in the properties of a subsystem of the complete system  $S_{tot}$  or a physical quantity  $A$  depends only on the states of a subsystem.

Examples are

1. system  $S$  and reservoir  $R$  forming together the total system  $S_{tot}$ . A complete basis of  $S_{tot}$  can be chosen as the set of direct product states ("product of WF")

$$|n_S\rangle \otimes |n_R\rangle = |n_S, n_R\rangle \equiv |n\rangle \quad (6.23)$$

where  $\{|n_S\rangle\}$  and  $\{|n_R\rangle\}$  are complete basis sets of  $S$  and of  $R$ , respectively (without coupling between the two).

2. a single particle as a subsystem in a many-particle system  $S_{tot}$ .

The observable operators  $\hat{A}$  we are interested in act only on the states  $|n_S\rangle$  of the system and not on the states of the reservoir  $|n_R\rangle$ . Therefore, it is useful in a thermodynamic average to perform the averaging over the reservoir states first:

$$\langle n|\hat{A}|m\rangle = \langle n_S, n_R|\hat{A}|m_S, m_R\rangle \quad (6.24)$$

$$= \langle n_S|\hat{A}|m_S\rangle \cdot \langle n_R|m_R\rangle \quad (6.25)$$

$$= \langle n_S|\hat{A}|n_S\rangle \delta_{n_R m_R} \quad (6.26)$$

$$\langle A\rangle = tr(\hat{A}\hat{W}) \quad (6.27)$$

$$= \sum_n \langle n|\hat{A}\hat{W}|n\rangle \quad (6.28)$$

$$= \sum_{nm} \langle n|\hat{A}|m\rangle \langle m|\hat{W}|n\rangle \quad (6.29)$$

$$= \sum_{n_S, n_R, m_S, m_R} \langle n_S|\hat{A}|m_S\rangle \delta_{n_R m_R} \langle m_S m_R|\hat{W}|n_S n_R\rangle \quad (6.30)$$

$$= \sum_{n_S m_S} \langle n_S|\hat{A}|m_S\rangle \sum_{n_R} \langle m_S n_R|\hat{W}|n_S n_R\rangle \quad (6.31)$$

$$\langle A\rangle = \sum_{n_S} \langle n_S|\hat{A}\hat{W}_S|n_S\rangle = tr_S(\hat{A}\hat{W}_S) \quad (6.32)$$

with

$$\widehat{W}_S := \sum_{n_R} \langle n_R | \widehat{W} | n_R \rangle = \text{tr}_R(\widehat{W}_R) \quad (6.33)$$

the reduced density matrix in the system  $S$ .

**Note:**

Let the system have a  $d_S$  dimensional Hilbert space, and the reservoir a  $d_R$  dimensional Hilbert space. Then the total Hilbert space is  $d_S \cdot d_R = d$  dimensional.  $\widehat{W}$  corresponds to a  $d_R \cdot d_S$  dimensional matrix.

$\widehat{W}_S$  corresponds to a  $d_S$  dimensional matrix and acts only in the Hilbert space of  $S$ , since the reservoir states have been "traced out".

### 6.3 Thermodynamic perturbation theory for the canonical ensemble

In general, the trace  $Z_c = \text{tr } \widehat{W}_c = \text{tr } e^{-\frac{\widehat{H}}{k_B T}}$  cannot be evaluated in a straightforward way, because the eigenvalues of  $\widehat{H}$  are not known. To develop a perturbation theory, we separate the total Hamiltonian  $\widehat{H}$  as

$$\widehat{H} = \widehat{H}_0 + \widehat{V}, \quad (6.34)$$

where

- the eigenstate problem of  $\widehat{H}_0$  is assumed to be solved exactly, and
- $\widehat{V}$  is a perturbation assumed to be small.

The expansion of  $e^{-\frac{\widehat{H}}{k_B T}} = \widehat{W}_c$  in powers of  $g$  is still nontrivial, because  $[\widehat{H}_0, \widehat{V}] \neq 0$  in general. A perturbation theory can be developed, however, by observing the formal analogy of the canonical density matrix  $\widehat{W}_c(T)$  with the time evolution operator  $U(t)$  of quantum mechanics:

$$Z_c W_c(T) = e^{-\frac{\hat{H}}{k_B T}} \quad (6.35)$$

$$U(t) = e^{-\frac{i}{\hbar} \hat{H} t} \quad (6.36)$$

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle \quad (6.37)$$

with the identification

$$\boxed{\frac{1}{k_B T} \longrightarrow i \frac{t}{\hbar}} \quad (6.38)$$

i.e. the inverse temperature plays the role of an *imaginary time* ! (in appropriate units,  $\hbar = 1$ ,  $k_B = 1$ ).

Thus, we will first recall the quantum mechanical time dependent perturbation theory and then set  $i \frac{t}{\hbar} = \frac{1}{k_B T}$  at the end.

### Time-dependent perturbation theory

1. The *interaction picture* is chosen such that the arbitrary operator  $\hat{A}$  obeys the time evolution according to  $\hat{H}_0$ , i.e. it is known:

$$\langle \psi(t) | \hat{A} | \psi(t) \rangle = \langle \psi(0) | e^{\frac{i}{\hbar} \hat{H} t} \hat{A} \underbrace{e^{-\frac{i}{\hbar} \hat{H} t}}_{|\psi(t)\rangle} | \psi(0) \rangle \quad (6.39)$$

$$= \langle \psi(0) | e^{\frac{i}{\hbar} \hat{H} t} e^{-\frac{i}{\hbar} \hat{H}_0 t} \underbrace{e^{+\frac{i}{\hbar} \hat{H}_0 t} \hat{A} e^{-\frac{i}{\hbar} \hat{H}_0 t}}_{\hat{A}_I(t)} | \psi(0) \rangle \quad (6.40)$$

$$\begin{aligned} & \underbrace{e^{+\frac{i}{\hbar} \hat{H}_0 t} e^{-\frac{i}{\hbar} \hat{H} t}}_{|\psi_I(t)\rangle} | \psi(0) \rangle \\ &= \langle \psi_I(t) | \hat{A}_I(t) | \psi_I(t) \rangle \end{aligned} \quad (6.41)$$

with

$$\hat{A}_I(t) = e^{\frac{i}{\hbar}\hat{H}_0 t} \hat{A} e^{-\frac{i}{\hbar}\hat{H}_0 t} \quad (6.42)$$

$$|\psi_I(t)\rangle = e^{\frac{i}{\hbar}\hat{H}_0 t} e^{-\frac{i}{\hbar}\hat{H} t} |\psi(0)\rangle \equiv \hat{S}(t) |\psi(0)\rangle \quad (6.43)$$

In the interaction picture, the operators and the states obey the equations of motion (assuming no explicit  $t$ -dependence of the Schrödinger operators  $\hat{A}$ ,  $\hat{H}$ ,  $\hat{H}_0$ ):

•

$$i\hbar \frac{d}{dt} \hat{A}_I(t) = [\hat{A}_I(t), \hat{H}_0] \quad (6.44)$$

$$\text{and} \quad (6.45)$$

$$i\hbar \frac{d}{dt} |\psi_I(t)\rangle = \left( -e^{\frac{i}{\hbar}\hat{H}_0 t} \hat{H}_0 e^{-\frac{i}{\hbar}\hat{H} t} + e^{\frac{i}{\hbar}\hat{H}_0 t} (\hat{H}_0 + \hat{V}) e^{-\frac{i}{\hbar}\hat{H} t} \right) |\psi(0)\rangle \quad (6.46)$$

$$= \underbrace{e^{\frac{i}{\hbar}\hat{H}_0 t} \hat{V} e^{-\frac{i}{\hbar}\hat{H}_0 t}}_{\hat{V}_I(t)} \underbrace{e^{\frac{i}{\hbar}\hat{H}_0 t} e^{-\frac{i}{\hbar}\hat{H} t} |\psi(0)\rangle}_{|\psi_I(t)\rangle} \quad (6.47)$$

•

$$i\hbar \frac{d}{dt} |\psi_I(t)\rangle = \hat{V}_I(t) |\psi_I(t)\rangle \quad (6.48)$$

$$\text{or} \quad (6.49)$$

$$i\hbar \frac{d}{dt} \hat{S}(t) = \hat{V}_I(t) \hat{S}(t), \quad \hat{S}(t=0) = 1. \quad (6.50)$$

Knowing that  $\hat{S}(t)$ , the total time evolution operator is given by

$$U(t) = e^{-\frac{i}{\hbar}\hat{H} t} = e^{-\frac{i}{\hbar}\hat{H}_0 t} \hat{S}(t) \quad (6.51)$$

2. *Formal integration and iterative solution of (\*)*:

$$\hat{S}(t) = 1 - \frac{i}{\hbar} \int_0^t dt' \hat{V}_I(t') \hat{S}(t') \quad (6.52)$$

$$= 1 - \frac{i}{\hbar} \int_0^t dt' \hat{V}_I(t') + \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt'' \hat{V}_I(t') \hat{V}_I(t'') + \dots \quad (6.53)$$

$$= \hat{T} e^{-\frac{i}{\hbar} \int_0^t dt' \hat{V}_I(t')} \quad (6.54)$$

(power series of  $\hat{S}$  in terms of  $\hat{V}$ )

with the  $t$ -ordering operator  $\widehat{T}$ .

