

3 Classical Statistical Mechanics

As already mentioned in Chapter 1.3.2, Statistical mechanics derives predictions with the help of statistical methods based on physical, microscopical laws.

3.1 Introduction Classical Mechanics for a particle in one dimension

Newton's equation of motion is of course

$$\begin{aligned}
 m\ddot{x}(t) - f(x, t) &= 0 && \text{where } F(x, t) \text{ denotes the force} && (3.1) \\
 f(x, t) &= -\frac{\partial V(x, t)}{\partial x} && \text{acting on the particle which} && (3.2) \\
 \dot{p}(t) &= \frac{d}{dt}(m\dot{x}(t)) && \text{follows from a potential } V(x, t) && (3.3) \\
 &= \frac{d}{dt} \frac{\partial}{\partial \dot{x}} \left(\frac{m\dot{x}^2}{2} \right) && \text{according to} && (3.4) \\
 &= \frac{d}{dt} \frac{\partial}{\partial \dot{x}} T(\dot{x}) && \text{where } T \text{ denotes the kinetic} && (3.5) \\
 &&& \text{energy} &&
 \end{aligned}$$

It follows

Knowing that Newton's equation can be rewritten as

$$0 = \frac{d}{dt} \frac{\partial}{\partial \dot{x}} T(\dot{x}) + \frac{\partial V}{\partial x} \quad (3.6)$$

With this the Lagrange function and the Euler-Lagrange equation can be written.

$$\begin{aligned}
 L(x, \dot{x}) &= T(\dot{x}) - V(x) && (3.7) \\
 \frac{d}{dt} \frac{\partial L(x, \dot{x})}{\partial \dot{x}} - \frac{\partial L(x, \dot{x})}{\partial x} &= 0 && (3.8)
 \end{aligned}$$

This formalism is very useful when there is a problem with many constraints. In statistical mechanics however it is not useful. Instead the Hamiltonian approach is used. To derive Hamiltonian mechanics the Lagrangian $L(x, \dot{x})$ is replaced by the Hamiltonian $\mathbb{H}(x, p)$ via the Legendre transform.

$$\begin{aligned}
 p &= \frac{\partial L}{\partial \dot{x}} = \frac{\partial T}{\partial \dot{x}} && (3.9) \\
 \mathbb{H}(x, p, t) &\equiv \dot{x}p - L(x, \dot{x}, t) && (3.10)
 \end{aligned}$$

3 Classical Statistical Mechanics

This is called the Hamilton function. Now the total differential can be calculated.

$$d\mathbb{H} = \dot{x}dp + p d\dot{x} - \frac{\partial L}{\partial x} dx - \frac{\partial L}{\partial \dot{x}} d\dot{x} - \frac{\partial L}{\partial t} dt \quad (3.11)$$

with

$$\frac{\partial L}{\partial \dot{x}} = p \quad (3.12)$$

this becomes

$$d\mathbb{H} = \dot{x}dp - \frac{\partial L}{\partial x} dx - \frac{\partial L}{\partial t} dt \quad (3.13)$$

$$= \dot{x}dp - \dot{p}dx - \frac{\partial L}{\partial t} dt \quad (3.14)$$

$$= \frac{\partial \mathbb{H}}{\partial p} dp + \frac{\partial \mathbb{H}}{\partial x} dx + \frac{\partial \mathbb{H}}{\partial t} dt \quad (3.15)$$

$$\dot{x} = \frac{\partial \mathbb{H}}{\partial p} \quad (3.16)$$

$$-\dot{p} = \frac{\partial \mathbb{H}}{\partial x} \quad (3.17)$$

$$-\frac{\partial L}{\partial t} = \frac{\partial \mathbb{H}}{\partial t} \quad (3.18)$$

$$(3.19)$$

In general the total differential of a function $\mathbb{H}(x, p, t)$ is

$$d\mathbb{H} \equiv \frac{\partial \mathbb{H}}{\partial x} dx + \frac{\partial \mathbb{H}}{\partial p} dp + \frac{\partial \mathbb{H}}{\partial t} dt \quad (3.20)$$

By comparing the coefficients the Hamiltonian equations can be written as

$$\frac{\partial \mathbb{H}}{\partial p} \Big|_{x,t} = \dot{x}(t) \quad (3.21)$$

$$\frac{\partial \mathbb{H}}{\partial x} \Big|_{x,t} = -\dot{p}(t) \quad (3.22)$$

$$\frac{\partial \mathbb{H}}{\partial t} \Big|_{x,t} = -\frac{\partial L}{\partial t} \quad (3.23)$$

$$(3.24)$$

With these the time derivatives of the solutions of the equations of motion are determined by \mathbb{H} .

Conservation of Energy

$$\frac{d\mathbb{H}(x(t), p(t), t)}{dt} = \underbrace{\frac{\partial \mathbb{H}}{\partial x} \frac{dx(t)}{dt}}_{\text{chain rule}} + \frac{\partial \mathbb{H}}{\partial p} \frac{dp(t)}{dt} + \frac{\partial \mathbb{H}}{\partial t} \quad (3.25)$$

$$= -\dot{p}(t)\dot{x}(t) + \dot{x}(t)\dot{p}(t) + \frac{\partial \mathbb{H}}{\partial t} \quad (3.26)$$

$$(3.27)$$

So the total time derivative of \mathbb{H} is the partial time derivative of \mathbb{H} .

$$\frac{\partial \mathbb{H}}{\partial x} = \frac{d\mathbb{H}}{dx} \quad (3.28)$$

If $\mathbb{H}(x, p, t) = \mathbb{H}(x, p)$ is not explicitly dependent on time, then \mathbb{H} is constant in time. \mathbb{H} is a constant of motion. But what information does \mathbb{H} hold?

$$\mathbb{H} = \dot{x}p - L \quad (3.29)$$

$$= 2T - (T - V) \quad (3.30)$$

$$= T + V \quad (3.31)$$

So \mathbb{H} is the total energy of the system, which is conserved.

3.2 Liouville Equation and Theorem

A gas of N atoms ^{is} specified by $3N$ spatial coordinates q_1, \dots, q_{3N} and $3N$ momentum coordinates p_1, \dots, p_{3N} . The $6N$ dimensional coordinate space is called phase space (sometimes also referred to as Γ space). A point in phase space completely specifies the system. This is called a micro state of the system, which moves according to the Hamilton equations

$$\dot{q}_i(t) = \frac{\partial \mathbb{H}(q^{3N}, p^{3N})}{\partial p_i} \quad (3.32)$$

$$\dot{p}_i(t) = -\frac{\partial \mathbb{H}(q^{3N}, p^{3N})}{\partial q_i} \quad (3.33)$$

is infleb

$$(3.34)$$

Here $i \in \mathbb{N}$. This yields $6N$ equations. \mathbb{H} does not depend on t, \dot{p}_i, \dots . This uniquely determines $q_{3N}(t)$ and $p_{3N}(t)$ for all times t . The total energy is conserved.

$$\frac{d\mathbb{H}}{dt} = \frac{\partial \mathbb{H}}{\partial t} = 0 \quad (3.35)$$

3 Classical Statistical Mechanics

make progress

Since $q_{3N}(t)$ and $p_{3N}(t)$ are unique, their trajectories must not cross. Because if they would, then at the crossing point there would be two different derivatives and the trajectory would not know what to do. The trajectories are closed or never cross. In statistical mechanics following the $6N$ dimensional coordinates is not possible because there is just too much information. Many points in phase space are interchangeable or equivalent (via permutation) that may lead to similar macroscopic properties such as temperature, pressure and others. To solve this a probabilistic description is necessary (Gibbs around 1960). Now as p is used for momentum every point in phase space has probability $\rho(q_{3N}, p_{3N}, t)$ which can be normalised as

$$\int_{q_{3N}, p_{3N}} \rho(q_{3N}, p_{3N}, t) = 1 \quad (3.36)$$

So the expectation value of any observable like the pressure or energy $A(q_{3N}, p_{3N})$ can be calculated *by*

$$\langle A \rangle = \int d^{3N}q d^{3N}p A(q_{3N}, p_{3N}) \rho(q_{3N}, p_{3N}, t) \quad (3.37)$$

$$= \langle A(t) \rangle \quad (3.38)$$

Since a state does not disappear,

A distribution $\rho(q_{3N}, p_{3N}, t)$ defines an ensemble. A micro state, dependent on q_{3N} and p_{3N} with a certain probability $\rho(q_{3N}, p_{3N}, t)$ at time t moves according to the Hamilton equation. It must obey a conservation law. Now Ω be a fixed volume in phase space. The change in probability ρ integrated over Ω is balanced by fluxes of probability through the surface $S(\Omega)$ of Ω .

$$-\frac{d}{dt} \int_{\Omega} d^{3N}q d^{3N}p \rho(q_{3N}, p_{3N}, t) = \int_{S(\Omega)} dS \vec{n}(s) \cdot \vec{v}(S) \rho(S, t) \quad (3.39)$$

$$\vec{v} = (\dot{q}_1, \dots, \dot{q}_{3N}, \dot{p}_1, \dots, \dot{p}_{3N}) \quad (3.40)$$

Here $\vec{v}(s)$ is the six-dimensional velocity in phase space. Using Gauß' theorem this can be written as

$$-\int_{\Omega} d^{3N}q d^{3N}p \frac{\partial}{\partial t} \rho(q_{3N}, p_{3N}, t) = \int_{\Omega} d^{3N}q d^{3N}p \vec{\nabla} \cdot (\vec{v}(q_{3N}, p_{3N}) \rho(q_{3N}, p_{3N}, t)) \quad (3.41)$$

$$\int_{\Omega} d^{3N}q d^{3N}p \left(\frac{\partial}{\partial t} \rho(q_{3N}, p_{3N}, t) + \vec{\nabla} \cdot (\vec{v}(q_{3N}, p_{3N}) \rho(q_{3N}, p_{3N}, t)) \right) = 0 \quad (3.42)$$

define $\vec{\nabla}$!

