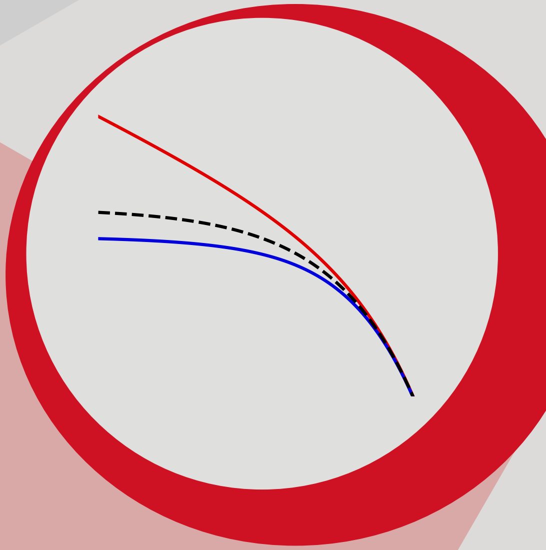
Lecture Notes
Physik

Statistical Physics

Linking the Microscopic with the Macroscopic World

BJÖRN MALTE SCHÄFER



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A STATISTICAL PHYSICS

The purpose of this script is an introduction into the fundamental concepts of thermodynamics and how they are determined from a microscopic model of matter. This includes especially the concept of the state variables temperature, pressure and chemical potential, and how changes of entropy, volume and particle number introduce changes in the internal energy; as well as how well thermal energy can be used in mechanical devices. Restricting ourselves to thermal equilibria where a notion of temperature exists, it is possible to set up partition sums over the microscopic states that a system might be in and to link these partition sums to thermodynamic potentials: Ideally, this bridges the gap between thermodynamics as a continuum theory with no particular assumption about the microscopic properties of a system, and the partition sum as a reflection of exactly these microscopic properties. Thermodynamics and statistical physics as the fundamental theory behind it are incredibly general and require temperature as a concept, joined with occupation statistics of the respective states of a system and a counting scheme for these states, whether they form a continuum or are discrete. We will end this lecture by looking at the phenomena of statistical systems like magnetism or Bose-Einstein-condensation and the dynamics of statistical systems with the Langevin-equation and the Fokker-Planck-equation. Perhaps the best way to view the relation between thermodynamics and statistical physics is that of an effective field theory: Thermodynamics describes systems without any recourse to their actual microscopic structure, which makes concepts like entropy so difficult to understand.

Statistical physics is a branch of physics that uses methods of probability theory and statistics, and particularly the mathematical tools for dealing with large populations and approximations, in solving physical problems. It can describe a wide variety of physical systems with an inherently stochastic nature on the microscopic level. Its applications include many problems in the fields of physics, biology, chemistry, neuroscience, and even some social sciences, such as sociology and linguistics. Its main purpose is to clarify the properties of matter in aggregate, in terms of physical laws governing atomic motion.

statistical physics is so incredibly general that you find applications in all branches of physics including gravity

Without any idea about atoms and molecules in the time before Ludwig Boltzmann one would have imagined the atmosphere to be a continuum described by field quantities like density, pressure and velocity, obeying the Euler-equation

$$\partial_t \boldsymbol{\upsilon} + (\boldsymbol{\upsilon} \cdot \nabla)\boldsymbol{\upsilon} = -\frac{\nabla p}{\rho} - \nabla\Phi \tag{A.1}$$

relating the accelerations of the fluid elements to gradients in pressure p and gravitational potential Φ, for an ideal fluid. Assuming that the atmosphere is static, $\boldsymbol{\upsilon} = 0$, and stationary, $\partial_t \boldsymbol{\upsilon} = 0$, results in the hydrostatic equation

$$\frac{\nabla p}{\rho} = -\nabla\Phi \tag{A.2}$$

For continuing, one needs a (possibly phenomenological) relation between pressure and density, i.e. an equation of state. If there is a proportionality $p \sim \rho$ one gets

$$\frac{\nabla p}{\rho} \sim \frac{\nabla \rho}{\rho} = \nabla \ln \rho = -\nabla\Phi \quad \rightarrow \quad \rho \sim \exp(-\Phi). \tag{A.3}$$

Assuming that the gravitational potential is homogeneous,

$$\boldsymbol{g} = -\nabla\Phi = \text{const} \quad \rightarrow \quad \Phi = gh \quad \rightarrow \quad \rho \sim \exp(-h) \tag{A.4}$$

i.e. the barometric formula with an exponential decrease of density with height h.

The reasoning in statistical physics is very different: Matter is not a continuum but made of discrete particles, which experience thermal fluctuations in their energy, due to a continuous reshuffling of energy between all mutually interacting degrees of freedom. In thermal equilibrium, however, it is possible to write down the probability of a thermal fluctuation of a certain size, i.e. the probability that the energy ϵ is borrowed from the system by a single particle or degree of freedom: According to Ludwig Boltzmann, this probability is given by

$$p(\epsilon) \sim \exp\left(-\frac{\epsilon}{k_B T}\right) \tag{A.5}$$

such that large fluctuations in energy are rare, but become less rare when the temperature T is increased. After a particle has borrowed the energy ϵ, it can climb in the gravitational field of the Earth to a height $\epsilon \propto gh$, and the fraction $p(\epsilon)$ of all particles must be the density at height h

$$\rho \sim \exp(-h) \tag{A.6}$$

While the result is certainly consistent with the one from continuum mechanics, it seems to involve a lot of intuition. In particular, eqn. A.5 makes a deep statement about the probability of a thermal fluctuation to occur: Clearly only applicable in thermal equilibrium and for systems with a defined temperature but without any specification of the internal structure of the system there is a universal probability distribution of a rather simple shape. The only parameter in eqn. A.5 is the Boltzmann-constant k_B with the numerical value

$$k_B \simeq 1.3806503 \times 10^{-23} \frac{\text{J}}{\text{K}} \tag{A.7}$$

which is an incredibly tiny number: Macroscopic objects do not move spontaneously, in contract to microscopic objects such as atoms or molecules, which are in a state of constant motion. At room temperature $T \simeq 300\text{K}$ there is typically a fluctuating thermal energy of $\epsilon = k_B T = 4.2 \times 10^{-21}\text{J}$, which is irrelevant compared to e.g. typical kinetic or potential energies of a macroscopic object.

B THERMODYNAMICS

Thermodynamics is the branch of physics that deals with heat, temperature and their relation to energy and work. The relation between these quantities is defined by the four laws of thermodynamics, irrespective of the composition or specific properties of system in question, neither its constituents nor its composition: As such, thermodynamics is incredibly general and finds applications almost everywhere where thermal equilibria are possible and temperatures are defined. Statistical physics is the microscopic theory behind thermodynamics: Here, the actual microscopic properties of a system matter, and under the assumption of thermal equilibrium statistical physics provides a relation between thermodynamic quantities through partition sums. It was the grand accomplishment of Ludwig Boltzmann to realise that thermal energy is energy distributed in the microscopic degrees of freedom of a system if it is fundamentally discrete. With a continuum model of matter one does not have a chance to have this thought, rather, one is forced to think of thermal energy as a ”fluid” that can be absorbed by any substance, increasing its temperature.

Systems in thermodynamics are characterised by state variables, which fall into two groups: Extensive state variables are proportional to the amount of matter or the physical size of the system, and include volume V, entropy S, particle number N, electric charge ρ or magnetisation $\mathbf{M}$. Each of these state variables has an intensive state variables as a partner that does not depend on the size of the system, for instance the pressure p, the temperature T, the chemical potential μ, the external electric potential Φ and the external magnetic field $\mathbf{B}$. Extensive and intensive state variables are combined into the Euler-relation, stating that the internal energy U is

$$U = TS - pV + \mu N + \Phi\rho + \mathbf{B}\cdot\mathbf{M} + \dots \tag{B.8}$$

Changes dU of the internal energy can be introduced by changing the extensive state variables and performing abstract work against the intensive state variables,

$$dU = TdS - pdV + \mu dN + \Phi d\rho + \mathbf{B}\cdot d\mathbf{M} + \dots \tag{B.9}$$

Commonly, we will restrict ourselves to just three of the terms, $U = TS - pV + \mu N$ and $dU = TdS - pdV + \mu dN$. There are cases where the separation between intensive and extensive state variables is not as clear, for instance in systems with self-interactions, i.e. when the potential is sourced by the electric charge density itself, making it depend on the physical size of the system, too.

B.1 *Ideal classical gases*

The behaviour of an ideal gas in terms of the three relevant state variables volume V, pressure p, and temperature T realised as being very dilute, is determined through three relationships: Firstly, the Boyle-Mariotte law, specifying that pV =const at fixed T, secondly, the Gay-Lussac law, requiring that V/T =const at fixed p, and thirdly, the Amontons law, making sure that p/T =const at fixed V. These three statements can be combined into the ideal gas law

$$pV = Nk_BT \tag{B.10}$$

by realising that the combination pV/T =const= Nk_B is extensive (well, p and T are certainly not extensive but V is) and depends on the amount of substance N.

B.1.1 Van der Waals-gases

The ideal gas law applies only to idealised systems, which are approximated by dilute gases, so the particle density N/V has to be a relevant quantity. In fact, real gases are well described the van der Waals-equation,

$$\left(p + a\left(\frac{N}{V}\right)^2\right)\cdot\left(V - Nb\right) = Nk_BT \tag{B.11}$$

with two empirical constants a and b. The second factor is due to the fact that not the entire volume V of a system is accessible by the particles, as they are extended and occupy a tiny but nonzero volume themselves, and the mutual attractive interaction between the particles leads to an effectively higher pressure. Both effects result naturally out of the Lennart-Jones-potential between atoms or molecules with a long-range attractive interaction mediated by electric forces and a short range repulsive force generated by the exclusion principle.

It should be emphasised that the validity of the ideal gas equation or the van der Waals-equation does not rely at all on the existence of atoms or molecules as fundamental constituents, but would be perfectly applicable to a continuum. Then, the particle number N would get replaced by the gas constant R, and the amount of substance is characterised by the number n of moles, $k_BN = Rn$. For a single mole, $n = 1$, suggesting the relation $k_BN_A = R$ with Avogadro's number N_A.

B.1.2 Phenomenological temperature measurements

The ideal gas law can be used to determine temperatures, for instance with Gay-Lussac's law: $T \propto V$ at fixed p, such that a measurement of the volume V is indicative of the temperature T. Surely this measurement is phenomenological as it depends on a particular substance, and furthermore, it is a bit unclear how a measurement of T in one system would change under e.g. Lorentz- or Galilei-transformations. For that purpose, one would like to carry out measurements of temperature mechanically and convert thermal energy into measurable mechanical energy, with a clear transformation behaviour under frame changes: This is achieved by Carnot-engines, as we will see in a second.

It is curious that an ideal gas reaches $V = 0$ at a given pressure at a finite temperature of -273 degrees Celsius, which is set to be the zero-point of the Kelvin scale. Although that temperature can never be reached in practice, it can be determined by means of extrapolation from finite T.

B.2 *Zeroth law of thermodynamics*

Two systems that are brought into thermal contact exchange thermal energy until they have reached thermal equilibrium characterised by a common temperature. In thermal equilibrium the flux thermal energy subsides. Typically the time scale of reaching thermal equilibrium (if it is defined at all, there are mind-blowing counter examples) would be determined by the content of thermal energy and the magnitude of heat flux.

Typically, the change δQ in thermal energy Q associated with a change dT in temperature T is related by

$$\delta Q = C\mathrm{d}T \tag{B.12}$$

with the heat capacity C. In contrast to the change dT of the state variable, the change is thermal energy depends on how exactly the change in state is achieved: Therefore, it is not an exact differential. The relation $\delta Q = c\mathrm{d}T$ served historically as the definition of the calorie by the amount of thermal energy to be added to a quantity of water to raise the temperature by a certain amount.

Thermal energy is proportional to the amount of substance in a system (again, there are counterexamples) and is therefore an extensive quantity unlike temperature. Therefore, it makes sense to define the specific heat c_X

$$C = mc_X \tag{B.13}$$

The index X is meant to illustrate that it matters how the change in state is achieved. For instance, an ideal gas can change the amount of thermal energy that it contains if the temperature is increased, but that increase can be conducted while keeping the pressure p fixed or by keeping the volume V fixed, leading to different results for c_X.

B.2.1 Exact and closed differentials

It is commonly the case in changes in state of a thermodynamical system that it matters how that change in state has been achieved. For instance, an equation state $p(T,V)$ would exhibit a differential change dp

$$\mathrm{d}p = \left.\frac{\partial p}{\partial T}\right|_V \mathrm{d}T + \left.\frac{\partial p}{\partial V}\right|_T \mathrm{d}V \tag{B.14}$$

so that a pressure change can be done increasing the temperature while keeping the volume fixed: In this case, the system would react according to $\left.\frac{\partial p}{\partial T}\right|_V$. Alternatively, the volume can be changed while keeping the temperature fixed, such that $\left.\frac{\partial p}{\partial V}\right|_T$ becomes relevant. Or even more general, one can combine the two changes dT and dV.

When trying to answer the question when exactly a change in state is independent of the way how it has been achieved, the criterion of integrability comes in: If a change in state is path-independent, it only can reflect the initial and final state,

$$F = \int_A^B \mathrm{d}F = F(B) - F(A) \tag{B.15}$$

so changing the system from A to B and back to A along a different path should yield zero,

$$\oint \mathrm{d}F = 0 \tag{B.16}$$

For a function F with the differential

$$\mathrm{d}F = \frac{\partial F}{\partial x}\mathrm{d}x + \frac{\partial F}{\partial y}\mathrm{d}y = A(x,y)\mathrm{d}x + B(x,y)\mathrm{d}y \tag{B.17}$$

one can use the Stokes-theorem in an advantageous way and find

$$\oint \mathrm{d}F = \oint A(x,y)\mathrm{d}x + B(x,y)\mathrm{d}y = \int \mathrm{d}x\mathrm{d}y \left(\frac{\partial B}{\partial x} - \frac{\partial A}{\partial y}\right) \tag{B.18}$$

That integral vanishes if

$$\frac{\partial B}{\partial x} = \frac{\partial A}{\partial y} \tag{B.19}$$

which is made sure by

$$\frac{\partial B}{\partial x} = \frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x} = \frac{\partial A}{\partial y} \tag{B.20}$$

with the interchangeability of the second partial derivatives according to the Schwarz-theorem. Therefore, the path-independence is made sure by the condition $\partial B/\partial x = \partial A/\partial y$.

In the general case one could imagine a inexact differential

$$\delta F = C(x,y)\mathrm{d}x + D(x,y)\mathrm{d}y \tag{B.21}$$

without $C = \partial F/\partial x$ nor $D = \partial F/\partial y$, so that $\partial C/\partial y \neq \partial D/\partial x$, and no valid integrability condition applies. In these cases, integrals over δF would become path-dependent and loop integrals will not vanish in general.

B.3 *First law of thermodynamics*

The foundational idea of the first law of thermodynamics is that thermal energy (or heat) is a form of energy: It can be converted to and from other forms of energy, while a global energy conservation law for the sum of all energy forms is fulfilled. For instance, the change $\mathrm{d}U$ in internal energy of a system would consist of the changes δW of the mechanical (or electromagnetic) energy content as well as of the change δQ of the thermal energy content:

$$\mathrm{d}U = \delta W + \delta Q \tag{B.22}$$

In contrast to the changes δW and δQ, which depend on the exact way in which the change in state is done, the internal energy is conserved: If one takes a system to a certain state and back to the original state along a second path, there can not be any net change in internal energy. Therefore, $\mathrm{d}U$ is an exact differential and the path-independence of the changes in state are summarised by

$$\oint \mathrm{d}U = 0 \tag{B.23}$$

The conservation of total energy contained in a system as the sum of heat and mechanical energy can be expressed pictorially by the statement, that it is impossible to construct a perpetuum mobile of the first kind: That would be a machine that delivers mechanical work without any changes to its internal state. For the first law of thermodynamics it is irrelevant if the changes in state are performed over a sequence of equilibrium states (called reversible changes) or in an arbitrary way such that not at every instance thermodynamical equilibrium is maintained (called irreversible changes, although we will not deal with those in this course):

$$\mathrm{d}U = \delta W_{\mathrm{rev}} + \delta Q_{\mathrm{rev}} = \delta W_{\mathrm{irr}} + \delta Q_{\mathrm{irr}} \tag{B.24}$$

B.3.1 Isochoric changes of state

Let's consider an ideal gas as an example, with state variables T and V, on which the internal energy U(T, V) of the system is thought to depend. Changes dU in the internal energy are given by

$$\mathrm{d}U = \left.\frac{\partial U}{\partial T}\right|_V \mathrm{d}T + \left.\frac{\partial U}{\partial V}\right|_T \mathrm{d}V \tag{B.25}$$

For isochoric changes in state, the volume V is fixed and consequently $\mathrm{d}V = 0$. There can not be any work being performed against the pressure, so $\delta W = 0$ and the change in internal energy is necessarily $\mathrm{d}U = \delta Q$, such that:

$$\delta Q = \left.\frac{\partial U}{\partial T}\right|_V \mathrm{d}T \quad \rightarrow \quad \left.\frac{\partial U}{\partial T}\right|_V = c_V \tag{B.26}$$

leading to the definition of heat capacity at fixed volume V.

B.3.2 Adiabatic changes of state

The situation is very different if one changes the internal energy content of a substance $\mathrm{d}U = \delta Q + \delta W$ by increasing the temperature through the addition of thermal energy and simultaneously by performing mechanical work $-p\mathrm{d}V$ against the pressure:

$$\delta Q = \mathrm{d}U + p\mathrm{d}V = \left.\frac{\partial U}{\partial T}\right|_V \mathrm{d}T + \left.\frac{\partial U}{\partial V}\right|_T \mathrm{d}V + p\mathrm{d}V \quad \rightarrow \quad \delta Q = c_V\mathrm{d}T + \left(\left.\frac{\partial U}{\partial V}\right|_T + p\right)\mathrm{d}V \tag{B.27}$$

in the general case. If, however, the change in state is adiabatic $\delta Q = 0$ and no thermal energy ist exchanged for instance through a perfect insulation of the system,

$$c_V\mathrm{d}T + \left(\left.\frac{\partial U}{\partial V}\right|_T + p\right)\mathrm{d}V = 0 \quad \rightarrow \quad \left.\frac{\partial T}{\partial V}\right|_{\mathrm{ad}} = -\frac{\left.\frac{\partial U}{\partial V}\right|_T + p}{c_V} \tag{B.28}$$

suggesting that the rate at which the temperature changes with changes in the volume is indeed different for the two cases.

B.3.3 Isobaric changes of state

Changing the volume at constant pressure is an isobaric change of state. Then, the volume $V(T, p)$ is dependent on temperature T and pressure p, implying

$$\mathrm{d}V = \left.\frac{\partial V}{\partial p}\right|_T \mathrm{d}p + \left.\frac{\partial V}{\partial T}\right|_p \mathrm{d}T \tag{B.29}$$

where the first term would vanish due to the isobaric condition, $\mathrm{d}p = 0$. Defining the specific heat at constant p is then

$$c_p = \left(\frac{\delta Q}{dT}\right) = c_V + \left(\left.\frac{\partial U}{\partial V}\right|_T + p\right) \left.\frac{\partial V}{\partial T}\right|_p \tag{B.30}$$

and is related to the change in temperature with volume by

$$\left(\left.\frac{\partial U}{\partial V}\right|_T + p\right) = (c_p - c_V) \left.\frac{\partial T}{\partial V}\right|_p \tag{B.31}$$

Picking up loose threads in the previous calculation then shows that

$$\left.\frac{\partial T}{\partial V}\right|_{\mathrm{ad}} = -\frac{c_p - c_V}{c_V} \left.\frac{\partial T}{\partial V}\right|_p \tag{B.32}$$

for the adiabatic versus the isobaric change of temperature with volume.

B.3.4 Adiabatic index of a gas

The adiabatic index is the ratio of the heat capacity at constant pressure c_p to heat capacity at constant volume c_V: These two heat capacities are not identical because they correspond to different ways in which energy is added to the system.

$$\frac{c_p}{c_V} = \kappa \tag{B.33}$$

For an ideal gas one can compute the rate of change of temperature with volume at constant pressure to be

$$\frac{p}{Nk_B} = \frac{T}{V} \quad \rightarrow \quad \left.\frac{\partial \ln T}{\partial \ln V}\right|_p = 1 \quad \text{and} \quad \left.\frac{\partial T}{\partial V}\right|_p = \frac{T}{V} \tag{B.34}$$

such that substitution gives

$$\left.\frac{\partial T}{\partial V}\right|_{\mathrm{ad}} = -(\kappa - 1)\frac{T}{V} \tag{B.35}$$

resulting in

$$\mathrm{d}\ln T = -(\kappa - 1)\mathrm{d}\ln V \quad \text{integrated to} \quad T \sim V^{-(\kappa-1)} \quad \text{or} \quad pV^{\kappa} = \text{const.} \tag{B.36}$$

An adiabatic process occurs without transfer of heat or mass of substances between a thermodynamic system and its surroundings. In an adiabatic process, energy is transferred to the surroundings only as mechanical work, for instance through $-p\mathrm{d}V$, $\mathbf{B}\cdot\mathrm{d}\mathbf{M}$ or $\Phi\mathrm{d}\rho$.

B.3.5 Entropy

The amount of exchanged thermal energy δQ is not an exact differential as it depends on the particular way in which the change in state has been performed. But it is possible to construct a quantity which is in fact an exact differential: Sticking to our example with $\delta Q = \mathrm{d}U + p\mathrm{d}V$ as well as $\mathrm{d}U = c_V\mathrm{d}T$ and an ideal gas with the equation of state $pV = Nk_BT$ suggests that

$$\frac{\delta Q}{T} = c_V\frac{\mathrm{d}T}{T} + Nk_B\frac{\mathrm{d}V}{V} \tag{B.37}$$

is an exact differential called dS,

$$\mathrm{d}S \equiv \frac{\delta Q}{T} \quad\rightarrow\quad S(T,V) = \int_{T_0}^{T} c_V\frac{\mathrm{d}T}{T} + nk_B\int_{V_0}^{V}\frac{\mathrm{d}V}{V} \tag{B.38}$$

provided that the first term only depends on T and the second term only on V. While this is clear for the second term, it is made sure for the first term by Boyle's experiment showing that the specific heat c_V does only depend on T: For U(T, V) the differential reads

$$\mathrm{d}U = \left.\frac{\partial U}{\partial T}\right|_V \mathrm{d}T + \left.\frac{\partial U}{\partial V}\right|_T \mathrm{d}V \tag{B.39}$$

c_V is defined as the change of internal energy with temperature and corresponds to the first term. Boyle observed that in having an isolated gas expand into a larger volume the temperature does not change: Insolation implies that the change dU of internal energy must be zero, and the empirical observation of $\mathrm{d}T = 0$ then suggests that the internal energy can not depend on volume (although we can not know that yet, makes a lot of sense because internal energy in a gas is the kinetic energy of the particles, and that would obviously not depend on volume):

$$\mathrm{d}U = \left.\frac{\partial U}{\partial V}\right|_T \mathrm{d}V = 0 \tag{B.40}$$

Therefore, internal energy is a function of temperature alone, and so is c_V.

S is called the entropy and the differential dS is exact,

$$\oint \mathrm{d}S = 0 \tag{B.41}$$

so that a cyclic change of state always results in a zero change in entropy, and the change in entropy does not depend on the way a change in state is done, in contrast to δQ or δW. Please keep in mind that we do not deal with irreversible changes in state, as they proceed along non-equilibrium states and temperature would not be defined at every instance.

B.4 *Second law of thermodynamics*

After the realisation that mechanical energy can be converted into thermal energy and vice versa, and that there is a corresponding energy conservation law for the total internal energy U, it should be clarified to what extend thermal energy can be transformed back into mechanical energy; after all, it is clear that mechanical energy can be completely converted into thermal energy, for instance by friction.

The second law states that a engine, which works in cycles and returns to its initial state after performing each cycle (so that no energy is stored somehow in the engine) is not allowed to perform mechanically usable work by just cooling down an energy reservoir: It is impossible to gain mechanical work out of thermal equilibrium. One can, however, construct engines that convert thermal energy into mechanical energy, but they require energy reservoirs at two different temperatures and a temperature non-equilibrium. Ideally, those Carnot-engines are able to convert thermal energy into mechanical work, at a given conversion efficiency (that only depends on the temperatures) which is strictly smaller than unity (as long as we're dealing with positive absolute temperatures, we'll revisit this amazingly interesting point later).

B.4.1 Conversion from thermal to mechanical energy

The Carnot-engine is the prime example of an idealised thermodynamical engine, which can use mechanical energy to pump thermal energy from a cold reservoir to a hot reservoir against the natural tendency of thermal energy to flow from hot to cold, or it can be used to gain mechanical energy from the flux of thermal energy from a hot reservoir to a cold reservoir. A Carnot-engine is working in a cyclic fashion, so it does not retain any energy for itself and returns exactly back to its initial state.

One possible realisation of a Carnot-engine is a series of isothermal and adiabatic changes of state of an ideal gas at two different temperatures: The engine absorbs a quantity Q_1 at temperature T_1 from the hot reservoir, and passes a lower quantity Q_2 of thermal energy onto the cold reservoir at temperature T_2, possibly delivering work W. I'd like to emphasise that is any number of possible Carnot-engines, with the common property that they absorb thermal energy in a reversible way: Because dS is an exact differential,

$$\oint \mathrm{d}S = \oint \frac{\delta Q}{T} = 0 \quad \rightarrow \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \tag{B.42}$$

Energy conservation implies that $Q_1 = W + Q_2$ and therefore for the efficiency η of the Carnot-engine

$$\eta = \frac{W}{Q_1}\left(1 - \frac{T_2}{T_1}\right) \tag{B.43}$$

For the case of thermal equilibrium, $T_2 = T_1$, $\eta = 0$ and $W = 0$, so no mechanical work can be performed. All Carnot engines necessarily run at the same efficiency: If you construct a system where the first engine gains work by having heat flow from T_1 to T_2 and use that work for powering a second engine to reverse the heat flow, both the heat flows and the flow of mechanical work should be perfectly balanced and no net changes can be observed: Otherwise, the more efficient engine would deliver mechanical work while no changes in temperature are observed, in contradiction with the second law of thermodynamics.

A highly unusual Carnot-engine is the ratchet and pawl-engine: A propeller is set into motion by impacting air molecules, but a ratchet-mechanism only allows it to turn into a single direction. Then one could use the thermal energy contained in the unordered motion of the air molecules to turn the propeller and possibly lift a weight, thus performing mechanical energy. If that was possible, one would have converted thermal energy into mechanical energy in a perfect way, so there must be a catch. So, for turning the contraption one needs to disengage the ratched by investing δ as an energy in addition to the energy ϵ for lifting the weight, supplied at temperature T_1 of the air. But the ratchet might just disengage randomly, when the energy δ might be randomly supplied by an impacting air molecule, possibly at a different temperature T_2. The probabilities for both cases to happen are given by Boltzmann-probabilities:

$$\exp\left(-\frac{\epsilon+\delta}{k_B T_1}\right) = \exp\left(-\frac{\delta}{k_B T_2}\right) \quad \rightarrow \quad \frac{\epsilon}{\delta} = \eta = 1 - \frac{T_2}{T_1} \tag{B.44}$$

so that the engine runs at the Carnot-efficiency, and at $\eta = 0$ in thermal equilibrium $T_1 = T_2$. In this context reversibility implies that the universally applicable Boltzmann-probabilities are characterised by temperature only: If that changes, they probabilities adjust at once, and there is no lag of the machine to a change in T. I find it very funny to imagine that both the idealised steam engine and the ratchet and pawl-machine operate at the same efficiency: Plugging them together such that the ratchet uses the work provided by the steam engine heats up the air at the propeller relative to the ratchet in exactly the proportion that is used by the steam engine to perform work from the non-equilibrium between propeller and ratchet.