3. Replacing  $\frac{i}{\hbar}t$  by the “inverse temperature”  $\beta = \frac{1}{k_B T}$ , we obtain a power series for  $W_c(T)$ :

$$\widehat{S}(\beta) = \widehat{T} e^{-\int_0^\beta d\beta' \widehat{V}_I(\beta')} \quad (6.55)$$

$$= 1 - \int_0^\beta d\beta' \widehat{V}_I(\beta') + (-1)^2 \int_0^\beta d\beta' \int_0^{\beta'} d\beta'' \widehat{V}_I(\beta') \widehat{V}_I(\beta'') + \dots \quad (6.56)$$

where

$$\widehat{V}_I(\beta) = e^{\beta \widehat{H}_0} \widehat{V} e^{-\beta \widehat{H}_0}, \quad \beta = \frac{1}{k_B T} \quad (6.57)$$

and

$$\begin{aligned} Z_c W_c(T) &= e^{-\beta \widehat{H}_0} \widehat{S}(\beta) \\ &= e^{-\beta \widehat{H}_0} - e^{-\beta \widehat{H}_0} \int_0^\beta d\beta' \widehat{V}_I(\beta') + \dots \\ &\quad + (-1)^n \int_0^\beta d\beta^{(1)} \int_0^{\beta^{(1)}} d\beta^{(2)} \dots \int_0^{\beta^{(n)}} d\beta^{(n)} \widehat{V}_I(\beta^{(1)}) \dots \widehat{V}_I(\beta^{(n)}) \\ &\quad + \dots \end{aligned}$$

We obtain explicitly in first order in the perturbation:

- *Partition sum:*

$$Z_c^{(0)} = \text{tr} e^{-\beta \widehat{H}_0} \quad (6.58)$$

$$Z_c = Z_c^{(0)} - \text{tr} \left\{ e^{-\beta \widehat{H}_0} \int_0^\beta d\beta' \widehat{V}_I(\beta') \right\} \quad (6.59)$$

$$= Z_c^{(0)} - \text{tr} \int_0^\beta d\beta' \left\{ e^{-\beta \widehat{H}_0} e^{\beta' \widehat{H}_0} \widehat{V} e^{-\beta' \widehat{H}_0} \right\} \quad (6.60)$$

$$\begin{array}{c} \text{cyclic} \\ \text{invariance of tr} \\ \downarrow \end{array} \quad (6.61)$$

$$= Z_c^{(0)} - \text{tr} \int_0^\beta d\beta' e^{-\beta \widehat{H}_0} \widehat{V} + \mathcal{O}(\widehat{V}^2) \quad (6.62)$$

$$\begin{aligned}
Z_c &= Z_c^{(0)} - \frac{1}{k_B T} \operatorname{tr} \left\{ e^{-\frac{\hat{H}_0}{k_B T}} \hat{V} \right\} \\
&= Z_c^{(0)} \left( 1 - \frac{\langle \hat{V} \rangle_0}{k_B T} + \mathcal{O}(\hat{V}^2) \right) \\
&= Z_c^{(0)} \left( 1 + \frac{Z_c^{(1)}}{Z_c^{(0)}} + \mathcal{O}(\hat{V}^2) \right)
\end{aligned} \tag{6.63}$$

with  $\langle \hat{V} \rangle_0 = \frac{\operatorname{tr} \left\{ e^{-\frac{\hat{H}_0}{k_B T}} \hat{V} \right\}}{Z_c^{(0)}} = \operatorname{tr} \left\{ \hat{W}_c^{(0)} \hat{V} \right\}$  the canonical thermal average of  $\hat{V}$  with respect to  $\hat{H}_0$ .

$$Z_c = Z_c^{(0)} \left( 1 + \frac{Z_c^{(1)}}{Z_c^{(0)}} \right) \tag{6.64}$$

$$Z_c^{(1)} = -Z_c^{(0)} \frac{\langle \hat{V} \rangle_0}{k_B T} + \mathcal{O}(\hat{V}^2) \tag{6.65}$$

- *Density operator*

$$\hat{W}_c = \frac{1}{Z_c} e^{-\beta \hat{H}_0} \left( 1 - \int_0^\beta d\beta' \hat{V}_I(\beta') \right) + \mathcal{O}(\hat{V}^2) \tag{6.66}$$

$$= e^{-\beta \hat{H}_0} \left( \frac{1}{Z_c^{(0)}} - \frac{Z_c^{(1)}}{Z_c^{(0)2}} - \frac{1}{Z_c^{(0)}} \int_0^\beta d\beta' \hat{V}_I(\beta') \right) \tag{6.67}$$

$$\hat{W}_c = \underbrace{\frac{1}{Z_c^{(0)}} e^{-\beta \hat{H}_0}}_{\hat{W}_c^{(0)}} \left( 1 - \int_0^\beta d\beta' \left[ \hat{V}_I(\beta') - \langle \hat{V} \rangle_0 \right] + \mathcal{O}(\hat{V}^2) \right) \tag{6.68}$$

- *Free energy:*

$$F = -k_B T \ln Z_c = -k_B T \ln Z_c^{(0)} - k_B T \cdot \frac{Z_c^{(1)}}{Z_c^{(0)}} \tag{6.69}$$

$$F = -k_B T \ln Z_c^{(0)} + \langle \hat{V} \rangle_0 \tag{6.70}$$



Expressions of higher order in  $\hat{V}$  can be obtained successively.

From  $F$  all other thermodynamic quantities can be obtained.

**Remark:**

Based on the analogy  $\frac{i}{\hbar}t \leftrightarrow \frac{1}{k_B T}$  and using the time dependent perturbation theory for Green's functions (QMII), a field theory for finite  $T$  can be developed.

## 6.4 The classical limit: equipartition theorem and virial theorem

For the classical limit it is crucial that the kinetic energy and the potential energy effectively commute in the high-temperature limit.

The thermal average of the commutator is in a momentum eigenbasis:

$$\bar{C} = \frac{1}{Z_c} \sum_{\vec{p}} \left\langle \vec{p} \left| e^{-\frac{\hat{H}}{k_B T}} \left[ \frac{\hat{\vec{p}}^2}{2m}, V(\vec{x}) \right] \right| \vec{p} \right\rangle \quad (6.71)$$

with

$$\left[ \frac{\hat{\vec{p}}^2}{2m}, V(\vec{x}) \right] = \frac{\hbar}{2mi} \left( \hat{\vec{p}} \cdot \vec{\nabla} V(\vec{x}) + \hat{\vec{p}} V(\vec{x}) \cdot \vec{\nabla} - V(\vec{x}) \hat{\vec{p}} \cdot \vec{\nabla} \right) \quad (6.72)$$

$$= \frac{\hbar}{2mi} \left( \hat{\vec{p}} \cdot \vec{\nabla} V + \vec{\nabla} V(\vec{x}) \cdot \hat{\vec{p}} \right) \quad (6.73)$$

Using a typical thermal momentum

$$\langle p \rangle_T \approx p_T = \frac{2\pi\hbar}{\lambda_T} = \sqrt{2mk_B T} \quad (6.74)$$

$$\bar{C} \approx \left\langle \vec{p}_T \left| \left[ \frac{\hat{\vec{p}}^2}{2m}, V(\vec{x}) \right] \right| \vec{p}_T \right\rangle \quad (6.75)$$

$$= \frac{\hbar}{2mi} 2p_T \left\langle \vec{p}_T \left| \vec{\nabla} V \right| \vec{p}_T \right\rangle \quad (6.76)$$

with  $\vec{\nabla} V \approx \frac{V(\vec{x})}{a_0}$  and  $a_0$ : typical length scale on which  $V$  varies:

$$\bar{C} \approx \frac{\hbar}{2mi} 2 \frac{p_T}{a_0} \langle V \rangle_T \quad (6.77)$$

$$\stackrel{p_T^2 \approx \langle p^2 \rangle}{\approx} -i \left\langle \frac{p_T^2}{2m} \right\rangle \langle V \rangle \cdot \frac{1}{2\pi} \left( \frac{\lambda_T}{a_0} \right) \quad (6.78)$$

This estimate can be extended to many-particle systems and to interacting particles. Then

$$a_0 = \min\{\text{range of interaction potential, average particle spacing}\} \quad (6.79)$$

### Conclusion:

In the  $T \rightarrow \infty$  limit,  $\frac{\lambda_T}{a_0} \ll 1$ , the commutator  $[\hat{H}_{\text{kin}}, \hat{V}]$  approaches  $\infty$  more slowly than the product of the thermal averages and can, therefore, be neglected in  $\left\langle e^{-\frac{H_{\text{kin}} - V}{k_B T}} \right\rangle$ . Note that the criterion  $\frac{\lambda_T}{a_0} \ll 1$  for this classical limit coincides with the heuristic argument given in the section about Bose systems.