Since Ω is fixed, but arbitrary, the integrand must vanish.

$$-\frac{\partial \rho}{\partial t} = \vec{\nabla} \cdot (\vec{v} \rho) \quad (3.43)$$

$$= \sum_{i=1}^{3N} \left[\frac{\partial}{\partial q_i} (\dot{q}_i(t) \rho) + \frac{\partial}{\partial p_i} (\dot{p}_i(t) \rho) \right] \quad (3.44)$$

This yields the Liouville equation, where \hat{L} is the Liouville operator. *step missing!*

$$-\frac{\partial \rho(q_{3N}, p_{3N}, t)}{\partial t} = \sum_{i=1}^{3N} \left[\dot{q}_i \frac{\partial}{\partial q_i} + \dot{p}_i \frac{\partial}{\partial p_i} \right] \rho \equiv \hat{L} \rho \quad (3.45)$$

3.3 Postulate of Equal A Priori Probability

The Liouville equation describes how ρ changes in time at a fixed position in phase space (q_{3N}, p_{3N}) . What happens if the observer moves along with the trajectory?

$$\frac{d\rho(q_{3N}(t), p_{3N}(t), t)}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial \rho}{\partial p_i} \frac{dp_i}{dt} \right) \quad (3.46)$$

$$= 0 \quad (3.47)$$

This is the Liouville theorem. The density along a trajectory does not change in time. ρ moves in phase space like an incompressible fluid.

3.3 Postulate of Equal A Priori Probability

If a trajectory visits every point in phase space compatible with energy conservation ($\mathbb{H} = \text{const.}$), then the Liouville theorem tells us that

$$\begin{cases} \rho(\vec{q}, \vec{p}, t) = \text{const.} & |U < \mathbb{H}(\vec{q}, \vec{p}) < U + \Delta \\ = 0 & \text{otherwise} \end{cases} \quad (3.48)$$

This defines the micro canonical ensemble (isolated system).

Remark

If we more generally consider an ensemble where different energies are populated with different probabilities, that is

we obtain from $\rho(\vec{q}, \vec{p}, t) = \rho(\mathbb{H}(\vec{q}, \vec{p}), t) \quad (3.49)$

then ~~this results in~~ the Liouville equation

$$-\dot{\rho}(\vec{q}, \vec{p}, t) = \sum_{i=1}^{3N} \left[\dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right] \quad (3.50)$$

$$= \sum_{i=1}^{3N} \left[\frac{\partial \mathbb{H}}{\partial p_i} \frac{\partial \rho}{\partial \mathbb{H}} \frac{\partial \mathbb{H}}{\partial q_i} - \frac{\partial \mathbb{H}}{\partial q_i} \frac{\partial \rho}{\partial \mathbb{H}} \frac{\partial \mathbb{H}}{\partial p_i} \right] \quad (3.51)$$

$$= 0 \quad (3.52)$$

So we obtain that $\rho(\mathbb{H}(\vec{q}, \vec{p})) = \rho(\mathbb{H}(\vec{q}, \vec{p})) \quad (3.53)$

which is independent of time! This ~~whole~~ statement is true for arbitrary systems for a general $\mathbb{H}(\vec{q}, \vec{p})$.

and

A distribution that depends on the Hamiltonian only and not on phase space variables directly is stationary.

0. κ,

3.4 Concepts of Entropy and Temperature

The number of all micro states in the energy range $U < \mathbb{H}(\vec{q}, \vec{p}) < U + \Delta$ is given by

$$\Gamma(U, V, N) = \int_{U < \mathbb{H} < U + \Delta} d^{3N}q d^{3N}p \quad (3.54)$$

This is the allowed volume in phase space with $\mathbb{H}(\vec{q}, \vec{p}) \approx U$. This relates to the density of states. The total number of states with the energy $\mathbb{H} < U$ is

$$\Sigma(U) = \int_{\mathbb{H} < U} d^{3N}q d^{3N}p \quad (3.55)$$

$$\Gamma(U) = \Sigma(U + \Delta) - \Sigma(U) \quad (3.56)$$

$$\approx \Sigma(U + \Delta) - \Sigma(U) \quad (3.57)$$

$$= \Delta \dot{\Sigma}(U) \quad (3.58)$$

we define the density of states as

$$\omega(U) = \lim_{\Delta \rightarrow 0} \frac{\Gamma(U)}{\Delta} \quad (3.59)$$

$$= \dot{\Sigma}(U) \quad (3.60)$$

$$\Sigma(U) = \int_{-\infty}^U dU' \omega(U') \quad (3.61)$$

~~Two coupled systems~~

3.4.1 Example with Two Compound Systems

The following two systems 1 and 2 are coupled, which means that they can exchange energy U . They can not however exchange neither particles N , nor volume V . U_1 and U_2 are not constant, but V_1, V_2, N_1 and N_2 are obviously.

Thus

Example of Two Coupled Systems

Two

A distribution that depends on the Hamiltonian and not on the space variables is stationary.

Figure 3.1

It is a compound system
 consisting of two subsystems
 which are in thermal contact
 with each other.

Figure 3.1: Compound System

The number of total states $\Gamma(U, V, N)$ is calculated by

$$\Gamma(U, V, N) = \int dU_1 \Gamma_1(U_1) \Gamma_2(U - U_1) \quad (3.62)$$

For a fixed energy U_1 the number of micro states of the total system is the product of the number of micro states of each of the subsystems. This originates from the product rule in probability calculus. But the Energy can vary, so that is why the integral over U_1 is necessary.

Definition 6. A new function $S(U)$ is introduced. Later it will be shown that this is

3 Classical Statistical Mechanics

the entropy in thermodynamics. It is calculated by the following equation.

$$\frac{S(U)}{k_B} = \ln(\Gamma(U)) \quad (3.63)$$

With this the problem can be further evaluated.

$$\frac{S(U)}{k_B} = \ln\left(\int dU_1 e^{\frac{S_1(U_1) + S_2(U - U_1)}{k_B}}\right) \quad \text{at } U_1' \quad (3.64)$$

Assuming that the integrand has a maximum, $S_1 + S_2$ has a maximum, too, as the exponential is a monotonic equation. This can be Taylor expanded.

$$S_1(U_1) + S_2(U - U_1) \approx S_1(U_1') + S_2(U - U_1') + (U_1 - U_1')(S_1'(U_1') + S_2'(U - U_1')) + \frac{1}{2}(U_1 - U_1')^2(S_1''(U_1') + S_2''(U - U_1')) + O((U - U_1')^3) \quad (3.65)$$

$$\frac{S(U)}{k_B} = \ln\left(\int dU_1 e^{\frac{S_1(U_1) + S_2(U - U_1)}{k_B}}\right) = \ln\left(\int dU_1 e^{\frac{(U_1 - U_1')(S_1'(U_1') + S_2'(U - U_1'))}{k_B}} \dots\right) \quad (3.66)$$

$$S(U) = S_1(U_1') + S_2(U - U_1') + k_B \ln\left(\sqrt{\frac{2\pi k_B}{S_1''(U_1') + S_2''(U - U_1')}}\right) \quad (3.67)$$

This is done with the assumption that $S''(U) < 0$ at the maximum, which is always true.

- Therefore
- The entropy of the total system is the sum of the entropies of the subsystems. Here the entropy $S(U)$ is extensive. So $S(U)$ is proportional to the system size. $S(U) \propto N$. Extensive variables are the mass m , the volume V and the energy U . Intensive variables on the other hand do not scale with the system's size. Examples of intensive variables are the temperature T and the pressure p .

$$S''(U) = \frac{d^2 S(U)}{dU^2} \quad (3.68)$$

$$= \frac{d^2(Ns(u))}{d(Nu)^2} \quad (3.69)$$

$$= \frac{1}{N} \frac{d^2 s(u)}{du^2} \quad (3.70)$$

Where s and u are...
 Thus the Gaussian concentration term scales logarithmically $\ln(N) \ll N$ as $N \rightarrow \infty$.
 With this equation 3.67 becomes

$$S(U) = S_1(U_1') + S_2(U - U_1') \quad (3.71)$$

This is exact in the thermodynamic limit ($N \rightarrow \infty$).