B.4.2 Generalised Carnot-engines

Carnot-engines do not have to be constructed in a specific way: Neither do they need a specific substance like the ideal gas, nor is the term by which mechanical energy is gained $p\mathrm{d}V$, and the ratchet and pawl-machine is a cute example for that; reversibility as a condition is enough. All Carnot-engines operate at the same fundamental efficiency, which can only be a function of the two temperatures

$$Q_2 = Q_1 f(T_1, T_2) \tag{B.45}$$

with efficiency:

$$\eta = 1 - f(T_1, T_2) \tag{B.46}$$

To get some insight into the functional form of f one can build a chain of two Carnot engines, the first one links a reservoir at T_1 with a second reservoir at T_2; it takes in an amount Q_1 of thermal energy, generates mechanical work W and dumps Q_2 into the second reservoir: $W = Q_1(1 - f(T_1, T_2))$ with the wasted thermal energy $Q_2 = Q1 f(T_1, T_2)$. Then, a second Carnot-engine absorbs exactly Q_2 at T_2, generates W' in work and passes Q_3 onto T_3: $W' = Q_2(1 - f(T_2, T_3))$ with the wasted thermal energy $Q_3 = Q_2 f(T_2, T_3)$.

💀 *Carnot-engines are mechanical devices to measure temperatures, they convert thermal to mechanical energy at a fixed efficiency that only depends on the temperatures.*

The sum of mechanical work $W + W' = Q_1(1 - f(T_1, T_2)f(T_2, T_3))$,

$$W + W' = Q_1(1 - f(T_2, T_3)) \tag{B.47}$$

needs to be equal to that of an imaginary Carnot-engine linking the first and the third reservoir directly, i.e. one needs to have transitivity in the efficiencies:

$$f(T_1, T_2) \cdot f(T_2, T_3) = f(T_1, T_3) \tag{B.48}$$

Taking the logarithm of the transitivity relation

$$\ln f(T_1, T_2) + \ln f(T_2, T_3) = \ln f(T_1, T_3) \tag{B.49}$$

and computing the derivative $\partial/\partial T_1$ yields

$$\frac{\partial}{\partial T_1} \ln f(T_1, T_2) = \frac{\partial}{\partial T_1} \ln f(T_1, T_3) \tag{B.50}$$

with $f(T_2, T_3)$ dropping out as it does not depend on T_1. Such a differential equation suggest a separation ansatz $\ln f(T_1, T_2) = A(T_1) + B(T_2)$ because both sides of the equation need to be proportional to the same function in T_1 and the differentiation can not mix in a dependence on the other variable. Reverting the logarithm this would then imply $f(T_1, T_2) = A(T_1) \cdot B(T_2)$ and transitivity is naturally fulfilled if $A(T_2) = 1/B(T_2)$. Substituting back gives

$$f(T_1, T_2) = \frac{B(T_2)}{B(T_1)} \tag{B.51}$$

and for the efficiency

$$\eta = 1 - \frac{B(T_2)}{B(T_1)} \tag{B.52}$$

Therefore, we would call $B(T)$ the thermodynamic temperature as measured by the Carnot-engine: It is a bit circumstantial at this point that it corresponds to the temperature T measured with Boyle's law in an ideal gas. Carnot-engines measure temperature differences or ratios only, so one needs to have a reference point relative to which actual temperatures are determined: $T = 0$ would be an obvious attractive choice from a practical point of view, but there, the Carnot-efficiency η would be undefined! The common definition is taken to be the triple point of water. At a temperature of $T = 273.15$ K and at a pressure of $p = 611.657$ Pa the solid, liquid and gaseous state of water exist simultaneously which is easy to observe.

B.4.3 Entropy and energy conversion

The amounts of thermal energy Q_i exchanged with the heat baths at temperature T_i follow the relation

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{B.53}$$

for any Carnot engine operating between two reservoirs. In the continuum limit this implies

$$\sum_i \frac{\delta Q_i}{T_i} = 0 \tag{B.54}$$

for a chain of Carnot engines, while the usable mechanical work is given by

$$W = \sum_i \delta Q_i \tag{B.55}$$

but we need to invest mechanical work W' to put the amount of δQ_i back into the reservoir i at temperature T_i:

$$W' = \sum_i \delta Q_i \frac{T_i - T_n}{T_i} = \sum_i \delta Q_i - T_n \sum_i \frac{\delta Q_i}{T_i} \tag{B.56}$$

so that the net gain is:

$$W - W' = T_n \sum_i \frac{\delta Q_i}{T_i} \tag{B.57}$$

with $W = W'$ for a loop. Therefore,

$$\sum_i \frac{\delta Q_i}{T_i} \rightarrow \oint \frac{dQ}{T} = \oint dS = 0 \tag{B.58}$$

showing the consistency between the Carnot-efficiency and the exactness of the entropy differential dS. Substituting $dS = \delta Q/T$ into the first law of thermodynamics yields

$$dU = \delta Q + \delta W = TdS - pdV \tag{B.59}$$

where we could replace the inexact differential δQ with the exact dS, introducing T as the function that makes it integrable or exact. The corresponding Euler-relation then assumes the form $U = TS - pV + \mu N + \ldots$.

B.4.4 Irreversible processes and entropy increase in closed systems

Typically, the net change in entropy in a reversible change in state is zero, $dS = 0$. But when for instance to systems with different temperature are brought into thermal contact, the first law of thermodynamics requires that there is a flow of thermal energy from the hot to the cold body, equilibrating their temperatures. That process happens spontaneously as a consequence of disequilibrium, and the entropy will increase.

From the first law of thermodynamics and from the definition of entropy as an exact differential one gets

$$dU = TdS \quad \rightarrow \quad dS = \frac{dU}{T} \tag{B.60}$$

Defining the specific heat $dU = c dT$ allows us to write the entropy differential as

$$dS = c\frac{dT}{T} = c d\ln T \quad \text{with the solution} \quad S = c\ln T + S_0 \tag{B.61}$$

where S_0 is an integration constant. Comparing the entropy before thermal contact

$$S_i = c(\ln T_1 + \ln T_2) \tag{B.62}$$

with that after thermal contact:

$$S_f = 2c\ln\left(\frac{T_1 + T_2}{2}\right) \tag{B.63}$$

shows that the difference in entropy is in fact positive,

$$\Delta S = S_f - S_i = c \cdot \left[2\ln\left(\frac{T_1 + T_2}{2}\right) - (\ln T_1 + \ln T_2)\right] \geq 0 \tag{B.64}$$

because of Jensen's inequality.

B.4.5 Concave functions and Legendre transforms

One has the freedom to replace state functions by performing Legendre transforms. The integration of the entropy into the Euler-relation would only be sensible a replacement of S by T and vice versa can be done in a defined way, and for that entropy needs to be a convex or concave function of T: Then, the Legendre-transform is defined yielding a concave or convex function in return, so that the inverse Legendre-transform is defined just as well.

In general, convex functions obey the inequality

$$g(\theta x + (1-\theta)y) \geq \theta g(x) \cdot (1-\theta) g(y) \tag{B.65}$$

for every value of θ. For the particular choice of $\theta = 1/2$ and the logarithm $g(x) = \ln x$ one gets:

$$\ln\left(\frac{x+y}{2}\right) \geq \frac{1}{2}(\ln x + \ln y) \tag{B.66}$$

By comparison with eqn.B.64 one immediately recognises that the entropy is a convex function of T.

Furthermore, by writing $dU = TdS$ as the first term in the differential Euler-relation and noticing that typically the internal energy is proportional to temperature and the amount of matter a system is composed of, $dU = CdT$ with the heat capacity C, one realises that entropy should (normally, again, there might be counterexamples) be extensive, and can be paired with temperature T as an intensive quantity.

B.5 *Third law of thermodynamics*

There is a rather obscure third law of thermodynamics, which determines the zero-point of entropy: As we are only concerned with changes in the thermodynamic variables and potentials only differences matter, and there is a priori no reference relative to which entropy is measured, unlike temperature T or any form of energy.

Therefore, one postulates that the entropy takes on a constant value, possibly to be set to zero, as the temperature approaches absolute zero.

C PROBABILITY THEORY

C.1 *Kolmogorov axioms for probability*

Probabilities serve as a quantification of the chances of success in a game, when an element of randomness is involved. A random experiment consists in a random selection from a **finite** and non-empty set of events Ω consisting of individual outcomes. The power set $\mathcal{P}(\Omega)$ is the set of all possible subsets (including the empty set) of Ω. The probability measure is now assigning a probability to each of the possible selections $\mathcal{P}(\Omega)$ from the set Ω, and this probability is required to be a real number between 0 and 1.

☠ *If Ω has n elements, the power set $\mathcal{P}(\Omega)$ contains 2^n elements.*

The probability measure is a probability if it fulfils Kolmogorov's axioms:

1. $p(\Omega) = 1$
2. $p(A) \geq 0$ for all $A \subset \Omega$
3. $p(A \cup B) = p(A) + p(B)$ if $A \cap B = \emptyset$, otherwise $p(A \cup B) = p(A) + p(B) - p(A \cap B)$

The first axiom says that the probability of some event in Ω is certainly to come up, and the second axiom makes sure that the probabilities are always positive. Probabilities of mutually exclusive events add, as stated by the third axiom. From these axioms one can draw a number of important conclusions:

1. $p(A) + P(\mathcal{C}(A)) = p(\Omega) = 1$, because $\Omega = A \cup \mathcal{C}(A)$
2. $p(A) \leq p(B)$ for $A \subset B$
3. $p(A \cup B) + p(A \cap B) = p(A) + p(B)$
4. $p(A \backslash B) = p(A) - p(A \cup B)$
5. $p(\emptyset) = 0$, from the previous statement with $\emptyset = A \backslash A$

Generalisations to **infinite** sets is possible by replacing the set of Kolmogorov-axioms with a Borel-σ algebra.

C.2 *Laplace probability*

We can narrow down the set A to contain a single element, $\omega \in \Omega$ in the set of possible outcomes Ω. Then, the probability for a single element is given by

$$p(A) = p\left(\bigcup_i A_i\right) = \sum_i p(A_i) = \sum_i p(\omega_i) \quad \text{for} \quad A \subset \Omega \tag{C.67}$$

where $A_i \cap A_j = \emptyset$ for $i \neq j$, such that straightforward additivity is given. $\omega \rightarrow p(\omega)$ is the probability function which assigns a probability to each ω.

If the elements ω_i are equally likely to be selected, like identical lottery tickets, the probability of selecting an individual one must be the inverse of how many tickets are available, i.e. the cardinality $\#(\Omega)$ of the set Ω

$$p(\omega) = \frac{1}{\#\Omega} \quad \text{and therefore} \quad p(A) = \frac{\#A}{\#\Omega} \tag{C.68}$$

for any set A grouping a couple of elements ω_i into a set. This is exactly Laplace's idea about a probability being the number of favourable cases divided by the number of possible cases.

C.3 *Conditional probabilities and Bayes' law*

Conditional probabilities refer to a random experiment that is carried out in two steps: Firstly, a subset $A \subset \Omega$ is selected in the first step, so that the events in the complement $\omega \in \mathcal{C}(A)$ have been assigned a probability $= 0$ in the successive second step of the random experiment: Then, from these preselected objects a new random selection is made, $\omega \in B$ under the condition $\omega \in A$. The conditional probability of selecting objects from B under the condition that they have been members of the selection of A is given by

$$P(B|A) = \frac{\#(A \cap B)}{\#(A)} \quad \text{with the Laplacian probability} \quad P(A) = \frac{\#(A)}{\#(\Omega)} \tag{C.69}$$

Extending the expression by the cardinality $\#(\Omega)$ of Ω gives

$$P(B|A) = \frac{\#(A \cap B)}{\#(\Omega)} \cdot \frac{\#(\Omega)}{\#(A)} = \frac{P(A \cap B)}{P(A)} \tag{C.70}$$

Then, Bayes' law appears naturally from the realisation that $P(A \cap B)$ is symmetric

$$P(A \cap B) = P(B \cap A) \tag{C.71}$$

so that one obtains:

$$P(B|A) \cdot P(A) = P(A \cap B) = P(B \cap A) = P(A|B) \cdot P(B) \tag{C.72}$$

implying in particular that $P(A|B) \neq P(B|A)$. A classic example to remember this result is the following idea: If A corresponds to a person being female (in a biological or medical sense) and B corresponds to a person being pregnant, $P(B|A) \simeq 10^{-2}$ (which can be easily estimated from the number of children per woman, and the duration of a pregnancy in relation to the life expectancy). On the contrary, $P(A|B)$ is essentially unity. So the gist of Bayes' law is that switching condition and random outcome of a conditional random process needs to be corrected by the ratio of the so-called prior probabilities $p(A)$ and $p(B)$,

$$P(B|A) = P(A|B)\frac{p(B)}{p(A)} \tag{C.73}$$

C.4 *Random variables*

Up to this point, the outcome of a random experiment was a selection of events from the set Ω, all contained in the power set $\mathcal{P}(\Omega)$. The idea of a random variable x now is to assign a value $x(\omega)$ to each of the possible individual outcomes, and to think of the probability $p(x)$ in terms of the value rather than the randomly selected elements. A straightforward example would be the value assigned to lottery tickets: The ticket that are drawn in a lottery would form the elements in Ω and the random variable x would be the money that is paid to the winner.

$$p(x) = P(\omega \in \Omega | x(\omega) = x) \tag{C.74}$$

In this case, the probabilities $p(x)$ as a function of x are called a distribution. Clearly, the same value of the random variable x could correspond to different elements in Ω, so the probability $p(x)$ collects up the contribution from each element ω which is assigned the value x.

The expectation value $\langle x\rangle$ or the first moment of the random variable x following the distribution $p(x)$ is given by

$$\langle x\rangle = \sum_{\omega\in\Omega} \mathrm{P}(\omega)\cdot x(\omega) = \sum_i x_i p(x_i) = \int \mathrm{d}x\, p(x)\cdot x \tag{C.75}$$

glossing over a fundamental difference between finite and infinite sets Ω. Similarly, the variance $\langle x^2\rangle$ or the second moment is defined

$$\langle x^2\rangle = \sum_{\omega\in\Omega} \mathrm{P}(\omega)\cdot x^2(\omega) = \sum_i x_i^2 p(x_i) = \int \mathrm{d}x\, p(x)\cdot x^2 \tag{C.76}$$

which immediately generalises to moments $\langle x^n\rangle$ of arbitrary order,

$$\langle x^n\rangle = \sum_{\omega\in\Omega} \mathrm{P}(\omega)\cdot x^n(\omega) = \sum_i x_i^n p(x_i) = \int \mathrm{d}x\, p(x)\cdot x^n \tag{C.77}$$

where it is interesting to note that the moments can be defined by summing over the set of possible events ω or by integrating over the possible range of values for x, as the probabilities $\mathrm{P}(\omega)$ and $p(x)$ are not identical.

The normalisation required by the Kolmogorov-axioms suggests a transformation law for continuous probabilities,

$$1 = \int \mathrm{d}x\, p_x(x) = \int \mathrm{d}y\, \left|\frac{\mathrm{d}x}{\mathrm{d}y}\right|\cdot p_x(x(y)) = \int \mathrm{d}y\, p_y(y) \quad \text{such that} \quad p(x)\mathrm{d}x = p(y)\mathrm{d}y \tag{C.78}$$

from the Jacobian appearing in the variable change when integrating by substitution.

Summing random numbers $z = x + y$ from two distributions $p_x(x)$ and $p_y(y)$ leads to a distribution of the sum z which is given by convolution of the two original distributions,

$$p_z(z) = \int \mathrm{d}x p_x(x) \int \mathrm{d}y p_y(y)\delta_\mathrm{D}(z-(x+y)) = \int \mathrm{d}x p_x(x)p_y(z-x) = \int \mathrm{d}y p_x(z-y)p_y(y) \tag{C.79}$$

where the δ_D-distribution selects from all possible values x and y the ones that make the sum $x + y$ equal to a predefined z. Similarly, the distribution of differences, products and ratios of random numbers can be computed. Of course everybody knows that convolutions are most practically computed in Fourier-space, so would the Fourier-transform of a distribution be a sensible mathematical object?

C.5 *Characteristic function and moment generating function*

The characteristic function $\varphi(t)$ of a distribution $p(x)$ is defined as the Fourier-transform,

$$\varphi(t) = \int \mathrm{d}x\, p(x)\exp(-\mathrm{i}tx) = \langle\exp(-\mathrm{i}tx)\rangle \tag{C.80}$$

Substituting the series expansion of the exponential then yields

$$\varphi(t)=\int \mathrm{d}x p(x)\sum_n\frac{(-\mathrm{i}tx)^n}{n!}=\sum_n\frac{(-\mathrm{i}t)^n}{n!}\cdot\int \mathrm{d}x\, p(x)\cdot x^n=\sum_n\frac{(-\mathrm{i}t)^n}{n!}\langle x^n\rangle \qquad \text{(C.81)}$$

That actually implies that the moments $\langle x^n\rangle$ can be computed by a differentiation

$$\langle x^n\rangle=\frac{1}{(-\mathrm{i})^n}\cdot\frac{\mathrm{d}^n}{\mathrm{d}t^n}\varphi(t)\bigg|_{t=0} \qquad \text{(C.82)}$$

instead by an integration process: The n-fold differentiation isolates the nth moment $\langle x^n\rangle$ in the series, because the differentiation of the lower powers in t vanish and the higher order powers of t are set to zero, leaving just $\langle x^n\rangle$. Related to the characteristic function is the moment generating function, defined as the Laplace- instead of the Fourier-transform,

$$\mathrm{M}(t)=\int \mathrm{d}x\, p(x)\exp(-tx)=\langle\exp(-tx)\rangle \qquad \text{(C.83)}$$

such that

$$\langle x^n\rangle=\frac{1}{(-1)^n}\cdot\frac{\mathrm{d}^n}{\mathrm{d}t^n}\mathrm{M}(t)\bigg|_{t=0} \qquad \text{(C.84)}$$

without having to worry about i. The above result about convolving distributions is now particularly simple,

$$\varphi_z(t)=\varphi_x(t)\cdot\varphi_y(t) \qquad \text{(C.85)}$$

for the sum $z=x+y$ of two random variables. The Taylor-expansion of $\ln\varphi(t)$ yields the cumulants κ_n as coefficients,

$$\ln\varphi(t)=\sum_n\kappa_n\cdot\frac{t^n}{n!} \qquad \text{(C.86)}$$

which are different compared to the moments, $\langle x^n\rangle\neq\kappa_n$ in general! First of all, cumulants add when random numbers are added, because $\ln\varphi_z(t)=\ln\varphi_x(t)+\ln\varphi_y(t)$, and they serve as a quantification, how close a distribution is to a Gauß-distribution.

The Gauß-distribution has the specific functional form

$$p(x)=\frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right) \qquad \text{(C.87)}$$

and the characteristic function follows straight away to be of equal Gaußian shape, $\varphi(t)=\exp(-\frac{1}{2}\sigma^2t^2)$ with the corresponding logarithm $\ln\varphi(t)\sim -it\mu-t^2\sigma^2$. Consequently, only the first three cumulants are nonzero $\kappa_0=1$ as a reflection of normalisation, the mean $\kappa_1=\mu$ and the variance $\kappa_2=\sigma^2$. One should be very cautious at this point: Cumulants and moments are not identical, and in general one needs Faa' di Bruno's formula to convert between them. Hence, the cumulant series truncates after κ_2, so that any higher-order cumulant must contain information about the non-Gaußian shape of a distribution.

C.6 *Information entropies*

It is an abstract but very interesting question how much randomness is contained in a random process with probabilities p_i in the discrete and $p(x)\mathrm{d}x$ in the continuous case. For that quantification one computes Shannon's information entropy S

$$S = -\sum_i p_i \ln p_i = -\int \mathrm{d}x\, p(x) \ln p(x) \tag{C.88}$$

which has the properties

1. $S \geq 0$ for $0 < p_i \leq 1$
2. $S = 0$ for $p_i = 1$ (certain outcome)
3. $p_i = \frac{1}{\#\Omega}$ for equally probable outcomes according to Laplace. Then,

$$\sum_i p_i = \frac{1}{\#\Omega}\sum_i 1 = \frac{\#\Omega}{\#\Omega} = 1 \rightarrow S = -\sum_i \frac{1}{\#\Omega} \ln \frac{1}{\#\Omega} = \ln \#\Omega \tag{C.89}$$

Clearly, the first requirement is chosen to have S as a positive number, while the second and third requirement make sure that the information entropy increases (logarithmically) as there are more possible outcomes, starting from 0 if there is no randomness at all.

Information entropy in this definition is additive for independent subsystems. Having a factorising probability for the events i and j from two different sets $p_{ij} = p_i \cdot q_j$ and therefore statistical independence,

$$S = -\sum_{ij} p_{ij} \ln p_{ij} = -\sum_{ij} p_i q_j \left(\ln p_i + \ln q_j\right) = -\sum_{ij} p_1 q_j \ln p_i + p_i q_j \ln q_j \tag{C.90}$$

such that separation of the terms yields

$$S = -\sum_i \left(\sum_j q_j\right) p_i \ln p_i + \sum_j \left(\sum_i p_i\right) q_j \ln q_j = -\sum_i p_i \ln p_i - \sum_j q_j \ln q_j = S_p + S_q \tag{C.91}$$

i.e. the entropies of independent random processes are additive.

It should be emphasised that information entropies defined for a continuous distribution $p(x)\mathrm{d}x$ is not invariant under changes of the random variable, which is not an issue at all for the discrete probabilties. In fact, $p(x)\mathrm{d}x = p(y)\mathrm{d}y$ as the transformation law gives

$$S = -\int \mathrm{d}x\, p(x) \ln p(x) = -\langle \ln p(x) \rangle \quad \rightarrow \quad S = -\int \mathrm{d}y\, p(y) \ln\left(p(y)\frac{\mathrm{d}y}{\mathrm{d}x}\right) \tag{C.92}$$

with an additional Jacobian $\mathrm{d}y/\mathrm{d}x$. In order to remedy this, relative entropies such as the Kullback-Leibler divergence have been introduced

$$\Delta S = -\int \mathrm{d}x\, p(x) \ln\left(\frac{p(x)}{q(x)}\right) = -\left\langle \ln\left(\frac{p(x)}{q(x)}\right)\right\rangle \tag{C.93}$$

which measures the relative amount of randomness between two distributions $p(x)\mathrm{d}x$ and $q(x)\mathrm{d}x$. In fact, the same transformation Jacobian $\mathrm{d}y/\mathrm{d}x$ is introduced for both $p(x)$ and $q(x)$, thus canceling out.

It is a very interesting thought to consider Shannon's entropy as a functional for the distribution p_i or $p(x)\mathrm{d}x$ and ask for which distribution the information entropy as a functional is maximised. For instance, the variation of S would be

$$\delta S = -\sum_i (\ln p_i + 1)\delta p_i = 0 \tag{C.94}$$

which needs to be augmented by a boundary condition making sure that the resulting probabilities add up to one, as required by Kolmogorov's first axiom:

$$\sum_i p_i = 1 \rightarrow \delta \sum_i p_i = \sum_i \delta p_i = 0 \tag{C.95}$$

such that

$$\delta S + \lambda \sum_i \delta p_i = 0 \tag{C.96}$$

implying that $\sum(\ln p_i + 1 + \lambda)\delta p_i = 0$ and therefore

$$p_i = \exp(-(1+\lambda)) \tag{C.97}$$

i.e. a constant probability: Information entropy is maximal for the uniform distribution, which defines the microcanonical ensemble in statistical physics.

Maximising Shannon's entropy with additional constraint

$$U = \sum_i p_i E_i = \langle E \rangle \tag{C.98}$$

with a fixed expectation value U, where we have already chosen suggestive variable names, alongside the normalisation. Formulating both constraints as Lagrange multipliers for the variation δS entropy

$$\delta S = -\sum_i (\ln p_i + 1)\delta p_i = 0 \tag{C.99}$$

would require

1. $\sum_i p_i = 1 \rightarrow \delta \sum_i p_i = \sum_i \delta p_i = 0$

2. $\sum_i p_i E_i = U \rightarrow \delta \sum_i p_i E_i = \sum_i E_i \delta p_i = 0$

leading to

$$\delta S + \lambda \sum_i \delta p_i + \mu \sum_i E_i \delta p_i = 0 \tag{C.100}$$

which can be computed to yield $\sum(\ln p_i + 1 + \lambda + \mu E_i)\delta p_i = 0$ and solved for the probabilties to give

$$p_i = \exp(-(1+\lambda+\mu E_i)) \tag{C.101}$$

The two Lagrange multipliers can be determined by resubstituting p_i into the two boundary conditions:

$$\sum_i p_i = \sum_i \exp(-(1+\lambda+\mu E_i)) = 1 \quad \rightarrow \quad \exp(-(1+\lambda)) = \frac{1}{\sum_i \exp(-\mu E_i)} = \frac{1}{Z} \tag{C.102}$$

with the partition sum $Z = \sum_i \exp(-\mu E_i)$ as well as

$$\frac{\sum_i E_i \exp(-\mu E_i)}{\sum_i \exp(-\mu E_i)} = U = \frac{1}{Z}\sum_i E_i \cdot \exp(-\mu E_i) \tag{C.103}$$

with the probabitliy

$$p_i = \frac{1}{Z}\exp(-\mu E) \tag{C.104}$$

which looks a bit reminiscent of the Boltzmann-probability,

$$p_i \sim \exp\left(-\frac{E_i}{k_B T}\right) \tag{C.105}$$

if the identification $\mu = 1/(k_B T)$ is valid. This is the basis of the so-called canonical ensemble, where states at higher energy are less likely according to the Boltzmann probability. In summary I'd like to point out that the realisation of entropy maximising probabilities replaces the fundamental postulates of statistical physics: It is superfluous to define the equipartition of states or the Boltzmann-factor in an axiomatic way when in fact the two distributions are the ones that maximise Shannon's entropy, subject to boundary conditions. Perhaps it is much more intuitive to imagine that the equipartition of states is a condition with makes the least assumption about the system.

D MICROCANONICAL ENSEMBLE

Any system left unperturbed tends towards thermal equilibrium with a defined temperature T, which, along with the other state variables that characterise the system. The internal thermal energy is reflected by the temperature and the heat capacity and is stored in the system in its microscopic degrees of freedom. In thermal equilibrium a continuous reshuffling of energy between all degrees of freedom is taking place, and these microscopical degrees of freedom follow energy-conserving Hamiltonian equations of motion. Ludwig Boltzmann was the first to realise that in thermal equilibrium all states compatible with the same energy are equally likely, and that states of higher energy are less likely to be assumed, where the ratio of probabilities is given by the Boltzmann factor: A justification of these two properties of systems in thermodynamic equilibrium would be axiomatic in the sense of a fundamental postulate, or, it would in fact follow from the notion that the probability distributions have to maximise the Shannon-information entropy as a measure of randomness. Effectively, we will assume that in thermal equilibrium the randomness of how the states are occupied, is as random as possible, with a maximised Shannon-entropy. It is important to realise that statistical mechanics as the microscopic theory behind thermodynamics, is perfectly energy-conserving, despite the fact that it deals ultimately with thermal energy which is often a byproduct of dissipative processes: We can reconcile these two ideas:A mechanical system can be dissipative on large scales with e.g. kinetic energy being lost due to friction, but that the true microscopic degrees of freedom follow energy-conserving Hamiltonian dynamics. The second law of thermodynamics is an expression of the fact that it is incredibly improbable (but not) for all microscopic degrees of freedom to conspire and generate macroscopic motion out of a freak thermal fluctuation. In some sense, thermodynamics becomes then an effective theory for Hamiltonian systems with many (coupled) degrees of freedom.