In the  $T \rightarrow \infty$  limit, the canonical partition sum for a single particle reads:

$$Z_c = \text{tr} \left\{ e^{-\frac{\hat{\vec{p}}^2}{2mk_B T}} e^{-\frac{V(\vec{x})}{k_B T}} \right\}. \quad (6.80)$$

It can be evaluated using complete basis sets of momentum and position eigenstates:

$$\widehat{\vec{p}}|\vec{p}\rangle = \vec{p}|\vec{p}\rangle \quad \langle \vec{p}|\vec{p}'\rangle = \delta^3(\vec{p} - \vec{p}') \quad (6.81)$$

$$\widehat{\vec{x}}|\vec{x}\rangle = \vec{x}|\vec{x}\rangle \quad \langle \vec{x}|\vec{x}'\rangle = \delta^3(\vec{x} - \vec{x}') \quad (6.82)$$

$$\int d^3x |\vec{x}\rangle \langle \vec{x}| = 1 \quad (6.83)$$

$$\int \frac{d^3p}{(2\pi\hbar)^3} |\vec{p}\rangle \langle \vec{p}| = 1 \quad (6.84)$$

$$(6.85)$$

$$Z_c = \int \frac{d^3p}{(2\pi\hbar)^3} \left\langle \vec{p} \left| e^{-\frac{\widehat{\vec{p}}^2}{2mk_B T}} e^{-\frac{V(\vec{x})}{k_B T}} \right| \vec{p} \right\rangle \quad (6.86)$$

$$= \int \frac{d^3p}{(2\pi\hbar)^3} \int d^3x \left\langle \vec{p} \left| e^{-\frac{\widehat{\vec{p}}^2}{2mk_B T}} \right| \vec{x} \right\rangle \left\langle \vec{x} \left| e^{-\frac{V(\vec{x})}{k_B T}} \right| \vec{p} \right\rangle \quad (6.87)$$

$$= \int \frac{d^3p}{(2\pi\hbar)^3} \int d^3x e^{-\frac{\widehat{\vec{p}}^2/2m + V(\vec{x})}{k_B T}} \underbrace{\langle \vec{p}|\vec{x}\rangle \langle \vec{x}|\vec{p}\rangle}_{|\psi_p(x)|^2 = \frac{1}{v} \text{ (density)}} \quad (6.88)$$

$$\boxed{\begin{aligned} Z_c &= \int \frac{d^3p}{(2\pi\hbar)^3} \int \frac{d^3x}{v} e^{-\frac{H(\vec{p}, \vec{x})}{k_B T}} \\ H(\vec{p}, \vec{x}) &= \frac{\vec{p}^2}{2m} + V(\vec{x}) \quad \text{classical Hamiltonian function} \end{aligned}} \quad (6.89)$$

In the classical limit, the canonical partition function  $Z_c$  is the classical Boltzmann factor integrated over the complete phase space of  $(\vec{x}, \vec{p})$ .

### Liouville theorem:

The “volume of a classical system in phase space”  $\Gamma$ , is conserved in time:

$$\Gamma = \int \frac{d^3p}{2\pi\hbar} \int d^3x \rho(\vec{x}, \vec{p}) \quad (6.90)$$

$$\frac{d\Gamma}{dt} = 0 \quad (6.91)$$

$$\rho(\vec{x}, \vec{p}) = \sum_i \delta^3(\vec{x} - \vec{x}_i) \delta^3(\vec{p} - \vec{p}_i) \quad (6.92)$$

Can be proved using the classical Hamiltonian equations of motion.

### 6.4.1 Equipartition and virial theorems

In the canonical ensemble for one particle in 1 dimension one has *in the classical limit*:

$$\left\langle p \frac{\partial H(\vec{p}, \vec{x})}{\partial p} \right\rangle = \frac{1}{Z_c} \int \frac{dp dx}{2\pi\hbar \cdot v} p \frac{\partial H}{\partial p} e^{-\frac{H}{k_B T}} \quad (6.93)$$

$$= \frac{1}{Z_c} \int \frac{dp dx}{2\pi\hbar \cdot v} (-k_B T) p \frac{\partial}{\partial p} e^{-\frac{H}{k_B T}} \quad (6.94)$$

$$\stackrel{\text{p.i.}}{=} k_B T \frac{1}{Z_c} \int \frac{dp dx}{2\pi\hbar \cdot v} e^{-\frac{H}{k_B T}} \quad (6.95)$$

$$= k_B T \quad (6.96)$$

For the quadratic momentum dependence of the classical  $H$  function,

$H = \frac{p^2}{2m} + V(x)$ , this implies

$$\langle H_{\text{kin}} \rangle = \left\langle \frac{\vec{p}^2}{2m} \right\rangle = \frac{1}{2} \left\langle p \frac{\partial H}{\partial p} \right\rangle = \frac{1}{2} k_B T. \quad (6.97)$$

Similarly, one can show the *Virial theorem*:

$$\begin{aligned} \left\langle x \frac{\partial H}{\partial x} \right\rangle &= k_B T \\ \left\langle x \frac{\partial V}{\partial x} \right\rangle &= k_B T \end{aligned} \quad (6.98)$$

For a harmonic potential  $V_h(x) \sim x^2$ , it follows:

$$\langle V_h(x) \rangle = \frac{1}{2} \left\langle x \frac{\partial V}{\partial x} \right\rangle = \frac{1}{2} k_B T \quad (6.99)$$

Generalizing this to many-particle systems, this proves the

**Equipartition theorem (classical thermodynamics):**

Each degree of freedom (momentum, position, or other) which appears quadratically in the Hamilton function, gives a contribution  $\frac{1}{2}k_B T$  to the internal energy.

This result has already been obtained for several explicit systems in the high- $T$ -limit of the specific heat (e.g. Fermi gas, classical gas).



# Chapter 7

## Interacting Systems in Thermodynamic Equilibrium: Phase Transitions

### 7.1 Thermodynamic considerations and outline

When there are interactions between the particles ( or spins) of a many-body system, the eigenstates of the system, and hence its full thermodynamics, cannot, in general, be determined exactly.

However, it can be understood from a very general thermodynamic argument that in an interacting system the states at low and at high temperature can be different in a *qualitative* way and, thus, separated by a phase transition.

These concepts will be made more concrete in this chapter<sup>1</sup>

1. Phase transitions with spontaneous symmetry breaking:

In a thermodynamic system controlled by temperature, the free energy

$$F = U - TS \tag{7.1}$$

---

<sup>1</sup>The Bose- Einstein condensation is the only example of a system without interaction which has a phase transition, induced only by statistical correlations.

is always minimized in thermodynamic equilibrium.

- (a) For  $T \rightarrow 0$ , this means that  $U$  is minimized, since  $-TS$  gives a vanishing contribution. With interactions,  $U$  is often minimal for an *ordered state*.

**Example:** Spin system with ferromagnetic interactions.

The ground state is a ferromagnetic state with all spins aligned parallel to each other.

This ground state is unique (3rd law of thermodynamics) e.g. the ferromagnetic state with given magnetization direction.

- (b) For sufficiently high  $T$ ,  $F$  is always dominated by the term  $-TS$ , since for  $T \rightarrow \infty$  the classical limit is approached, where  $U \sim T$  and  $-TS \sim -T \ln T$  ( see chapter 6.4.1, equipartition theorem).