* as we will show later

- The function

$$S(U) = S_1(U'_1) + S_2(U - U'_1) \quad (3.72)$$

is maximised with respect to the free variable U_1 at the value U'_1 , the composite system automatically goes to the ~~that~~ state that maximises $S(U)$. ~~The system takes the state that maximises the total entropy~~

$$S(U) = S_1(U_1) + S(U - U_1). \quad (3.73)$$

This is so that $U_1 = U'_1$. This is the second law of thermodynamics.

- At that equilibrium $U_1 = U'_1$

$$\frac{dS_1(U'_1)}{dU'_1} = \frac{dS_2(U'_2)}{dU'_2}. \quad (3.74)$$

So per definition $\frac{dS(U)}{dU} = \frac{1}{T}$. Here T is the absolute temperature.

Definition 7. Systems in heat contact (that can exchange energy) have the same temperatures. This is the zeroth law of thermodynamics.

3.5 Canonical Ensemble

coupled to each other

Again two systems are ~~compound~~ so that they are in heat contact and can exchange energy. The figure 3.1 still holds for this case. The total number of micro states for a given energy U_1 is

$$\Gamma(U, U_1) \propto \Gamma_1(U_1)\Gamma_2(U - U_1) \quad (3.75)$$

The number of micro states of the composite system per micro state of system one is the probability of a certain micro state of system one.

$$\rho(U_1, N_1, V_1) = \frac{\Gamma(U_1, V_1, N_1)\Gamma(U - U_1, V - V_1, N - N_1)}{\Gamma(U, V, N)} \quad (3.76)$$

$$= \Gamma(U - U_1, V - V_1, N - N_1) \quad (3.77)$$

$$\rho(U_1) = e^{\frac{S(U - U_1)}{k_B}} \leftarrow S(U - U_1, V - V_1, N - N_1) \quad (3.78)$$

$$= e^{\frac{S(U)}{k_B} - \frac{U_1 S'(U)}{k_B} + \frac{U_1^2 S''(U)}{2 k_B} + \dots} \quad \text{functions as} \quad (3.79)$$

This expansion was done at $U_1 = 0$. ~~so one can safely~~ assume that $N_2 = N - N_1 \gg N_1$ so that $U - U_1 \approx U \gg U_1$. ~~Here system two takes the form of a reservoir that is big enough that none of its properties change when coupled to a small system like system one.~~ ($N_2 = N - N_1 \approx N, V_2 = V - V_1 \approx V, U_2 = U - U_1 \approx U$). With the knowledge that

$$\frac{dS(U)}{dU} = \frac{1}{T} \quad (3.80)$$

Therefore $U_1^2 \frac{d^2 S(U)}{dU^2}$ ~~it can be neglected as~~ scales like N_1^2/N and can be neglected.

is the inverse temperature of the system the Boltzmann distribution ~~can be derived~~ *has been derived*

$$\rho(U_1) \propto e^{-U_1/k_B T} = e^{-U_1/2k_B T} \quad (3.81)$$

This is of course not (yet) normalised. The Boltzmann (or canonical) distribution for a closed system that can exchange energy with the reservoir: All states are possible, even high energy states are not impossible, but they are very, very unlikely as $k_B T$ with $T = 300K$ is around $k_B \cdot 300K \approx 4 \text{ pN} \cdot \text{nm} = 4 \cdot 10^{-21} \text{ J}$.

holds

We assume a system with

3.5.1 Expectation Values and Variances in the Canonical Ensemble

The following discrete states i have the energy U_i .

that $\langle U \rangle = \sum_i U_i \rho(U_i)$ ~~$\langle U \rangle = \sum_i U_i$~~ $\langle U \rangle = \sum_i U_i \rho(U_i)$ (3.82)

$$= \frac{\sum_i U_i e^{-\frac{U_i}{k_B T}}}{\sum_i e^{-\frac{U_i}{k_B T}}} \quad (3.83)$$

$$= \frac{\sum_i U_i \rho(U_i)}{\sum_i \rho(U_i)} \quad (3.84)$$

with the definition

To save some writing in literature often $\beta = \frac{1}{k_B T}$. *we have*

$$\langle U \rangle = \frac{\sum_i U_i e^{\beta U_i}}{\sum_i e^{\beta U_i}} \quad (3.85)$$

$$= \frac{-\frac{\partial}{\partial \beta} \sum_i e^{\beta U_i}}{\sum_i e^{\beta U_i}} \quad (3.86)$$

$$= -\frac{\partial}{\partial \beta} \ln \left(\sum_i e^{\beta U_i} \right) \quad (3.87)$$

$$Z = \sum_i e^{\beta U_i} \quad (3.88)$$

$$\langle U \rangle = -\frac{\partial}{\partial \beta} \ln Z \quad (3.89)$$

Here Z is the partition function. It is the central object in statistical mechanics. It allows to calculate the expectation values, the variances and much more. The variance

of the energy

Therefore $\langle U \rangle = -\frac{\partial}{\partial \beta} \ln Z$ and $\langle U^2 \rangle = \frac{\partial^2}{\partial \beta^2} \ln Z$ and so on.

is

$$\frac{\partial^2}{\partial \beta^2} \ln(Z) = -\frac{\partial}{\partial \beta} \langle U \rangle \quad (3.90)$$

$$= -\frac{\partial}{\partial \beta} \left(\frac{\sum_i U_i e^{-\beta U_i}}{\sum_i e^{-\beta U_i}} \right) \quad (3.91)$$

$$= \frac{\sum_i U_i^2 e^{-\beta U_i}}{\sum_i U_i e^{-\beta U_i}} + \frac{\sum_i U_i e^{-\beta U_i}}{(\sum_i U_i e^{-\beta U_i})^2} \frac{\partial}{\partial \beta} \sum_i e^{-\beta U_i} \quad (3.92)$$

$$= \frac{\sum_i U_i^2 e^{-\beta U_i}}{\sum_i e^{-\beta U_i}} - \frac{(\sum_i U_i e^{-\beta U_i})^2}{(\sum_i e^{-\beta U_i})^2} \quad (3.93)$$

$$= \langle U^2 \rangle - \langle U \rangle^2 \quad (3.94)$$

$$= \frac{\partial^2 \ln Z}{\partial \beta^2} \quad (3.95)$$

This now is the variance of the energy.

3.5.2 Connection to Thermodynamics

$$-\frac{\partial}{\partial \beta} \langle U \rangle = -\frac{\partial T}{\partial \beta} \frac{\partial}{\partial U} \langle U \rangle \quad (3.96)$$

$$\frac{\partial}{\partial T} \beta = \frac{\partial}{\partial T} \frac{1}{k_B T} \quad (3.97)$$

$$= -\frac{1}{k_B T^2} \quad (3.98)$$

$$\frac{\partial}{\partial T} \langle U \rangle = \frac{\partial}{\partial T} U|_{V,N} \quad (3.99)$$

$$= C_v \quad (3.100)$$

3 Classical Statistical Mechanics

Here C_v is the (always positive) heat capacity, which describes the increase of the system's energy with temperature. It is an extensive quantity. *We conclude that*

$$\langle U^2 \rangle - \langle U \rangle^2 = -\frac{\partial}{\partial \beta} \langle U \rangle \quad (3.101)$$

$$= -\frac{\partial T}{\partial \beta} \frac{\partial}{\partial T} \langle U \rangle \quad (3.102)$$

$$= k_B T^2 C_v \quad (3.103)$$

$$\propto N \quad (3.104)$$

$$\frac{\Delta U}{U} = \frac{\sqrt{\langle (U - \langle U \rangle)^2 \rangle}}{U} \quad (3.105)$$

$$= \frac{\sqrt{k_B T^2 C_v}}{U} \quad (3.106)$$

$$= \frac{N^{\frac{1}{2}}}{N} \quad (3.107)$$

$$= \frac{1}{\sqrt{N}} \quad (3.108)$$

~~And~~ this again is the law of large numbers. The energy fluctuations around $\langle U \rangle$ are negligible as $N \rightarrow \infty$. *This means that the canonical ensemble,*

where the energy of a system can fluctuate, and the microcanonical ensemble, where the energy is fixed, are

Concept of Free Energy

Consider the

~~canonical~~ partition function $Z(T, V, N) = \sum_i e^{-\beta \mathbb{H}_i}$ with $\beta = \frac{1}{k_B T}$. Here i is the summation over all micro states. *Using the unity operator*

$$1 = \int_{-\infty}^{\infty} dU \delta(U - \mathbb{H}_i) \quad \text{we obtain} \quad (3.109)$$

$$Z = \sum_i \int_{-\infty}^{\infty} dU \delta(U - \mathbb{H}_i) e^{-\beta \mathbb{H}_i} \quad (3.110)$$

$$= \sum_i \int_{-\infty}^{\infty} dU \delta(U - \mathbb{H}_i) e^{-\beta U} \quad (3.111)$$

$$= \int_{-\infty}^{\infty} dU \sum_i \delta(U - \mathbb{H}_i) e^{-\beta U} \quad (3.112)$$

$$\equiv \int_{-\infty}^{\infty} \omega(U) e^{-\beta U} dU \quad (3.113)$$

an index that enumerates

equivalent.

$$= \sum_i \delta(U - H_i)$$

Here $\omega(U)$ is the density of states.

