NON-EQUILIBRIUM STATISTICAL MECHANICS

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Chapter 1

Thermostatics

1.1. Equation of state

We wish to recall the basics of thermostatics starting from the internal energy of the system $U(V, S, N)$ which we write in the differential form

$$dU = \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \tag{1.1}$$

In this equation there are all the thermodynamic informations. Writing

$$dU = -pdV + TdS + \mu dN \tag{1.2}$$

we can identify

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad -p = \left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{1.3}$$

and then get the differential form of the entropy $S(U, V, N)$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN \tag{1.4}$$

With the Legendre transformations for the internal energy we obtain the Helmholtz free energy, the Enthalpy and the Gibbs free energy respectively given by

$$dF = d(U - TS) = -pdV - SdT + \mu dN \tag{1.5}$$

$$dH = d(U + pV) = Vdp + TdS + \mu dN \tag{1.6}$$

$$dG = d(U - TS + pV) = Vdp - SdT + \mu dN \tag{1.7}$$

Because G depends only on extensive variables we can assume $G \sim N$. From the differential expression of G it follows $\partial G/\partial N = \mu$ and then one gets $G = \mu N$. Differentiating this results gives

$$dG = \mu dN + Nd\mu = Vdp - SdT + \mu dN \tag{1.8}$$

from which it follows the Gibbs-Duhem relation

$$\boxed{Nd\mu = Vdp - SdT} \tag{1.9}$$

There are also 4 additional potentials: $\Omega(T, V, \mu)$, $R(S, V, \mu)$, $J(S, p, \mu)$, $K(T, p, \mu)$. The grand potential, sometimes called the Landau free energy, is defined by

$$\Omega = U - TS - \mu N = F - \mu N = F - G = -pV \tag{1.10}$$

Starting from $U(S, V, N)$ we can generate $2^3 = 8$ potentials, which in principle can be done also from $S(U, V, N)$, $V(U, S, N)$ and $N(U, V, S)$.

Maxwell relations are conditions equating certain derivatives of state variables which follow from the exactness of the differentials of the various state functions. Taking the mixed second derivatives of (1.2) and using (1.3), we find

$$\frac{\partial^2 U}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N} = \frac{\partial^2 U}{\partial V \partial S} \tag{1.11}$$

$$\frac{\partial^2 U}{\partial S \partial N} = \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \tag{1.12}$$

$$\frac{\partial^2 U}{\partial V \partial N} = -\left(\frac{\partial p}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N} \tag{1.13}$$

In the following we consider a system with a fixed number of particles. From the previous results we have

$$\left(\frac{\partial T}{\partial V}\right)_{S} = -\left(\frac{\partial p}{\partial S}\right)_{V} \tag{1.14}$$

For a gas p, V, T are easy to measure and the functional relation is unique so that

$$p(V,T) = -\left(\frac{\partial F}{\partial V}\right)_T \tag{1.15}$$

$$V(p,T) = \left(\frac{\partial G}{\partial p}\right)_T \tag{1.16}$$

$$T(p,V) = \left(\frac{\partial H}{\partial S}\right)_p \tag{1.17}$$

Then the equation of state (1.2) follows from first derivatives of the potentials but it does not describe the thermodynamics completely. For example given $p(V,T)$ if we want to calculate $F(V,T)$ we need the expression for the entropy $S(V,T)$.

We define the response functions with the second derivatives of the thermodynamic potentials as

$$\boxed{\begin{array}{ll} \kappa_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_T = -\dfrac{1}{V}\dfrac{\partial^2 G}{\partial p^2} & \textit{isothermal compressibility} \quad (1.18) \\ \kappa_S = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial p}\right)_S = -\dfrac{1}{V}\dfrac{\partial^2 H}{\partial p^2} & \textit{adiabatic compressibility} \quad (1.19) \\ \alpha_P = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_p & \textit{thermal expansivity} \quad (1.20) \end{array}}$$

Then we can express the volume differential as function of this quantities

$$dV(p,T,N) = -V\kappa_T dp + V\alpha_P dT + \rho dN \tag{1.21}$$

where $\rho = V/N$ is the particles density.

Recall the first law as a statement of energy conservation in a differential form

$$dU = \delta Q - \delta W \tag{1.22}$$

where the work $\delta W = -pdV + \mu dN$ in this equation is considered as done by the system since it has a minus sign in front. While the second law of thermodynamics states that

$$dS \geq \frac{\delta Q}{T} \tag{1.23}$$

The heat capacity of a body is the ratio of the amount of heat absorbed by the body to the associated infinitesimal change in temperature

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{1.24}$$

$$C_p = \left(\frac{\delta Q}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{1.25}$$

1.2. Equilibrium conditions

Consider a closed system with fixed particles number which is thermally isolated (i.e. no heat exchange with the exterior). If the system is in a thermal bath with a reservoir at fixed temperature T_0 from the second law of thermodynamics

$$dS_T = dS + dS_0 \geq \frac{\delta Q}{T} = 0 \tag{1.26}$$

and also

$$dU + dU_0 = 0 \tag{1.27}$$

where the zero lower index denotes the reservoir quantities. From (1.22) it follows

$$dS_0 = \frac{\delta Q}{T_0} = \frac{dU_0}{T_0} = -\frac{dU}{T_0} \tag{1.28}$$

where δQ is the amount of heat absorbed by the reservoir from the system. Then the second law becomes

$$dS + dS_0 = dS - \frac{dU}{T_0} \geq 0 \tag{1.29}$$

From this equation it follows that the Helmholtz free energy is minimized since using the definition (1.5) we have $dF = d(U - T_0 S) \leq 0$.