Thus, for  $T \rightarrow \infty$  the system maximizes the entropy  $S$  ( instead of minimizing  $U$ ) and forms a *disordered state*, realized by a large number of microstates.

**Example:**

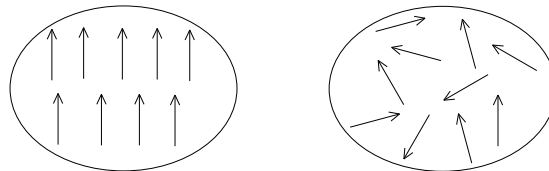


Figure 7.1: Paramagnetic state

The ordered state has often ( not always! counterexample: liquid- gas) a reduced symmetry compared to the disordered one.

**Example:** In the ferromagnetic state the rotational symmetry is broken.

Therefore, the thermodynamic states at high and at low  $T$  must be separated by a phase transition. The existence of a phase transition as a function of  $T$  can be inferred alone from the thermodynamic



interplay of energy minimization and entropy maximization, if the interactions tend to form a ground state which has lower symmetry than the Hamiltonian itself.

There are, however, phase transitions which cannot be understood in this way:

2. Phase transitions without spontaneous symmetry breaking or long-range ordering.

**Example:** Liquid-gas transition

3. Phase transitions at  $T = 0$ , controlled by other parameters (coupling strength, particle density, ...)  
 $\rightarrow$  “quantum phase transitions”.

In this chapter we will first consider examples of real systems using approximate methods, in order to formulate the phenomenon “phase transition” and several concepts connected with it more precisely.

Starting from the approximate treatment, we will then, in particular, formulate the concept of universality near phase transitions, which will lead us to the renormalization group method (RG).

A classification of the different types of phase transitions will be briefly discussed at the end.

As examples we will describe

- (a) Ordering transitions in magnetic systems
- (b) Liquid-gas transitions in a classical, interacting gas.

## 7.2 Spin systems with interactions

### 7.2.1 Origin of the spin-spin interaction and models

The nucleus as well as the electron system of a single atom can carry a finite magnetic moment or spin. The magnetic moment of the electron system of an

atom is comprised of the orbital angular momentum and of the spin of the electrons. It is in general non-zero for atoms with incompletely filled shells and must be finite, if the number of electrons is odd.

### Types of spin-spin interactions

(a) Direct dipole interaction:

This interaction is very weak because of the smallness of the individual magnetic moments involved and can usually be neglected.

(b) Exchange interaction:

This interaction is induced by the symmetry of the quantum mechanical many-body wave function and by the ( large!) Coulomb interaction between the electrons. Therefore, this interaction can be large.

- **Hund's rule ferromagnetic interaction**

between electrons in orbitals which are *spatially close* ( large Coulomb-interaction) but ( almost) *orthogonal* to each other (no hybridization mixing)

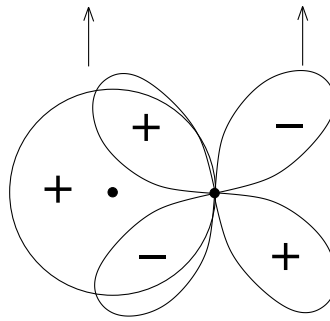


Figure 7.2: Ferromagnetic interaction

$$|\psi\rangle = |\phi\rangle_{\text{orbital}} \otimes |\chi\rangle_{\text{spin}} \quad (7.2)$$

Spatial part of 2-particle wave function antisymmetric to minimize strong Coulomb repulsion.

$\Rightarrow$  Spin part of wave function symmetric  $\rightarrow$  triplet

$\Rightarrow$  Coulomb induced ferromagnetic interaction.

- **Hopping-induced antiferromagnetic interaction**

between electrons in orbitals which are *spatially separated* (small Coulomb interaction), but have large overlap (strong hopping between orbitals)

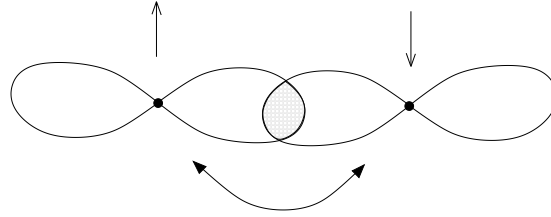


Figure 7.3: Antiferromagnetic interaction

Kinetic energy minimized by virtual hopping of an electron between the two orbitals. This is only possible, if the electrons in the two orbitals are antiferromagnetically oriented, because of the Pauli principle.

$\Rightarrow$  antiferromagnetic coupling.

Using these microscopic couplings one can write down effective spin models for the electrons which do not involve the details of the orbitals any longer but only the spin couplings.

We will consider only spin- $\frac{1}{2}$  systems here.

### 1. Heisenberg model

Localized interacting spins on a lattice.

$$H_{\text{Heisenb.}} = - \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j - \mu \vec{B} \cdot \sum_i \vec{S}_i \quad (7.3)$$

most often: nearest neighbor coupling:

$$J_{ij} = \begin{cases} J & , \quad i, j, \text{ n.n.} \\ 0 & , \quad \text{else} \end{cases} \quad (7.4)$$

$$J_{i,j} > 0 \quad : \quad \text{ferromagnetic} \quad (7.5)$$

$$J_{i,j} < 0 \quad : \quad \text{antiferromagnetic} \quad (7.6)$$

$$\vec{B} \quad : \quad \text{external magnetic field} \quad (7.7)$$

$$\vec{S}_i = \frac{1}{2} \begin{pmatrix} \vec{\sigma}_x \\ \vec{\sigma}_y \\ \vec{\sigma}_z \end{pmatrix} \quad : \quad \text{vector of Pauli matrices} \quad (7.8)$$

$$\sigma_x(0) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y(0) = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z(0) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (7.9)$$

which have quantum dynamics according to the Heisenberg equation of motion.

→ In general not exactly solvable.

## 2. Ising model

$$H_{\text{Ising}} = - \sum_{i,j} J_{ij} S_{iz} S_{jz} - \mu B \sum_i S_z \quad (7.10)$$

Since all the  $x, y$  components are *set equal to zero*, the spins have no temporal dynamics in this model, but can only take the values  $S_{iz} = \pm \frac{1}{2}$  in a statistical manner.

→ classical spin model

## 3. x-y model

Planar spins on a lattice

$$H_{x-y} = - \sum_{i,j} J_{ij} (S_{ix} S_{jx} + S_{iy} S_{jy}) - \mu B \sum_i S_{ix} \quad (7.11)$$

## 4. Stoner model

Itinerant electrons with short-range (screened) Coulomb repulsion  $U$  on a lattice

$$H_{\text{Stoner}} = \sum_{\vec{k}, \sigma} \epsilon_{\vec{k}} c_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma} + U \sum_{i,j} \delta_{i,j} \hat{n}_{i\uparrow} \hat{n}_{j\downarrow}, \quad U > 0 \quad (7.12)$$

$$\hat{n}_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}, \quad \sigma = \uparrow, \downarrow: \quad \text{electron number on site } i \text{ with spin } \sigma.$$

### 7.2.2 Mean-field theory for the Heisenberg model

The ferromagnetic Spin- $\frac{1}{2}$  Heisenberg model with nearest neighbor coupling reads

$$H = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - \mu \vec{B} \cdot \sum_i \vec{S}_i, \quad J > 0 \quad (7.13)$$

where  $\langle \cdot, \cdot \rangle$  denotes nearest neighbor sites.

- Ground state ( $T = 0$ ):  
All spins aligned, ferromagnetic long-range order
- High- $T$  limit ( $k_B T \gg J$ ):  
Independent spins, paramagnetic

Since for the quantum model the excited many-body states and energies cannot be found exactly, one must apply an approximation to describe the thermodynamics.

#### Mean-field (MF) approximation:

We select an arbitrary single spin  $\vec{S}_i$  at lattice site  $i$  and assume that the effect of all the surrounding spins on  $\vec{S}_i$  can be described in an averaged way by an effective field  $\vec{B}_{MF}$  (Weißfield). The resulting mean-field Hamiltonian is then

$$H_{MF} = -\mu(\vec{B} + \vec{B}_{MF}) \cdot \sum_i \vec{S}_i \quad (7.14)$$

Since  $H_{MF}$  is non-interacting, it can be solved exactly. However,  $\vec{B}_{MF}$  is now a variational parameter which must be determined in an optimal way so as to minimize the free energy.