Hamiltonian systems with conserved energies are a consequence of Lagrange-functions that do not explicitly depend on time. In classical mechanics, the Lagrange-function $\mathcal{L}$ defines the action S

$$S = \int_{t_i}^{t_f} \mathrm{d}t\, \mathcal{L}(q, \dot{q}) \tag{D.106}$$

which for the mechanics of a particle is actually the non-relativistic limit of the arc-length of the trajectory through spacetime, measured in terms of proper time:

$$\mathrm{d}s^2 = c^2\mathrm{d}t^2 - dx^2 = c^2\mathrm{d}\tau^2 \quad \rightarrow \quad \mathrm{d}\tau = \sqrt{1 - \left(\frac{1}{c}\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2}\mathrm{d}t \quad \rightarrow \quad \mathrm{d}\tau = \frac{1}{\gamma}\mathrm{d}t \tag{D.107}$$

such that the arc length $S = \int \mathrm{d}s = c\int \mathrm{d}\tau = c\int \mathrm{d}t\; 1/\gamma$ with the Lorentz-factor γ. As $1/\gamma \rightarrow= 1 - (\upsilon/c)/2$ for small velocities $\upsilon = \mathrm{d}x/\mathrm{d}t \ll c$, one recovers the classical Lagrange-function, where overall pre-factors and signs do not matter in the Euler-Lagrange equation.

Hamilton's principle now stipulates that the physical trajectory taken by the system corresponds to an extremum of the action, i.e. $\delta S = 0$

$$\delta S = \int_{t_i}^{t_f} \mathrm{d}t \left(\frac{\partial \mathcal{L}}{\partial q}\delta q + \frac{\partial \mathcal{L}}{\partial \dot{q}}\right) = \int_{t_i}^{t_f} \mathrm{d}t \left(\frac{\partial \mathcal{L}}{\partial q} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathcal{L}}{\partial \dot{q}}\right)\delta q \tag{D.108}$$

with an integration by parts on $\delta\dot{q} = \mathrm{d}\delta q/\mathrm{d}t$ and a successive integration by parts, where the boundary terms do not contribute as the Lagrange-function is kept fixed at the boundary: This rearrangement gives the Euler-Lagrange equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathcal{L}}{\partial \dot{q}} + \frac{\partial \mathcal{L}}{\partial q} = 0 \tag{D.109}$$

as a tool serving the purpose of isolating the action-extremising trajectory $q(t)$ as a differential equation.

The canonical momentum of the coordinate q is given by the relation

$$p = \frac{\partial \mathcal{L}}{\partial \dot{q}} \tag{D.110}$$

and helps to identify conserved quantities: If a coordinate is cyclic, $\mathcal{L}$ does not depend on it directly (and only on its derivative), so that $\partial\mathcal{L}/\partial q = 0$. Then, the Euler-Lagrange equation has the canonical momentum conserved in time evolution,

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathcal{L}}{\partial \dot{q}} = \frac{\mathrm{d}p}{\mathrm{d}t} = 0 \tag{D.111}$$

The conservation of energy in classical mechanics works in a different way, though, because the time t plays the role of a parameter describing motion, not that of a coordinate.

Typical Lagrange-functions in classical mechanics have the form

$$\mathcal{L} = \frac{m}{2}\dot{x}^2 - \Phi(x) \tag{D.112}$$

for a particle moving in a potential Φ, such that $\delta S = 0$ implies the Newtonian equation of motion $m\ddot{q} = -\mathrm{d}\Phi/\mathrm{d}x$. But there might be other systems that are perfectly amenable to a Lagrangian description, for instance an LC-circuit in electrical engineering:

$$\mathcal{L} = \frac{L}{2}\dot{Q}^2 - \frac{1}{2C}Q^2 \quad \rightarrow \quad \ddot{Q} + \frac{1}{LC}Q = 0 \tag{D.113}$$

with the charge Q and the current $\dot{Q}$: Recognising the Lagrange-function of a harmonic oscillator immediately suggests the angular frequency $\omega = 1/\sqrt{LC}$ and the corresponding equation of motion. Very often the kinetic and potential terms of the Lagrange-function are separate but that is not a necessity. If $\partial\mathcal{L}/\partial\dot{q}$ still depends on q the differentiation $\mathrm{d}/\mathrm{d}t$ in the Euler-Lagrange equation will read:

$$\ddot{q}\frac{\partial^2 \mathcal{L}}{\partial \dot{q}\partial \dot{q}} + \dot{q}\frac{\partial^2 \mathcal{L}}{\partial q \partial \dot{q}} - \frac{\partial \mathcal{L}}{\partial q} = 0 \tag{D.114}$$

A cute example for this would be the harmonic oscillator $\mathcal{L} = \dot{q}^2/2 - \omega^2 q^2/2$ in coordinates $x_\pm = \dot{q} \pm \omega q$, such that $\mathcal{L} = x_+ x_-/2$. While in one dimension the only requirement would now be that $\partial^2\mathcal{L}/\partial\dot{q}/\partial\dot{q}$ is non-zero, in more than one dimension $\partial^2\mathcal{L}/\partial\dot{q}^i/\partial\dot{q}^j$ would need to be an invertible matrix for isolating $\ddot{q}$.

D.1 *Virial theorem*

Is kinetic or potential energy the preferred form of energy of a system? Clearly, a physical system follow its dynamical equation and continuously reshuffles energy from one energy form to another, but taking averages is time, the system might preferentially be in a state where one energy form dominates over the others. To show this might be the case, let's start at the Euler-Lagrange-equation for any system,

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{q}} - \frac{\partial\mathcal{L}}{\partial q} = 0 \tag{D.115}$$

and it with the coordinate q. Then, using the Leibnitz-rule,

$$q\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{q}} - q\frac{\partial\mathcal{L}}{\partial q} = \frac{\mathrm{d}}{\mathrm{d}t}\left(q\frac{\partial\mathcal{L}}{\partial\dot{q}}\right) - \dot{q}\frac{\partial\mathcal{L}}{\partial\dot{q}} - q\frac{\partial\mathcal{L}}{\partial q} = 0 \tag{D.116}$$

We can break into this relation by individual inspection of the three terms:

1. time everage of the Lagrange-function $\mathcal{L}$ over $\Delta t \gg$ many dynamical time scales

$$\frac{1}{\Delta t}\int_0^{\Delta t}\mathrm{d}t\,\frac{\mathrm{d}}{\mathrm{d}t}\left(q\frac{\partial\mathcal{L}}{\partial\dot{q}}\right) = \frac{1}{\Delta t}\left(q\frac{\partial\mathcal{L}}{\partial\dot{q}}\right)\Bigg|_0^{\Delta t} = \frac{1}{\Delta t}\,(qp)|_0^{\Delta t} \leq \frac{1}{\Delta t}(q_\mathrm{max}\cdot p_\mathrm{max}) \tag{D.117}$$

   where the result of the integration is estimated to be less than the product of the largest values for p and q that the integrand assumes between 0 and Δt. Clearly, this requires that the integrand and therefore the range of motion is bounded in p and q. Taking the limit $\Delta t \rightarrow \infty$, makes the term disappear, as Δt grows without bounds and $q_\mathrm{max}\cdot p_\mathrm{max}$ is finite.

2. $\mathcal{L}_\mathrm{kin}$ is homogeneous of degree 2 in $\dot{q}$ for non-relativistic mechanics:

$$\mathcal{L}_\mathrm{kin} = \mathrm{T} = \frac{m}{2}\dot{q}^2 \quad\rightarrow\quad \dot{q}\frac{\partial\mathcal{L}_\mathrm{kin}}{\partial\dot{q}} = 2\mathcal{L}_\mathrm{kin} = 2\mathrm{T} \tag{D.118}$$

3. $\mathcal{L}$ is homogeneous of degree k in q for power-law potentials $\Phi \propto q^k$

$$\mathcal{L}_\mathrm{pot} = \Phi = q^k \quad\rightarrow\quad q\frac{\partial\mathcal{L}_\mathrm{pot}}{\partial q} = k\mathcal{L}_\mathrm{pot} = k\Phi \tag{D.119}$$

Therefore, we obtain the relation

$$2\langle\mathrm{T}\rangle = k\langle\Phi\rangle \tag{D.120}$$

between the time-averages of the kinetic and potential energies, with the definition of the average kinetic energy $\langle\mathrm{T}\rangle$,

$$\lim_{\Delta t\to\infty}\frac{1}{\Delta t}\int_0^{\Delta t}\mathrm{d}t\;\mathrm{T}(t)=\langle\mathrm{T}\rangle \tag{D.121}$$

with an analogous average for $\langle\Phi\rangle$.

The harmonic oscillator has a potential $\Phi\propto q^2$ with the potential being a harmonic function of degree $k=2$, and consequently, $\langle\mathrm{T}\rangle=\langle\Phi\rangle$, and both forms of energy are on average equal, which is a rather obvious result. After all, $q\propto\exp(\mathrm{i}\omega t)$ and $\dot{q}\propto\mathrm{i}\omega\exp(\mathrm{i}\omega t)$, such that the averages $\omega^2\langle q^2\rangle$ and $\langle\dot{q}^2\rangle$ are necessarily equal. For a Coulomb-potential we have $\Phi\propto 1/q$, and therefore $k=-1$ and $2\langle\mathrm{T}\rangle=-\langle\Phi\rangle$, which is fine, because Φ is negative. It is illustrative to increase k to high positive values: Then, the kinetic energy becomes on average dominant over the potential energy, $\langle\mathrm{T}\rangle=k/2\,\langle\Phi\rangle$. For high positive k one obtains a flat potential with very steep walls, where a particle zooms around in a state of high kinetic energy most of the time and spends only little time being deflected at the walls where the potential energy is high. A fun idea is the impossibility of a gravitationally bound ball of photons: There, the kinetic energy for ultra-relativsitic particles is a homogeneous function of order $k=1$ such that the virial theorem would become $\langle\mathrm{T}\rangle=-\langle\Phi\rangle$, implying that the total energy is zero - but it would have to be negative for a bound system!

In summary, the virial theorem makes a statement about the average kinetic and potential energies in the course of the time evolution and is perfectly valid for a system with a single degree of freedom, as long as the motion is bounded in position and momentum. Often it is the case, thought, that systems consist of many particles and one might wonder if the average of kinetic and potential energy could be determined instead at a fixed time over the many particles, whether these ensemble averages are identical to the temporal averages, and whether the virial theorem applies to ensemble averages as well. Ergodic systems have in fact this property, although ergodicity is in particular systems difficult to demonstrate.

D.2 *Energy conservation*

Energy conservation is, from an arithmetic point of view, very similar: Instead of q we multiply the Euler-Lagrange-equation with $\dot{q}$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{q}}-\frac{\partial\mathcal{L}}{\partial q}=0 \tag{D.122}$$

to arrive at

$$\dot{q}\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{q}}-\dot{q}\frac{\partial\mathcal{L}}{\partial q}=m\dot{q}\ddot{q}+\dot{q}\frac{\mathrm{d}\Phi}{\mathrm{d}q}=\frac{m}{2}\frac{\mathrm{d}}{\mathrm{d}t}\dot{q}^2+\frac{\mathrm{d}}{\mathrm{d}t}\Phi(q)=\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{m}{2}\dot{q}^2+\Phi(q)\right)=0 \tag{D.123}$$

with the replacements $\partial\mathcal{L}/\partial\dot{q}=m$ and $\partial\mathcal{L}/\partial q=-\Phi$ in the first step, followed by the time derivative $\dot{q}\mathrm{d}\Phi/\mathrm{d}q=\mathrm{d}\Phi/\mathrm{d}t$, suggested by the chain rule. The quantity $\mathcal{H}$

$$\mathcal{H}(q,\dot{q})=\frac{m}{2}\dot{q}^2+\Phi(q) \tag{D.124}$$

is the Hamilton-function of the system, which comes out as conserved, $\mathrm{d}\mathcal{H}/\mathrm{d}t=0$.

D.3 *Legendre transforms and the Hamilton-function*

To be quite exact, $\mathcal{H}(q,\dot{q})$ is not yet the energy, because it is assumed to depend on $\dot{q}$ but not yet on the canonical momentum,

$$p = \frac{\partial\mathcal{L}}{\partial\dot{q}} \tag{D.125}$$

The Legendre-transform of the Lagrange-function $\mathcal{L}$

$$\mathcal{H}(q,p) = p\dot{q} - \mathcal{L}(q,\dot{q}(p)) \tag{D.126}$$

which replaces the variable $\dot{q}$ by the variable p, can be shown to be conserved using this argument:

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} = \dot{p}\dot{q} + p\ddot{q} - \dot{q}\frac{\partial\mathcal{L}}{\partial q} - \ddot{q}\frac{\partial\mathcal{L}}{\partial\dot{q}} = \frac{\partial\mathcal{L}}{\partial q}\dot{q} - \dot{q}\frac{\partial\mathcal{L}}{\partial q} = 0 \tag{D.127}$$

which is known as the Beltrami-identity. In the first step, we used the derivative of the canonical momentum,

$$\dot{p} = \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{q}} = \frac{\partial\mathcal{L}}{\partial q} \tag{D.128}$$

together with the Euler-Lagrange equation. With the definition of the canonical momentum as the derivative $p = \partial\mathcal{L}/\partial\dot{q}$ one needs an invertible expression to be able to write down $\dot{q}(p)$ from $p(\dot{q})$, which is made sure by the convexity of the functional $\mathcal{L}$. Then, the Legendre-transform $\mathcal{H}$ is likewise convex, ensuring the existence of the inverse Legendre transform.

I am a bit picky to call only $p^2/(2m)$ kinetic energy and not $m\dot{q}^2/2$, for a very specific reason, even though the Legendre transform of a parabola $\dot{q}^2$ is of course a parabola p^2: The classical Lagrange-function is the non-relativistic limit of the arc-length of a spacetime-trajectory and acquires the interpretation of energy only after Legendre-transformation.

D.4 *Hamilton-equations of motion*

Instead of the Euler-Lagrange equations, which naturally lead to second-order equations of motions, one can write down equivalent coupled first-order equations of motions operating on the Hamilton-function $\mathcal{H}$ instead of the Lagrange-function $\mathcal{L}$.

$$\frac{\partial\mathcal{H}}{\partial p} = \dot{q} + p\frac{\partial\dot{q}}{\partial p} - \frac{\partial\dot{q}}{\partial p}\frac{\partial\mathcal{L}}{\partial\dot{q}} = \dot{q} \quad\text{and}\quad \frac{\partial\mathcal{H}}{\partial q} = p\frac{\partial\dot{q}}{\partial q} - \frac{\partial\mathcal{L}}{\partial q} - \frac{\partial\dot{q}}{\partial q}\frac{\partial\mathcal{L}}{\partial\dot{q}} = -\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{q}} = -\dot{p} \tag{D.129}$$

The form of Hamilton's equation of motion allow an incredibly interesting notation, in particular for the harmonic oscillator, where $\mathcal{H} = p^2/2 + \omega^2 q^2/2$: Then, $\partial\mathcal{H}/\partial p = p = \dot{q}$ and $\partial\mathcal{H}/\partial q = \omega^2 q = -\dot{p}$, such that

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\begin{array}{c} p \\ q \end{array}\right) = \left(\begin{array}{cc} 0 & -\omega^2 \\ 1 & 0 \end{array}\right)\left(\begin{array}{c} p \\ q \end{array}\right) \tag{D.130}$$

which is the archetypical form of a symplectic differential equation. The solution to the system can be written in terms of a matrix exponential,

$$\begin{pmatrix} p \\ q \end{pmatrix} = \exp\left(\begin{pmatrix} 0 & -\omega^2 \\ 1 & 0 \end{pmatrix} t\right)\begin{pmatrix} p_0 \\ q_0 \end{pmatrix} \tag{D.131}$$

applied to the initial conditions. Summing up the exponential series with this so-called symplectic matrix yields the familiar sine and cosine functions.

The question on energy conservation is answered in view of Hamilton's equation of motion in a completely different way: Forming the derivative of $\mathcal{H}$ which only depends on p and q (and not on t directly) yields

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} = \frac{\partial\mathcal{H}}{\partial q}\dot{q} + \frac{\partial\mathcal{H}}{\partial p}\dot{p} = \frac{\partial\mathcal{H}}{\partial q}\frac{\partial\mathcal{H}}{\partial p} - \frac{\partial\mathcal{H}}{\partial p}\frac{\partial\mathcal{H}}{\partial q} = 0 = \{\mathcal{H},\mathcal{H}\} \tag{D.132}$$

with the definition of Poisson-brackets,

$$\frac{\partial\mathcal{A}}{\partial q}\frac{\partial\mathcal{B}}{\partial p} - \frac{\partial\mathcal{B}}{\partial q}\frac{\partial\mathcal{A}}{\partial p} = \{\mathcal{A},\mathcal{B}\} \tag{D.133}$$

for any two functions A and B dependent on the canonical momenta and coordinates. Then, the time evolution of any of such functions is determined by the Poisson equation of motion,

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\partial A}{\partial t} + \dot{q}\frac{\partial A}{\partial q} + \dot{p}\frac{\partial A}{\partial p} = \frac{\partial A}{\partial t} + \{\mathcal{H},\mathcal{A}\} \tag{D.134}$$

Alternatively, the Lagrange-function can be thought to depend directly on (q,p) instead of $(q,\dot{q})$. From the definition of the Legendre-transformation

$$\mathcal{L}(p,q) = p\dot{q} - \mathcal{H}(p,q) \tag{D.135}$$

one obtains from the two independent Euler-Lagrange equations for the coordinates p and q directly

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{q}} - \frac{\partial\mathcal{L}}{\partial q} = 0 = \dot{p} + \frac{\partial\mathcal{H}}{\partial q} \tag{D.136}$$

as well as

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot{p}} - \frac{\partial\mathcal{L}}{\partial p} = 0 = -\dot{q} + \frac{\partial\mathcal{H}}{\partial p} \tag{D.137}$$

i.e. again the two Hamilton equations of motion.

D.5 *Canonical transforms*

Within Hamiltonian mechanics there exists a class of coordinate transitions with covariant transformation of the equations of motion: Effectively, the states of a mechanical system form a manifold that is parameterised by coordinates p and q, and transitions to new coordinates $Q = Q(p,q)$, $P = P(p,q)$ lead to new coordinates for which the same type of equation of motion is valid:

$$\dot{Q} = \frac{\partial\bar{\mathcal{H}}}{\partial P}, \quad \dot{P} = -\frac{\partial\bar{\mathcal{H}}}{\partial\dot{Q}}, \quad \text{with} \quad \bar{\mathcal{H}} = \mathcal{H}(p(P,Q), q(P,Q)) \tag{D.138}$$

the equation of motion in (Q, P) needs to follow from the same variation of the Lagrange-function $\mathcal{L} = Q\dot{P} - \bar{\mathcal{H}}$ as the one in (q, p), so that

$$S = \int_{t_i}^{t_f} \mathrm{d}t\, \bar{\mathcal{H}}(P,Q) - Q\dot{P} = \int_{t_i}^{t_f} \mathrm{d}t\, \mathcal{H}(p,q) - \dot{q}p + \int_{t_i}^{t_f} \mathrm{d}t\, \frac{\mathrm{d}\bar{W}}{\mathrm{d}t} \tag{D.139}$$

where the two actions can at most be different by a total time derivative, as

$$\int_{t_i}^{t_f} \mathrm{d}t\, \frac{\mathrm{d}\bar{W}}{\mathrm{d}t} = \bar{W}(t_f) - \bar{W}(t_i) \tag{D.140}$$

does not contribute to the variation, which is fixed at t_i and t_f. But this new function can be used constructively to generate a canonical transform: For instance, the specific choice

$$\bar{W}(q, P) = W(q, P) - QP \tag{D.141}$$

for $\bar{W}$ with variables q and P

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \dot{q}\underbrace{\frac{\partial\bar{W}}{\partial q}}_{=p} + \dot{P}\underbrace{\frac{\partial W}{\partial P}}_{=Q} \tag{D.142}$$

is equivalent, if $\mathcal{H}(p, q) = \bar{\mathcal{H}}(P, Q)$ and if $p = \frac{\partial W}{\partial q}$ and $Q = \frac{\partial W}{\partial P}$. Then, in addition, the functional determinant is

$$\det\left(\frac{\partial(p,q)}{\partial(P,Q)}\right) = 1 \tag{D.143}$$

A truly novel concept are infinitesimal canonical transformations: The identity transform $W = q \cdot P$ does not change anything

$$p = \frac{\partial W}{\partial q} = P\frac{\partial q}{\partial q} = P \quad \text{and} \quad Q = \frac{\partial W}{\partial P} = q\frac{\partial P}{\partial P} = q \tag{D.144}$$

such that we can define an infinitesimal transform $W(\epsilon) = qP + \epsilon w(q, P)$ controlled by a small $\epsilon > 0$

$$p = \frac{\partial W}{\partial q} = P + \epsilon\frac{\partial w}{\partial q} \quad \rightarrow \quad \Delta p = p - P = \epsilon\frac{\partial w}{\partial q} \tag{D.145}$$

as well as

$$Q = \frac{\partial W}{\partial P} = q + \epsilon\frac{\partial w}{\partial P} \quad \rightarrow \quad \Delta q = q - Q = -\epsilon\frac{\partial w}{\partial P} \tag{D.146}$$

In the spirit of a Lie-generator we take the limit $\epsilon \to 0$

$$\lim_{\epsilon\to 0} \frac{\Delta p}{\epsilon} = \frac{\partial W}{\partial q} \quad \text{and} \quad \lim_{\epsilon\to 0} \frac{\Delta q}{\epsilon} = \frac{\partial W}{\partial p} \tag{D.147}$$

Setting $\epsilon = \Delta t$ and $W = \mathcal{H}(p, q)$

$$\lim_{\Delta t\to 0} \frac{\Delta q}{\Delta t} = \dot{q} = -\frac{\partial \mathcal{H}}{\partial p} \quad \text{and} \quad \lim_{\Delta t\to 0} \frac{\Delta p}{\Delta t} = \dot{p} = \frac{\partial \mathcal{H}}{\partial q} \tag{D.148}$$

In summary, the time evolution of a Hamiltonian system is itself a canonical transformation, and the Hamilton equations of motion are the Lie-generators of the transform: Therefore, the entire dynamical evolution of the system can be mapped onto evolution equations for the coordinates and the evolution becomes just a coordinate transform. The phase space volume is invariant under canonical transformations, and therefore the phase space volume needs to be conserved in time evolution too: This is exactly the statement of Liouville's theorem.

E PHASE SPACE DYNAMICS

E.1 *Phase space* Γ

Statistical mechanics as the theory behind thermodynamics is concerned with systems with many degrees of freedom which follow Hamiltonian, energy-conserving dynamical laws. For linking mechanical microscopic properties of these systems with thermodynamic concepts like entropy and temperature we need to introduce some conceptual ideas.

The phase space of a Hamiltonian system is made up from all coordinates $\{q_i, p_i\}$. For a system like a collection of point particles interacting with potentials as the microscopic idea behind a real gas, it would be $6n$-dimensional for n particles. As the Lagrange-function $\mathcal{L}(q_i, \dot{q}_i)$ does not explicitly depend on time, the value of the Hamilton-function $\mathcal{H}(q_i, p_i)$ interpreted as the energy of the system is conserved: It is a straightforward visualisation that the system moves on a surface of fixed energy through phase space Γ. If we combine the phase space coordinates into a vector $\boldsymbol{x} = (q_i, p_i)$ the phase space motion proceeds at velocity $\boldsymbol{\upsilon}$

$$\boldsymbol{\upsilon} = \dot{\boldsymbol{x}} = (\dot{q}_i, \dot{p}_i) = \left(\frac{\partial\mathcal{H}}{\partial p_i}, -\frac{\partial\mathcal{H}}{\partial q_i}\right) \tag{E.149}$$

At the same time, the gradient of the Hamilton-function is given by

$$\nabla\mathcal{H}(q_i, p_i) = \left(\frac{\partial\mathcal{H}}{\partial q_i}, \frac{\partial\mathcal{H}}{\partial p_i}\right) \tag{E.150}$$

such that we can conclude two things:

$$\boldsymbol{\upsilon}\cdot\nabla\mathcal{H} = 0 \quad \text{as well as} \quad |\boldsymbol{\upsilon}| = |\nabla\mathcal{H}| \tag{E.151}$$

i.e. that the velocity and the gradient are equal in magnitude but perpendicular to each other.

E.2 *Phase space density* ρ

Populating the phase space Γ with an ensemble of physically equivalent systems (with identical Hamilton-functions) leads to a density ρ of encountering systems at a certain phase space coordinate. There should be a continuity equation making sure that in the course of time evolution systems are not spontaneously lost or added to the ensemble,

$$\frac{\partial\rho}{\partial t} + \mathrm{div}(\rho\boldsymbol{\upsilon}) = \frac{\partial\rho}{\partial t} + \nabla\rho\cdot\boldsymbol{\upsilon} + \rho\,\mathrm{div}\boldsymbol{\upsilon} = 0 \tag{E.152}$$

with the application of the Leibnitz-rule to $\mathrm{div}(\rho\boldsymbol{\upsilon})$ and the successive definition of the advective derivative: As the density $\rho(t, x^i)$ is a function of both time and the full phase space coordinates bundled in $\boldsymbol{x}$ one gets:

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(t, x^i) = \frac{\partial\rho}{\partial t} + \dot{x}^i\frac{\partial\rho}{\partial x^i} = \frac{\partial\rho}{\partial t} + \upsilon^i\frac{\partial\rho}{\partial x^i} \tag{E.153}$$

The divergence of the velocity $\boldsymbol{\upsilon}$ vanishes, as one can quickly see

$$\mathrm{div}\boldsymbol{\upsilon} = \sum_i \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = \sum_i \frac{\partial}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i} = 0 \tag{E.154}$$

through substitution of the Hamilton equations of motion. With the advective derivative,

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} \equiv \frac{\partial \rho}{\partial t} + \boldsymbol{\upsilon}\cdot\nabla\rho \tag{E.155}$$

in the laboratory frame in which the coordinates are defined, and

$$\frac{\partial \rho}{\partial t} = 0 \tag{E.156}$$

for a comoving observer that is advected with the flow, as for that observer $\boldsymbol{\upsilon} = 0$. But is there something that we can say about $\partial\rho/\partial t$ in the laboratory frame? This is a surprising result, as

$$\mathrm{div}\,(\rho\boldsymbol{\upsilon}) = \sum_i \frac{\partial \rho}{\partial p_i}\dot{p}_i + \frac{\partial \rho}{\partial q_i}\dot{q}_i = \sum_i \frac{\partial \rho}{\partial p_i}\frac{\partial \mathcal{H}}{\partial p_i} + \frac{\partial \rho}{\partial q_i}\frac{\partial \mathcal{H}}{\partial q_i} = -[\rho, \mathcal{H}] \tag{E.157}$$

where the Hamilton equations of motion and then the Poisson-bracket was substituted. For the derivatives of ρ with respect to the phase space coordinates one can do an intermediate step by differentiating with respect to $\mathcal{H}$ first and then continue the differentiation with the chain rule.

$$\mathrm{div}\,(\rho\boldsymbol{\upsilon}) = \frac{\partial \rho}{\partial \mathcal{H}}\sum_i \frac{\partial \mathcal{H}}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \mathcal{H}}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} = \frac{\partial \rho}{\partial \mathcal{H}}[\mathcal{H}, \mathcal{H}] = 0 \tag{E.158}$$

where the Poisson-bracket of the Hamilton-function with itself vanishes, setting the divergence of $\rho\boldsymbol{\upsilon}$ to zero. That implies in turn that the partial derivative of ρ in the laboratory frame

$$\frac{\partial \rho}{\partial t} = 0 \tag{E.159}$$

vanishes: The distribution of the systems in phase space is non-evolving, neither for the comoving observer nor for an observer in the laboratory frame. Being advected with the flow, observers would see a constant density around them, and observing the flow at any point from the laboratory frame would always yield the same density, too.