$$\int_{-\infty}^U dU' \omega(U') = \sum_i d(U' - H_i) \quad (3.114)$$

$$= \sum_{i, H_i < U} \int_{-\infty}^{\infty} dU' \delta(U' - H_i) \quad (3.115)$$

$$= \sum_{i, H_i < U} 1 \quad (3.116)$$

$$= \Sigma(U) \quad (3.117)$$

$\Sigma(U)$

with energy smaller than U

This now, of course is the number of states. With this

~~$$Z = \int_{-\infty}^{\infty} dU \sum_i \delta(U - H_i) e^{-\beta U} \quad (3.118)$$~~

becomes

We can write

$$Z = \int_{-\infty}^{\infty} dU e^{\ln \omega(U) - \beta U} \quad (3.119)$$

Previously $\frac{S(U)}{k_B T}$ was defined as

$$\frac{S(U)}{k_B T} = \ln \Gamma(U) \quad (3.120)$$

$$= \ln(\omega(U) \Delta) \quad (3.121)$$

$$= \underbrace{\ln(\omega(U))}_{\text{extensive}} + \underbrace{\ln \Delta}_{\text{non-extensive}} \quad (3.122)$$

With this 3.119 becomes

$$Z = \int_{-\infty}^{\infty} dU e^{-\beta[U - TS(U)]} \quad (3.124)$$

And the free energy can be written as

$$F = U - TS \quad (3.125)$$

3 Classical Statistical Mechanics

and the partition function becomes

$$Z = \int_{-\infty}^{\infty} dU \rho(U) \quad (3.126)$$

$$= \int_{-\infty}^{\infty} dU e^{-\beta F(U)}. \quad (3.127)$$

$$\left. \frac{dF(U)}{dU} \right|_{U'} = \left. \frac{d}{dU} (U - TS(U)) \right|_{U'} \quad (3.128)$$

$$= 1 - T \left. \frac{dS(U)}{dU} \right|_{U'} \quad (3.129)$$

$$= 1 - T \frac{1}{T} \quad (3.130)$$

$$= 0 \quad (3.131)$$

$$\left. \frac{d^2 F(U)}{dU^2} \right|_{U'} = -T \left. \frac{d^2 S(U)}{dU^2} \right|_{U'} \quad (3.132)$$

$$= -T \left. \frac{dT^{-1}(U)}{dU} \right|_{U'} \quad (3.133)$$

$$= \frac{1}{T} \left. \frac{dT(U)}{dU} \right|_{U'} \quad (3.134)$$

$$= \frac{1}{T} \left(\frac{dU}{dT} \right)_T^{-1} (U') \quad (3.135)$$

$$= \frac{1}{TC_v} \geq 0 \quad (3.136)$$

Some conclusions from this are:

- U' is determined by the minimum of $F(U)$.
- The most probable U' does exist since $d^2 F/dU^2|_{U'} \geq 0$.
- The variance of the energy $\langle (U - U')^2 \rangle \approx C_v \propto N$ is extensive.
- The relative deviation is $\sqrt{\langle (\frac{U}{U'} - 1)^2 \rangle} \propto \frac{1}{\sqrt{N}} \rightarrow 0$.
- ~~$\rho(U) = e^{-\beta F} = e^{-\beta(U - TS)}$~~ *
- The most probable energy results from equilibrium between minimising the energy U and maximising the entropy.

* It follows that the integral over U is dominated by the extremum of the integrand and thus $Z \approx e^{-\beta F(U')}$ and therefore $F = -k_B T \ln Z$

3.6 Application of Canonical Distribution, Maxwell-Boltzmann Distribution and the Barometric (Height) Formula

The Hamiltonian of a gas is given by

$$\mathbb{H}_{\text{tot}} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i=1}^N V(\vec{q}_i) + \sum_{i=1}^N \sum_{j=i+1}^N V_2(\vec{q}_i, \vec{q}_j) \quad (3.137)$$

The first term is the kinetic energy. The second term is the external potential (energy). The third term is the two-body-interaction, but this is neglected here. So the Hamiltonian becomes

$$\mathbb{H}_{\text{tot}} = \sum_{i=1}^N \left(\frac{\vec{p}_i^2}{2m} + V(\vec{q}_i) \right) \quad (3.138)$$

$$Z = \int_{-\infty}^{\infty} d\vec{p}_1 \dots d\vec{p}_N \int_V d\vec{q}_1 \dots \vec{q}_i q e^{-\beta \mathbb{H}_{\text{tot}}} \quad (3.139)$$

$$Z_N = \left[\int d\vec{p} e^{-\beta \frac{\vec{p}^2}{2m}} \int d\vec{q} e^{-\beta \frac{V(\vec{q})}{2m}} \right]^N \quad (3.140)$$

$$= Z_1^N \quad (3.141)$$

We see that

Here Z_1 is the single particle partition function. So the ideal many-body partition function factorises into the single-particle partition function. The kinetic energy of one gas atom is $E_{\text{kin}} = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$. For an isotropic system the expectation values of the momenta are equal: $\langle p_x^2 \rangle = \langle p_y^2 \rangle = \langle p_z^2 \rangle$. Each of them can be written as

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \int dp_x \frac{p_x^2}{2m} e^{-\beta \frac{p_x^2}{2m}} \int dp_y p_y^2 e^{-\beta \frac{p_y^2}{2m}} \int dp_z p_z^2 e^{-\beta \frac{p_z^2}{2m}} \int dp_x e^{-\beta \frac{p_x^2}{2m}} \int dp_y p_y^2 e^{-\beta \frac{p_y^2}{2m}} \int dp_z p_z^2 e^{-\beta \frac{p_z^2}{2m}} \quad (3.142)$$

$$= \frac{-\partial}{\partial \beta} \ln \left(\int dp_x \frac{p_x^2}{2m} e^{-\beta \frac{p_x^2}{2m}} \right) \quad (3.143)$$

$$= \frac{\partial}{\partial \beta} \ln Z \quad (3.144)$$

$$= \frac{-\partial}{\partial \beta} \ln \sqrt{\frac{2\pi m}{\beta}} \quad (3.145)$$

$$= \frac{\partial}{\partial \beta} \frac{1}{2} \ln \beta \quad (3.146)$$

$$= \frac{1}{2\beta} \quad (3.147)$$

$$= \frac{k_B T}{2} \quad (3.148)$$

$$= E_{\text{kin}} \quad (3.149)$$

3.6.1 Velocity-Distribution and Kinetic Energy of Gases

The kinetic energy of one coordinate is $\frac{k_B T}{2}$. This is called the equipartition theorem. Each atom has the kinetic energy of $\frac{3}{2} k_B T$

$$E_{kin} = 3 \left\langle \frac{p_x^2}{2m} \right\rangle = \frac{3}{2} k_B T \quad (3.150)$$

For N atoms this becomes

$$E_{kin} = \frac{3N}{2} k_B T \quad (3.151)$$

$$= U \quad (3.152)$$

More generally for a Hamiltonian defined by a total of f degrees of freedom and a quadratic Hamiltonian from

$$\mathbb{H} = \sum_{i=1}^f \frac{k_i}{2} x_i^2 \quad (3.153)$$

and a partition function

$$Z = \int_{-\infty}^{\infty} dx_1 \dots dx_f e^{-\beta \mathbb{H}} \quad (3.154)$$

we obtain

it results that

$$\mathbb{H} = U \quad (3.155)$$

$$= \frac{f}{2} k_B T. \quad (3.156)$$

Here the degrees of freedom can be momenta, positions, anything! The heat capacity is constant as a function of temperature.

$$C = \frac{dU}{dT} \quad (3.157)$$

$$= \frac{f k_B}{2} \quad (3.158)$$

For a monatomic gas $f = 3N$ and for a diatomic gas $f = (6 + 1)N$ (6 momenta and 1 distance coordinate). The kinetic energy of a gas atom is

$$\langle E_{kin} \rangle = \left\langle \frac{p^2}{2m} \right\rangle \quad (3.159)$$

$$= \left\langle \frac{p_x^2 + p_y^2 + p_z^2}{2m} \right\rangle \quad (3.160)$$

$$= \left\langle \frac{p_x^2}{2m} \right\rangle \quad (3.161)$$

$$= \frac{3}{2} k_B T \quad (3.162)$$

3.6 Application of Canonical Distribution, Maxwell-Boltzmann Distribution and the Barometric (Height) Fo

now we can calculate what we had only assumed in

Since $k_B T$ at $T = 300\text{ K}$ is $4 \cdot 10^{-21}\text{ J}$, the kinetic energy of a gas atom at room temperature is a very small. The velocity can be calculated by setting the energy equal to the formula for the kinetic energy.

the introduction

$$\frac{3}{2} k_B T = \left\langle \frac{mv^2}{2} \right\rangle \quad (3.163)$$

$$\langle v^2 \rangle = \frac{3 k_B T}{m} \quad (3.164)$$

$$\sqrt{\langle v^2 \rangle} = 460 \frac{m}{s} \quad (3.165)$$

So the velocity is very fast: of the order of the speed of sound.