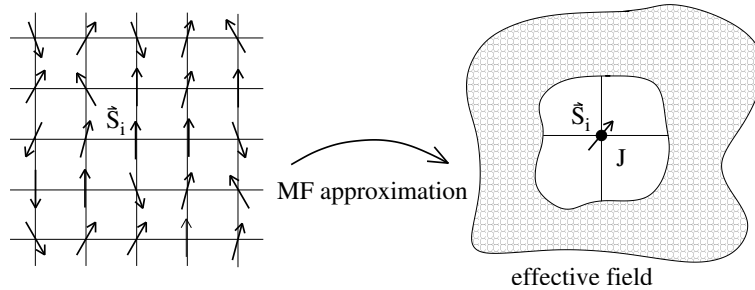


Figure 7.4: Mean-field approximation

In mean-field approximation the equilibrium density operator is

$$\widehat{W}_{MF} = \frac{1}{Z_{MF}} e^{-\frac{\widehat{H}_{MF}}{k_B T}} \quad (7.15)$$

with the MF partition sum (system of  $N$  free spins  $\frac{1}{2}$ )

$$Z_{MF} = \text{tr} \{ e^{-\frac{\widehat{H}}{k_B T}} \} = (2 \cosh x)^N \quad (7.16)$$

with the abbreviations

$$x = \frac{\mu(B + B_{MF})}{2k_B T}, \quad h = \frac{\mu B}{2k_B T} \quad (7.17)$$

( $\vec{B}_{MF} \parallel \vec{B} \parallel \hat{z}$  without loss of generality).

The MF thermal average of any quantity is the average taken with respect to  $\widehat{W}_{MF}$ , e.g. the average spin and the spin-spin correlation function (see free spin  $\frac{1}{2}$ , chapter 3):

$$\langle \vec{S}_i \rangle_{MF} = \frac{1}{2} \hat{e}_z \tanh x \quad (7.18)$$

$$\langle \vec{S}_i \cdot \vec{S}_j \rangle_{MF} = \langle \vec{S}_i \rangle_{MF} \cdot \langle \vec{S}_j \rangle_{MF} \quad (7.19)$$

$$= \frac{1}{4} \tanh^2 x, \quad (7.20)$$

and the MF free energy

$$F\{\widehat{W}_{MF}\} = U - TS = \text{tr} \{ \widehat{H} \widehat{W}_{MF} + k_B T \widehat{W}_{MF} \ln(\widehat{W}_{MF}) \} \quad (7.21)$$

$$= -k_B T \ln Z_{MF} + \langle \widehat{H} - \widehat{H}_{MF} \rangle_{MF} \quad (7.22)$$

$$= -k_B T \ln Z_{MF} - J \sum_{\langle i,j \rangle} \langle \vec{S}_i \cdot \vec{S}_j \rangle_{MF} + \mu \vec{B}_{MF} \cdot \sum_i \langle \vec{S}_i \rangle_{MF} \quad (7.23)$$

$$F = F(B_{MF}) \quad (7.24)$$

$$= N \left[ -k_B T \ln(2 \cosh x) - J \frac{Z}{2} \cdot \frac{1}{4} \tanh^2 x + k_B T (x - h) \tanh x \right] \quad (7.25)$$

$Z$  = number of nearest neighbors.

To find the optional field  $B_{MF}$  we find the minimal (stationary) point of  $F$  wrt.  $B_{MF}$ :

$$0 = \frac{\partial F}{\partial x} = \left[ \frac{1}{4} JZ \tanh x + k_B T (x - h) \right] \frac{1}{\cosh^2 x} \quad (7.26)$$

or

$$\boxed{\mu B_{MF} = \frac{1}{2} JZ \tanh \frac{\mu(B_{MF} + B)}{2k_B T}} \quad \text{variational condition for } B_{MF}. \quad (7.27)$$

This result can be understood pictorially in that  $B_{MF}$  is the effective field acting on  $\vec{S}_i$ , created by the surrounding spins, i.e. comparing equations (7.13), (7.14):

$$\mu B_{MF} = J \sum_{j,n,n,i} \langle \vec{S}_j \rangle_{MF} = JZ \cdot \frac{1}{2} \tanh x \quad (7.28)$$

in agreement with the variational result.

Since  $\langle \vec{S}_j \rangle_{MF}$  of the surrounding spins is the same as for the central spin  $\langle \vec{S}_i \rangle_{MF}$  (because of translational invariance),  $B_{MF}$  is also called "selfconsistent field" (similar to Hartree-Fock approximation).

### Graphical solution of the selfconsistency equation

1.  $B = 0$  (no external field)

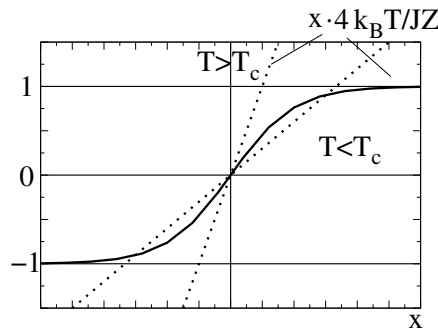


Figure 7.5: Graphical solution for  $B = 0$  (no external field)

(a) For  $T > T_c$ ,

$$\boxed{T_c = \frac{JZ}{4k_B}} \quad \begin{array}{l} \text{f.m. transition temperature} \\ \text{(Curie temperature)} \end{array} \quad (7.29)$$

only the solution  $x = 0$ ,  $B_{MF} = \langle \vec{S}_i \rangle_{MF} = 0$  exists.

→ Paramagnetic high-T phase.

(b) For  $T < T_c$  two solutions  $x \neq 0$  exist with the non-zero magnetization

$$M = - \left. \frac{\partial F}{\partial B} \right|_{B=0} = \mu N \langle |\vec{S}_j| \rangle_{MF} = M_0 \tanh x|_{B=0} , \quad (7.30)$$

$M_0 = \mu N s$  ( $s = \frac{1}{2}$ ) saturation magnetization with  $x =$  solution of selfconsistency equation.

(c) For  $T \lesssim T_c$  one obtains by expanding  $\tanh(x)$  for small  $x$

$$\frac{\mu B_{MF}}{2k_B T} = x = \pm \sqrt{3} \sqrt{1 - \frac{4k_B T}{JZ}} = \pm \sqrt{3} \sqrt{1 - \frac{T}{T_c}} \quad (7.31)$$

and a finite, spontaneous magnetization

$$M(T) = M_0 \tanh \sqrt{3 \left( 1 - \frac{4k_B T}{JZ} \right)} \approx M_0 \sqrt{3 \left( 1 - \frac{4k_B T}{JZ} \right)} + O(T_c - T) \quad (7.32)$$

(ferromagnetism).

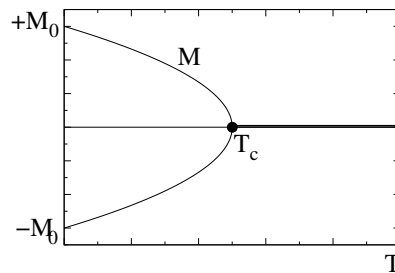


Figure 7.6:



2.  $B \neq 0$ :

In finite external field, the magnetization curve is shifted.

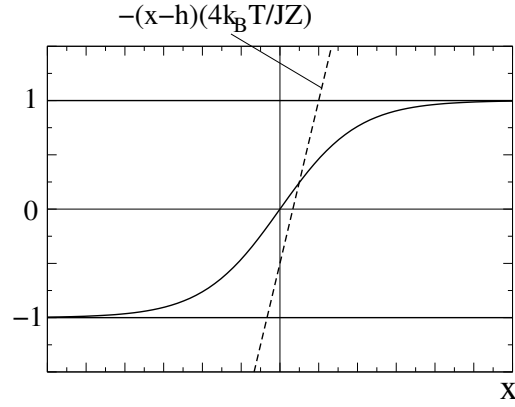


Figure 7.7:

### Magnetic susceptibility:

For small external field  $B$  and  $T \approx T_c$ :  $x \ll 1$ , the selfconsistency equation reads

$$(x - h) \frac{4k_B T}{JZ} = \tanh x \approx x - \frac{1}{3}x^3 + O(x^5) \quad (7.33)$$

$$\frac{\partial x}{\partial B} = 2k_B T \frac{\partial x}{\partial h} \quad (7.34)$$

$$\left( \frac{\partial x}{\partial h} \Big|_{B=0} - 1 \right) \underbrace{\frac{4k_B T}{JZ}}_{\frac{T}{T_c}} = \frac{\partial x}{\partial h} \Big|_{B=0} - x^2 \Big|_{B=0} \frac{\partial x}{\partial h} \Big|_{B=0} \quad (7.35)$$

$$\frac{\partial x}{\partial h} \Big|_{B=0} = \frac{\frac{T}{T_c}}{\frac{T}{T_c} - 1 + x^2 \Big|_{B=0}} \quad (7.36)$$

$$= \frac{\frac{T}{T_c}}{\frac{T}{T_c} - 1 + 3 \left| 1 - \frac{T}{T_c} \right|} \quad (7.37)$$

$$= \begin{cases} \frac{1}{2} \frac{\frac{T}{T_c}}{1 - \frac{T}{T_c}} & , \quad T < T_c \\ \frac{1}{4} \frac{\frac{T}{T_c}}{\frac{T}{T_c} - 1} & , \quad T > T_c \end{cases} \quad (7.38)$$