E.3 *Phase space volume: surface and volume*

The volume of the phase space Γ as bounded by a surface of constant energy $\mathcal{H} \leq \mathrm{E}$ would be

$$\phi^*(\mathrm{E}) = \int_{\mathcal{H}\leq \mathrm{E}} \prod_i \mathrm{d}^3 q_i \mathrm{d}^3 p_i \tag{E.160}$$

where we have introduced the asterisk for the time being as it needs to be corrected by the Gibbs factor. Adding or removing energy from the system leads to a change in volume, as the surface of constant energy will move to a different location and enclose a different amount of volume in Γ: The rate of change of the volume with energy is simply the derivative of $\phi^*(E)$,

$$\omega^*(E) = \frac{d}{dE}\phi^*(E) = \frac{d}{dE}\int_{\mathcal{H}\leq E}\prod_i d^3q_i d^3p_i \tag{E.161}$$

E.4 *Microcanonical ensemble*

With these ideas it is possible to define the microcanonical ensemble: One populates the phase space Γ with a large number of physically equivalent systems with the same Hamilton-function $\mathcal{H}$ on the surface of constant energy E. In doing that, one needs to make an assumption how this ensemble of systems will be distributed on the hypersurface at constant E. For continuing, one can adopt now the fundamental postulate of statistical physics and require axiomatically that this distribution ρ is constant in thermodynamic equilibrium, or, perhaps a bit more insightful, we ask what distribution ρ would maximise the information entropy as an expression about the largest possible amount of randomness, which we would suspect to be present in thermodynamic equilibrium. A constant distribution would in fact extremise Shannon's entropy (if there are no boundary conditions to be fulfilled), so we will work with that! The previous section showed that for a conservative Hamiltonian system this density ρ, once initialised, is stationary $\partial\rho/\partial t = 0$ but that does not mean that there is no dynamics going on. The every system in the ensemble is pursuing its path in phase space Γ, but it is the case that the number of systems that evolve away from a certain volume in phase space are replaced by new systems moving into that volume, keeping the density constant.

Therefore, the distribution of systems on the surface of constant energy (or to be more exact, in an infinitesimally thin shell between energies E and E + δE, for mathematical convenience) is chosen to be constant, because that imposes the least assumption on the phase space density.

$$\rho(E) = \begin{cases} 1, & \text{if } E \leq \mathcal{H} \leq E + \delta E \\ 0, & \text{elsewhere} \end{cases} \tag{E.162}$$

such that the number n of systems becomes proportional to the volume between E and E + dE,

$$n = \rho\omega^*(E)dE = \omega^*(E)dE \tag{E.163}$$

using the phase space volume element defined above.

E.5 *Equipartition theorem*

Suppose one would like to determine the average $\langle A\rangle$ of a function $A(p_i, q_i, t)$ that can depend on the coordinates (q_i, p_i) and possibly on time t. The average should be characterised by a predefined energy E (which the Hamiltonian system conserves). There are fundamentally two ways of computing the average, first summing over the ensemble,

$$\langle \mathrm{A} \rangle = \frac{\displaystyle\int\limits_{\mathrm{E}\leq\mathcal{H}\leq\mathrm{E}+\delta\mathrm{E}} \prod_i \mathrm{d}^3q_i\mathrm{d}^3p_i\ \mathrm{A}(p_i,q_i,t)}{\displaystyle\int\limits_{\mathrm{E}\leq\mathcal{H}\leq\mathrm{E}+\delta\mathrm{E}} \prod_i \mathrm{d}^3q_i\mathrm{d}^3p_i} = \frac{\frac{\mathrm{d}}{\mathrm{dE}}\displaystyle\int_0^{\mathrm{E}} \prod_i \mathrm{d}^3q_i\mathrm{d}^3p_i\ \mathrm{A}(p_i,q_i,t)}{\frac{\mathrm{d}}{\mathrm{dE}}\displaystyle\int_0^{\mathrm{E}} \prod_i \mathrm{d}^3q_i\mathrm{d}^3p_i} \tag{E.164}$$

where the averages are normalised by the volume. The idea in this equation is that the ensemble of statistically equivalent systems is distributed evenly over the allowed phase space volume at coordinates (q_i, p_i). Every system of the ensemble contributes to this average with a specific value for $\mathrm{A}(p_i, q_i, t)$. The denominator in the ensemble average is just $\omega^*(\mathrm{E})$.

Secondly, if the system is ergodic, the ensemble average is equal to the average of a single system in its time evolution,

$$\langle \mathrm{A} \rangle = \lim_{\Delta t\to\infty} \frac{1}{\Delta t} \int_0^{\Delta t} \mathrm{d}t\ (p_i(t), q_i(t), t); \tag{E.165}$$

the idea being that a single system in its time evolution comes by every point of the allowed phase space volume the exactly the same even measure.

For a specific choice of the phase space function $\mathrm{A} = p_1\partial\mathcal{H}/\partial p_1$ one can compute the expectation value of the phase space average by an integration by parts,

$$\int \mathrm{d}^3p_1\ p_1\frac{\partial\mathcal{H}}{\partial p_1} = \int \mathrm{d}^3p_1\ \frac{\partial}{\partial p_1}(p_1\mathcal{H}) - \int \mathrm{d}^3p_1\ \mathcal{H} \tag{E.166}$$

because obviously $\partial p_1/\partial p_1 = 1$, and the first term will simply be the evaluation of the integrand at the boundaries, where $\mathcal{H} = \mathrm{E}$.

Applying this simplification to the entire integrand,

$$\int_0^{\mathrm{E}} \prod_i \mathrm{d}^3p_i\mathrm{d}^3q_i\ p_1\frac{\partial\mathcal{H}}{\partial p_1} = \mathrm{E}\cdot(p_{1,\mathrm{max}} - p_{1,\mathrm{min}}) \int_0^{\mathrm{E}} \prod_{i\geq 2} \mathrm{d}^3p_i\mathrm{d}^3q_i - \int_0^{\mathrm{E}} \prod \mathrm{d}^3p_i\mathrm{d}^3q_i\mathcal{H} \tag{E.167}$$

such that a differentiation with respect to the energy E would yield

$$\frac{\mathrm{d}}{\mathrm{dE}}\int_0^{\mathrm{E}} \prod_i \mathrm{d}^3p_i\mathrm{d}^3q_i\mathcal{H} = \frac{1}{\delta\mathrm{E}}\int_{\mathrm{E}}^{\mathrm{E}+\delta\mathrm{E}} \prod_i \mathrm{d}^3p_i\mathrm{d}^3q_i\mathcal{H} = \mathrm{E}\frac{1}{\delta\mathrm{E}}\prod_i \mathrm{d}^3p_i\mathrm{d}^3q_i = \mathrm{E}\omega^*(\mathrm{E}) \tag{E.168}$$

$$\frac{\mathrm{d}}{\mathrm{dE}}\int_0^{\mathrm{E}} \prod_i \mathrm{d}^3p_i\mathrm{d}^3q_ip_1\frac{\partial\mathcal{H}}{\partial p_1} = \phi^*(\mathrm{E}) \tag{E.169}$$

$$\left\langle p_i\frac{\partial\mathcal{H}}{\partial p_i}\right\rangle = \left\langle q_i\frac{\partial\mathcal{H}}{\partial q_i}\right\rangle = \frac{\phi^*}{\omega^*} = \frac{1}{\frac{\mathrm{d}\ln\phi^*}{\mathrm{dE}}} \tag{E.170}$$

The equipartition theorem then follows from these considerations: If

$$\frac{\mathrm{d}\ln\phi^*}{\mathrm{d}E} = \frac{1}{k_B T} \tag{E.171}$$

then the average kinetic energy for a non-relativistic system follows from

$$\left\langle p_i \frac{\partial\mathcal{H}}{\partial p_i}\right\rangle = 2\langle T\rangle \sim k_B T \tag{E.172}$$

As a consequence of the virial theorem,

$$\left\langle q_i \frac{\partial\mathcal{H}}{\partial q_i}\right\rangle \sim \left\langle p_i \frac{\partial\mathcal{H}}{\partial p_i}\right\rangle \sim k_B T \tag{E.173}$$

as well: This is a far-reaching result, and shows that every degree of freedom carries on average a typical amount of $k_B T$ of the total thermal energy of the system.

E.6 *Entropy for Hamiltonian systems*

Let's introduce a parameter a in the Hamilton-function $\mathcal{H}$

$$\mathcal{H} = \mathcal{H}(p_i, q_i, a) \tag{E.174}$$

which can be controlled from the outside and changes the mechanics of the system: For instance, it could be the length of a pendulum or the distance between the capacitor plates in an LC-circuit or in fact the volume of a gas in a container. If changes in a have an influence on the Hamilton-function, energy can be added to or removed from the system:

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} = \dot{a}\frac{\partial\mathcal{H}}{\partial a} \quad\rightarrow\quad \mathrm{d}\mathcal{H} = \frac{\partial\mathcal{H}}{\partial a}\mathrm{d}a \tag{E.175}$$

which leads to an energy gain

$$\mathrm{d}E = \lim_{\Delta t\to\infty}\int_t^{t+\Delta t}\mathrm{d}t\,\frac{\partial\mathcal{H}}{\partial a}\dot{a} \tag{E.176}$$

over the interval Δt. For an entire ensemble of systems one would write for the average gain in energy

$$\mathrm{d}E = \left\langle\frac{\partial\mathcal{H}}{\partial a}\right\rangle\mathrm{d}a \tag{E.177}$$

where the quantity $\langle\partial\mathcal{H}/\partial a\rangle$ could be interpreted in an ensemble-average sense, or if ergodicity is given, as a time average

$$\left\langle\frac{\partial\mathcal{H}}{\partial a}\right\rangle = \lim_{\Delta t\to\infty}\frac{1}{\Delta t}\int_t^{t+\Delta t}\mathrm{d}t\,\frac{\partial\mathcal{H}}{\partial a} \tag{E.178}$$

For the particular case of a being the volume V of a container filled with gas, the change in energy would be

$$\left\langle\frac{\partial\mathcal{H}}{\partial V}\right\rangle = -p \tag{E.179}$$

and correspond to the pressure, such that one can write $dE = -p dV$ with $dE = \langle\partial\mathcal{H}/\partial V\rangle dV$, identical to $dU = -p dV$! Relations like this one start to bridge the gap between ensembles of Hamiltonian systems with many degrees of freedom at thermodynamic quantities. Surely, the next building block of the theory that we need to understand is the relation between a term like $dU = TdS$ with the underlying Hamiltonian dynamics.

E.7 *Adiabatic invariance of entropy*

The phase space volume $\phi^*(\mathcal{H}, a)$ and its differential change $\omega^*(\mathcal{H}, a)$ are defined as

$$\phi^*(\mathcal{H}, a) = \int\limits_{\mathcal{H}\leq E}\prod_i d^3p_i d^3q_i \quad \text{and} \quad \omega^*(\mathcal{H}, a) = \frac{d}{dE}\phi^*(E, a) \tag{E.180}$$

where both quantities depend through the Hamilton-function $\mathcal{H}$ on the control parameter a, which in fact can change the energy and therefore the accessible phase space volume of the system:

$$\frac{\partial\phi^*}{\partial a}da = \phi^*(E, a+\delta a) - \phi(E, a) \tag{E.181}$$

This quantity exactly corresponds to the volume contained between

$$\mathcal{H}(p,q,a) = E \quad \text{and} \quad \mathcal{H}(p,q,a+\delta a) = E - \frac{\partial\mathcal{H}}{\partial a}\delta a \tag{E.182}$$

with the idea that $\partial H/\partial a$ points into the direction of smaller energies, but in the formula we need the inverse gradient, pointing towards higher energies.

$$\frac{\partial\phi^*}{\partial a}\delta a = \int \delta s dO \tag{E.183}$$

δS is parallel to $\nabla\mathcal{H}$

$$d\mathcal{H} = \frac{\partial\mathcal{H}}{\partial S}\delta S \tag{E.184}$$

and consequently,

$$|\nabla\mathcal{H}|\delta s = -\frac{\partial\mathcal{H}}{\partial a}\delta a \quad \rightarrow \frac{\partial\phi^*}{\partial a}da = \int\frac{\partial\mathcal{H}}{\partial a}\frac{dO}{|\nabla\mathcal{H}|}\delta a \tag{E.185}$$

In the average defined by the microcanonical ensemble one obtains for the average change in energy

$$\left\langle\frac{\partial\mathcal{H}}{\partial a}\right\rangle = \frac{1}{\omega^*(E)}\int\frac{\partial\mathcal{H}}{\partial a}\frac{dO}{|\nabla\mathcal{H}|} \quad \rightarrow \quad \frac{\partial\phi^*}{\partial a} = -\omega^*(E)\left\langle\frac{\partial\mathcal{H}}{\partial a}\right\rangle \tag{E.186}$$

Therefore, for an arbitrary change in $\phi^*(E, a)$ by $\mathrm{d}a$ one would obtain

$$\mathrm{d}\phi^* = \omega^* \left[\mathrm{dE} - \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a\right] \tag{E.187}$$

Both changes (dE and da) affect the phase space volume and therefore the entropy

$$\mathrm{dE} = \frac{1}{\omega^*} d\phi^* + \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a \tag{E.188}$$

which is a formula reminiscent of the first law of thermodynamics,

$$\mathrm{dU} = \delta Q + \delta W \tag{E.189}$$

Should we continue by analogy? If this is the case, one would identify the thermal energy with $\delta Q = \frac{1}{\omega^*}\mathrm{d}\phi^*$, and consequently the entropy with $S = k_B\phi^*$:

$$\frac{k_B}{\phi^*}\frac{\mathrm{d}\phi^*}{\omega^*} = \frac{k_B}{\phi^*}\left[\mathrm{dE} - \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a\right] \tag{E.190}$$

Using logarithmic derivatives this can be rewritten as

$$k_B \mathrm{d}\ln\phi^* = k_B\frac{\omega^*}{\phi^*} = k_B\frac{1}{\phi^*}\frac{\mathrm{d}\phi^*}{\mathrm{dE}}\left[\mathrm{dE} - \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a\right] = k_B\frac{\mathrm{d}\ln\phi^*}{\mathrm{dE}}\left[\mathrm{dE} - \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a\right] \tag{E.191}$$

$$k_B \mathrm{d}\ln\phi^* = k_B\frac{\mathrm{d}\ln\phi^*}{\mathrm{dE}}\left[\mathrm{dE} - \left\langle \frac{\partial \mathcal{H}}{\partial a} \right\rangle \mathrm{d}a\right] \tag{E.192}$$

Comparison with the second law of thermodynamics, $\mathrm{dS} = \frac{1}{T}\left[\mathrm{dE} - \delta W\right]$, would imply that the change dS in entropy

$$\mathrm{dS} = k_B \cdot \mathrm{d}\ln\phi^* \tag{E.193}$$

is just given by the change in logarithmic phase space volume, with k_B as a prefactor fixing the units. Then, comparing with the definition of temperature as $1/(k_B T) = \partial S/\partial E$, consistency implies that

$$\frac{1}{k_B T} = \frac{\partial \ln\phi^*}{\partial E} \tag{E.194}$$

The phase space volume of a system and how that volume changes with changing energy determine entropy and temperature.

E.7.1 Example: adiabatic invariance in a string pendulum

Adiabatic invariance of the phase space volume ϕ^* when changing a control parameter is an incredibly abstract and interesting concept as it defines entropy and what exactly corresponds to adiabatic changes of state in the underlying mechanics of a system. We should consolidate this idea by considering a mechanical string pendulum of length $l = a$ which serves as the control parameter. It performs oscillations in angle φ with time t according to the differential equation $\ddot{\varphi} + \omega^2\varphi = 0$ with $\omega^2 = g/l$, which follow from variation of the Lagrange-function,

$$\mathcal{L} = \frac{m}{2}(l\dot{\varphi})^2 + mgl\cos\varphi \simeq \frac{m}{2}(l\dot{\varphi})^2 + mgl\left(1 - \frac{\varphi^2}{2}\right) \tag{E.195}$$

The canonical momentum p_φ is just the angular momentum L,

$$p_\varphi = \frac{\partial\mathcal{L}}{\partial\dot{\varphi}} = ml^2\dot{\varphi} = \mathrm{L} \tag{E.196}$$

so that the Legendre-transform replacing $\dot{\varphi}$ with L yields the Hamilton-function

$$\mathcal{H}(\varphi, \mathrm{L}, l) = \frac{\mathrm{L}^2}{2ml^2} + \frac{mgl}{2}\varphi^2 - mgl = \mathrm{E} \tag{E.197}$$

where we keep the explicit dependence of $\mathcal{H}$ on the control parameter l. The phase space volume ϕ^* is given as the integral

$$\phi^* = \int_{\mathcal{H}\leq\mathrm{E}} \mathrm{d}\varphi\mathrm{d}\mathrm{L} \tag{E.198}$$

which in the case of the harmonic oscillator is just and ellipse bounded by the surface of constant energy, specifically by the semi axes in L

$$a^2 = l^2 2m(\mathrm{E} + mgl) \quad \text{and} \quad b^2 = \frac{2\mathrm{E} + mgl}{mgl} \tag{E.199}$$

in φ, such that the volume (which is really the area of a 2-dimensional ellipse, therefore the factor 2π) becomes

$$\phi^*(\mathrm{E}, l) = 2\pi\sqrt{\frac{l}{g}}(\mathrm{E} + mgl) \tag{E.200}$$

The corresponding rate of change of this volume

$$\mathrm{d}\phi^*(\mathrm{E}, l) = 2\pi\sqrt{\frac{l}{g}}\left[\mathrm{dE} + \left(\frac{\mathrm{E} + 3mgl}{2l}\right)\mathrm{d}l\right] \tag{E.201}$$

implying that one can operate on $\mathrm{d}\phi^*$ both by adding energy dE or by changing the control parameter dl.

Changing l very slowly in comparison to the typical time scale of the system would require a force F, as the weight needs to be lifted against the centrifugal force as well as the outside gravity,

$$\mathrm{F} = -\frac{\partial\mathcal{H}}{\partial l} = \frac{\mathrm{L}^2}{ml^3} - \frac{mg\varphi^2}{2} + mg \tag{E.202}$$

The change to the system is required to be slow such that the ensemble is not disrupted: One needs to maintain an even distribution of the members of the ensemble over phase space, and a sudden change in the control parameter could potentially mess up the distribution. On the side of time averages it is imperative that the virial theorem is not affected, which relates the average kinetic and potential energies: Any rapid change in the control parameter would affect the ratio between the two energy forms. Specifically for a harmonic oscillator one gets $\langle T \rangle = \langle \phi \rangle$ and therefore

$$\frac{\langle L^2 \rangle}{2ml^2} = \frac{mgl}{2}\langle \varphi^2 \rangle = \frac{1}{2}(E + mgl) \tag{E.203}$$

and therefore for the average force

$$\langle F \rangle = -\left\langle \frac{\partial \mathcal{H}}{\partial l} \right\rangle = -\frac{1}{2l}(E + 3mgl) \tag{E.204}$$

with $\langle L^2 \rangle$ and $\langle \varphi^2 \rangle$ re-expressed with the energy E. Changes dE in energy then take place in performing work by changing the control parameter against this force,

$$dE = -\langle F \rangle dl = -\frac{E + 3mgl}{2l} dl \tag{E.205}$$

Comparison with eqn. E.201 then implies directly that the change in phase space volume is in fact vanishing, $d\phi^* = 0$ and, using the results of the previous chapter, that the corresponding energy is unchanged, $dS = d\ln(k_B \phi^*) = 0$. With this, we have gained a mechanical intuition about adiabatic changes and the invariance of the phase space volume.

E.8 *Entropy as phase space volume at fixed energy*

Up to this point, the idea of phase space volume was driven by the geometry of the boundary surface defined by energy. For continuing one needs to get a bit more specific, for instance with the example of an ideal gas, consisting of N point particles with no mutual interaction following a classical dispersion relation

$$\mathcal{H} = \sum_i \frac{\boldsymbol{p}_i^2}{2m} \tag{E.206}$$

The corresponding phase space volume ϕ^* bounded by $\mathcal{H}$ is given by

$$\phi^* = \int_{\mathcal{H} \leq E} \prod_i d^3 p_i d^3 q_i \tag{E.207}$$

While the spatial part of the integration is easy,

$$\int \prod_i d^3 q_i = \prod_i \int d^3 q_i = \prod_i V = V^N \tag{E.208}$$

and yields just the total physical volume of the system, taken to the Nth power, the integral over momentum space is bounded,

$$\sum_i \frac{\boldsymbol{p}_i^2}{2m} \leq \mathrm{E}, \quad \text{or} \quad \sum_i \boldsymbol{p}_i^2 \leq 2m\mathrm{E} \tag{E.209}$$

Effectively, this is the volume $\mathrm{C}(3\mathrm{N})r^{3\mathrm{N}}$ of a 3N-dimensional sphere of radius $r = \sqrt{2m\mathrm{E}}$.

$$\phi^* = \mathrm{C}(3\mathrm{N}) \cdot (2m\mathrm{E})^{\frac{3\mathrm{N}}{2}} \cdot \mathrm{V}^{\mathrm{N}} = \left(\frac{4\pi}{3} \cdot \frac{m\mathrm{E}}{\mathrm{N}} e\right)^{\frac{3\mathrm{N}}{2}} \cdot \mathrm{V}^{\mathrm{N}} \tag{E.210}$$

Moving towards the entropy requires the logarithm of the phase space volume,

$$k_{\mathrm{B}} \ln \phi^* = \frac{3\mathrm{N}}{2} k_{\mathrm{B}} \ln \mathrm{E} + \mathrm{N} k_{\mathrm{B}} \ln \mathrm{V} + \frac{3\mathrm{N}}{2} k_{\mathrm{B}} \ln(2m) \tag{E.211}$$

with the last two terms being constant. If the relationship between entropy and phase space volume would be given by $\mathrm{S} = k_{\mathrm{B}} \ln \phi^*$, the definition of temperature would be sensible,

$$\frac{\partial \mathrm{S}}{\partial \mathrm{E}} = \frac{\frac{3}{2}\mathrm{N}k_{\mathrm{B}}}{\mathrm{E}} = \frac{1}{\mathrm{T}} \tag{E.212}$$

as it corresponds to what we expect from equipartition, $\mathrm{E} = 3/2\, \mathrm{N}k_{\mathrm{B}}\mathrm{T}$, as well as the change of entropy with volume,

$$\frac{\partial \mathrm{S}}{\partial \mathrm{V}} = \frac{\mathrm{N}k_{\mathrm{B}}}{\mathrm{V}} = \frac{p}{\mathrm{T}} \tag{E.213}$$

as it corresponds to the ideal gas law, $p\mathrm{V} = \mathrm{N}k_{\mathrm{B}}\mathrm{T}$. But what about the scaling of the entropy S with particle number?

E.9 *Gibbs-paradox*

The Gibbs paradox is a thought experiment that shows that eqn. E.211 with terms that are all proportional to the particle number N is incompatible with the idea that entropy should be additive. Writing

$$\mathrm{S} = \frac{3}{2}\mathrm{N}k_{\mathrm{B}} \ln \mathrm{T} + \mathrm{N}k_{\mathrm{B}} \ln \mathrm{V} - \mathrm{N}k_{\mathrm{B}} \ln \mathrm{N} + \mathrm{N}\sigma_0 = \frac{3}{2}\mathrm{N}k_{\mathrm{B}} \ln \mathrm{T} + \mathrm{N}k_{\mathrm{B}} \ln \left(\frac{\mathrm{V}}{\mathrm{N}}\right) + \mathrm{N}\sigma_0 \tag{E.214}$$

with an additional factor $\propto \mathrm{N} \ln \mathrm{N}$ would remedy this: Imagine a system with $\mathrm{N} = \mathrm{N}_1 + \mathrm{N}_2$ particles in the total volume $\mathrm{V} = \mathrm{V}_1 + \mathrm{V}_2$, which can be separated by inserting a wall, such that two partial systems with N_1 and N_2 particles in volumes V_1 and V_2 exist. In doing that, the density N/V is equal to $\mathrm{N}_1/\mathrm{V}_1$ and to $\mathrm{N}_2/\mathrm{V}_2$.

Before the barrier is removed, the entropies read

$$\mathrm{S}_1 = \frac{3}{2}\mathrm{N}_1 k_{\mathrm{B}} \ln \mathrm{T} + \mathrm{N}_1 k_{\mathrm{B}} \ln \frac{\mathrm{V}_1}{\mathrm{N}_1} + \mathrm{N}_1\sigma_0 \tag{E.215}$$

$$\mathrm{S}_2 = \frac{3}{2}\mathrm{N}_2 k_{\mathrm{B}} \ln \mathrm{T} + \mathrm{N}_2 k_{\mathrm{B}} \ln \frac{\mathrm{V}_2}{\mathrm{N}_2} + \mathrm{N}_2\sigma_0 \tag{E.216}$$

and after removing the barrier, the two entropies need to be combined in an additive way: $\mathrm{S}_1 + \mathrm{S}_2 = \mathrm{S}$. Separating or combining the volumes can be done without any physical change to the system, neither thermal energy nor mechanical work is needed to insert the separating wall.

Let's inspect the terms one by one. The last term is clearly additive, $N_1\sigma_0 + N_2\sigma_0 = (N_1 + N_2)\sigma_0$, and so is the first term, $\frac{3}{2}N_1 k_B \ln T + \frac{3}{2}N_2 k_B \ln T = \frac{3}{2}(N_1 + N_2)k_B \ln T$. The second term is slightly more complicated:

$$N_1 k_B \ln \frac{V_1}{N_1} + N_2 k_B \ln \frac{V_2}{N_2} = k_B \ln \left[\left(\frac{V_1}{N_1}\right)^{N_1} \left(\frac{V_2}{N_2}\right)^{N_2}\right] \tag{E.217}$$

but the density $V/N = V_1/N_1 = V_2/N_2$ is unchanged:

$$\ldots = k_B \ln \left[\left(\frac{V}{N}\right)^{N_1} \left(\frac{V}{N}\right)^{N_2}\right] = k_B \ln \left[\left(\frac{V}{N}\right)^{N_1+N_2}\right] \tag{E.218}$$

The required additional term $-N k_B \ln N$ can be generated by changing the definition of entropy,

$$S = k_B \ln \frac{\phi^*}{N!} \simeq k_B \ln \phi^* - k_B N \ln N \tag{E.219}$$

with the approximative Stirling-formula:

$$\ln N! \simeq N \ln N. \tag{E.220}$$

The physical origin of the Gibbs-factor is the following: When removing the barrier, each of the N_1 particles in the volume V_1 can change place with each of the N_2 particles in the volume V_2, for which there are $N!/N_1!/N_2!$ possibilities. Just by removing the barrier the phase space volume ϕ^* would get enlarged by this factor. This is unphysical, just exchanging the particles would not have any influence on the physical properties of the system. If one distributes N particles onto N placeholders, there would be a total of N! possibilities. So one should counteract the increase in phase space volume by setting

$$S = k_B \ln \frac{\phi^*}{N!} \tag{E.221}$$

and by the rules of the logarithms, this becomes $S/k_B = \ln \phi^* - \ln N! = \ln \phi^* - N \ln N$ using Stirling's approximation. The inclusion of this so-called Gibbs-factor provides exactly the right correction to the entropy.