3.6.2 Maxwell Boltzmann Distribution

The unnormalised velocity distribution of one component v_x is according to the Boltzmann distribution given by

! $P_{v_x^2}$

$$\rho v_x \propto e^{-\frac{p v_x^2 \beta}{2m}} \quad (3.166)$$

$$\propto e^{-\frac{\beta m v_x^2}{2}} \quad (3.167)$$

The expectation value of the second moment of \vec{v} is

$$\langle v^2 \rangle = \frac{\int d\vec{v} v^2 \rho(\vec{v})}{\int d\vec{v} \rho(\vec{v})} \quad (3.168)$$

$m\beta(v_x^2 + v_y^2 + v_z^2)$

$$= \frac{\int dv_x dv_y dv_z v^2 e^{-\frac{m v_x^2 + v_y^2 + v_z^2 \beta}{2}}}{\int dv_x dv_y dv_z e^{-\frac{m v_x^2 + v_y^2 + v_z^2 \beta}{2}}} \quad (3.169)$$

dv not $d\vec{v}$!

$$= \int_0^\infty d\vec{v} 4\pi v^2 v^2 e^{-\frac{m\beta v^2}{2}} \quad (3.170)$$

$$= \int_0^\infty d\vec{v} 4\pi v^2 e^{-\frac{m\beta v^2}{2}} \quad (3.171)$$

$$= \int_0^\infty d\vec{v} v^2 e^{-\frac{m\beta v^2}{2}} \quad (3.172)$$

$$\equiv \int_0^\infty d\vec{v} v^2 \rho_{MB}(\vec{v}) \quad (3.172)$$

Here $\rho_{MB}(\vec{v})$ is

denotes the Maxwell-Boltzmann velocity distribution which is given by

$$\rho_{MB}(\vec{v}) = v^2 e^{-\frac{m\beta v^2}{2}} \cdot 4\pi \left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} \quad (3.173)$$

3 Classical Statistical Mechanics

since

$$\int_0^\infty d\vec{v} v^2 e^{-\frac{m\beta v^2}{2}} = \frac{1}{2} \int_{-\infty}^\infty d\vec{v} v^2 e^{-\frac{m\beta v^2}{2}} \quad (3.174)$$

$$= -\frac{1}{2} \frac{d}{d(m\beta/2)} \int_{-\infty}^\infty d\vec{v} e^{-\frac{m\beta v^2}{2}} \quad (3.175)$$

$$= -\frac{1}{2} \frac{d}{d(m\beta/2)} \left(\frac{2\pi}{m\beta} \right)^{\frac{1}{2}} \quad (3.176)$$

$$= \frac{1}{2} \pi^{\frac{1}{2}} \frac{1}{2} \left(\frac{m\beta}{2} \right)^{\frac{3}{2}} \quad (3.177)$$

$$= \frac{\pi^{\frac{1}{2}}}{4} \left(\frac{2}{m\beta} \right)^{\frac{3}{2}} \quad (3.178)$$

$$= \frac{1}{4\pi} \left(\frac{2\pi k_B T}{m} \right)^{\frac{3}{2}} \quad (3.179)$$

The maximum of $\rho_{MB}(\vec{v})$ is at

$$\frac{d\rho_{MB}(\vec{v})}{dv^2} = 4\pi \left(\frac{m\beta}{2\pi} \right)^{\frac{3}{2}} \left(e^{-\frac{m\beta v^2}{2}} - \frac{v^2 m\beta}{2} e^{-\frac{m\beta v^2}{2}} \right) \quad (3.180)$$

$$v_{\max}^2 = \frac{2}{m\beta} \quad (3.181)$$

$$= \frac{2k_B T}{m} \quad (3.182)$$

Compared with equation (3.164) this yields

$$\frac{\langle \vec{v}^2 \rangle}{\vec{v}_{\max}^2} = \frac{3}{2} \quad (3.183)$$

So the mean and the maximum are not the same. The law of large numbers does not hold, as this only about one atom.

apply here;

the Maxwell-Boltzmann distribution only deals with a single atom,

3.6.3 Barometric Height Formula

Close to the ground of the earth the total Hamiltonian for N particles is

$$\mathbb{H}_{\text{total}} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + mgz_i \quad (3.184)$$

The height distribution of one atom is

$$\rho(z) = e^{-\beta mgz} \quad (3.185)$$

where g is the gravitational acceleration which is given by

The momentum and position distribution factorizes, so

3 Classical Statistical Mechanics

function is dependant on those $Z(T, V, N)$ *has variables* and the free energy as well $\{F(T, V, N)\}$ *as well as*

$$Z = \frac{1}{N!} \prod_{j=1}^N \left[\frac{1}{h^3} \int d^3 p_j \int_V d^3 q_j \right] e^{-\beta \sum_{i=1}^N \frac{p_i^2}{2m}} \quad (3.194)$$

$$= \frac{1}{N!} \left[\frac{1}{h^3} \int d^3 p e^{-\beta \frac{p^2}{2m}} \int_V d^3 q \right]^N \quad (3.195)$$

$$= \frac{1}{N!} \left(\frac{V}{h^3} \right)^N \left[\int_{-\infty}^{\infty} dp e^{-\beta \frac{p^2}{2m}} \right]^{3N} \quad (3.196)$$

$$= \frac{1}{N!} \left(\frac{V}{h^3} \right)^N \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} \quad (3.197)$$

$$= \frac{1}{N!} \left(\frac{V}{\lambda_t^3} \right)^N \quad (3.198)$$

$$\lambda_t = \frac{h}{\sqrt{2\pi m k_B T}} \quad (3.199)$$

Here λ_t is the de-Broglie wavelength at temperature T . *The free energy follows as*

$$F = -k_B T \ln(Z) \quad (3.200)$$

$$= k_B T N \ln \left(\frac{\lambda_t^3}{V} \right) + k_B T \ln(N!) \quad (3.201)$$

$$\approx k_B T N \left[\ln \left(\frac{N \lambda_t^3}{V} \right) - 1 \right] \quad (3.202)$$

where we used the Stirling approximation in the last step

and with that the expectation value for the height z is

$$\langle z \rangle = \frac{\int_{-0}^{\infty} z e^{-\beta mgz} dz}{\int_{-0}^{\infty} e^{-\beta mgz} dz} = -\frac{d}{d(\beta mg)} \int_{-0}^{\infty} e^{-\beta mgz} dz \quad (3.186)$$

$$= -\frac{d}{d(\beta mg)} \ln\left(\frac{1}{\beta mg}\right) \quad (3.187)$$

$$= \frac{1}{\beta mg} \quad (3.188)$$

Put in numbers for β , m , and g !

3.7 Ideal Gas in the Canonical Ensemble

$$Z = \frac{1}{N!} \prod_{j=1}^N \left[\frac{1}{N^3} \int d^3 p_j \int d^3 q_j \right] e^{-\beta \mathbb{H}(p_{3N}, q_{3N})} \quad (3.189)$$

$$Z(N, V, T) = \frac{1}{N!} \prod_{j=1}^N \left[\frac{1}{N^3} \int d^3 p_j \int d^3 q_j \right] e^{-\beta \mathbb{H}(p_{3N}, q_{3N})} \quad (3.190)$$

gas particles

This is the partition function for an ideal gas of N identical mono-atomic atom in a volume V is given by

- The pre-factor $\frac{1}{N!}$ avoids over counting of micro-states due to permutation of indices. From this follows the Gibbs paradox of non-extensive entropy.
- h is Planck's constant and has units of an action ($J s$). It makes the integral over phase space and thus Z itself unitless. For all physical observable, the value of h is not important since $F = -k_B T \ln(Z)$. and therefore h becomes an additive constant of F .
- The (inverse) pre-factor $(N!h^3)$ follows from quantum statistics.

- $\mathbb{H}(p_{3N}, q_{3N}) = \sum_{i=1}^N \frac{p_i^2}{2m}$ and no dependence on \vec{q}_i for an ideal gas and the finite volume V enters via integration boundaries.

there is

$$\int_V d^3 q_i = \int_0^L dq_i^x \int_0^L dq_i^y \int_0^L dq_i^z 1 \quad (3.191)$$

$$= L^3 \quad (3.192)$$

$$= V \quad (3.193)$$

- Clearly Z depends on the thermodynamic parameters N, T, V so the partition

while

proportional to

3.7 Ideal Gas in the Canonical Ensemble

The free energy is extensive and scales like N . Without the factorial it would be $F \propto N \ln(N)$. We now proceed to calculate other state variables from F .

$$F(N, T, V) = k_B T N \left[\ln \left(\frac{N}{V} h^3 (2\pi m k_B T)^{-\frac{3}{2}} \right) - 1 \right] \quad (3.203)$$

$$= k_B T N \left[\ln \left(\frac{N}{V} h^3 \right) - \frac{3}{2} \ln(2\pi m k_B T) - \frac{3}{2} \ln(T) - 1 \right] \quad (3.204)$$

$$-S = \frac{\partial F}{\partial T} \quad (3.205)$$

$$= \frac{F}{T} - \frac{3}{2} k_B N \quad (3.206)$$

$$S = -\frac{F}{T} + \frac{3}{2} k_B N \quad (3.207)$$

$$= -k_B N \quad (3.208)$$

$$= -k_B N \left[\ln \left(\frac{N}{V} \lambda_t^3 \right) - 1 \right] + \frac{3}{2} k_B N \quad (3.209)$$

$$= -k_B N \left[\ln \left(\frac{N \lambda_t^3}{V} \right) - \frac{5}{2} \right] \quad (3.210)$$

$$F = U - TS \quad (3.211)$$

$$U(N, T, V) = F + TS \quad (3.212)$$

$$= \frac{3}{2} N k_B T \quad (3.213)$$

$$= U(T, N) \quad (3.214)$$

we see that the internal energy of the ideal gas does not depend on the volume V .