Hence,

$$\chi(T) = \left. \frac{\partial M}{\partial B} \right|_{B=0} \quad (7.39)$$

$$= - \left( \left. \frac{\partial^2 F}{\partial B^2} \right) \right|_{B=0} = M_0 \frac{\partial}{\partial B} \tan x(B, T) \Big|_{B=0} \quad (7.40)$$

$$= M_0 \frac{1}{\cosh^2 x(0, T)} \cdot \frac{1}{2k_B T} \frac{\partial x}{\partial h} \quad (7.41)$$

$B = 0, T \approx T_c$ :  $x \approx 0$

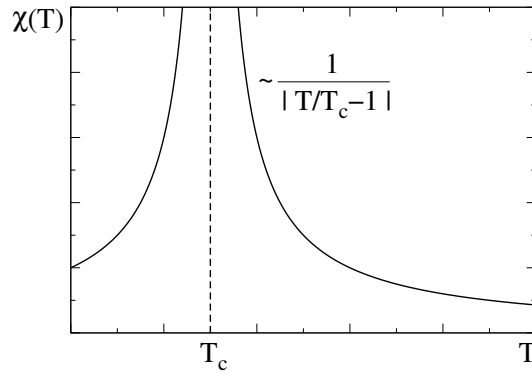


Figure 7.8:

$$\chi(T) = \frac{M_0}{2k_B T_c} \frac{\alpha}{\left| \frac{T}{T_c} - 1 \right|}, \quad \alpha = \begin{cases} \frac{1}{2} & , \quad T < T_c \\ \frac{1}{4} & , \quad T > T_c \end{cases} \quad (7.42)$$

The magnetic susceptibility diverges at the transition with a power law  $\left| \frac{T}{T_c} - 1 \right|^{-1}$ .

From the mean-field solution of the ferromagnetic transition one can extract several important, general concepts of phase transitions:

### 1. Classification of phase transitions

For  $T < T_c$  the thermodynamic state is qualitatively different than for  $T > T_c$ , e.g. finite magnetization broken rotational symmetry below  $T_c$ .

The transition between the two types of states is called *phase transition*.

**Remark:** Definition of qualitative change non-trivial

For the f.m. transition the susceptibility  $\chi = -\frac{\partial^2 F}{\partial B^2}$  diverges at the transition, while  $M = -\frac{\partial F}{\partial B}$  is continuous.

**Definition:**

A *phase transition is of  $n$ th order*, if the  $n$ -th derivatives of  $F$  wrt. to intensive variables diverges at the transition and all lower-order derivatives are continuous.

We first consider 2nd order phase transitions.

### 2. Long-range order and order parameter

In all the thermodynamic states at  $T < T_c$  the spins have a finite component  $\langle \vec{S}_i \rangle_{MF}$  aligned parallel to each other over an infinite distance, i.e. there is *long-range order*.

The states for  $T < T_c$  have a finite spontaneous (i.e. even for  $\vec{B} = 0$ ) magnetization  $M(T < T_c) \neq 0$ . This region of states is called *ordered phase*.

For  $T > T_c$  the magnetization vanishes,  $\vec{M}(T \geq T_c) = 0$ . This region is called *disordered phase*.

A quantity (like  $\vec{M}$ ) which vanishes in the disordered phase and is finite in the ordered phase and which can, hence, be used to characterize the phases, is called *ordered parameter* (OP).

### 3. Spontaneous symmetry breaking

The states with finite magnetization  $|\vec{M}|$  are infinitely degenerate, since the direction of  $\vec{M}$  is arbitrary. For a given state, however, the direction of  $\vec{M}$  is fixed: The ordered state does not have the full 3D rotational symmetry of the Hamiltonian. This fact is called spontaneous *symmetry breaking*. The spontaneous breaking of a *continuous* symmetry has important consequences. They result from the fact, that the (symmetry-breaking) ground

state is infinitely degenerate:

- (a) Existence of gapless collective excitations which "mix" in the degenerate ground states in a position-dependent way: *Goldstone modes*

**Example:** Magnons (spin waves) in a ferromagnet

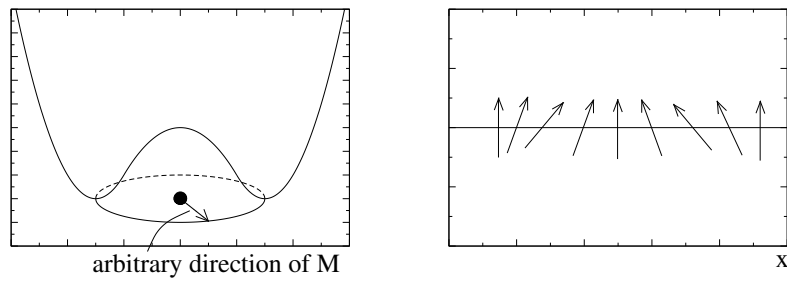


Figure 7.9:

- (b) Existence of *domains* with different orientation of  $\vec{M}$ .

Since Goldstone modes are gapless, they dominate the low-energy excitation spectrum. The Goldstone modes are not included in the MF theory since no spatial dependence is considered. Therefore, the MF theory does not give  $T$ -dependencies correctly, like specific heat.

#### 4. Critical exponents

At a 2nd order transition the order parameter vanishes with a power law

$$\vec{M}(T) \sim \left(1 - \frac{T}{T_c}\right)^\beta \quad (7.43)$$

The susceptibilities (2nd derivatives of  $F$ , response functions) diverge with a power law

$$\chi(T) \sim \left|1 - \frac{T}{T_c}\right|^{-\gamma} \quad (7.44)$$

$$c_V(T) \sim \left|1 - \frac{T}{T_c}\right|^{-\alpha} \quad (7.45)$$

The exponents  $\alpha, \beta, \gamma, \dots$  are called critical exponents; "critical behavior" of physical quantities at the transition.

In mean field theory:

$$\beta = \frac{1}{2}, \quad \gamma = 1, \quad \alpha = 0 \quad (\text{step}) \quad (7.46)$$

This result is universal for any 2nd order transition in MF approximation (will be shown in G.-L.-theory). The exact exponents are in general different from the MF result. The reason is that thermal fluctuations (caused by Goldstone modes) are not taken into account in MF approximation.

### 7.2.3 Ginzburg-Landau-Theory for 2nd order phase transitions

The free energy density is a function of the mean field  $\frac{\mu B_{MF}}{2k_B T} = x$ , i.e. of the order parameter field (see 6.2.2):

$$\frac{M}{M_0} = m = \tanh \frac{\mu(B + B_{MF})}{2k_B T} = \begin{cases} 0 & , \text{ paramagnet} \\ \neq 0 & , \text{ ferromagnet} \end{cases} \quad (7.47)$$

In equilibrium, the value of  $B_{MF}$  (and thus  $m$ ) is determined by the stationarity condition on  $F$  (selfconsistency equation). However, in a general state  $F$  has the form

$$F = \int d^3x f \quad (7.48)$$

$$f(T, m, h) = \frac{N}{V} \left[ -k_B T \ln(2 \cosh x) - J \frac{Z}{2} \cdot \frac{1}{4} \tanh^2 x + k_B T (x - h) \tanh x \right] \quad (7.49)$$

In order to learn general properties of a 2nd-order transition, one can exploit that the order parameter  $m$  vanishes continuously at the transition and, hence, that  $f$  can be expanded in powers of  $m$ :

$$f = \overbrace{-nk_B T \ln 2}^{f_0} + \underbrace{\frac{1}{2} A \frac{T - T_c}{T_c}}_{\tau} m^2 + \frac{1}{4} B m^4 - m h + O(m^6) \quad (7.50)$$

The coefficients  $A$ ,  $B$  can be calculated from a microscopic theory for a given system.