The phase space volume ϕ^* bounded by the energy was defined to be

$$\phi^* \equiv \int_{\mathcal{H}\leq E} \prod_i^N d^3p_i d^3q_i \tag{E.222}$$

and has units of an action^{3N}, but should really be dimensionless. Without any particular deeper meaning in classical mechanics we can choose any scale h with units of an action to make the phase space volume dimensionless, although it will become apparent in quantum statistics that this is exactly the right thing to do. Choosing specifically the Planck-constant h and including the 1/N!-factor already in the definition of the phase space volume then yields

$$\phi = \frac{1}{h^{3N}N!}\int_{\mathcal{H}\leq E}\prod_i^N d^3p_i d^3q_i \tag{E.223}$$

Then, for the ideal gas one would obtain the result

$$\phi = \frac{1}{h^{3N}}\left(\frac{4\pi}{3}\frac{mE}{N}\right)^{\frac{3N}{2}}\left(\frac{V}{N}\right)^N \exp\left(\frac{5N}{2}\right) \tag{E.224}$$

In summary, there are two places where quantum mechanics showed up: The proper de-dimensionalisation of the phase space volume and the Gibbs-factor due to the indistinguishability of the particles!

E.10 *Thermal wavelength λ_{th}*

We already made use of the Planck-constant h to make the phase space volume ϕ dimensionless, up to this point it appears naturally in many quantities without any particular reference to quantum mechanics, where the de Broglie-wavelength of a wave packet with momentum p is given by h/λ. Therefore, the classical dispersion relation suggests that we can assign a length scale λ_{th} to any temperature T,

$$E = \frac{p^2}{2m} = \frac{1}{2m}\left(\frac{h}{\lambda_{\mathrm{th}}}\right)^2 = k_B T \quad \rightarrow \quad \lambda_{\mathrm{th}} = \frac{h}{\sqrt{2mk_BT}} \tag{E.225}$$

assuming equipartition of the thermal energy k_BT. By convention, one usually absorbs additional factors of π into the definition $\lambda_{\mathrm{th}} = h/\sqrt{2\pi mk_BT}$ for the thermal wavelength.

With λ_{th} one can write for the phase space volume of an ideal classical gas,

$$\phi = \left(\frac{V}{\lambda_{\mathrm{th}}^3}e^{\frac{5}{2}}\right)^N \tag{E.226}$$

such that the entropy S becomes

$$S = k_B \ln\phi = k_B N\left(\ln\frac{V}{\lambda_{\mathrm{th}}^3} + \frac{5}{2}\right) \tag{E.227}$$

It increases with particle number N because it is an extensive quantity, and compares the total available volume V with the fundamental size λ_{th}^3 of the wave packets representing the particles, alluding at the number of possibilities to distribute the wave packets in the volume.

The ensemble average of the phase space function $A(p_i, q_i)$ would be given by

$$\langle A\rangle = \int_{E\leq\mathcal{H}\leq E+\delta E}\frac{1}{N!h^{3N}}\prod_i d^3p_i d^3q_i\; A(p_i,q_i)\rho(p_i,q_i) \tag{E.228}$$

for an arbitrary density $\rho(p_i, q_i)$, where the fundamental postulate stipulates that this density is constant. If, specifically, it is set to $\rho(p_i, q_i) = 1/\omega(E)$ the average becomes compatible with

$$\langle A\rangle = \frac{\int\limits_{E\leq\mathcal{H}\leq E+\delta E} \frac{1}{N!h^{3N}} \prod_i d^3p_i d^3q_i \; A(p_i, q_i)}{\int\limits_{E\leq\mathcal{H}\leq E+\delta E} \frac{1}{N!h^{3N}} \prod_i d^3p_i d^3q_i} = \frac{\frac{d}{dE}\int\limits_0^E \frac{1}{N!h^{3N}} \prod_i d^3p_i d^3q_i \; A(p_i, q_i)}{\frac{d}{dE}\int\limits_0^E \frac{1}{N!h^{3N}} \prod_i d^3p_i d^3q_i} \tag{E.229}$$

where the denominator is by definition the differential phase space density $\omega(E)$

$$\omega(E) = \frac{d}{dE}\int\limits_0^E \frac{1}{N!h^{3N}} \prod_i d^3p_i d^3q_i \tag{E.230}$$

There is no contradiction between eqn. E.228 and eqn. E.229 with $\rho(p_i, q_i) = 1/(\omega(E)\delta E)$. At the same time, the entropy S is given by the logarithmic phase space volume

$$S = k_B \ln \phi \tag{E.231}$$

so would it be possible to write S as a phase space average as well? And if yes, of what function? Let's try out the logarithmic phase space density $-\ln\rho$, with a prefactor of k_B to fix the units:

$$S = \int\limits_{E\leq\mathcal{H}\leq E+\delta E} \frac{1}{N!h^{3N}} \prod_i d^3p_i d^3q_i \; \rho(-k_B \ln\rho) = \int \frac{1}{N!h^{3N}} \prod_i d^3p_i d^3q_i \; \frac{1}{\omega\delta E}\left(-k_B \ln\frac{1}{\omega\delta E}\right) \tag{E.232}$$

with the inverse differential volume $\rho = \frac{1}{\omega(E)}$ and the corresponding logarithm $\ln\omega(E) = -\ln\rho$ the entropy becomes

$$S = \frac{1}{\omega\delta E} k_B \ln(\omega\delta E) \int\limits_{E\leq\mathcal{H}\leq E+\delta E} \frac{1}{N!h^{3N}} \prod_i d^3p_i d^3q_i \tag{E.233}$$

where the integral is just $\omega\delta E$, canceling with the prefactor. In general, entropy is the ensemble average of the logarithmic phase space density

$$S = -k_B\langle\ln\rho\rangle \tag{E.234}$$

obtained by resubstitution of ρ, which is exactly Boltzmann's iconic finding. At the same time, this formula is very reminiscent of Shannon's entropy for any distribution, and again there is a deep relationship between statistics and thermodynamics.

F CANONICAL ENSEMBLE

The canonical ensemble is characterised by temperature T, volume V and particle number N, instead of energy E, volume V and particle number N (or any other series of extensive state variables), effectively, the temperature is controlled instead of the energy. Physically one can reach that by putting the system into thermal contact with a larger system acting as an energy reservoir: The zeroth law of thermo dynamics will then make sure that a common equilibrium temperature is reached. If the second system is very large compared to the first one, it will determine this temperature.

As there are two microcanonical systems in thermal contact with an exchange of thermal energy, one would write down a common Hamilton function with an interaction term $h(p_i, q_i, \mathrm{P}_j, \mathrm{Q}_j)$ that allows the coupling of the two systems,

$$\mathcal{H} = \mathcal{H}(p_i, q_i) + \mathcal{H}(\mathrm{P}_j, \mathrm{Q}_j) + h(p_i, q_i, \mathrm{P}_j, \mathrm{Q}_j) \tag{F.235}$$

The first Hamilton-function describes a system with f degrees of freedom, the second Hamilton-function a system with F degrees of freedom, and usually $f \ll \mathrm{F}$. If the interaction term $h(p_i, q_i, \mathrm{P}_j, \mathrm{Q}_j)$ is zero, the two systems are isolated. We will assume that the interaction $h(p_i, q_i, \mathrm{P}_j, \mathrm{Q}_j)$ is nonzero to allow coupling, but small compared to the two energies $\mathcal{H}(p_i, q_i)$ and $\mathcal{H}(\mathrm{P}_i, \mathrm{Q}_i)$, such that the thermodynamical properties follow from these two energies alone.

F.1 *Marginalisation procedure*

For a given phase space coordinate (p_i, q_i) of the smaller system with an associated energy $\mathcal{H}_1$, the larger system is left with all configurations that are compatible with the energy $\mathrm{E} - \mathcal{H}_1 \leq \mathcal{H}_2 \leq \mathrm{E} + \delta\mathrm{E} - \mathcal{H}_1$ which is an immediate consequence of $\mathrm{E} \leq \mathcal{H}_1 + \mathcal{H}_2 \leq \mathrm{E} + \delta\mathrm{E}$. The probability of finding the smaller system at (p_i, q_i) needs to take into account all states $(\mathrm{P}_j, \mathrm{Q}_j)$, which are compatible with the energies $\mathcal{H}_1$ and $\mathcal{H}_2$. Therefore, this probability is given by

$$\mathrm{W}(p_i, q_i)\prod_i \mathrm{d}^3p_i\mathrm{d}^3q_i \propto \prod_i \mathrm{d}^3p_i\mathrm{d}^3q_i \int\limits_{\mathrm{E}-\mathcal{H}_1\leq\mathcal{H}_2\leq\mathrm{E}+\delta\mathrm{E}-\mathcal{H}_1} \prod_j \mathrm{d}^3\mathrm{P}_j\mathrm{d}^3\mathrm{Q}_j \tag{F.236}$$

with the identification

$$\omega_2(\mathrm{E}) = \frac{\mathrm{d}\phi_2(\mathrm{E})}{\mathrm{dE}} = \int\limits_{\mathrm{E}-\mathcal{H}_1\leq\mathcal{H}_2\leq\mathrm{E}+\delta\mathrm{E}-\mathcal{H}_1} \prod_j \mathrm{d}^3\mathrm{P}_j\mathrm{d}^3\mathrm{Q}_j \tag{F.237}$$

as the phase space volume of the second system. Mathematically, this is called a marginalisation: We are interested in the distribution of the smaller system *irrespective* of the particular distribution over $(\mathrm{Q}_j, \mathrm{P}_j)$, so we are *integrating out* that part of the distribution.

By integrating of the phase space (p_i, q_i) with $\mathrm{E} \leq \mathcal{H} \leq \mathrm{E} + \delta\mathrm{E}$ we get

$$\mathrm{W}(\mathrm{E}_1)\delta\mathrm{E}_1 \propto \omega_1(\mathrm{E}_1)\omega_2(\mathrm{E} - \mathrm{E}_1)\delta\mathrm{E}_1 \tag{F.238}$$

which should have a maximum at a certain value $\tilde{\mathrm{E}}_1$ for the energy E_1. In fact, in thermodynamic equilibrium the energy should be distributed among the two parts of the system in a way that the temperatures become equal. In order to get a feeling for this, let's look at a Bernoulli-probability as a model, as in the case of ideal gases. Then,

$$W(E_1) = E_1^{n_1}(E - E_1)^{n_2}, \qquad n_1, n_2 \sim 10^{23} \tag{F.239}$$

with the logarithm

$$\ln W(E_1) = n_1 \ln E_1 + n_2 \ln(E - E_1) \tag{F.240}$$

and a maximum at

$$\frac{d \ln W(E_1)}{dE_1} = 0 \quad \text{yields} \quad \tilde{E}_1 = E\frac{n_1}{n_1 + n_2}, \quad \tilde{E}_2 = E - \tilde{E}_1 = E\frac{n_2}{n_1 + n_2} \tag{F.241}$$

We expand this probability around the maximum $\tilde{E}_1$ and write $E_1 = \tilde{E}_1 + \epsilon$

$$\ln W(\tilde{E}_1 + \epsilon) = n_1 \ln \tilde{E}_1 + n_2 \ln \tilde{E}_2 + n_1 \ln\left(1 + \frac{\epsilon}{\tilde{E}_1}\right) + n_2 \ln\left(1 + \frac{\epsilon}{\tilde{E}_2}\right) \tag{F.242}$$

in a parabolic expansion. Then, the probability around $\tilde{E}_1$ becomes

$$\ln W(\tilde{E}_1 + \epsilon) = \text{const} - \frac{\epsilon^2}{2}\frac{n_1 + n_2}{\tilde{E}_1\tilde{E}_2} \tag{F.243}$$

as the linear term is = 0 at the maximum. Consequently, there will be a Gaussian distribution

$$W(\tilde{E}_1 + \epsilon) = W(\tilde{E}_1)\exp\left(-\frac{\epsilon^2}{2}\frac{n_1 + n_2}{\tilde{E}_1\tilde{E}_2}\right) \tag{F.244}$$

around $\tilde{E}_1$, with the variance approaching zero for large $n_1 + n_2$, such that the contribution to the phase space appears at a single, well-defined energy $\tilde{E}_1$, leaving $E - \tilde{E}_1$ to the second system.

Let's return to the probability $W(E_1)$, whose most probable value is defined by

$$\frac{\partial}{\partial E_1}(\omega_1(E_1)\omega_2(E - E_2)) = 0 \tag{F.245}$$

Because the logarithm is monotonic we can conclude

$$\frac{\partial}{\partial E_1} \ln \omega_1(E_1)\bigg|_{E_1=\tilde{E}_1} = \frac{\partial}{\partial E_1} \ln \omega_2(E_2)\bigg|_{E_2=\tilde{E}_2=E-\tilde{E}_1} \tag{F.246}$$

which would suggest the identification

$$S = k_B \ln \omega \quad \text{and} \quad \frac{\partial \ln \omega}{\partial E} = \frac{1}{k_B T} \tag{F.247}$$

in contradiction with previous results where

$$S = k_B \ln \phi \quad \text{and} \quad \frac{\partial \ln \phi}{\partial E} = \frac{1}{k_B T} \tag{F.248}$$

i.e. the actual phase space volume was replaced by the differential phase space volume. There is actually no issue because for a highly dimensional phase space most of the volume is contained in an incredibly thin layer just below the surface such that the two measures become approximately equal,

$$\lim_{N\to\infty} \frac{\ln \phi}{N} = \lim_{N\to\infty} \frac{\ln \omega}{N} \tag{F.249}$$

such that

$$\phi \sim \omega\delta E \tag{F.250}$$

Specifically for an ideal gas one would write

$$\phi = CE^{\frac{3N}{2}} \quad \text{as well as} \quad \omega = \frac{3N}{2}CE^{\frac{3N}{2}-1} = \frac{3N}{2}\frac{\phi}{E} \tag{F.251}$$

such that the temperature in both definition coincides,

$$\frac{\partial}{\partial E}k_B \ln \phi = \frac{1}{T} = \frac{\frac{3}{2}Nk_B}{E} = \frac{1}{T} = \frac{\left(\frac{3}{2}N - 1\right)k_B}{E} = \frac{\partial}{\partial E}k_B \ln \omega \tag{F.252}$$

as the difference between N and N − 1 becomes irrelevant.

We are missing now the actual shape of the phase space distribution for a canonical system, which is defined to be the distribution over the degrees of freedom of the smaller system by a temperature defined through the larger system, acting as a reservoir of thermal energy. The energy is shared among both systems, but effectively in a way that $\mathcal{H}_1(p_i, q_i) \ll E$ and from the argument in the previous example, such that the energy of both parts is well defined and fixed to $\tilde{E}_1$ and $E - \tilde{E}_1 \simeq E$, in particular if the thermostat is huge compared to the controlled system:

$$\ln \omega_2(E - \mathcal{H}_1) = \ln \omega_2(E_2)|_{E_2=E} - \frac{\partial}{\partial E_2} \ln \omega_2(E_2)|_{E_2=E}\mathcal{H}(p_i, q_i) \tag{F.253}$$

in the limit $E_1 = \mathcal{H}_1 \ll E_2 \simeq E$. But at the same time, $\frac{\partial}{\partial E} \ln \omega_2 = \frac{1}{k_B T}$, such that

$$W(p_i, q_i)\prod_i d^3p_i d^3q_i \propto \prod_i d^3p_i d^3q_i \omega_2(E - \mathcal{H}_1)dE \propto \prod_i d^3p_i d^3q_i \exp\left(-\frac{\mathcal{H}(p_i, q_i)}{k_B T}\right) \tag{F.254}$$

and similarly

$$W(E_1)dE_1 \propto \omega_1(E_1)\exp\left(-\frac{E_1}{k_B T}\right)dE_1 \tag{F.255}$$

with the Boltzmann-factor appearing, with the effect of down-weighting states of high energy.

F.2 *Canonical ensemble*

For defining a new ensemble where temperature T is controlled instead of energy E we need to be aware of the fact that energy is not fixed anymore, clearly the system can exchange energy with the thermostat through the interaction term of the common Hamilton-function. Recapitulating the argument about the maximisation of Shannon-entropy and the search for the "most random" distribution that is normalised and for which the expectation value of energy is fixed led to the Boltzmann-factor: For a given energy all states are equally probable, and states of higher energy are less probable according to $\exp(-\mathrm{E}/(k_\mathrm{B}\mathrm{T}))$. Defining an ensemble average of a phase space function $\mathrm{A}(p_i, q_i)$ this entire ensemble (not just the $(\mathcal{H} = \mathrm{E})$-surface!), leads to

$$\langle \mathrm{A}(p_i, q_i)\rangle = \frac{\int \prod_i \mathrm{d}^3p_i \mathrm{d}^3q_i\ \mathrm{A}(p_i, q_i) \exp\left(-\frac{\mathcal{H}(p_i,q_i)}{k_\mathrm{B}\mathrm{T}}\right)}{\int \prod_i \mathrm{d}^3p_i \mathrm{d}^3q_i\ \exp\left(-\frac{\mathcal{H}(p_i,q_i)}{k_\mathrm{B}\mathrm{T}}\right)} \tag{F.256}$$

i.e. with the weighting function is now being $\rho \sim \exp\left(-\frac{\mathcal{H}(p_i,q_i)}{k_\mathrm{B}\mathrm{T}}\right)$ instead of a constant $\rho = 0, 1$; where in addition the normalising factor $\mathrm{N}!h^{3\mathrm{N}}$ has been dropped. Then, the expectation value of energy would be

$$\langle \mathrm{E}\rangle = \frac{\int \prod_i \mathrm{d}^3p_i \mathrm{d}^3q_i\ \mathcal{H} \exp(-\beta\mathcal{H}(p_i, q_i))}{\int \prod_i \mathrm{d}^3p_i \mathrm{d}^3q_i\ \exp(-\beta\mathcal{H}(p_i, q_i))} \tag{F.257}$$

and of pressure

$$\langle p\rangle = \frac{\int \prod_i \mathrm{d}^3p_i \mathrm{d}^3q_i\ (-\frac{\partial\mathcal{H}}{\partial\mathrm{V}}) \exp(-\beta\mathcal{H}(p_i, q_i)}{\int \prod_i \mathrm{d}^3p_i \mathrm{d}^3q_i\ \exp(-\beta\mathcal{H}(p_i, q_i))} \tag{F.258}$$

with $p = -\partial\mathcal{H}/\partial\mathrm{V}$, and the inverse temperature $\beta = \frac{1}{k_\mathrm{B}\mathrm{T}}$.

F.3 *Equipartition theorem*

Remembering how difficult it was in the microcanonical ensemble to derive the equipartition theorem, we should try to rederive it in the canonical ensemble. Exploiting the virial law implies

$$\left\langle p_i \frac{\partial\mathcal{H}}{\partial p_i}\right\rangle = 2\langle\mathcal{H}_\mathrm{kin}\rangle = k\langle\mathcal{H}_\mathrm{pot}\rangle \tag{F.259}$$

if the Hamilton-function has the archetypical form $\mathcal{H} \sim p^2 + q^k$ with the potential being a homogeneous function of order k. Then,

$$\left\langle p_i \frac{\partial\mathcal{H}}{\partial p_i}\right\rangle = \frac{\int \prod_i \mathrm{d}^3p_i \mathrm{d}^3q_i p_i\ \frac{\partial\mathcal{H}}{\partial p_i} \exp(-\beta\mathcal{H}(p_i, q_i)}{\int \prod_i \mathrm{d}^3p_i \mathrm{d}^3q_i\ \exp(-\beta\mathcal{H}(p_i, q_i))} \tag{F.260}$$

Rewriting the term in the numerator involving the Boltzmann-factor as

$$\frac{\partial\mathcal{H}}{\partial p_i} \exp\left(-\frac{\mathcal{H}}{k_\mathrm{B}\mathrm{T}}\right) = -k_\mathrm{B}\mathrm{T}\frac{\partial}{\partial p_i} \exp\left(-\frac{\mathcal{H}}{k_\mathrm{B}\mathrm{T}}\right) \tag{F.261}$$

with the chain rule gives

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i}\right\rangle = \frac{\int \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i \; (-k_\mathrm{B} T p_i) \frac{\partial}{\partial p_i} \exp(-\beta \mathcal{H}(p_i, q_i))}{\int \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i \; \exp(-\beta \mathcal{H}(p_i, q_i))} = +k_\mathrm{B} T \tag{F.262}$$

with a sign change due to an integration by parts to obtain $\partial p_i / \partial p_i = 1$. Therefore, we can conclude that on average the kinetic energy and the potential energy for every degree of freedom are similar and of order $k_\mathrm{B} T$, essentially in a one-line calculation!

F.4 *Canonical partition function*

The idea of the canonical partition function Z is again that the weighting function in the numerator is the normalisation function in the denominator, such that for instance the state variable $E = \mathcal{H}$ can be generated by differentiation with respect to $\beta = 1/(k_\mathrm{B} T)$. Just as in the discussion of characteristic functions one would proceed by interchanging differentiation and integration, and have the differentiation act on the partition function as a carried-out integral:

$$Z(T, V, N) = \int \frac{1}{N! h^{3N}} \prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i \exp\left(-\frac{\mathcal{H}(p_i, q_i)}{k_\mathrm{B} T}\right) \tag{F.263}$$

now with the normalising factor $N! h^{3N}$, yielding the expectation value for the energy as a logarithmic derivative: The logarithm makes sure that exactly the right shape of the canonical average is generated, with a normalisation from the differentiation of the logarithm, and the state variable to be averaged over as the internal derivative required by the chain rule:

$$\langle E \rangle = k_\mathrm{B} T^2 \frac{\partial \ln Z}{\partial T} = k_\mathrm{B} T^2 \frac{1}{Z} \frac{\partial Z}{\partial T} \tag{F.264}$$

The expecation value for the pressure p follows in analogy through differentation with respect to its extensive partner V

$$\langle p \rangle = k_\mathrm{B} T \frac{\partial \ln Z}{\partial V} = k_\mathrm{B} T \frac{1}{Z} \frac{\partial Z}{\partial V} \tag{F.265}$$

Given the form of these expressions we should start looking for a suitable thermodynamic potential:

$$-\frac{F}{k_\mathrm{B} T} = -\beta F \tag{F.266}$$

called the Helmholtz-free energy F.

F.5 *Helmholtz-free energy* F

The Helmholtz-free energy F is obtained through Legendre-transform of the energy E by replacing the dependence on volume V as an extensive quantity through pressure p. Therefore, we write

$$F = E - TS \quad \text{with the differential} \quad \mathrm{d}F = \mathrm{d}E - T\mathrm{d}S - S\mathrm{d}T \tag{F.267}$$

together with the Euler relation

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V \quad \rightarrow \quad \mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V \tag{F.268}$$

Therefore, including $1/(k_B T)$ into the definition of F gives for the differential

$$\mathrm{d}\left(-\frac{F}{k_B T}\right) = \frac{F}{k_B T^2}\mathrm{d}T - \frac{1}{k_B T}\mathrm{d}F = \frac{F + TS}{k_B T^2}\mathrm{d}T + \frac{p}{k_B T}\mathrm{d}V = \underbrace{\frac{E}{k_B T^2}}_{\frac{\partial \ln Z}{\partial T}}\mathrm{d}T + \underbrace{\frac{p}{k_B T}}_{\frac{\partial \ln Z}{\partial p}}\mathrm{d}V \tag{F.269}$$

And therefore

$$\mathrm{d}\left(-\frac{F}{k_B T}\right) = \frac{\partial \ln Z}{\partial T}\mathrm{d}T + \frac{\partial \ln Z}{\partial V}\mathrm{d}V \tag{F.270}$$

which strongly suggests the definition $F(T, V) = -k_B T \ln Z$ for obtaining the Helmholtz-free energy F from the logarithmic canonical partition function, in analogy to $S = k_B \ln \phi$ in the microcanonical case. Alternatively, one can argue that

$$Z = \int \frac{\prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i}{N! h^{3N}} \exp\left(\frac{-\mathcal{H}(p_i, q_i)}{k_B T}\right) = \int_0^\infty \mathrm{d}E \underbrace{\int \frac{\prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i}{N! h^{3N}}}_{=\omega(E)} \exp\left(-\frac{\mathcal{H}}{k_B T}\right) \tag{F.271}$$

or equivalently

$$Z = \int_0^\infty \mathrm{d}E \underbrace{\frac{\mathrm{d}}{\mathrm{d}E} \underbrace{\int_0^E \frac{\prod_i \mathrm{d}^3 p_i \mathrm{d}^3 q_i}{N! h^{3N}}}_{=\phi(E)}}_{=\omega(E)} \exp\left(-\frac{\mathcal{H}}{k_B T}\right) \tag{F.272}$$

such that the canonical partition function originates directly from a reweighting of the microcanonical phase space density with the Boltzmann-factor: That is in fact an incredibly intuitive result, as extremisation of Shannon-entropy yields naturally a uniform distribution at fixed energy and an exponentially decreasing probability with increasing energy, in accordance with the fundamental postulate of statistical physics.

F.6 *Gibbs-enthalpy*

The Helmholtz free energy $F(T, V, N)$ has the temperature being controlled as an intensive state variable, while V and N are clearly extensive. Physically, this would mean that there is a larger thermal reservoir acting as a thermostat for the system. But often, the pressure p is fixed rather than the volume V, for instance in a chemical reaction at atmospheric pressure if one does not use a closed container for the chemical substances. A suitable thermodynamic potential with T, p and N controlled is the Gibbs enthalpy $G(T, p, N)$. Here, apart from being a thermostat the second system is in pressure equilibrium with the first system, such that $E = E_1 + E_2$ and $V = V_1 + V_2$.

In this case one can write

$$W(E_1, V_1)dE_1dV_1 \sim \omega(E_1, V_1)\omega_2(E - E_1, V - V_1)dE_1dV_1 \tag{F.273}$$

extending the previous relation by volume. An expansion of the logarithm $\ln\omega_2$ in terms of energy and volume yields

$$\ln\omega_2(E - E_1, V - V_1) = \ln\omega_2(E, V) - \underbrace{\frac{\partial\ln\omega_2}{\partial E_1}}_{=\frac{1}{k_BT}} E_1 - \underbrace{\frac{\partial\ln\omega_2}{\partial V_1}}_{=\frac{p}{k_BT}} V_1 \tag{F.274}$$

and because $S = k_B\ln\omega$,

$$\frac{\partial S}{\partial E} = \frac{1}{k_BT}\frac{\partial\ln\omega}{\partial E} = \frac{1}{k_BT}$$

$$\frac{\partial S}{\partial V} = \frac{1}{k_B}\frac{\partial\ln\omega}{\partial V} = \frac{p}{k_BT}$$

Looking a the Legendre-transform relation

$$dE = TdS - pdV \quad \rightarrow \quad dS = \frac{1}{T}(dE + pdV) \tag{F.275}$$

such that

$$\ln\omega_2(E - E_1, V - V_2) = \ln\omega_2(E, V) - \frac{1}{k_BT}(E_1 - pV_1) \tag{F.276}$$

and the Boltzmann-factor is extended to include pressure work. Using this extended Boltzmann-factor to compute expectation values in the canonical ensemble gives for instance for $\langle E + pV\rangle$,

$$\langle E + pV\rangle = \frac{\int dEdV\,(E + pV)\omega(E, V)\exp\left(-\frac{E+pV}{k_BT}\right)}{\int dEdV\,\omega(E, V)\exp\left(-\frac{E+pV}{k_BT}\right)} = k_BT^2\frac{\partial}{\partial T}\ln\int dEdV\,\omega(E, V)\exp\left(-\frac{E + pV}{k_BT}\right) \tag{F.277}$$

and for $\langle V\rangle$,

$$\langle V\rangle = \frac{\int dEdV\,V\omega(E, V)\exp\left(-\frac{E+pV}{k_BT}\right)}{\int dEdV\,\omega(E, V)\exp\left(-\frac{E+pV}{k_BT}\right)} = -k_BT\frac{\partial}{\partial p}\ln\int dEdV\,\omega(E, V)\exp\left(-\frac{E + pV}{k_BT}\right) \tag{F.278}$$

where again the variables $E + pV$ or V alone have been generated by suitable differentiation of the partition function, and interchanging differentiation and integration determines the expectation values as suitable derivatives of the logarithmic partitions functions. These relations lead naturally to the definition of the Gibbs-enthalpy

$G(T, p, N)$

$$G(T, p, N) = -k_B T \ln \int dE dV \omega(E, V) \quad \rightarrow$$

$$E + pV = k_B T^2 \frac{\partial}{\partial T}\left(-\frac{G}{k_B T}\right) \quad \text{and} \quad V = \frac{\partial G}{\partial p} \tag{F.279}$$

Linking this up to the Legendre-transform of F for the replacement of V with p

$$G = E - TS + pV \quad \rightarrow \quad dG = -SdT + Vdp + \mu dN \tag{F.280}$$

makes it possible to write

$$d\left(-\frac{G}{k_B T}\right) = \frac{G}{k_B T^2} dT - \frac{1}{k_B T} dG = \frac{E + pV}{k_B T^2} dT - \frac{V}{k_B T} dp - \frac{\mu}{k_B T} dN \tag{F.281}$$

Such that a differentiation in T will yield $E + pV$ and a differentiation in p the corresponding volume. Separating the combined Boltzmann-factor the allows to compute the partition function for the enthalpy G as following from the canonical partition function Z defining the Helmholtz free energy F

$$G(T, p, N) = -k_B T \ln \int dV\, Z(T, V, N) \exp\left(-\frac{pV}{k_B T}\right) \tag{F.282}$$

with an interesting picture emerging: Replacement of a state variable by Legendre-transform corresponds to a reweighting of the partition function with a modified Boltzmann-factor. Naturally we would ask now if a replacement of N with the chemical potential μ would be possible: This leads to the macrocanonical partition function. Please keep in mind that a thermodynamic potential can not depend on all intensive state variables as a consequence of the Gibbs-Duhem relation, so we are aiming at macrocanonical partitions and their corresponding potentials as functions of T, V and μ.