$$-\frac{\partial F}{\partial V} = \frac{\partial}{\partial V} [k_B T N (\ln(N \lambda_t^3) - \ln(V) - 1)] = \frac{k_B T N}{V} \quad (3.215)$$

$$= \frac{k_B T N}{V} \quad (3.216)$$

$$\equiv P(T, V, N) \quad (3.217)$$

This is called the thermal equation of state of an ideal gas. (*)

$$dF = \frac{\partial F}{\partial T} |_{V, N} dT + \frac{\partial F}{\partial V} |_{T, N} dV + \frac{\partial F}{\partial N} |_{T, V} dN \quad (3.218)$$

$$= -S(T, V, N) dT - P(T, V, N) dV \quad (3.219)$$

$$dU = -S dT - P dV + T dS + S dT \quad (3.220)$$

$$dU = -P dV + T dS \quad (3.221)$$

$$= -P(V, S) dV + T(V, S) dS \quad (3.222)$$

from $U = F + TS$ we obtain

for N constant we obtain

To summarise

$$P = -\frac{\partial U}{\partial V} \quad (3.223)$$

$$T = +\frac{\partial U}{\partial S} \quad (3.224)$$

$$\frac{1}{T} = +\frac{\partial S}{\partial U} \quad (3.225)$$

(*) We can now write down the total differential of the free energy,

3.7.1 First law of Thermodynamics in Differential Form

The total differential of U corresponds to the first law of Thermodynamics (3.226)

$$dU(S, V) = TdS - PdV \quad \text{Thermodynamics (3.226)}$$

$$dU(S, V) = \Delta Q - \Delta W \quad (3.227)$$

where $\Delta W = PdV$ is the mechanical work done by the gas and $\Delta Q = TdS$ is the heat transferred to the gas.

3.8 Ideal Gas in the Microcanonical Ensemble

$$\Omega = \int_{U < \mathbb{H} < U + \Delta} d^3q_1 \dots d^3q_N d^3p_1 \dots d^3p_N \quad (3.228)$$

$$d^{3N}q d^{3N}p \quad (3.229)$$

Here Ω is the number of micro-states in the energy range $U < \mathbb{H} < U + \Delta$. So the number of micro-states with the energy $\mathbb{H} < U$ is given by

$$\Sigma = \int_{\mathbb{H} < U} d^3q_1 \dots d^3q_N d^3p_1 \dots d^3p_N \quad (3.230)$$

$$= \Sigma(U, V, N, \dots) \quad (3.231)$$

and $\frac{d\Sigma}{dU} = \omega(U) \quad (3.232)$

$$= \frac{\Omega}{\Delta} \quad (3.233)$$

For a mono atomic ideal gas of N atoms at volume V the shape of the container is not relevant. To calculate Σ a (quantum mechanical) correction factor has to be introduced.

$$\Sigma = \frac{1}{N! h^{3N}} \int_{\mathbb{H} < U} d^3q_1 \dots d^3q_N d^3p_1 \dots d^3p_N \quad (3.234)$$

lower case \vec{p} !

$$\mathbb{H} = \sum_{i=1}^N \left[\frac{\vec{p}_i^2}{2m} + V_{\text{wall}}(\vec{q}_i) \right] \quad (3.235)$$

$$V_{\text{wall}} = \begin{cases} 0 & |\vec{q}_i \in V \\ \infty & |\vec{q}_i \notin V \end{cases} \quad (3.236)$$

$$= \infty \quad (3.237)$$

*

As we will discuss later in detail, ΔQ and ΔW are not total differentials, that means that Q and W are not state functions.

3.8 Ideal Gas in the Microcanonical Ensemble

So $\mathbb{H} > 0$ does not contribute to the integral.

$$\Sigma(U) = \frac{1}{N!h^{3N}} \int_V d\vec{q}_1 \dots \int_V d\vec{q}_N \int_{\sum_{i=1}^N \frac{p_i^2}{2m} < U} d\vec{p}_1 \dots d\vec{p}_N \quad (3.238)$$

$$= \frac{V^N}{N!h^{3N}} (2m)^{\frac{3N}{2}} \int_{\sum_{i=1}^{3N} dx_i < U} dx_1 \dots dx_{3N} \quad (3.239)$$

$$x_1 = \frac{p_i}{\sqrt{2m}} \quad (3.240)$$

$$dp_1 = (2m)^{\frac{1}{2}} dx_1 \quad (3.241)$$

$$\Sigma(U) = \frac{V^N}{N!h^{3N}} (2m)^{\frac{3N}{2}} \nu_{3N}(U^{\frac{1}{2}}) \quad (3.242)$$

$$(3.243)$$

Here ν_{3N} is the volume ~~integral over~~ a $3N$ dimensional hypersphere which is $\nu_n(R) = c_n R^n$. The coefficient c_n turns out to be $c_n = \frac{\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2}+1)}$. With this the volume becomes

$$\nu_n(R) = \frac{\pi^{\frac{n}{2}}}{\Gamma(\frac{n}{2}+1)} R^n \quad (3.244)$$

The calculation is in my notes!

$$\Gamma(U) = \Delta \frac{d\Sigma}{dU} \quad (3.245)$$

$$= \left(V \left(\frac{2\pi m U}{h^2} \right)^{\frac{3N}{2}} \right) \frac{1}{N!} \frac{1}{\Gamma(\frac{3N}{2}+1)} \frac{3N \Delta}{2 U} \quad (3.246)$$

$$S = k_B \ln(\Gamma(U)) \quad (3.247)$$

$$= k_B N \left(\ln \left(V \left(\frac{2\pi m U}{h^2} \right)^{\frac{3}{2}} \right) - \ln(N!) - \ln \left(\Gamma \left(\frac{3N}{2} \right) \right) + \ln \left(\frac{\Delta}{U} \right) \right) \quad (3.248)$$

For very large systems ($N \gg 1, V \gg 1$) $N \gg \ln(N)$ and the Stirling approximation ($\ln(N!) = N \ln(N) - N$) the expression simplifies a lot.

$$S = k_B N \left(\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right) \quad (3.249)$$

show complete calculation!

So the entropy S is extensive, but only because the $\frac{1}{N!}$ factor was introduced in the beginning. With the thermal wavelength λ_t , introduced earlier, this yields

and using that $U = \frac{3}{2} N k_B T$

we can write

$$S = k_B N \left(\ln \left(\frac{V}{N} \lambda_t^{-3} \right) + \frac{5}{2} \right) \quad (3.250)$$

$$= -k_B N \left(\ln \left(\frac{N}{V} \lambda_t^3 \right) - \frac{5}{2} \right) \quad (3.251)$$

Which is the same result we derived in the canonical ensemble, see Eq xx

3.8.1 Exercise Heat capacity of a solid

A very simple model for a ~~mono atomic~~ solid is just a cube lattice with localised atoms that can be modelled a $3N$ harmonic oscillators with the same frequency ω . The Hamiltonian \mathbb{H} is given by

$$\mathbb{H} = \sum_{i=1}^N \left(\frac{p_i^2}{2m} + \frac{1}{2} m \omega^2 q_i^2 \right) \quad (3.252)$$

As the particles are distinguishable at all times, so no $\frac{1}{N!}$ is needed.

since they are localised on lattice sites,

$$Z(\beta) = \frac{1}{h^{3N}} \int_{\mathbb{H}} d\vec{q}_1 \dots d\vec{q}_N d\vec{p}_1 \dots d\vec{p}_N \quad (3.253)$$

$$= \frac{1}{h^{3N}} \left(\frac{2\pi}{\omega} \right)^{3N} \int_{\mathbb{H}} dx_1 \dots dx_{6N} \quad (3.254)$$

$$= \frac{1}{h^{3N}} \left(\frac{2\pi}{\omega} \right)^{3N} \nu_{6N}(U^{\frac{1}{2}}) \quad (3.255)$$

$$U = 3N k_B T \quad (3.256)$$

$$S = 3N k_B \left(\ln \left(\frac{2\pi U}{3h\omega N} \right) \right) \quad \text{calculate } C_V! \quad (3.257)$$

not from my lecture

3.9 Grand Canonical Ensemble

This is important

Now also the particle number can fluctuate, which is relevant for a open system, where particles can exchange with the reservoir, for example in cells, chemical reactions, etc.