However, we are here interested in the general behavior near the transition without calculating the coefficients explicitly. From very general principles they have the properties

1. Only even powers of  $m$  appear in the expansion (spatial inversion symmetry) if there is no external field  $h$ .
2. The minima of  $f(m)$  are at the equilibrium values of  $m$ . This implies that the coefficient of the  $m^2$  term is (see figure)

$$\begin{cases} > 0 & , \quad T \geq T_c \\ < 0 & , \quad T < T_c \end{cases} \quad (7.51)$$

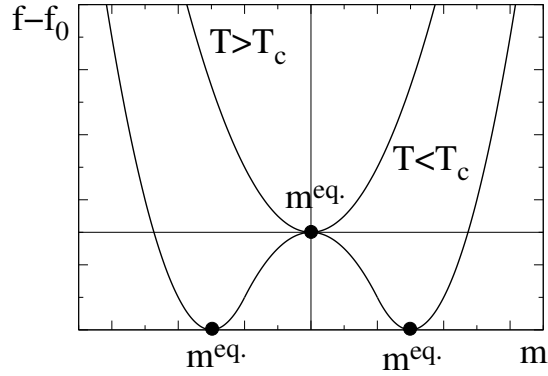


Figure 7.10:

This has been taken into account in the factor

$$\tau = \frac{T - T_c}{T_c} \quad \text{reduced temperature} \quad (7.52)$$

and  $A > 0$ .

3. The coefficient of the  $m^4$  term and of all higher-order terms must be  $R > 0$  in order to stabilize the system.

In order to include spatial fluctuations, the free energy density can be considered position dependent, which introduces a gradient term ("rigidity" of the OP field)

$$\Delta f = f - f_0 = \bar{f} \left\{ \frac{1}{2} \xi_0^2 (\vec{\nabla} \vec{m})^2 + \frac{1}{2} \tau \vec{m}^2 + \frac{1}{4} b (\vec{m}^2)^2 - \vec{m} \cdot \vec{h} \right\} \quad (7.53)$$

$$\vec{m} = \vec{m}(\vec{x}), \quad \xi_0 : \text{OP coherence length.}$$

Although the G.-L. theory has been developed here for a ferromagnetic transition, it can be written for any 2nd order transition and allows to explore general properties of a transition in MF approximation, eg. spec. heat, critical exponents etc.

### 7.2.4 Principle of the Higgs mechanism

One of the important problems of the standard model of elementary particle physics is the question, how the gauge bosons obtain their non-zero rest mass. Gauge bosons are the particles which mediate the elementary interactions. They are the field quanta of the gauge fields, e.g.  $W^\pm$  and  $Z^0$  bosons for the weak interaction (SU(2) symmetry), photons for the electromagnetic interaction (U(1) symmetry) and gluons for the strong interaction (SU(3) symmetry). The gauge symmetry prohibits a rest mass of the gauge bosons. For the example of the electromagnetic interaction we show in this chapter first, how the U(1) gauge symmetry implies that photons are massless, and second, as an application of a Ginzburg-Landau theory, how spontaneous symmetry breaking can lead to a finite rest mass of the gauge bosons. The latter is called the Anderson-Higgs mechanism.

#### U(1) gauge symmetry

We consider a scalar boson matter field  $\psi(\underline{x})$  with rest mass  $m$ , the Higgs boson field, obeying the Klein-Gordon equation ( $\hbar = 1, c = 1$ )

$$(-\partial_\mu \partial^\mu + m^2) \psi = 0. \quad (7.54)$$

The free energy density of the field  $\psi(\underline{x})$  is

$$f_\psi = \psi^* (-\partial_\mu \partial^\mu + m^2) \psi - Ts, \quad (7.55)$$

where  $s$  is the entropy density considered later. Note that in the Klein-Gordon theory  $n = i\psi^* (\partial_t \psi)$  is interpreted as a particle density.

From equation (7.55) we see that the prefactor of the modulus squared of  $\psi$  in the free energy density,  $m^2|\psi|^2$ , indicates the square of the rest mass. This is, hence, the general place where the rest mass of a particle appears in a field theory.

The electromagnetic 4-vector potential is

$$A^\mu = (\phi, \vec{A}), \quad A_\mu = g_{\mu\nu} A^\nu \quad (7.56)$$

and the field tensor in covariant form

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu. \quad (7.57)$$

The electromagnetic free energy density is ( neglecting the energy contribution  $-Ts_{\text{e.m.}}$  at low  $T$ )

$$f_{\text{e.m.}} = \frac{1}{8} F_{\mu\nu} F^{\mu\nu} = \frac{1}{8\pi} (\vec{E}^2 + \vec{B}^2). \quad (7.58)$$

The U(1) gauge symmetry of the total free energy density with respect to local phase transformations of  $\psi$ ,

$$\psi(\underline{x}) \longmapsto e^{i\Theta(\underline{x})} \psi(\underline{x}) \quad (7.59)$$

implies that the derivatives of  $\psi$  are replaced according to

$$i\partial_\mu \longmapsto i\partial_\mu - eA_\mu(\underline{x}) \quad (7.60)$$

( “minimal coupling”), where a gauge field  $A_\mu(\underline{x})$  has been introduced which must transform as

$$A_\mu(\underline{x}) \longmapsto A_\mu(\underline{x}) - \frac{1}{e} \partial_\mu \Theta(\underline{x}) \quad (7.61)$$

in order to obey the local U(1) gauge symmetry.

The total free energy density of the interacting system is, hence,

$$\begin{aligned} f\{\psi, \psi^*, A^\mu\} &= \psi^* [(-i\partial_\mu - eA_\mu)(-i\partial^\mu - eA^\mu) + m^2] \psi \\ &\quad -Ts + \frac{1}{8\pi} F_{\mu\nu} F^{\mu\nu} \end{aligned} \quad (7.62)$$



The free electromagnetic field in vacuum (no charges) is a transverse field,  $\partial_\mu A^\mu = 0$ . This additional constraint means that the 4-vector  $A^\mu$  consists of 3 independent fields, i.e. is a 3-dim. representation of the rotation group. Hence,  $A^\mu$  carries an integer spin  $S = 1$ , and its field quanta are bosons.  $A^\mu$  is identified with the electromagnetic field and its field quanta are the photons.

It is seen that the energy density  $u$  is invariant under the local U(1) gauge transformations (7.59), (7.61), and that a mass term for the gauge field,

$$M_{\text{ph}}^2 A_\mu A^\mu \quad (7.63)$$

would break the gauge symmetry (see (7.61)).

### Spontaneous symmetry breaking

We will now describe a condensation transition of the bosonic matter field  $\psi$ . To that end we will derive a Ginzburg-Landau form of the free energy.

- a) In order to have a condensation the number of bosons ( $\psi$ - field) must be fixed by a chemical potential  $\mu(T)$ .

Therefore, we transform to the grand canonical potential density  $w$  with the natural variable  $\mu$ :

$$w\{\psi, \psi^*, A^\mu\} = f\{\psi, \psi^*, A^\mu\} - \mu n\{\psi, \psi^*\}. \quad (7.64)$$

We will be interested only in the condensate part  $\psi_0(\underline{x})$  of the matter field, which has momentum  $\vec{k}^{(0)} = 0$  and rest energy  $m$ ,

$$\psi_0(\underline{x}) = |\psi_0| e^{-ik_\mu^{(0)} x^\mu} = |\psi_0| e^{-imt} \quad (7.65)$$

$$n^{(0)} = i\psi^* \partial_t \psi = m|\psi_0|^2 \quad (7.66)$$

- b) The matter field has a repulsive interaction with itself. For our U(1) system this is the electromagnetic interaction (Coulomb repulsion), since the particles of the matter field  $\psi$  carry charge  $e$  due to the coupling to  $A^\mu$ . This interaction would be obtained in second order perturbation theory in the

coupling to the electromagnetic field  $A^\mu$ . For simplicity, we here assume a zero-range repulsive contact interaction, which gives the contribution

$$\frac{1}{4}b|\psi(\underline{x})|^2|\psi(\underline{x})|^2, \quad b > 0 \quad (7.67)$$

to the free energy density. It will stabilize the system against infinite condensate amplitude  $|\psi_0|$ .