G MACROCANONICAL ENSEMBLE

G.1 *Macrocanonical ensemble*

Similar to the case of the Gibbs-enthalpy and the extension of the canonical potential by an additional Boltzmann-like factor $\exp(pV/(k_B T))$ one could construct a new partition with an associated thermodynamical potential for the case where temperature and volume are controlled, but the particle number is allowed to fluctuate by exchange with a particle reservoir, in analogy to the thermostat regulating the temperature. The ease at which new particles are added to the system is regulated by the chemical potential μ, and the resulting ensemble is called macrocanonical or grand canonical ensemble.

The combined phase space volume of the two systems is given by

$$\omega^{*}\delta E = \int_{E\leq\mathcal{H}\leq E+\delta E} \prod_i d^3p_i d^3q_i = \int_{0\leq E_1\leq E} \omega_1^{*}(E_1, N_1)\omega_2^{*}(E-E_1, N-N_1)dE_1\delta E \quad (G.283)$$

If the systems are separated, one would put N_1 particles in the first system but let the energy fluctuate such that the temperature is controlled: That would define the canonical partition.

If now the barrier between the systems is openend there can be an exchange of particles. There is a number of

$$\frac{N!}{N_1!(N-N_1)!} = \binom{N}{N_1} \quad (G.284)$$

possibilities to select N_1 particles from $N = N_1 + N_2$ to be in the first system, implying

$$\omega^{*}(E, N)\delta E = \int \sum_{N_1} \binom{N}{N_1} \omega_1^{*}(E_1, N_1)\omega_2^{*}(E-E_1, N-N_1)dE_1\delta E \quad (G.285)$$

The binomial factor separates magically into exactly the Gibbs-factors that are needed for each term:

$$\frac{\omega^{*}(E, N)\delta E}{N!h^{3N}} = \sum_{N_1}\int \frac{\omega_1^{*}(E_1, N_1)}{N_1!h^{3N_1}} \frac{\omega_2^{*}(E-E_1, N-N_1)}{(N-N_1)!h^{3(N-N_1)}} dE_1\delta E \quad (G.286)$$

and with the proper definition of Gibbs-corrected phase space volumes, including the powers of $h^{3N} = h^{3N_1} \times h^{3N_2}$,

$$\omega(E, N)\delta E = \sum_{N_1}\int \omega_1(E, N_1)\omega_2(E-E_1, N-N_1)dE_1\delta E \quad (G.287)$$

The probability of finding the system in a state characterised by E_1 and N_1 is then given by

$$W(E_1, N_1)dE_1 \sim \omega_1(E_1, N_1)\omega_2(E-E_1, N-N_1)dE_1 \quad (G.288)$$

from which we continue as before by expanding the logarithm of ω_2 around the maximum of W

$$\ln \omega_2(E - E_1, N - N_1) = \ln \omega_2(E, V) - \underbrace{\frac{\partial \omega_2}{\partial E}}_{=\frac{1}{k_B T}=\beta} E_1 - \underbrace{\frac{\partial \ln \omega_2}{\partial N}}_{=\frac{\mu}{k_B T}=z=} N_1 \tag{G.289}$$

from $S = k_B \ln \omega$ such that $\frac{\partial S}{\partial E} = \frac{1}{k_B T}$ and $\frac{\partial S}{\partial N} = \frac{\mu}{k_B T}$. With the definition of fugacity

$$z = \frac{\mu}{k_B T} \tag{G.290}$$

as the chemical potential in units of the thermal energy in analogy to the inverse temperature $\beta = \frac{1}{k_B T}$ we find for the probability

$$W(E_1, N_1) dE_1 \sim \omega(E_1, V_1, N_1) \exp\left(-\frac{E_1 - \mu N}{k_B T}\right) dE_1 \tag{G.291}$$

such that the fugacity plays the role of an analogous Boltzmann-factor to introduce the replacement of N by μ.

G.2 *Macrocanonical potential* J *and macrocanonical partition* $\mathcal{Z}$

The associated thermodynamical potential to the macrocanonical partition $\mathcal{Z}$ is the macrocanonical potential J, naturally as a function of the state variables T, V and μ, the latter replacing N:

$$J(T, V, \mu) = -k_B T \ln \mathcal{Z} \tag{G.292}$$

as the logarithm of the macrocanonical partition $\mathcal{Z}$

$$\mathcal{Z} = \sum_N \int_E dE\, \omega(E, V, N) \exp\left(-\frac{E - \mu N}{k_B T}\right) \tag{G.293}$$

Derivatives of the macrocanonical potential J with respect to T, V and μ are then linked to entropy S, pressure p and particle number N, respectively.

G.3 *Chemical potential* μ *and fugacity* z

A fun example for a canonical, discrete system is a microscopic model for a polymer, i.e. an elastic string: We'll set up a canonical partition and extend it to a macrocanonical partition in order to get some intuition about the chemical potential and the associated fugacity. Let's assume that the string is a chain of N monomers which can be in two configurations, the long configuration with length a and the short configuration with length b. The string is kept under tension σ, such that there is mechanical work σdl performed, if the the length l of the chain is changed, in analogy to the work performed by pressure $p dV$. As in this system the state variables T, σ and

N are controlled, we chose the enthalpy $G(T, \sigma, N)$ as the thermodynamical potential, with the associated canonical partition $Z_G(T, p, N)$:

$$Z_G = \sum_i \binom{N}{i} \exp\left(-\frac{\sigma l(i)}{k_B T}\right) =$$

$$\sum_i \binom{N}{i} \exp\left(-\frac{\sigma}{k_B T}[ia + (N-i)b]\right) = \left[\exp\left(-\frac{a\sigma}{k_B T}\right) + \exp\left(-\frac{b\sigma}{k_B T}\right)\right]^N \qquad (G.294)$$

with a factorising partition sum, $Z_G T, \sigma, N = Z_G(T, \sigma, 1)^N$. Clearly, the length of the polymer chain $l(i)$ depends on the number i of long elements a and the number $N - i$ of short elements b. The combinatorial factor $\binom{N}{i} = N!/i!/(N-i)!$ counts the number of possibilities to distribution i long elements in a chain of N elements in total.

Then, he Gibbs-enthalpy then follows from the canonical partition as

$$G(T, \sigma) = -k_B T \ln Z_G = \sigma l - TS \qquad (G.295)$$

with the corresponding differential dG,

$$dG = -SdT + l d\sigma \qquad (G.296)$$

such that the length of the chain at fixed tension and temperature is given by

$$l = \frac{\partial G}{\partial \sigma} = N \frac{a \exp\left(-\frac{a\sigma}{k_B T}\right) + b \exp\left(-\frac{b\sigma}{k_B T}\right)}{\exp\left(-\frac{a\sigma}{k_B T}\right) + \exp\left(-\frac{b\sigma}{k_B T}\right)} \qquad (G.297)$$

in thermodynamical equilibrium: Immediately, one would interpret equation G.297 as a weighted sum of $N\exp(-a\sigma/(k_B T))$ monomers in the a-configuration and of $N\exp(-b\sigma/(k_B T))$ monomers in the b-configuration, to form the expectation value for the total length l. In complete analogy, differentiation with respect to temperature yields the entropy, $S = -\frac{\partial G}{\partial T}$.

Figs. 1 and 2 show the equation of state, i.e. the relation between tension σ, length l and temperature T for this model, and compare the analytic solution derived from Z_G with the expectation values of samples drawn from the canonical ensemble my means of a Monte-Carlo Markov-chain method, namely, the Metropolis-Hastings algorithm. Perhaps a bit surprisingly, the polymer chain in fact contracts at fixed tension with increasing temperature, as the Boltzmann-probability for replacing a long monomer with a short one increases. And there is, at least for small tensions, a linear relationship between length and force reminiscent of Hooke's law. Only for large tensions, when the chain is almost fully elongated, the curve is significantly steeper, as there are fewer configurations consistent with increasing length.

We can extend the idea of a polymer chain to include a chemical potential μ: The polymer chain could be in a solution of monomers, which can leave the solution and be built into the polymer chain, controlled by the parameter μ. For the corresponding macrocanonical partition we need the Gibbs-factor $\frac{1}{j!}$, the canonical partition $Z(T, \sigma, j)$ now as a function of l and a weighting with fugacity:

$$\mathcal{Z}(T, \sigma, \mu) = \sum_j \frac{1}{j!}\left[\sum_i^j \binom{j}{i} \exp\left(-\frac{\sigma l(i)}{k_B T}\right)\right] \exp\left(\frac{\mu j}{k_B T}\right) \qquad (G.298)$$

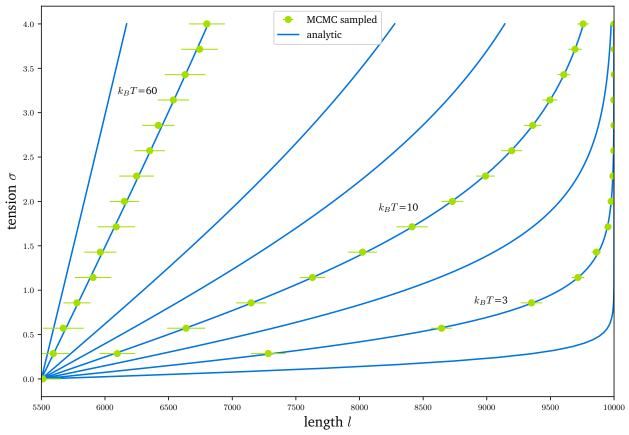

Figure 1: Relation between tension σ and length l of the rubber band, parameterised by temperature k_BT, as it would result from the partition sum Z_G and with the most likely value and its dispersion as determined numerically with a Metropolis-Hastings-algorithm for sampling from the canonical ensemble (reference: bachelor-thesis M. Kretschmer)

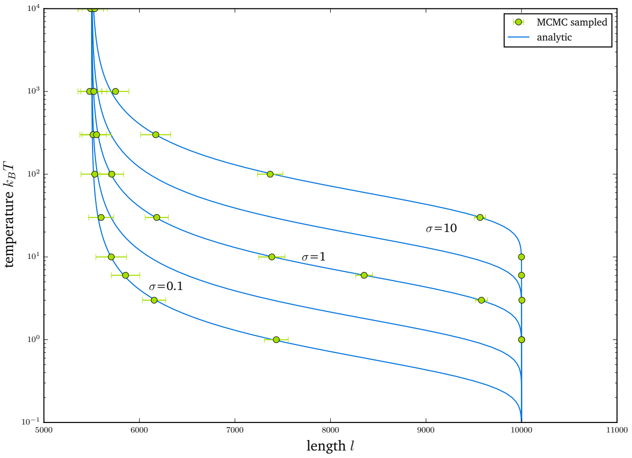

Figure 2: Relation between temperature k_BT and length l of the rubber band, parameterised by tension σ, as it would result from the partition sum Z_G and with the most likely value and its dispersion (reference: bachelor-thesis M. Kretschmer)

such that the macrocanonical potential J(T, σ, μ) is given by

$$J(T,\sigma,\mu) = -k_B T \ln \mathcal{Z}(T,\sigma,\mu) \tag{G.299}$$

with corresponding derivatives

$$\frac{\partial J}{\partial T} = -S, \quad \frac{\partial J}{\partial l} = -\sigma, \quad \frac{\partial J}{\partial \mu} = -N \tag{G.300}$$

The canonical partition sum factorises, $Z(T,\sigma,N) = Z(T,\sigma,1)^N$ into powers of the canonical partition of a single chain link,

$$Z(T,\sigma,1) = \exp\left(-\frac{a\sigma}{k_B T}\right) + \exp\left(-\frac{b\sigma}{k_B T}\right) \tag{G.301}$$

Collecting all results then yields for the macrocanonical partition

$$\mathcal{Z}(T,\sigma,\mu) = \sum_j \frac{1}{j!} Z(T,\sigma,1)^j \exp\left(\frac{\mu}{k_B T}\right)^j =$$

$$\sum_j \frac{1}{j!}\left[Z(T,\sigma,1)\exp\left(\frac{\mu}{k_B T}\right)\right]^j = \exp\left(\exp\left(\frac{\mu}{k_B T}\right) Z(T,\sigma,1)\right) \tag{G.302}$$

where the double exponential is typical for the structure of the macrocanonical partition sum $\mathcal{Z}$. For this case, S, l and N can be computed by differentiating $J = -k_B T \ln \mathcal{Z}$. It is a funny side effect that by providing a high chemical potential μ and pulling on the string with σ the system assembles the chain spontaneously! There is an inconsistency though, which does not invalidate the macrocanonical ensemble: To have a partition function that depends entirely on intensive variables is at odds with the Gibbs-Duhem relation, which disallows all intensive state variables in the potential for making statements about extensive state variables, as all information of the system is lost.

We have seen how the macrocanonical partition is assembled from fugacity-weighted canonical partitions, but can this process be inverted? It is possible to recover the canonical partition Z from the macrocanonical partition $\mathcal{Z}$. Their relation is given by

$$\mathcal{Z}(T,V,\mu) = \sum_N \exp\left(\frac{\mu}{k_B T}\right)^N Z(T,V,N) \tag{G.303}$$

as a fugacity-weighted summation over the canonical partition, which in turn factorises

$$Z(T,V,N) = \frac{1}{N!} Z(T,V,1)^N \tag{G.304}$$

into powers over the canonical partition pertaining to a single particle, N = 1. Introducing the fugacity explicitly,

$$\mathcal{Z}(T,V,z) = \sum_N Z(T,V,N) z^N = \sum_N \frac{1}{N!}\left(z\, Z(T,V,N)\right)^N \tag{G.305}$$

with $z = \exp\left(\frac{\mu}{k_B T}\right)$ shows that $\mathcal{Z}$ is in fact a power series in z with the canonical partition as prefactors. The variable for the fugacity is already aptly named: When performing an analytic continuation of $\mathcal{Z}$ from real-valued z to complex-valued z, the series becomes a Laurent series. Then, the canonical partition is obtained through complex differentiation

$$Z(T, V, N) = \frac{d^N}{dz^N} \mathcal{Z}(T, V, z)\bigg|_{z=0} \tag{G.306}$$

where the N-fold differentiation can be rewritten as a complex integration around a loop at $z = 0$

$$Z(T, V, N) = \frac{1}{2\pi i} \oint \frac{\mathcal{Z}(T, V, z)}{z^{N+1}} \tag{G.307}$$

which can be evaluated using the tools of complex analysis, i.e. the residue theorem.

H QUANTUM STATISTICS

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

H.1 *Averages in classical and quantum physics*

In classical physics, ensemble averages would be defined as

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

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

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

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

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

in position representation.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

with the final result

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

The time evolution of the density matrix is determined from

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

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

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

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

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

if the operator does not depend explicitly on time.

H.2 *Quantum mechanical partitions*

H.2.1 Construction of phase space densities

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

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

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

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

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

H.2.2 Canonical ensemble in quantum statistics

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

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

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

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

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

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

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

we would compute

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

H.2.3 Canonical averages of arbitrary observables

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

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

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

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

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

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

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

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

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

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

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

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

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

continuing we can write decomposing the logarithm of the fraction,

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

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

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

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

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

H.2.4 Macrocanonical ensembles in quantum statistics

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

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

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

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

such that one can define a quantum mechanical macrocanonical partition sum

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

with weights depending on the sign of the permutation:

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

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

H.4 *Non-interacting systems*

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

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

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

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

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

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

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

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

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

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

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

H.5 *Macrocanonical ensembles in quantum statistics*

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

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

or, completely equivalently, in terms of energy eigenstates as

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

This particular representation is practical, because the partition separates:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

with the normalising macrocanonical partition function

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

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

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

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

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

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

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

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

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

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

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

where one can continue with the geometric series,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

as well as through a differentiation with respect to β

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

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

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

H.5.1 Ultrarelativistic ideal Bose-gas

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

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

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

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

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

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

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

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

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

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

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

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

which follows from this argument:

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

with a geometric series

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned}
\text{entropy:}\quad & S = -\frac{\partial J}{\partial T} = \frac{32\pi^5 V}{90(hc)^3}(k_B T)^3 k_B \\
\text{pressure:}\quad & p = -\frac{\partial J}{\partial V} = \frac{8\pi^5}{90(hc)^3}(k_B T)^4 \\
\text{Euler-relation:}\quad & E = TS - pV = \frac{24\pi^5 V}{90(hc)^3}(k_B T)^4 \\
\text{free energy:}\quad & F = E - TS = -pV = -\frac{8\pi^5 V}{90(hc)^3}(k_B T)^4 \\
\text{Gibbs enthalpy:}\quad & G = E + pV - TS = F + pV = 0 \quad (= \mu N)
\end{aligned}$$

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

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

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

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

H.5.2 Planck-spectrum

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

yields an expression reminiscent of the Bose-factor,

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

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

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

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

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

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

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

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

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

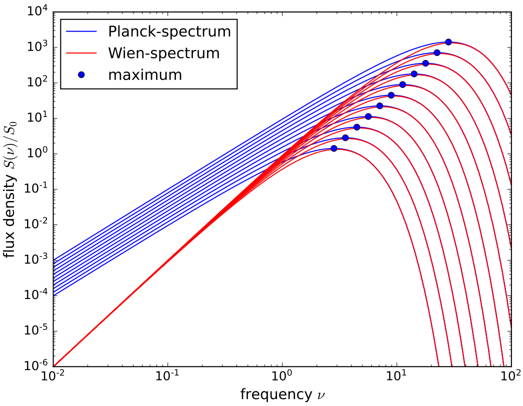

Figure 3: Planck-spectrum for ultrarelativistic bosons, in comparison to the Wien-approximation using classical instead of quantum statistics, both for a range of temperatures T. *The maxima in frequency for different temperatures clearly follow a linear Wien-displacement law.*

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

H.6 *Fluctuations in quantum and classical statistics*

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

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

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

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

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

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

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

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

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

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

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

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

or through the expectation value of the occupation number operator,

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

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

This implies for the three distributions that

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

because each occupation number can be isolated through differentiation by ϵ_k

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

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

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

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

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

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

suggest for the variance

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

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

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

as well as for the expectation value

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

such that the final result becomes

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

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

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

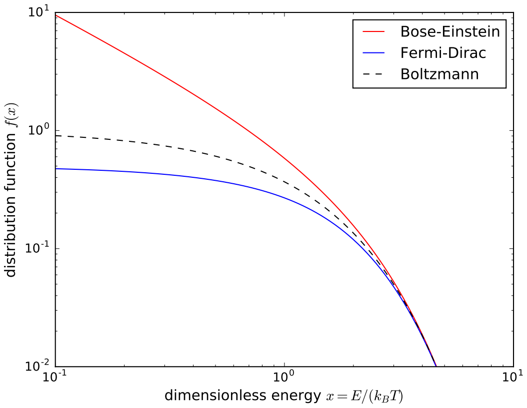

Figure 4: Bose-Einstein and Fermi-Dirac distribution in comparison to the Boltzmann-distribution, as a function of energy E*, expressed in terms of thermal energy* $k_B T$.

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

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

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

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

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

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

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

and the entropy S through differentiation,

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

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

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

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

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

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

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

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

H.8 *Fermionic statistics and the exclusion principle*

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

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

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

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

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

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

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

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

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

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

H.8.1 Density of states for non-relativistic fermions

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

$$\int \mathrm{d}^3x \int \mathrm{d}^3p = \mathrm{V}4\pi\int \mathrm{d}p\, p^2 = \mathrm{V}4\pi\int \mathrm{d}\epsilon\, 2m\epsilon\frac{m}{p} = \mathrm{V}2\pi(2m)^{\frac{3}{2}}\int \mathrm{d}\epsilon\,\sqrt{\epsilon} \tag{H.421}$$

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

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

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

and similarly for the particle number

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

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

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

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

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

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

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

The Fermi-Dirac distribution can be reformulated as

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

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

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

and for the special case $s = 0$

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

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

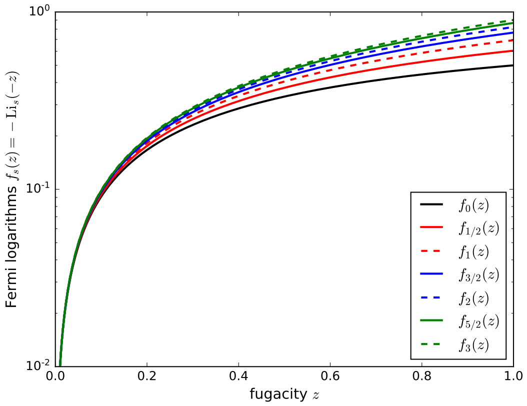

Figure 5: Fermi logarithms $f_s(z) = -\mathrm{Li}_s(-z)$ *as a function of fugacity* z.

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

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

$$z\frac{\partial}{\partial z} f_s(z) = \frac{1}{\Gamma(s)} \int\limits_0^\infty \mathrm{d}x \frac{x^{s-1} z^{-1}\exp(x)}{(z^{-1}\exp(x)+1)^2} \tag{H.431}$$

which can be integrated by parts to yield

$$\ldots = \frac{1}{\Gamma(s)}\Bigg(\underbrace{-\left.\frac{x^{s-1}}{z^{-1}\exp(x)+1}\right|_0^\infty}_{=0,\text{ for } s>1} + (s-1)\int\limits_0^\infty \frac{x^{s-2}}{z^{-1}\exp(x)+1}\Bigg) =$$

$$\frac{s-1}{\Gamma(s)} \int\limits_0^\infty \mathrm{d}x \frac{x^{s-2}}{z^{-1}\exp(x)+1} = f_{s-1}(z) \tag{H.432}$$

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

H.8.2 Fermi-gases

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

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

implying

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

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

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

which is typical for non-relativistic systems.

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

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

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

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

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

as well as

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

such that the energy per particle becomes

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The continuum for large systems would be given by

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

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

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

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

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

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

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

for the logarithmic macrocanonical partition and

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

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

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

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

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

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

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

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

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

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

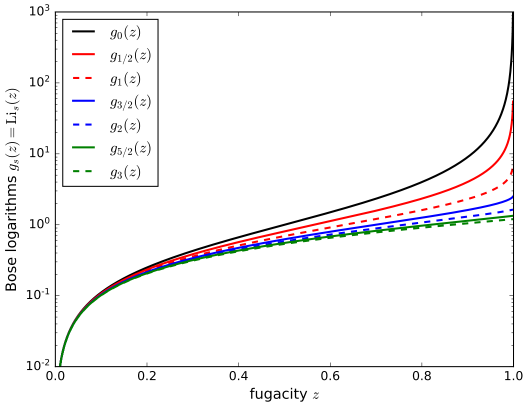

Figure 6: Bose logarithms $g_s(z) = \mathrm{Li}_s(z)$ *as a function of fugacity* z*.*

number,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

such that one immediately recognises the two cases

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

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

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

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

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

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

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

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

I PHASE TRANSITIONS

Phase transitions are phenomena related to *interacting* systems with many degrees of freedom, where the particles show a collective behaviour if the state variables are changed. Examples include the condensation of a van der Waals-gas, which liquefies at low temperatures, the ferromagnetic states of coupled spin systems or the condensation of quarks and gluons into nuclei. From this point of view, Bose-Einstein-condensation is very different: It takes place already in ideal systems, purely as a consequence of the symmetry requirement on the bosonic wave function, without any interaction between the particles.

I.1 *Van der Waals-gases*

The Hamilton-function of ideal non-relativistic kinetic systems is given by

$$H(p_i, q_i) = \sum_i^N \frac{\boldsymbol{p}_i^2}{2m} \tag{I.463}$$

as a straightforward sum over the individual kinetic energies. The canonical partition function is then computed as

$$Z(T, V, N) = \frac{1}{N!}\left[\frac{1}{h^3}\int d^3p \exp\left(-\beta\frac{\boldsymbol{p}^2}{2m}\right)\right]^N \cdot V^N = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \tag{I.464}$$

where the integral has units of an inverse length cubed, so we set it to λ^{-3} to make Z dimensionless. From the logarithmic partition function one obtains the Helmholtz free energy F,

$$F(T, V, N) = -k_B T \ln Z(T, V, N) \tag{I.465}$$

and through logarithmic derivatives $p = -\partial F/\partial V = Nk_B T/V$ the equation of state of the ideal gas. The spatial integration $\int d^3q$ contributions one power of V for every particle, therefore $Z \propto V^N$. The spatial integration is non-trivial, if there are interactions in the system, for instance through a (pairwise) potential in the Hamilton-function,

$$H(\{p_i\}, \{q_i\}) = \sum_i^N \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j}^N V(|\boldsymbol{q}_i - \boldsymbol{q}_j|) \tag{I.466}$$

where the summation condition $i < j$ makes sure that every interaction is only counted once. The potential keeps the partition function from separating.

$$Z(T, V, N) \neq \frac{1}{N!} Z(T, V, 1)^N \tag{I.467}$$

unlike in the non-interacting case. In summary, the effect of the mutual interaction between the particles is to introduce as a more elaborate d^3q-integration, leading to a new expression for the accessible spatial part of phase space, depending on the interaction potential.

I.1.1 Typical shapes of interaction potentials

Non-ideal gases are characterised by interactions between their particles, for instance through a Lennard-Jones-potential

$$V(r) = 4\epsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right] \tag{I.468}$$

where the physical idea would be that at small distances there is repulsion between the atoms, caused by Pauli-exclusions of the electron shells (called Born-repulsion), and at large distances one gets induced electrical dipoles, leading to a Coulomb-attraction. The equilibrium position is given by

$$\frac{dV}{dr} = 0 = \left[-12\left(\frac{r_0}{r}\right)^{11} + 6\left(\frac{r_0}{r}\right)^{5}\right]\cdot\frac{r_0}{r^2} \quad\rightarrow\quad \left(\frac{r_0}{r}\right)^{6} = \frac{1}{2} \quad \text{and therefore} \quad r \simeq 1.12 r_0 \tag{I.469}$$

The canonical (We assume that the particle number N is fixed and that volume and temperature are controlled) partition sum is then given by

$$\begin{aligned} Z(T,V,N) &= \frac{1}{N!}\left[\frac{1}{h^3}\int d^3p\,\exp\left(-\frac{\beta \boldsymbol{p}_i^2}{2m}\right)\right]^N \cdot \int \prod_i d^3q_i \cdot \exp\left(-\beta\sum_{i<j} V(q_{ij})\right) \\ &= Z_{\mathrm{id}}(T,V,N)\cdot \underbrace{\int \prod_i d^3q_i \cdot \exp\left(-\beta\sum_{i<j} V(q_{ij})\right)}_{\sim Z_{\mathrm{int}}(T,V,N),\ \text{not factorisable!}} \end{aligned}$$

with the abbreviation $q_{ij} = |\boldsymbol{q}_i - \boldsymbol{q}_j|$; and the most important observation would be that this partition does not separate due to the integral involving the relative distances between the particle pairs.