Here $\mathbb{H}(p_{3N}, q_{3N}, N) \approx \mathbb{H}(p_{3N_1}, q_{3N_1}, N_1) + \mathbb{H}(p_{3N_2}, q_{3N_2}, N_2) + \text{interactions}$. The canonical partition function becomes

and $N_2 = N - N_1$

Again we consider two coupled systems and

$$Z_N(V, T) = \frac{1}{h^{3N} N!} \sum_{N_1=1}^N \frac{N!}{N_1! N_2!} \int d^{3N_1} p_1 d^{3N_1} q_1 \quad (3.258)$$

$$Z(N, V, T) = \sum_{N_1=0}^N Z_{N_1}(V_1, T) Z_{N_2}(V_2, T) \quad (3.259)$$

missing formula!

definition of S missing!

which is normalized

$$\sum_{N_1=0}^N \int d^{3N_1} p_1 d^{3N_1} q_1 \rho(p_1, q_1, N_1) = \frac{Z_1(V_1, T) Z_2(V_2, T)}{h^{3N_1} N_1!} \quad \text{wrong!} \quad (3.260)$$

Here the probability distribution is

$$\rho(p_{3N_1}, q_{3N_2}, N_1) \equiv \frac{Z_{N_2}(V_2, T) e^{-\beta \mathbb{H}(p_{3N_1}, q_{3N_1}, N_1)}}{Z_N} \frac{1}{h^{3N_1} N_1!} \quad (3.261)$$

make schematic figure!

free energy

$Z(N, V, T)$

3.9 Grand Canonical Ensemble

With the function $F(N, V, T) = -k_B T \ln(Z_N(V, T))$ follows - we obtain

$$\frac{Z_{N_2}(V_2, T)}{Z_N(V, T)} = e^{-\beta(F(N-N_1, V-V_1, T) - F(N, V, T))} \quad (3.262)$$

Now $N_1 \ll N$, which means that system 2 is a particle and volume reservoir. Now $F(N - N_1, V - V_1, T)$ can be expanded around $N_1 = 0$ and $V_1 = 0$.

$$\left. \frac{\partial F(N, V, T)}{\partial V} \right|_{N, T} = -P(N, V, T) \quad (3.263)$$

Here $\left. \frac{\partial F(N, V, T)}{\partial N} \right|_{V, T} \equiv \mu(N, V, T)$ is the chemical potential. Furthermore μ is the free energy needed to add a particle to the system.

$$F(N - N_1, V - V_1, T) \approx F(N, V, T) - N_1 \mu + V_1 P \quad (3.264)$$

$$\frac{Z_{N_2}(V_2, T)}{Z_N(V, T)} = e^{\beta N_1 \mu - \beta P V_1} \quad (3.265)$$

$$\rho(p, q, N) = \frac{e^{-\beta(PV - \mu N + \mathbb{H}(p, q))}}{N! h^{3N}} \quad (3.266)$$

With this the grand canonical partition function can be written

$$Z_\mu(V, T) \equiv \sum_{N=0}^{\infty} e^{\beta N \mu} Z_N(V, T) \quad (3.267)$$

$$= \sum_{N=0}^{\infty} e^{\beta N \mu} \int \frac{d^{3N} q d^{3N} p}{N! h^{3N}} e^{-\beta \mathbb{H}(p_{3N}, q_{3N}, N)} \quad (3.268)$$

$$= e^{\beta P V} \sum_{N=0}^{\infty} d^{3N} q d^{3N} p \rho(p, q, N) \quad (3.269)$$

$$= e^{\beta P V} \quad (3.270)$$

$$k_B T \ln(Z_\mu(V, T)) = -\Omega(\mu, V, T) \quad (3.271)$$

$$= P V \quad (3.272)$$

$$= P(\mu, V, T) V(\mu, T) \quad (3.273)$$

we have derived

the grand-canonical

equation of state

Here $\Omega(\mu, V, T)$ is the grand (canonical) potential.

3.9.1 Properties of Particles in the Grand (Canonical) Ensemble

Mean Number of Particles

from the definition of the grand-canonical partition function in

$$\langle N \rangle = \frac{\partial \ln Z_\mu}{\beta \partial \mu} \quad (3.274)$$

Eq. xx we

see that

We next calculate particle number fluctuations

The Fluctuation $\langle N^2 \rangle - \langle N \rangle^2$.

$$\frac{\partial}{\partial \mu} \frac{\partial}{\partial \beta} \ln Z_\mu(V, T) = \frac{\partial}{\partial \mu} \frac{\partial}{\partial \beta} \ln \left(\sum_{N=0}^{\infty} e^{\beta N \mu} Z_N \right) \quad (3.276)$$

$$= \frac{\partial}{\partial \mu} \frac{\sum_N N e^{\beta N \mu} Z_N}{\sum_N e^{\beta N \mu} Z_N} \quad (3.277)$$

$$= \frac{\sum_N N^2 e^{\beta N \mu} Z_N}{\sum_N e^{\beta N \mu} Z_N} - \left(\frac{\sum_N N e^{\beta N \mu} Z_N}{\sum_N e^{\beta N \mu} Z_N} \right)^2 \quad (3.278)$$

$$= \langle N^2 \rangle - \langle N \rangle^2 \quad (3.279)$$

$$= \frac{\partial}{\partial \mu} \frac{\partial}{\partial \beta} \frac{PV}{k_B T} \quad (3.280)$$

$$= \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \Big|_{V, T} \frac{PV}{k_B T} \quad (3.281)$$

$$= k_B T V \frac{\partial^2 P}{\partial \mu^2} \Big|_{T, V} \quad (3.282)$$

$$= k_B T V \frac{\partial^2 P(\mu, T, V)}{\partial \mu^2} \quad (3.283)$$

$$\propto N \quad (3.284)$$

So (as for energy fluctuations in the canonical ensemble) the relative particle number deviations from the mean number are $\frac{\sqrt{\langle N^2 \rangle - \langle N \rangle^2}}{\langle N \rangle} \propto N^{-1/2}$. This tends to 0 as $N \rightarrow \infty$. This means that there are no particle fluctuations as N becomes large and thus $\langle N \rangle = N' = N$ for large systems.

where N' denotes the most probable particle number.

Conclusions

The important conclusion from this is that the grand canonical ensemble, the canonical ensemble and the micro canonical ensemble are equal. Therefore the grand canonical partition function $Z_\mu(V, T)$ becomes equivalent

$$Z_\mu(V, T) = \sum_{N=0}^{\infty} e^{\beta N \mu} Z_N(V, T) \quad (3.285)$$

$$\approx e^{\beta N' \mu} Z_{N'}(V, T) \quad (3.286)$$

Here N' is the most probable particle number which is of course equal to the mean. Thus the logarithm of the partition becomes

$$\ln Z_\mu(V, T) = \beta N' \mu + \ln Z_{N'} \quad (3.287)$$

$$(3.288)$$

Comments

results from the free energy via a Legendre transformation

The grand potential is $\Omega = F - \mu N$, which comes from $F = -k_B T \ln Z_{N'}$ and $\Omega = -k_B T \ln Z_\mu$.
where we used that

- The equation can be written as a function of μ, T, V or N, T, V or any other state variables and potentials.
- With $\Omega = -PV$ it follows $F = \mu N - PV$. And from $F = U - TS$ follows $U = TS + \mu N - PV$. This is a fundamental equation. All thermodynamic potentials (U, F, Ω, G) can be expressed in a bilinear form as products of extensive (S, N, V) and intensive (T, μ, P) state variables.

3.9.2 Total Differential of Ω

$$dF(T, V, N) = \mu dN - PdV - SdT \quad (3.289)$$

$$\Omega = F - \mu N \quad (3.290)$$

$$d\Omega = dF - d(\mu N) \quad (3.291)$$

$$= \mu dN - PdV - SdT - \mu dN - Nd\mu \quad (3.292)$$

$$= -PdV - SdT - Nd\mu \quad (3.293)$$

$$= d\Omega(\mu, T, V) \quad (3.294)$$

3.9.3 Gibbs-Duhem Equation

Since $\Omega = -PV$

$$d\Omega = -PdV - VdP \quad (3.295)$$

$$= -PdV - SdT - Nd\mu \quad (3.296)$$

With this the Gibbs Duhem equation is

$$0 = VdP - SdT - Nd\mu. \quad (3.297)$$

This is the Gibbs-Duhem equation, which is the most important relation between all intensive differentials.