The total grand potential density is then,

$$\begin{aligned} w\{\psi_0, \psi_0^*, A^\mu\} &= w_0\{\psi_0, \psi_0^*, A^\mu\} + e^2 A_\mu A^\mu |\psi_0|^2 \\ &\quad - \mu(T)m|\psi_0|^2 + \frac{1}{4}b(|\psi_0|^2)^2 \end{aligned} \quad (7.68)$$

There is no derivative of  $\psi_0(\underline{x})$  in  $w$ , since the condensate wave function  $\psi_0(\underline{x})$  has no spatial dependence and the time derivative cancels in  $f$ . The entropy of the condensate  $\psi_0(\underline{x})$  vanishes, since it is a single state. All non-condensate contributions, including  $-Ts$  and  $\frac{1}{8\pi}F_{\mu\nu}F^{\mu\nu}$  are absorbed in  $w_0$ . They behave continuously at the condensation transition (which will be considered below).

The quadratic term in  $w$  has a sign change at a critical temperature  $T_c$ , since

$$\mu(T=0) = m = \text{minimum energy of a matter particle} > 0 \quad (7.69)$$

$$\mu \xrightarrow{T \rightarrow \infty} -\infty \quad (\text{see bosonic systems}), \text{ and} \quad (7.70)$$

$$e^2 \langle A_\mu A^\mu \rangle > 0 \quad \text{is small,} \quad e^2 \langle A_\mu A^\mu \rangle_{T=0} = 0. \quad (7.71)$$

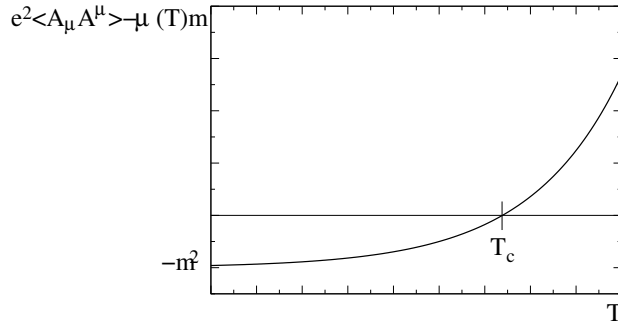


Figure 7.11:

Hence, the grand potential can be written as

$$w = w_0 + \frac{1}{2}a \frac{\overbrace{T - T_c}^{\tau}}{T_c} |\bar{\psi}_0|^2 + \frac{1}{4}b (|\bar{\psi}_0|^2)^2 + \dots, \quad a, b > 0. \quad (7.72)$$

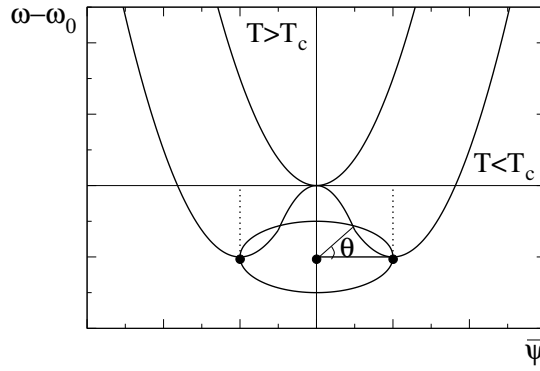


Figure 7.12:

For  $T > T_c$ ,  $w$  has minima for nonzero condensate amplitudes  $|\bar{\psi}_0|$

$$0 \stackrel{!}{=} \frac{\partial w}{\partial \bar{\psi}_0^*} a \tau \bar{\psi}_0 + b |\bar{\psi}_0|^3 \quad (7.73)$$

$$\bar{\psi}_0(T) = \sqrt{-\frac{a}{b}\tau} = \sqrt{\frac{a}{b}} \cdot \sqrt{1 - \frac{T}{T_c}}. \quad (7.74)$$

The symmetry-broken ground state has a continuous degeneracy due to an arbitrary global phase  $\Theta \in [0, 2\pi[$ :

$$\psi_0 = \bar{\psi}_0 e^{i\Theta} e^{-imt}. \quad (7.75)$$

In the condensate phase,  $T < T_c$ , the free energy of the photon field is

$$f_{A_\mu} = e^2 |\bar{\psi}_0|^2 A_\mu A^\mu + \frac{1}{8\pi} F_{\mu\nu} F^{\mu\nu}, \quad |\bar{\psi}_0| > 0. \quad (7.76)$$

This means that by the spontaneous symmetry breaking  $A_\mu$  has dynamically acquired a non-zero mass term with

$$M_{\text{ph}}^2 = e^2 |\bar{\psi}_0|^2 = e^2 \sqrt{\frac{a}{b}} \cdot \sqrt{1 - \frac{T}{T_c}}. \quad (7.77)$$

### Physical interpretation:

The physical interpretation can be found by considering the wave equation for  $A^\mu$  in the symmetry broken state

$$0 = (-\partial_t^2 + \partial_x^2 + M_{\text{ph}}^2) A^\mu \quad (c = 1) \quad (7.78)$$

$$A^\mu = \bar{A}^\mu e^{-i(\omega t - \vec{k} \cdot \vec{x})} \quad (7.79)$$

with

$$\omega = \sqrt{k^2 - M_{\text{ph}}^2} = \begin{cases} \sqrt{k^2 - M_{\text{ph}}^2}, & k \geq M_{\text{ph}} \\ -i\sqrt{M_{\text{ph}}^2 - k^2}, & k < M_{\text{ph}}. \end{cases} \quad (7.80)$$

For  $c\hbar k < mc^2$  the wave equation for  $A^\mu$  has only decaying solutions, i.e. the field  $A^\mu$  cannot statically exist inside the condensate.

Physically, this situation is realized in a superconductor.  $\bar{\psi}_0$  is the superconducting condensate amplitude. The fact that photons (i.e. an electromagnetic field) with energy  $\hbar\omega < M_{\text{ph}}c^2$  cannot exist inside a superconductor is the Meißner effect.

# Appendix A

## The Lagrange multiplier method (reminder)

Extremum of a function  $f(\underbrace{x_1, x_2, \dots}_{\vec{x}})$  under the constraint  $g(x_1, x_2, \dots) = g_0$ .

$$\tilde{f}(\vec{x}) = f(\vec{x}) + \lambda g(\vec{x}) \quad (\text{A.1})$$

$$\frac{\partial \tilde{f}}{\partial \vec{x}} = \frac{\partial f}{\partial \vec{x}} + \lambda \frac{\partial g}{\partial \vec{x}} = 0 \quad (\text{A.2})$$

- Add gradient of  $g$ ,  $\frac{\partial g}{\partial \vec{x}} \perp (g = \text{const. line})$  with weight factor  $\lambda$  such that  $\frac{\partial \tilde{f}}{\partial \vec{x}} \parallel (g = \text{const. line})$ .  
→ variation only along equipotential line
- The value of  $\lambda$  picks out the value  $g_0$  to which  $g$  is fixed.

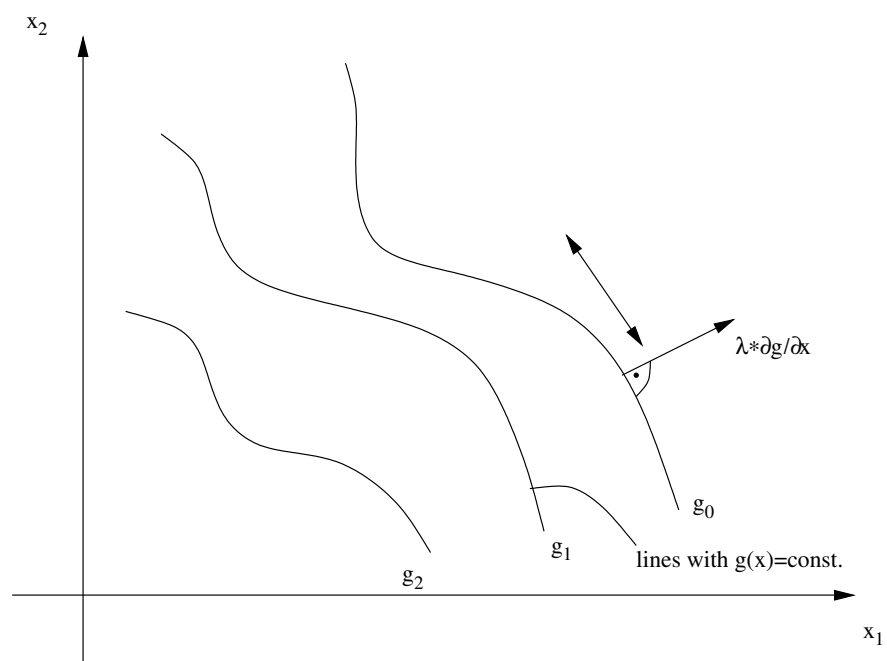


Figure A.1: Lagrange multiplier method

# Appendix B

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