Computing the equation of state by isolating the pressure as a function of temperature and volume from the derivative of the Helmholtz free energy $F(T,V,N) = -k_B T \ln Z(T,V,N)$, which in turn depends logarithmically on the canonical partition function yields

$$p = -\frac{\partial F}{\partial V} = p_{\mathrm{id}} + p_{\mathrm{int}} = \rho k_B T(1 + B\rho + ...) \tag{I.470}$$

such that one immediately notices a correction to the ideal equation of state parameterised by B. The correction is proportional to the number of particle pairs, $\rho^2 \sim N^2 \sim N(N-1)$.

The parameter B can be determined approximatively from a so-called virial expansion, weirdly enough, one can achieve this and make the problem simpler by making it more complicated: Using the macrocanonical partition $\mathcal{Z}(T,V,\mu)$ one can derive B. The first step is to write out a power-series in the fugacity $z = \exp(\beta\mu)$, where higher-order terms will be neglected. The chemical potential μ is re-introduced as being small but nonzero, and the same applies to the fugacity:

$$\mathcal{Z}(T,V,\mu) = \sum_N \underbrace{Z(T,V,N)}_{=Z_N}\cdot z^N = Z_0 + zZ_1 + z^2 Z_2 + \ldots \tag{I.471}$$

where $Z_0 = 1$, as can be easily checked. The interesting term is Z_2, because it will contain the d^3q-integration over particle pairs, whose mutual interactions make the gas non-ideal:

$$Z_2 = \frac{1}{2!\lambda^6}\int d^3q_1 \int d^3q_2 \exp(-\beta V(q_{12})) \tag{I.472}$$

For evaluating the integration one can introduce relative coordinates, $\boldsymbol{q}_2 = \boldsymbol{q}_1 + \boldsymbol{r}$ with corresponding volume elements, $d^3q_2 = d^3r$ for fixed $\boldsymbol{q}_1$. Then, Z_2 becomes

$$Z_2 = \frac{1}{2!\lambda^6}\int d^3q_1 \int d^3r \exp(-\beta V(r)) = \frac{4\pi V}{2\lambda^6}\int r^2 dr \exp(-\beta V(r)) \tag{I.473}$$

where the first integral becomes simply the volume and the second integral can be simplified using spherical symmetry of the interaction potential. The macrocanonical potential

$$J = -k_B T \ln \mathcal{Z} = -pV \quad \rightarrow \quad \frac{pV}{k_B T} = \ln \mathcal{Z} \simeq \ln(1 + zZ_1 + z^2 Z_2 + \ldots) \tag{I.474}$$

The logarithm can now be expanded using the smallness of the fugacities with the Taylor-expansion $\ln(1 + x) \simeq x - \frac{x^2}{2}$, such that the ideal gas law starts acquiring corrections from terms that reflect the number of particle pairs!

$$\frac{pV}{k_B T} \simeq zZ_1 + z^2 Z_2 - \frac{z^2}{z} Z_1^2 + \ldots \tag{I.475}$$

at order z^2, with the new quadratic term $\propto Z_1^2$ appearing due to the Taylor-expansion. Therefore, this can be compared with our previous result

$$\frac{pV}{k_B T} \simeq V(\rho + B\rho^2 + ...) \tag{I.476}$$

and B is then obtained through a comparison of coefficients. From the fugacity one can derive derivative expressions according to

$$z = \exp(\beta\mu) \quad \rightarrow \quad \mu = \frac{1}{\beta}\ln z \quad \text{and therefore} \quad \frac{\partial}{\partial\mu} = \beta z \frac{\partial}{\partial z} \tag{I.477}$$

such that the particle number N follows from the macrocanonical partition through differentiation by z instead of μ:

$$N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln \mathcal{Z} = z\frac{\partial}{\partial z}\ln \mathcal{Z} = \frac{\partial \ln \mathcal{Z}}{\partial \ln z} \simeq zZ_1 + z^2(2Z_2 + Z_1^2) \tag{I.478}$$

where we see a term $z = \frac{N}{Z_1} = \rho\lambda^3$ proportional to particle number, which reproduces the ideal gas, clearly from the 1-particle partition sum, as in the ideal, separating case. At quadratic order in z one first obtains an implicit relation

$$\frac{N}{Z_1} = z + \left(\frac{2Z_2 - Z_1^2}{Z_1}\right) z^2 \tag{I.479}$$

which is in fact a quadratic equation

$$Z = \frac{N}{Z_1}\left(1 - \frac{N}{Z_1}\frac{2Z_2 - Z_1^2}{Z_1}\right) \tag{I.480}$$

With the approximation $\sqrt{1+x} \sim 1 + \frac{x}{2} - \frac{x^2}{8}$ on the arrives, collecting all results, at

$$\frac{pV}{k_B T} = \ln \mathcal{Z} = Z_1 \frac{N}{Z_1}\left(1 - \frac{N}{N_1}\left(\frac{2Z_2 - Z_1^2}{Z_1}\right)\right) + \frac{N^2}{Z_1}\left(Z_2 - \frac{Z_1^2}{2}\right) = N \cdot \left[1 - \left(Z_2 - \frac{Z_1^2}{2}\right)\frac{N}{Z_1^2}\right] \tag{I.481}$$

Since N and V both extensive one can make a replacement in the last term which makes an identification of the term involving Z_1 and Z_2 with B(T) possible, keeping in mind that $\rho V = N$,

$$B(T) = -\frac{V}{Z_1^2} \cdot \frac{Z_2 - Z_1^2}{2} = -\frac{1}{2}\int d^3r[\exp(-\beta V(r)) - 1] = -2\pi \int r^2 dr[\exp(-\beta V(r)) - 1] \tag{I.482}$$

As an approximation to the potential we use a piecewise constant function,

$$B(T) = -2\pi \underbrace{\int_0^d dr\, r^2}_{\text{small } r} - \underbrace{\int_d^{d+\delta} dr\, r^2[\exp(\beta\epsilon) - 1]}_{\text{intermediate } r} \simeq \frac{2\pi}{3}d^3 \quad - \quad 2\pi d^2 \delta\beta\epsilon \tag{I.483}$$

which in the limit $\delta \ll d$ and $\beta\epsilon \ll 1$ gives as a final result a correction to the ideal gas law

$$\frac{pV}{k_B T} = N\left(1 + B(T)\frac{N}{V}\right) \tag{I.484}$$

in the form of a van der Waals-term, reflecting the interaction between the particles. The interaction strength, the shape of the interaction potential and the physical extension of the attractive and repulsive part determine together the numerical value of B.

I.2 *Ising-model for ferromagnetism*

The Ising-model is a discrete set of spin states, mostly arranged on a regular lattice, which can interact with an external magnetic field as well as mutually with the direct neighbours in the lattice. In contrast to paramagnetism where only the interaction with an external magnetic field and the corresponding term $\mathbf{B} \cdot d\mathbf{M}$ with a changing magnetisation $d\mathbf{M}$ exist, the collective interactions give rise to ferromagnetic effects such as spontaneous magnetisation. The Hamilton-function of interacting spins is given by

$$H = -J\sum_{(i,j)} S_i S_j - B\mu \sum_i S_i \quad \text{with} \quad \sum_{(i,j)} = \sum_i \sum_{i-n \leq j \leq i+n} \tag{I.485}$$

with a fixed summation over the neighbours of each spin at finite range while $i \neq j$ in the first term. Multiplying with β and defining $K = \beta J$ as well as $Q = \beta\mu B$ yields

$$\beta H = -K \sum_{(i,j)} S_i S_j - Q \sum_i S_i \tag{I.486}$$

The modelling of interactions between spins follows the idea that parallel orientation is energetically favoured and antiparallel orientation disfavoured. The construction of a (canonical) partition sum now involves a Boltzmann-weighted summation over all lattice sites,

$$Z(K, Q, N) = \underbrace{\sum_{S_1=\pm1} \sum_{S_2=\pm1} \cdots \sum_{S_N=\pm1}}_{2^N \text{ possible states}} \exp(-\beta H) \tag{I.487}$$

with possibly periodic boundary condition to avoid edge effects. If $J > 0$ (or $K > 0$), parallel alignment is preferred leading ultimately to a spontaneous magnetisation if the temperature is not too high (below the Curie-temperature), which is referred to as ferromagnetism. The magnetisation is given by

$$M(K, Q) = \mu \left\langle \sum_i S_i \right\rangle \tag{I.488}$$

The canonical partition sum for a 1-dimensional chain if $Q = 0$ is given by

$$\begin{aligned} Z &= \sum_{S_1=\pm1} \cdots \sum_{S_N=\pm1} \exp(K(S_1S_2 + S_2S_3 + \ldots + S_{N-1}S_N)) \\ &= \sum_{S_1=\pm1} \cdots \sum_{S_{N-1}=\pm1} \exp(K(S_1S_2 + S_2S_3 + \ldots + S_{N-2}S_{N-1})) \cdot \underbrace{\sum_{S_N=\pm1} \exp(K(S_{N-1}S_N))}_{=\exp(+K)+\exp(-K)=2\cosh K} \\ &= (2 \cdot \cosh K)^N \end{aligned}$$

so iteratively one obtains $Z = (2\cosh K)^N$, and therefore for the Helmholtz energy F

$$F = -k_B T N \cdot \ln\left(2\cosh\frac{J}{k_B T}\right) \tag{I.489}$$

which reminds us of the result for paramagnetism, and would not show any spin correlation over large distances; in 1-dimensional lattices one does not observe ferromagnetic phase transitions.

I.2.1 Transfer matrix method for the Ising-model

There is an alternative elegant way of computing the canonical partition including effects of Q, starting again with the Hamilton-function and an additional cyclic boundary condition on the spin chain, $S_{N+1} = S_1$:

$$\beta H = -K \sum_{(i,j)} S_i S_j - Q \sum_i S_i \tag{I.490}$$

Defining the transfer function

$$T(i, i+1) = \exp\left(KS_iS_{i+1} + \frac{1}{2}Q(S_i + S_{i+1})\right) \tag{I.491}$$

one can write the Boltzmann-factor as

$$\exp(-\beta H) = T(1,2) \cdot T(2,3) \cdots T(N,1) \tag{I.492}$$

including the periodic boundary, as mentioned before. There are only 3 possible values appearing in in the transfer function T for the possible choices ±1 for S_i and S_j:

$$T = \begin{pmatrix} \exp(K+Q) & \exp(-K) \\ \exp(-K) & \exp(K-Q) \end{pmatrix} \tag{I.493}$$

So let's introduce a quantum mechanical notation with state vectors,

$$|S_i = +1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |S_i = -1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{I.494}$$

such that the entries in the transfer function T follow from forming the expectation values

$$T(i, i+1) = \langle S_i|T|S_{i+1}\rangle \tag{I.495}$$

This helps us to write the canonical partition as

$$\begin{aligned} Z = \sum_{\{S_i\}} \exp(-\beta H) &= \sum_{\{S_i\}} \langle S_1|T\underbrace{|S_2\rangle\langle S_2|}_{=\mathrm{id}}T|S_3\rangle \cdots \langle S_N|T|S_1\rangle \\ &= \sum_{S_1=\pm 1} \langle S_1|T^N|S_1\rangle = (T^N)_{11} + (T^N)_{22} = \mathrm{tr}(T^N) = \lambda_1^N + \lambda_2^N \end{aligned}$$

as the sum of the two possible eigenvalues of the transfer matrix, which is diagonal, ensuring that the eigenvalues exist and are real. The fastest way for getting the eigenvalues is the computation of the characteristic polynomial:

$$\det\begin{pmatrix} \exp(K+Q) & \exp(-K) \\ \exp(-K) & \exp(K-Q) \end{pmatrix} = 0 \tag{I.496}$$

which is a polynomial of order 2,

$$\begin{aligned} &[\exp(K+Q) - \lambda] \cdot [\exp(K-Q) - \lambda] - \exp(-2K) = \\ &\qquad \lambda^2 - 2\exp(K)\cosh Q \cdot \lambda + \exp(2K) - \exp(-2K) = 0 \end{aligned} \tag{I.497}$$

Solving for the two zeros $\lambda_\pm$ yields

$$\lambda_\pm = \exp(K) \cdot \cosh Q \pm \sqrt{\cosh^2 Q - 2\exp(-2K)\sinh 2K} \tag{I.498}$$

such that the canonical partition becomes

$$Z = \lambda_+^N + \lambda_-^N = \lambda_+^N \left[1 + \left(\frac{\lambda_-}{\lambda_+}\right)^N\right] \rightarrow \lambda_+^N \text{ for large } N \tag{I.499}$$

The previous result is recovered if $Q = 0$: Then, the first eigenvalue is $\lambda_+ = \exp(K) + \exp(-K) = 2\cosh K$.

The magnetisation is determined either by direct summation or by differentiation of the canonical partition,

$$M(T, B) = \frac{1}{Z}\sum_{\{S_i\}} \mu \left(\sum_i S_i \exp(-\beta H)\right) = \mu\partial_Q \ln Z = \frac{\mu N}{\lambda_+}\partial_Q \lambda_+ \tag{I.500}$$

and comes out as

$$M(T, B) = \frac{\mu N \sinh Q}{\sqrt{\cosh^2 Q - 2\exp(-2K)\sinh 2K}} \tag{I.501}$$

which shows an interesting behaviour: For $B = 0$ and $T \neq 0$ the magnetisation $M(T, B) = 0$ so that one does not observe a spontaneous transition to a magnetised state. If the fields are strong, on the contrary, the magnetisation is $M(T, B) = \mu N$ as all spins are aligned. The entropy follows from differentiation of the Helmholtz free energy with respect to temperature,

$$F = -Nk_B T \ln(2\cosh K) \rightarrow S = -\frac{\partial F}{\partial T} = Nk_B(\ln(2\cosh K) - K \tanh K) \tag{I.502}$$

with the limit $S = Nk_B \ln Z$ at high temperature and $S = 0$ at low temperature, in accordance with the third law of thermodynamics.

I.2.2 Isothermal susceptibility χ

The rate of change of the magnetisation with the external magnetic field is the magnetic susceptibility, which in this model is determined to be

$$\chi = \frac{1}{N}\frac{\partial M}{\partial B} = \frac{\beta\mu}{N}\partial_Q M = \frac{\beta\mu^2}{N}\partial_Q^2 \ln Z = \beta\mu^2\partial_Q^2 \ln \lambda_+ = \frac{\beta\mu^2}{1 - \tanh K} \tag{I.503}$$

which behaves as $1/T$ for large T: This is the statement of the Curie-law. Looking at its microscopic interpretation by substitution of the Hamilton-function yields

$$\chi = \frac{\beta\mu^2}{N}\partial_Q\left(\frac{1}{Z}\sum_{\{S_i\}}\left(\mu\sum_i S_i\right)\exp\left(K\sum_{(i,j)} S_i S_j + Q\sum_i S_i\right)\right) =$$

$$\frac{\beta\mu^2}{N}\sum_{\{S_i\}}\left(\mu\sum_i S_i\right)\exp(-\beta H) = \frac{\beta\mu^2}{N}\left(\sum_{i,j}\langle S_i S_j\rangle\right) \tag{I.504}$$

such that the susceptibility χ is actually the variance in the spin-configurations.

There is no known computation for the Ising partition function in 3 dimensions or more, and only a very complicated expression for 2-dimensional lattices. Actually, it's a pity that the 1-dimensional chain does not go a lot beyond paramagnets and that phase transitions are reserved to the higher-dimensional cases. But it is one of the few examples where mutual interactions in non-ideal systems are exactly computable.

J STOCHASTIC DIFFERENTIAL EQUATIONS

Up to this point we considered mechanical Hamiltonian systems in thermal equilibrium and looked at the reversible addition of thermal energy, leading to adiabatic, i.e. entropy-conserving changes of state. But this picture is incomplete, as we should understand better how exactly the many microscopic degrees of freedom of a system provide thermal fluctuations and how the motion of a single degree of freedom is changed under the influence of random, stochastic forces, or better, how the distribution of amplitudes of a system with many degrees of freedom evolves with time, as every degree of freedom follows its own equation of motion.

An example of such a distribution could be the amplitude distribution $p(x)\mathrm{d}x$ of a harmonic oscillator: Going from $x = 0$ to x requires mechanical work $\delta W = kx^2/2$ with the spring constant k. The energy needed is supplied as thermal energy from the interaction with all other degrees of freedom in the system, $\delta Q = -ST$. Energy conservation would then imply that $\mathrm{d}E = \delta W + \delta Q$ and therefore that entropy can be expressed as a function of amplitude of the oscillator, $S(x) = kx^2/2/(k_B T)$, if there is no overall change in energy, $\mathrm{d}E = 0$.

$$S(x) \sim k_B \ln p(x) \quad \rightarrow \quad p(x) = \frac{\exp\left(\frac{S(x)}{k_B}\right)}{\int \mathrm{d}x \, \exp\left(\frac{S(x)}{k_B}\right)} \sim \exp\left(-\frac{k}{k_B T}\frac{x^2}{2}\right) \tag{J.505}$$

i.e. a Gaussian with variance $k_B T/k$, which seems reasonable, as the amplitude of the random motion should increase with higher temperature and decrease for a higher spring constant: One should really imagine that there is a trembling of the pendulum due to thermal fluctuations corresponding to this variance. An observation of $\langle x^2 \rangle$ would immediately determine k_B for a system with known spring constant k and temperature T, with the experimental challenge being the smallness of thermal fluctuations $k_B T$ for reasonable temperatures.

J.1 *Brownian motion*

Macroscopic objects suspended in a fluid perform a random motion, as first noticed by Robert Brown, who observed pollen in water under a microscope. Naturally, there are two types of forces acting on such an object: a frictional force and a random agitation due to collisions with atoms and molecules in the fluid. The two are not independent, as state by the fluctuation-dissipation theorem. Writing down an equation of motion with a friction coefficient D

$$m\ddot{x} = -D\dot{x} \quad \text{leads to the solution} \quad \dot{x}(t) \propto \exp\left(-\frac{t}{\tau}\right) \tag{J.506}$$

with a time constant $\tau = m/D$, under which all motion ceases. But what about the random impacting of atoms and molecules that provide fluctuations in energy of the amount $k_B T$ in thermal equilibrium?

J.1.1 Langevin-equation

The key point is to add an external, randomly fluctuation force $\eta(t)$, as realised by Paul Langevin:

$$m\ddot{x}(t) = -D\dot{x}(t) + \sigma\eta(t) \tag{J.507}$$

with amplitude σ. This external force has the property that it vanishes on average, $\langle\eta(t)\rangle = 0$ and that its magnitude at different times is uncorrelated, $\langle\eta(t)\eta(t')\rangle = 2\cdot\delta_D(t-t')$, expressed by the Dirac δ_D-function. As the equation of motion is still linear, the solution is given as a superposition of the friction term and the time-integrated effect of the random force:

$$\dot{x}(t) = \exp\left(-\frac{t}{\tau}\right)\cdot\left[\dot{x}(0) + \int_0^t dt\exp\left(+\frac{t}{\tau}\right)\frac{\sigma}{m}\eta(t)\right] \tag{J.508}$$

While there is no macroscopic, ordered motion due to $\langle\eta(t)\rangle = 0$,

$$\langle\dot{x}(t)\rangle = \dot{x}\cdot\exp\left(-\frac{t}{\tau}\right) \tag{J.509}$$

there is a diffusive motion as can be seen from the variance

$$\begin{aligned}&\langle\dot{x}(t)\dot{x}(t')\rangle = \\ &\dot{x}(0)^2\exp\left(-\frac{t+t'}{\tau}\right) + \left(\frac{\sigma}{m}\right)^2\exp\left(-\frac{t+t'}{\tau}\right)\int_0^t dt\int_0^{t'} dt'\exp\left(\frac{t+t'}{\tau}\right)\cdot 2\delta_D(t-t') = \\ &\underbrace{\exp\left(-\frac{t+t'}{\tau}\right)\left[\dot{x}(0)^2 - \frac{\sigma^2}{Dm}\right]}_{\rightarrow 0\text{ for }t,t'\gg\tau} + \frac{\sigma^2}{Dm}\exp\left(-\frac{t-t'}{\tau}\right)\end{aligned} \tag{J.510}$$

Therefore, random fluctuations keep the particle in motion with velocity variance:

$$\langle\dot{x}(t)^2\rangle = \frac{\sigma^2}{Dm}\quad\text{for } t = t' \tag{J.511}$$

Assuming equipartition between the kinetic and thermal energies then leads to

$$\frac{m}{2}\langle\dot{x}^2\rangle = \frac{1}{2}k_BT\quad\text{such that}\quad\sigma^2 = Dk_BT \tag{J.512}$$

i.e. the amplitude of thermal fluctuation is related to the friction coefficient: First of all, that seems to be a surprising result, as D was phenomenological and σ was a model of the agitation of the fluid due to thermal motion. That the two are related makes a lot of sense, though, because their microsopci origin is identical: The macroscopic motion of the object through a fluid causes a momentum transfer onto the atoms and molecules, and the thermal motion of the atoms and molecules give rise to a momentum transfer onto the object.

J.1.2 Random walks

The object suspended in a fluid undergoes a random walk under the influence of the thermal, random force $\eta(t)$: We can repeat the above reasoning for the position $x(t)$ instead of the velocity $\dot{x}(t)$. The time constant τ^{-2} can be used to constraint $\ddot{x}$ to be very small at late times, so an object always slows down. Then, the equation of motion reads

$$\mathrm{D}\dot{x}(t) = \sigma\eta(t) \quad \text{and is solved by} \quad x(t) = x_0 + \int_0^t \mathrm{d}t\, \frac{\sigma}{\mathrm{D}}\eta(t) \tag{J.513}$$

As before, we find that there is no net motion $\langle x(t)\rangle = 0$ but that the variance is nonzero

$$\langle x^2(t)\rangle = \frac{\sigma^2}{\mathrm{D}^2}\int_0^t \mathrm{d}t \int_0^{t'} \mathrm{d}t'\, 2\delta_\mathrm{D}(t-t') = 2\left(\frac{\sigma}{\mathrm{D}}\right)^2 \cdot t \quad \rightarrow \quad \langle x(t)^2\rangle \propto t \tag{J.514}$$

such that the variance increases proportional to t, which is typical for diffusive processes. The diffusion constant Q is derived as

$$\mathrm{Q} = \left(\frac{\sigma}{\mathrm{D}}\right)^2 = \frac{k_\mathrm{B}\mathrm{T}}{\mathrm{D}} \tag{J.515}$$

commonly known as Einstein's relation. Substitution of a Stokes-like friction law for a spherical object of radius r in a fluid with viscosity $\nu\rho$ yields the Stokes-Einstein-relation:

$$\mathrm{D} = 6\pi(\nu\rho)\cdot r \quad \rightarrow \quad \mathrm{Q} = \frac{k_\mathrm{B}\mathrm{T}}{b\pi(\nu\rho)\cdot r} \tag{J.516}$$

linking viscosity and temperature, in the spirit of the fluctuation-dissipation-theorem. Fig. 7 gives an impression of discretised random walks in two dimensions, in particular of the diffusive process scaling $\propto \sqrt{t}$, or rather $\propto \sqrt{n}$ in the discrete case.

J.2 *Fokker-Planck-equation and evolution of distributions*

Up to this point, the Langevin-equation has described the motion of a damped system under the influence of a thermal fluctuating force. An interesting generalisation is that of an entire ensemble of particles, which represent a distribution, and where every particle itself follows its Langevin-dynamics $\ddot{x} = -\mathrm{D}\dot{x} + \sigma\eta(t)$. On would expect that the distribution then widens and diffuses, and the time evolution of this distribution is given by the Fokker-Planck-equation.

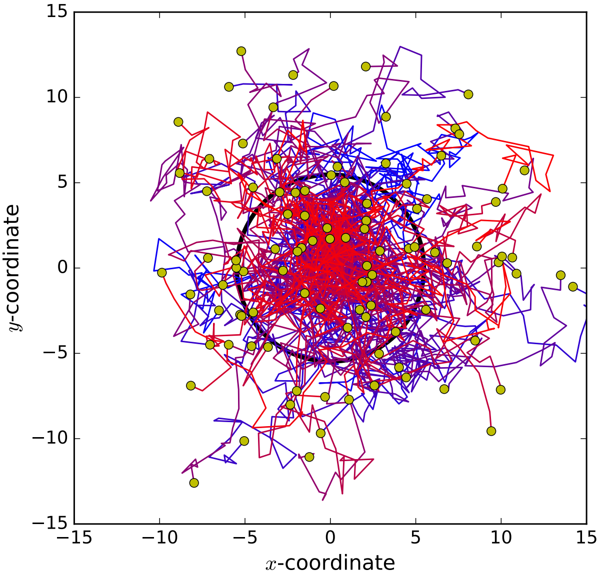

Figure 7: Discrete random walks in 2 dimensions with $n = 30$ *steps each drawn isotropically from a Gaussian distribution with variance* $\sigma^2 = 1$. *The walks are initialised at the origin and the endpoints are marked with a yellow dot. The typical distance that the random walks is able to cover is* $\sqrt{n}\sigma \simeq 5.47$, *indicated by the circle.*

If $\varphi(v, w)$ is the probability for a velocity change of a particle from v to $v + w$ on a time scale τ, one would write for the velocity distribution

$$p(v, t + \tau) = \int_{-\infty}^{+\infty} \mathrm{d}w \; p(v - w, t)\varphi(v - w, w) \tag{J.517}$$

as a convolution integral or a Green-like propagator: How often one observes a velocity v depends on how often the velocity $v - w$ appeared and how likely the transition from $v - w$ to v was.