3.9.4 Derivation of $\frac{\partial^2 P}{\partial \mu^2}|_{T, V}$

The free energy is $F(N, V, T) = Nf(N, V, T)$. By construction f is intensive, it can only depend on $\frac{V}{N} = v$, so $F(N, V, T) = Nf\left(\frac{V}{N}, T\right) = Nf(v, t)$, where v is the volume per

3 Classical Statistical Mechanics

particle. The chemical potential μ again is defined as

$$\mu = \frac{\partial F}{\partial N} |_{T,v} \quad (3.298)$$

$$= \frac{\partial}{\partial N} [Nf(v, T)] \quad (3.299)$$

$$= f(v, T) - v \frac{\partial f(v, T)}{\partial v} \quad (3.300)$$

$$= \mu(v, T) \quad (3.301)$$

The pressure P is

$$P = - \frac{\partial F}{\partial V} |_{T,N} \quad (3.302)$$

$$= - \frac{\partial}{\partial V} (Nf(v, T)) \quad (3.303)$$

$$= - \frac{\partial}{\partial v} f(v, T) \quad (3.304)$$

$$= P(v, T) \quad (3.305)$$

From this

$$P(v, T) = P(v(\mu, T), T) \quad (3.306)$$

$$\hat{=} P(\mu, T) \quad (3.307)$$

$$\frac{\partial P}{\partial \mu} |_{T,v} = \frac{\partial P}{\partial v} |_{T} \frac{\partial v}{\partial \mu} |_{T} \quad (3.308)$$

So with 3.301 $\frac{\partial \mu}{\partial v} |_{T}$ can be calculated.

$$\frac{\partial \mu}{\partial v} |_{T} = \frac{\partial f}{\partial v} |_{T} - \frac{\partial f}{\partial v} |_{T} - v \frac{\partial^2 f}{\partial v^2} |_{T} \quad (3.309)$$

$$= -v^2 \frac{\partial^2 f}{\partial v^2} |_{T} \quad (3.310)$$

$$\frac{\partial P}{\partial v} |_{T} = - \frac{\partial^2 f}{\partial v^2} |_{T} \quad (3.311)$$

$$\frac{\partial \mu}{\partial v} |_{T} = v \frac{\partial P}{\partial v} |_{T} \quad (3.312)$$

$$(3.313)$$

With all of this 3.308 magically becomes

$$\frac{\partial P}{\partial \mu} |_{T,v} = \frac{1}{v} \quad (3.314)$$

3.10 Ideal Gas in the Grand Canonical Ensemble

and

$$\left. \frac{\partial^2 P}{\partial \mu^2} \right|_{V,T} = \left. \frac{\partial^2 v}{\partial \mu^2} \right|_T \quad (3.315)$$

$$= -\frac{1}{v^2} \left. \frac{\partial v}{\partial \mu} \right|_T \quad (3.316)$$

$$= -\frac{1}{v^3} \left. \frac{\partial v}{\partial P} \right|_T \quad (3.317)$$

continue and
express this as isothermal

This is an important property of gases, the compressibility. It tells how much the volume of a gas changes if the pressure is changed (at constant temperature).

compressibility!

3.10 Ideal Gas in the Grand Canonical Ensemble

The grand-canonical partition function was defined as

$$\mathbb{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta N \mu} Z(N, V, T) \quad (3.318)$$

was derived as in Eq xx as

The free Energy is again $F(N, V, T) = k_B T N \ln\left(\frac{N \lambda^3}{V}\right) - k_B T N = N f(v, T)$ and the chemical potential is $\mu = \frac{\partial F}{\partial N} = k_B T \ln\left(\frac{N \lambda^3}{V}\right)$. So the partition function becomes

$$\mathbb{Z} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{V}{\lambda^3} e^{\beta \mu} \right)^N \quad (3.320)$$

$$= e^{\frac{V}{\lambda^3} e^{\beta \mu}} \quad (3.321)$$

And the grand potential Ω is

$$\Omega(\mu, V, T) = -k_B T \ln(\mathbb{Z}(\mu, V, T)) \quad (3.322)$$

$$= -k_B T \frac{V}{\lambda^3} e^{\beta \mu} \quad (3.323)$$

$$= -PV. \quad (3.324)$$

and from that follows

how?

$$-k_B T N = -PV \quad (3.325)$$

$$PV = N k_B T. \quad (3.326)$$

the ideal equation of state we calculate in Eq xx

3.10.1 Chemical Reactions

reactions

A simple example of chemical reactions are bimolecular ones. Here two atoms react to be one molecule which can split back into the two atoms again: $A + A \rightleftharpoons B$. Examples

3 Classical Statistical Mechanics

are gases like hydrogen $H + H \rightleftharpoons H_2$. Here μ_A and μ_B are the chemical potentials, V is the volume and T is the temperature. The partition function is

$$\mathbb{Z}(\mu_A, \mu_B, V, T) = \sum_{N_A=0}^{\infty} \sum_{N_B=0}^{\infty} e^{\beta N_A \mu_A} e^{\beta N_B \mu_B} Z_A(N_A, V, T) Z_B(N_B, V, T). \quad (3.327)$$

Here Z_A (and similar for Z_B) is (see Eq xx)

$$Z_A(N_A, V, T) = \frac{1}{N_A!} \left(\frac{V}{\lambda_{tA}^3} \right)^{N_A}. \quad (3.328)$$

$$\mathbb{Z} = \sum_{N_A=0}^{\infty} \frac{1}{N_A!} \left(e^{\beta \mu_A} \frac{V}{\lambda_{tA}^3} \right)^{N_A} \sum_{N_B=0}^{\infty} \frac{1}{N_B!} \left(e^{\beta \mu_B} \frac{V}{\lambda_{tB}^3} \right)^{N_B} \quad (3.329)$$

$$\mathbb{Z} = e^{e^{\beta \mu_A} \frac{V}{\lambda_{tA}^3} + e^{\beta \mu_B} \frac{V}{\lambda_{tB}^3}} \quad (3.330)$$

The expectation values of N_A and N_B are

$$\langle N_A \rangle = N_A \quad (3.331)$$

$$= \frac{1}{\beta} \frac{\partial \ln(\mathbb{Z})}{\partial \mu_A} \quad (3.332)$$

$$= e^{\beta \mu_A} \frac{V}{\lambda_{tA}^3} \langle N_B \rangle \quad (3.333)$$

$$= e^{\beta \mu_B} \frac{V}{\lambda_{tB}^3}. \quad (3.334)$$

The chemical energy of the reaction $2A \rightarrow B$ is divided by $\Delta\mu$ and given by $\Delta\mu = \mu_B - 2\mu_A$ (one B created, two A destroyed).

$$N_B = e^{\beta(\Delta\mu + 2\mu_A)} \frac{V}{\lambda_{tB}^3} \quad (3.335)$$

$$= e^{\beta \Delta\mu} \frac{V}{\lambda_{tB}^3} N_A^2 \frac{\lambda_{tA}^6}{V^6} \quad (3.336)$$

$$\frac{N_B}{V} \left(\frac{V}{N_A} \right)^2 = \frac{C_B}{C_A^2} \quad (3.337)$$

$$= e^{\beta \Delta\mu} \frac{\lambda_{tA}^6}{\lambda_{tB}^3} \quad (3.338)$$

$$\equiv K. \quad (3.339)$$

This is the law of mass action, K is the equilibrium reaction constant. The concentrations of constituents in a reaction are related by power law. The powers are given by the multiplicity in the reaction. The total or maximal concentration of A is given by C_A

3.10 Ideal Gas in the Grand Canonical Ensemble

$$+ 2 C_B = C_A^{\text{TOT}} \text{ (if } C_B = 0 \text{ then } C_A = C_A^{\text{TOT}} \text{ and if } C_A = 0 \text{ then } C_B = C_A^{\text{TOT}}/2).$$

$$\frac{C_B}{(C_A^{\text{TOT}} - 2C_B)^2} = K \quad (3.340)$$

$$\frac{C_B}{K} = (C_A^{\text{TOT}})^2 + 4(C_B)^2 - 4C_B C_A^{\text{TOT}} \quad (3.341)$$

$$0 = (C_B)^2 - C_B \left(C_A^{\text{TOT}} + \frac{1}{4K} \right) + \frac{(C_A^{\text{TOT}})^2}{4} \quad (3.342)$$

$$C_B = \frac{C_A^{\text{TOT}} + \frac{1}{4K}}{2} \pm \sqrt{\frac{(C_A^{\text{TOT}} + \frac{1}{4K})^2}{4} - \frac{(C_A^{\text{TOT}})^2}{4}} \quad (3.343)$$

Since C_B cannot be larger than $\frac{C_A^{\text{TOT}}}{2}$ the negative root is needed. *the correct one*

$$C_B = \frac{C_A^{\text{TOT}} + \frac{1}{4K}}{2} - \sqrt{\frac{1}{64K^2} + \frac{C_A^{\text{TOT}}}{8K}} \quad (3.344)$$

So this is the concentration of the ~~resulting molecule~~. *product*

Limit 1: Low Concentration

$$C_A^{\text{tot}} \ll \frac{1}{k} \quad (3.345)$$

Capital K!

$$C_B = \frac{C_A^{\text{tot}}}{2} + \frac{1}{8k} - \frac{1}{8k} (1 + 8k C_A^{\text{tot}})^{\frac{1}{2}} \quad (3.346)$$

show intermediate steps

$$\approx k (C_A^{\text{tot}})^2 \quad (3.347)$$

Limit 2: High Concentration

$$C_B \approx \frac{C_A^{\text{tot}}}{2} - \sqrt{\frac{C_A^{\text{tot}}}{8k}} \quad (3.348)$$

show intermediate steps

$$\approx \frac{C_A^{\text{tot}}}{2} - \frac{C_A^{\text{tot}}}{\sqrt{C_A^{\text{tot}} 8k}} \quad (3.349)$$

$C_A^{\text{tot}} \gg \frac{1}{k}$

So all molecules fall apart at low concentrations due to entropic effects ~~$F = U - TS$~~ .

~~$$k = e^{\frac{\Delta\mu}{k_B T}} \frac{\lambda_A^6}{\lambda_B^3} \quad (3.350)$$~~