If τ is chosen to be infinitesimally small then $\varphi \neq 0$ only for $|w| \ll |v|$ and one observes only small changes in velocity, suggesting a Taylor-expansion:

$$p(v, t + \tau) = \int \mathrm{d}w \left(p(v, t) - \frac{\partial p}{\partial v} w + \frac{\partial^2 p}{\partial v^2} \frac{w^2}{2}\right)\left(\varphi(v, w) - \frac{\partial \varphi}{\partial v} w + \frac{\partial^2 \varphi}{\partial v^2} \frac{w^2}{2}\right) \tag{J.518}$$

Multiplying out this relation and keeping all terms up to order w^2 yields these terms:

1. $\int \mathrm{d}w \; \varphi(v, w) = 1$
2. $\int \mathrm{d}w \; w\varphi(v, w) = \langle w \rangle$
3. $\int \mathrm{d}w \; w\frac{\partial \varphi}{\partial v} = \left\langle \frac{\partial w}{\partial v} \right\rangle = \frac{\partial}{\partial v}\langle w \rangle$
4. $\int \mathrm{d}w \; w^2\varphi(v, w) = \langle w^2 \rangle$
5. $\int \mathrm{d}w \; w^2\frac{\partial \varphi}{\partial v} = \frac{\partial}{\partial v}\langle w^2 \rangle$
6. $\int \mathrm{d}w \; w^2\frac{\partial^2 \varphi}{\partial v^2} = \frac{\partial^2}{\partial v^2}\langle w^2 \rangle$

Collection of these results and resubstitution into the distribution $p(v, t + \tau)$ yields

$$p(v, t + \tau) =$$

$$\int \mathrm{d}w \left(p(v, t) \cdot \underbrace{\varphi(v, w)}_{1} - p \cdot \underbrace{w \cdot \frac{\partial \varphi}{\partial v}}_{3} + p \underbrace{\frac{w^2}{2} \frac{\partial^2 \varphi}{\partial v^2}}_{6} - \frac{\partial p}{\partial v} \underbrace{w\varphi}_{2} + \frac{\partial p}{\partial v} \underbrace{\frac{\partial \varphi}{\partial v} w^2}_{5} + \frac{\partial^2 p}{\partial v^2} \underbrace{x \frac{w^2}{2}}_{4} \right) \tag{J.519}$$

such that the evolution equation becomes

$$p(v, t + \tau) = p(v, t)\left(1 - \frac{\partial}{\partial v}\langle w \rangle + \frac{\partial^2}{\partial v^2}\langle w^2 \rangle - \langle w \rangle - \frac{\partial}{\partial v}\langle w^2 \rangle + \langle w^2 \rangle\right) \tag{J.520}$$

From the Langevin-equation one can obtain an expression for the average change in velocity: v changes on the time scale τ, so $\dot{v} = w/\tau = -\mathrm{D}v$, such that

$$\frac{\partial}{\partial v}\langle w \rangle = -\mathrm{D}\tau. \tag{J.521}$$

The variance $\langle w^2\rangle = 2k_\mathrm{B}\mathrm{T}\frac{\mathrm{D}}{m}\tau$ is obtained from the Einstein-relation, which as well suggests that $\frac{\partial}{\partial v}\langle w^2\rangle = 0$. Therefore,

$$\frac{p(\upsilon, t+\tau) - p(\upsilon, t)}{\tau} = \mathrm{D}p + \mathrm{D}\upsilon\frac{\partial p}{\partial \upsilon} + k_\mathrm{B}\mathrm{T}\frac{\mathrm{D}}{m}\frac{\partial^2 p}{\partial \upsilon^2} \tag{J.522}$$

and in the limit $\tau \to 0$:

$$\frac{\partial}{\partial t}p(t,\upsilon) = \mathrm{D}\frac{\partial}{\partial \upsilon}\left[(p\upsilon) + \frac{k_\mathrm{B}\mathrm{T}}{m}\frac{\partial p}{\partial \upsilon}\right] \tag{J.523}$$

which is the sought-after Fokker-Planck-equation. It is a advection-diffusion equation for the probability distribution $p(t,\upsilon)$ and allows particular stationary solutions, for instance the Maxwell-Boltzmann-distribution

$$p \sim \exp\left(-\frac{m\upsilon^2}{2k_\mathrm{B}\mathrm{T}}\right) \tag{J.524}$$

for $\partial p/\partial t = 0$.

J.3 *Spectral decomposition of random forces $\sigma\eta(t)$*

The random force $\sigma\eta(t)$ is randomly fluctuating, and a Fourier-decomposition

$$\eta(t) = \frac{1}{2\pi}\int \mathrm{d}\omega\, \mathrm{C}(\omega)\cdot\exp(+\mathrm{i}\omega t) \quad \leftrightarrow \quad \mathrm{C}(\omega) = \int \mathrm{d}t\, \eta(t)\cdot\exp(-\mathrm{i}\omega t) \tag{J.525}$$

would be able to differentiate between fluctuations taking place on different time scales, by means of the Fourier-transform $\mathrm{C}(\omega)$. The Wiener-Khinchin-theorem states that the variances in real and Fourier-space are identical,

$$\langle \eta(t)^2\rangle = \int \mathrm{d}t\, \eta(t)^2 = \int \frac{\mathrm{d}\omega}{2\pi}|\mathrm{C}(\omega)|^2 \tag{J.526}$$

and tha tthe correlation function is the inverse Fourier-transform of the spectrum $|\mathrm{C}(\omega)|^2$,

$$\begin{aligned}\langle \eta(t)\eta(t+\tau)\rangle = &\\ &\frac{1}{(2\pi)^2}\int \mathrm{d}t \int \mathrm{d}\omega \int \mathrm{d}\omega'\, \mathrm{C}(\omega)\mathrm{C}^*(\omega')\cdot\exp(\mathrm{i}(\omega-\omega')t)\cdot\exp(-\mathrm{i}\omega'\tau) = \\ &\int \mathrm{d}\omega\, |\mathrm{C}(\omega)|^2\exp(-\mathrm{i}\omega\tau)\end{aligned} \tag{J.527}$$

With this idea, let's Fourier-decompose all terms in the Langevin-equation,

$$\dot{\upsilon} + \mathrm{D}\upsilon = \sigma\eta(t) \tag{J.528}$$

including the time derivatives:

$$\upsilon(t) = \int \frac{\mathrm{d}\omega}{2\pi}\upsilon(\omega)\exp(\mathrm{i}\omega t) \quad \rightarrow \quad \frac{\partial}{\partial t}\upsilon(t) = \int \frac{\mathrm{d}\omega}{2\pi}\mathrm{i}\omega\upsilon(\omega)\exp(\mathrm{i}\omega t) \tag{J.529}$$

and

$$\eta(t) = \int \frac{\mathrm{d}\omega}{2\pi}\mathrm{C}(\omega)\exp(\mathrm{i}\omega t) \tag{J.530}$$

The, the Langevin-equation can be written as $(\mathrm{i}\omega + \mathrm{D})\upsilon(\omega) = \sigma \cdot \mathrm{C}(\omega)$ in Fourier-space, which can be solved for $\upsilon(\omega)$ as

$$\upsilon(t) = \int \frac{\mathrm{d}\omega}{2\pi}\frac{\sigma\mathrm{C}(\omega)}{\mathrm{i}\omega + \mathrm{D}}\exp(\mathrm{i}\omega t) \tag{J.531}$$

with the corresponding variance

$$\langle\upsilon^2(t)\rangle = \int \mathrm{d}t\;\upsilon^2(t) = \int \frac{\mathrm{d}\omega}{2\pi}\frac{\sigma|\mathrm{C}(\omega)|^2}{\mathrm{D}^2 + \omega^2} = \frac{k_\mathrm{B}\mathrm{T}}{m} \tag{J.532}$$

using the Wiener-Khinchin-theorem in the second and equipartition in the last step. The result implies that the thermal energy is present in terms of kinetic energy in the system, and is assembled from fluctuations on all time scales, weighted by $1/\omega^2$ for large frequencies, but by D^2 for small frequencies, as clearly there is damping relevant for slow motion on large time scales.

J.4 *Irreversible processes*

J.4.1 Irreversibility in statistical physics

The fundamental physical laws are time reversible, and this is a true statement for the motion of particles or the dynamics of fields, in all branches of physics. For instance,

$m\frac{\mathrm{d}^2x^i}{\mathrm{d}t^2} = -\partial^i\Phi$ Newton's equation of motion

$\partial_\alpha\partial^\alpha\mathrm{A}^\mu = \frac{4\pi}{c}\jmath^\mu$ Maxwell's field equation (in Lorenz-gauge $\partial_\alpha\mathrm{A}^\alpha = 0$)

$\frac{\mathrm{d}^2x^\mu}{\mathrm{d}\tau^2} = -\frac{q}{c}\mathrm{F}^{\mu\nu}\frac{\mathrm{d}x_\nu}{\mathrm{d}\tau}$ Lorentz-equation of motion

$\mathrm{R}_{\mu\nu} - \frac{\mathrm{R}}{2}g_{\mu\nu} = -\frac{8\pi\mathrm{G}}{c^4}\mathrm{T}_{\mu\nu} - \Lambda g_{\mu\nu}$ gravitational field equation

$\frac{\mathrm{d}^2x^\alpha}{\mathrm{d}\tau^2} + \Gamma^\alpha_{\mu\nu}\frac{\mathrm{d}x^\mu}{\mathrm{d}\tau}\frac{\mathrm{d}x^\nu}{\mathrm{d}\tau} = 0$ geodesic equation of motion

In all of these examples, time reversibility is ensured by second derivatives (or squares of first derivatives), and the only case where a deeper explanation is necessary would be the Lorentz-equation of motion: The field tensor $F^{\mu\nu}$ is in fact a first derivative of the potential A^μ, so there is in fact a square of first derivatives as well.

Statistical systems with many degrees of freedom behave very different: While the dynamics of their fundamental constituents follows time-reversible laws like in the five examples, the Fokker-Planck equation as a diffusion equation is not time reversible. It is naturally to observe a widening distributions with time, but not the opposite. To understand this, let's have a look at a famous nonlinear equation:

$$\partial_t \upsilon^i + (\upsilon^j \partial_j)\upsilon^i = -\frac{\partial^i p}{\rho} - \partial^i \Phi + \nu\Delta\upsilon^i \quad \text{Navier-Stokes-equation} \tag{J.533}$$

for the evolution of the velocity υ^i of a fluid element on which pressure p and gravity Φ is acting, for the particular case of incompressible fluids, $\partial_i \upsilon^i = 0$. ν is the coefficient of viscosity, which encapsulates the microscopic dynamics of the atoms the fluid is made of. Ignoring this term for a second and setting $\nu = 0$ recovers the Euler-equation

$$\partial_t \upsilon^i + (\upsilon^j \partial_j)\upsilon^i = -\frac{\partial^i p}{\rho} - \partial^i \Phi \quad \text{Euler-equation} \tag{J.534}$$

for the motion of ideal inviscid fluids which is perfectly time-reversible: Making the replacements

$$t \to t, \quad \partial_t \to -\partial_t, \quad \upsilon^i \to -\upsilon^i \tag{J.535}$$

does not change anything in the Euler-equation, but this invariance is broken if $\nu \neq 0$, as $\Delta\upsilon^i \to -\Delta\upsilon^i$. Clearly, this has to do with the dichotomy between the microscopic degrees of freedom and the macroscopic motion.

Reversible changes of state, in which the entropy stays constant, proceed over a sequence of equilibria (such that temperature is defined at every point and changes because of the change in internal energy), while irreversible changes in state take place spontaneously under entropy generation. The rate of change of entropy with time would be given by

$$\frac{\partial S}{\partial t} = \frac{\partial x}{\partial t}\frac{\partial S}{\partial x} \tag{J.536}$$

with a control parameter x of the system, such as the length of a pendulum as discussed in the section about adiabatic changes. In equilibrium the condition $\partial S/\partial x = 0$ would hold,

$$\dot{x} = C\frac{\partial S}{\partial x} = \frac{C}{2}\left.\frac{\partial^2 S}{\partial x^2}\right|_{x_0}(x - x_0) \tag{J.537}$$

with a suitable Taylor expansion around the equilibrium value x_0.

This result is a bit surprising when thinking about second-order equations of motion so typical for e.g. mechanical systems. There, a force $\partial\Phi/\partial x$ would provide the reason for acceleration

$$m\ddot{x} = m\dot{v} = -\frac{\partial}{\partial x}\Phi \tag{J.538}$$

very unlike thermodynamics, where a first order equation appears:

$$\dot{x} = \mathrm{C}\frac{\partial \mathrm{S}}{\partial x} \tag{J.539}$$

and the gradient of the thermodynamic potential such as the entropy determines velocity instead of acceleration. But when including dissipative forces into a mechanical system

$$m\dot{v} + \beta v = -\frac{\partial}{\partial x}\Phi \tag{J.540}$$

in the limit of strong damping, $\beta v \gg m\dot{v}$ one falls back onto a perfectly non-reversible equation of motion

$$\beta v = \beta\dot{x} = -\frac{\partial}{\partial x}\Phi \tag{J.541}$$

This would exactly be the limit in which the gradient of a potential is related to a velocity rather than an acceleration.

An example illustrating this idea might be the following: Imagine a ball submersed in a liquid, on which a spring is attached. The liquid provides both a heavy damping of the system as well as a source of thermal fluctuations. The potential $\Phi = kx^2/2$ under which the ball moves is provided by the spring with spring constant k. The kinetic energy E of the ball is coupled to the heat bath as the impacting molecules of the liquid can transfer kinetic energy. So we would write $\mathrm{E} = \mathrm{E}_0 - \Phi(x)$ and consequently for the entropy $\mathrm{S}(x) = \mathrm{S}(\mathrm{E}_0 - \Phi(x), \mathrm{V}, \mathrm{N})$, in the microcanonical sense. A Taylor-expansion of the entropy gives

$$\mathrm{S}(x) = \mathrm{S}_0 - \frac{\partial \mathrm{S}}{\partial \mathrm{E}_0}\Phi(x) + \ldots = \mathrm{S}_0 - \frac{1}{k_\mathrm{B}\mathrm{T}}\Phi(x) + \ldots \tag{J.542}$$

where in the second equality we have substituted the definition of temperature with $\partial\mathrm{S}/\partial\mathrm{E} = 1/(k_\mathrm{B}\mathrm{T})$. There is a gradient in entropy collinear with the gradient in the potential,

$$\frac{\partial \mathrm{S}}{\partial x} = -\frac{1}{k_\mathrm{B}\mathrm{T}}\frac{\partial\Phi}{\partial x} = \frac{k}{k_\mathrm{B}\mathrm{T}}x \quad \rightarrow \quad \dot{x} = \mathrm{C}\frac{\partial \mathrm{S}}{\partial x} = -\mathrm{C}\frac{k}{k_\mathrm{B}\mathrm{T}}x \tag{J.543}$$

with a similar proportionality between $\dot{x}$ and the entropy gradient as before. Therefore, the solution for the equation of motion of the system is

$$x(t) \propto \exp\left(-\frac{k}{k_\mathrm{B}\mathrm{T}}x\right) \tag{J.544}$$

which is a non-reversible process because of the appearance of a first derivative $\dot{x}$ instead of a second derivative $\ddot{x}$ typical for a single, microscopic degree of freedom.

A second example would be two bodies in thermal contact. The total energy is simply $E = E_1 + E_2$, and under a perturbation ϵ in one of the bodies the total energy would be conserved, $(E_1 + \epsilon) + (E_2 - \epsilon) = E$. Writing the entropy S as an additive function dependent on the energies of the two subsystems as $S(\epsilon) = S_1(E_1 + \epsilon) + S_2(E_2 - \epsilon)$ on can Taylor-expand the entropy as

$$S(\epsilon) = S_1(E_1) + \epsilon \underbrace{\frac{\partial S_1}{\partial E_1}}_{=\frac{1}{k_B T}} + \frac{\epsilon^2}{2}\frac{\partial^2 S_1}{\partial E_1^2} + S_2(E_2) - \epsilon \underbrace{\frac{\partial S_2}{\partial E_2}}_{=\frac{1}{k_B T}} + \frac{\epsilon^2}{2}\frac{\partial^2 S_2}{\partial E_2^2} \tag{J.545}$$

to second order: Then, the two terms $\partial S_1/\partial E_1 = 1/(k_B T) = \partial S_2/\partial E_2$ in thermal equilibrium, and the higher-order terms are controlled by the smallness of ϵ. Changing the energy with time leads to a corresponding change in entropy,

$$\frac{\partial S}{\partial t} = \epsilon\dot{\epsilon}\left(\frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2}\right) \tag{J.546}$$

Contrarily, if there is no equilibrium,

$$\begin{aligned} \frac{1}{k_B T_1} &= \frac{\partial S_1}{\partial E_1}(E_1 + \epsilon) = \frac{1}{k_B T} + \frac{\partial^2 S_1}{\partial E_1^2} \\ \frac{1}{k_B T_2} &= \frac{\partial S_2}{\partial E_2}(E_2 - \epsilon) = \frac{1}{k_B T} + \frac{\partial^2 S_2}{\partial E_2^2} \end{aligned}$$

and both temperature become equal if there is no perturbation in energy $\epsilon = 0$, inducing the temperature imbalance. Therefore, the time evolution of entropy

$$\frac{\partial S}{\partial t} = \dot{\epsilon}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{J.547}$$

is driven by the rate of change of energy, and aims at establishing an equilibrium.

J.4.2 Reversibility in classical mechanics

Classical mechanics is perfectly time-reversible, not only in the Newtonian equation of motion, but in the Hamiltonian description as well: The Hamilton-function and the corresponding equations of motion

$$\mathcal{H} = \frac{p^2}{2m} \quad \rightarrow \quad \frac{\partial \mathcal{H}}{\partial p} = \dot{x}, \quad \frac{\partial \mathcal{H}}{\partial x} = -\dot{p} \tag{J.548}$$

are inveriant under the transformation $t \rightarrow -t$, because the canonical momentum transforms as

$$p = \frac{\partial \mathcal{L}}{\partial \dot{x}} \rightarrow -p \tag{J.549}$$

as a consequence of the sign change of $\dot{x}$, and keeping in mind that the time-derivative brings in another minus sign. While this is fundamentally true for any Hamiltonian system and while reversibility of the microscopic world is certainly given, observing reversible processes become very unlikely in the macroscopic world, where the system moves towards increasing its entropy in irreversible processes.

Coming back to the go-to example of the harmonic oscillator with spring constant k and invoking equipartition between potential and thermal energy

$$\frac{k}{2}\langle x^2\rangle = \frac{1}{2}k_\mathrm{B}\mathrm{T}, \quad \rightarrow \quad \langle x^2\rangle = \frac{k_\mathrm{B}\mathrm{T}}{k} \tag{J.550}$$

one can compute a typical amplitude for a fluctuation amounting to the thermal energy $k_\mathrm{B}\mathrm{T}$. The distribution of amplitudes of an ensemble of harmonic oscillators in thermal equilibrium is then given by the entropy, $\mathrm{S}(x) = k_\mathrm{B}\mathrm{T}\ln p(x)$ and comes out as being Gaussian distributed in the amplitude x (which is only the case of the harmonic oscillator, as potential energy is $\propto x^2$)

$$p(x) = \frac{\exp\left(\frac{\mathrm{S}}{k_\mathrm{B}}\right)}{\int \mathrm{d}x\, \exp\left(\frac{\mathrm{S}}{k_\mathrm{B}}\right)} = \sqrt{\frac{k}{2\pi k_\mathrm{B}\mathrm{T}}}\exp\left(-\frac{k}{k_\mathrm{B}\mathrm{T}}\frac{x^2}{2}\right) \tag{J.551}$$

The probability of observing large amplitudes $|x| \gg \sqrt{\frac{k_\mathrm{B}\mathrm{T}}{k}}$ in a system with a typical spring constant k in thermal equilibrium with temperatures that we are used to are very, very unlikely, as

$$k_\mathrm{B}\mathrm{T} \sim 10^{-21}\mathrm{J} \tag{J.552}$$

at room temperature. Vice versa, observing 1J of thermal energy acquired as a fluctuation out of thermal equilibrium happens at the probability of $\exp(-10^{21})$, which is an incredibly small number.

In summary, it is absolutely the case that the microscopic laws of Nature are time-reversible, but macroscopic objects are, in a probabilistic way exempt from thermal fluctuations, as the energies involved are much, much higher than typical thermal energies provided at sensible temperatures.

X MATHEMATICAL SUPPLEMENT

X.1 *Relative information entropies*

The Shannon-entropy S (or, equivalently, the Gibbs-entropy as it is called in the statistical physics community rather than in the information theory community)

$$\mathrm{S} = -\sum_i p_i \ln p_i \tag{X.553}$$

can be extended to measuring the relative entropy between two discrete distributions p_i and q_i, yielding the Kullback-Leibler divergence $\Delta\mathrm{S}$,

$$\Delta\mathrm{S} = -\sum_i p_i \ln\left(\frac{p_i}{q_i}\right) = \left\langle \ln\left(\frac{p_i}{q_i}\right)\right\rangle \tag{X.554}$$

which really plays its strength when generalised to continuous distributions $p(x)\mathrm{d}x$ and $q(x)\mathrm{d}x$,

$$\Delta\mathrm{S} = -\int \mathrm{d}x\, p(x) \ln\left(\frac{p(x)}{q(x)}\right) = -\left\langle \ln\left(\frac{p(x)}{q(x)}\right)\right\rangle \tag{X.555}$$

The relative entropy comes with a large advantage as it is invariant under transformations of the random variable in the continuous case (the problem does not arise in the discrete case, anyways). The transformation law is commonly written as $p(x)\mathrm{d}x = p(z)\mathrm{d}z$ and results from integration by substitution:

$$\int \mathrm{d}x\, p(x) = \int \mathrm{d}z\, p(x(z))\frac{\mathrm{d}x}{\mathrm{d}z} \tag{X.556}$$

with a transformation Jacobian $\mathrm{J} = \mathrm{d}x/\mathrm{d}z$. In contrast to the straightforward entropy $\mathrm{S} = -\int \mathrm{d}x\, p(x) \ln p(x)$ which transforms to $-\int \mathrm{d}z\, p(z)[\ln(p(z)) + \ln \mathrm{J}]$ and picks up an additional term depending on the transformation, this additional term cancels in the ratio $p(z)/q(z) = p(x)/q(x)$ of the relative entropy. That effectively means, that the continuum limit of the Shannon-entropy can not be defined in an invariant way:

$$\mathrm{S} = -\int \mathrm{d}x\, p(x) \ln p(x) = -\langle \ln p(x)\rangle\,. \tag{X.557}$$

Related entropy measures, that are likewise (i) positive definite and bounded by 0, (ii) additive for independent random processes and (iii) growing with the number of possible outcomes are Rényi-entropies S_α

$$\mathrm{S}_\alpha = -\frac{1}{\alpha - 1} \ln \int \mathrm{d}x\, p(x)p(x)^{\alpha-1} = -\frac{1}{\alpha - 1} \ln \left\langle p(x)^{\alpha-1}\right\rangle \tag{X.558}$$

for any constant $0 < \alpha \neq 1$. There are corresponding definitions of relative entropies $\Delta\mathrm{S}_\alpha$

$$\Delta\mathrm{S}_\alpha = -\frac{1}{\alpha - 1} \ln \int \mathrm{d}x\, p(x)\left(\frac{p(x)}{q(x)}\right)^{\alpha-1} = -\frac{1}{\alpha - 1} \ln \left\langle\left(\frac{p(x)}{q(x)}\right)^{\alpha-1}\right\rangle \tag{X.559}$$

One often runs into problems with Rényi-entropies when dealing with conditional and joint probabilities, which miraculously works with Kullback-Leibler divergences: Joint probabilities $p(x,z)$ can be generated in in a two-step random process as

$$p(x,z) = p(x|z)p(z) = p(z|x)p(x) \tag{X.560}$$

with conditional probabilities, which are obviously connected through Bayes' law. The conditional entropy $\mathrm{S}(z|x)$ of $p(x,z)$ relative to $p(x)$ is given by

$$\begin{aligned} \mathrm{S}(z|x) = -\int \mathrm{d}x \int \mathrm{d}z\, p(x,z) \ln\left(\frac{p(x,z)}{p(x)}\right) = \\ -\int \mathrm{d}x \int \mathrm{d}z\, p(x,z)\ln p(x,z) + \int \mathrm{d}x \int \mathrm{d}z\, p(x,z) \ln p(x) = \\ -\int \mathrm{d}x \int \mathrm{d}z\, p(x,z)\ln p(x,z) + \int \mathrm{d}x\, \ln p(x) \int \mathrm{d}z\, p(x,z) = \\ -\int \mathrm{d}x \int \mathrm{d}z\, p(x,z)\ln p(x,z) + \int \mathrm{d}x\, p(x) \ln p(x) = \mathrm{S}(x,z) - \mathrm{S}(x) \end{aligned} \tag{X.561}$$

because of the marginalisation $\int \mathrm{d}z\, p(x,z) = p(x)$ in the second term, such that we can write down the entropy-version of Bayes' law, making use of the symmetry of $\mathrm{S}(x,z)$:

$$\mathrm{S}(z|x) + \mathrm{S}(x) = \mathrm{S}(z,x) = \mathrm{S}(x,z) = \mathrm{S}(x|z) + \mathrm{S}(z) \tag{X.562}$$

which is impossible to formulate in terms of Rényi-entropies due to the logarithm acting on an integral.

Y PHYSICAL SUPPLEMENT

Y.1 *Gibbs-Duhem relation and intensive state variables*

When constructing the various ensembles, we started at the fully extensive $E(S, V, N)$ for the microcanonical ensemble and ended up at $J(T, V, \mu)$ for the macrocanoncial ensemble: Would there be a hypothetical ensemble with fully intensive state variables T, p and μ? The answer is no, as one would lose all information about the actual size of the system and the amount of matter involved, and the mathematically accurate formulation is the Gibbs-Duhem relation.

With the Euler-relation $U = TS - pV + \mu N$ as a starting point with the corresponding differential $dU = TdS - pdV + \mu dN$ for the case of three pairs of state variables variables we see that in every term there is always an intensive state variable associated with an extensive one. That means, that in principle one could define $8 = 2^3$ potentials, where 5 of those potentials have names

$U(S, V, N)$	energy	$dU = TdS - pdV + \mu dN$
$F(T, V, N)$	Helmholtz free energy	$dF = -SdT - pdV + \mu dN$
$G(T, p, N)$	free enthalpy (Gibbs)	$dG = -SdT + Vdp + \mu dN$
$H(S, p, N)$	enthalpy	$dH = TdS + Vdp + \mu dN$
$J(T, V, \mu)$	grand canonical potential	$dJ = -SdT - pdV - Nd\mu$

Computing the full differential of the Euler-relation $U = TS - pV + \mu N$ then suggests:

$$dU = TdS + SdT - pdV + Vdp + \mu dN + Nd\mu = TdS - pdV + \mu dN + SdT - Vdp + Nd\mu \tag{Y.563}$$

When substituting the differential $dU = TdS - pdV + \mu dN$ on arrives at a relation between the intensive state variables:

$$SdT - Vdp + Nd\mu = 0 \tag{Y.564}$$

implying that only 2 of the intensive state variables are actually independent, reducing the number of possible thermodynamic potentials for 3 pairs of state variables from 8 to 7.

Y.2 *Euler-relation*

The state variables S, V and N reflect the size of the thermodynamic system or the amount of matter present in the system, and for that purpose the energy U is necessarily a homogeneous functions of order $\lambda = 1$ in these variables: Naturally one would think that the total internal energy of the system has this property,

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N), \tag{Y.565}$$

and it is easy to imagine just λ copies of the system and to add up all extensive variables, such that the internal energy of the combined system is λ times larger, too. Differentiating this relation with respect to λ yields

$$U(S, V, N) = \frac{\partial U}{\partial(\lambda S)} \cdot \underbrace{\frac{\partial(\lambda S)}{\partial\lambda}}_{=S} + \frac{\partial U}{\partial(\lambda V)} \cdot \underbrace{\frac{\partial(\lambda V)}{\partial\lambda}}_{=V} + \frac{\partial U}{\partial(\lambda N)} \cdot \underbrace{\frac{\partial(\lambda N)}{\partial\lambda}}_{=N} \tag{Y.566}$$

Setting λ, which was arbitrary, to $\lambda = 1$ then gives the Euler-relation

$$U(S, V, N) = \underbrace{\frac{\partial U}{\partial S}}_{=T} \cdot S + \underbrace{\frac{\partial U}{\partial V}}_{=-p} \cdot V + \underbrace{\frac{\partial U}{\partial N}}_{=\mu} \cdot N = TS - pV + \mu N \tag{Y.567}$$

There is a differential version to the Euler-equation,

$$dU = TdS - pdV + \mu dN \tag{Y.568}$$

as a differential of $U(S, V, N)$, which is suggested from the first and second law of thermodynamics:

$$dU = \delta Q + \delta W = TdS - pdV + \mu dN \tag{Y.569}$$

which associate the change in thermal energy δQ with TdS and the change in mechanical energy δW with $-pdV + \mu dN$.

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INDEX

Statistical physics provides the microscopic theory for thermodynamic macroscopic properties of a physical system. These lecture notes introduce the necessary concepts of statistics and analytical mechanics for equilibrium thermodynamics with partition functions. They cover classical and quantum statistics, and treat advanced topics such as Langevin dynamics, the Fokker-Planck equation and phase transitions. Many systems like ideal classical and relativistic gases are worked out in detail.

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