Let's now consider a system divided in two equal parts. Then, being an extensive quantity, the Helmholtz free energy is $F(N, V, T) = 2F(\frac{N}{2}, \frac{V}{2}, T)$. We consider perturbation δ away from equilibrium keeping N and T fixed, and using the fact that at equilibrium F is minimized we can write

$$F\left(\frac{N}{2}, \frac{V}{2} + \delta V, T\right) + F\left(\frac{N}{2}, \frac{V}{2} - \delta V, T\right) \geq F(N, V, T) = 2F\left(\frac{N}{2}, \frac{V}{2}, T\right)$$

$$\Rightarrow \quad \left[F\left(\frac{V}{2} + \delta V\right) - F\left(\frac{V}{2}\right)\right] - \left[F\left(\frac{V}{2}\right) - F\left(\frac{V}{2} - \delta V\right)\right] \geq 0 \tag{1.30}$$

$$\Rightarrow \quad \delta V\left[F'\left(\frac{V}{2}+\frac{\delta V}{2}\right)-F'\left(\frac{V}{2}-\frac{\delta V}{2}\right)\right]=(\delta V)^2F''\left(\frac{V}{2}\right)\geq 0 \tag{1.31}$$

just by using the definition of derivative. Then we conclude that F must be a convex function

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_{N,T}=\left(\frac{\partial P}{\partial V}\right)_{N,T}=\frac{1}{V\kappa_T}\geq 0 \tag{1.32}$$

It is easy to show that the same applies to $\partial^2F/\partial N^2$ but not to $\partial^2F/\partial T^2$.

1.3. Fluctuations

In statistical mechanics a microstate is described by a point in the 6N-dimensional phase space Γ. In the microcanonical ensemble the fundamental quantity which gives the connection with the thermodynamics is the entropy defined as

$$\boxed{S(U,V,N)=k_B\ln\Omega(U,V,N)} \tag{1.33}$$

where $\Omega=\Omega(U)$ is the density of states at a fixed energy. An interpretation of the second law of thermodynamics is that to a maximum of the entropy corresponds a maximum of Ω. In the canonical ensemble for a generic configuration of the system $\boldsymbol{x}$, the Laplace transform of the density of states is the partition function

$$Z=\int e^{-\beta H(\boldsymbol{x})}d\boldsymbol{x} \tag{1.34}$$

while the internal and the Helmholtz free energy are respectively

$$U=\langle H\rangle=\int H(\boldsymbol{x})\rho(\boldsymbol{x})d\boldsymbol{x}=\frac{\int H(\boldsymbol{x})e^{-\beta H(\boldsymbol{x})}d\boldsymbol{x}}{Z}=-\frac{\partial\ln Z}{\partial\beta} \tag{1.35}$$

$$F(V,T,N)=-k_BT\ln Z \tag{1.36}$$

Combining these expressions and using $(\partial T/\partial\beta)=-k_BT^2$ and $-(\partial F/\partial T)=S$ we can also verify that

$$\begin{aligned}\frac{\partial(\beta F)}{\partial\beta} &= F + \beta\frac{\partial F}{\partial\beta} \\ &= F + \beta\frac{\partial T}{\partial\beta}\frac{\partial F}{\partial T} \\ &= F + \beta k_B T^2 S \\ &= F + TS \\ &= U \end{aligned} \tag{1.37}$$

For the heat capacity one finds

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{\partial\beta}{\partial T}\frac{\partial U}{\partial\beta}\bigg|_{V,T} = -\frac{1}{k_B T^2}\left(\frac{\partial U}{\partial\beta}\right)_{V,N} = \frac{1}{k_B T^2}[\langle H^2\rangle - \langle H\rangle^2] \tag{1.38}$$

while for the energy fluctuations in the limit of large particles number

$$\frac{\sqrt{\langle H^2\rangle - \langle H\rangle^2}}{\langle H\rangle} = \frac{\sqrt{k_B T^2 C_V}}{U} \sim \frac{1}{\sqrt{N}} \longrightarrow 0 \tag{1.39}$$

This last result assures the equivalence of the microcanonical and canonical ensemble in the thermodynamic limit.

In the grandcanonical ensemble the number of particles is not fixed. The gran partition function and the grandpotential are defined as

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N, V, T) \tag{1.40}$$

$$\Phi(V, T, N) = -k_B T \ln\Xi \tag{1.41}$$

The averaged number of particles and the fluctuations of density are

$$\langle N\rangle = -\frac{\partial\Phi}{\partial\mu} \tag{1.42}$$

$$\langle N^2\rangle - \langle N\rangle^2 = -k_B T\left(\frac{\partial^2\Phi}{\partial\mu^2}\right)_{V,T} = k_B T\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T} \tag{1.43}$$

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{V,T} = \frac{N}{V}\left(\frac{\partial\langle N\rangle}{\partial p}\right)_{V,T} = \frac{\langle N\rangle^2}{V}\kappa_T \tag{1.44}$$

$$\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle^2} = k_B T\frac{\kappa_T}{V} \tag{1.45}$$

Now we wish to consider a k-components system where the entropy is given by a generalization of (1.4)

$$\boxed{dS = \frac{1}{T}dU + \frac{p}{T}dV - \sum_{i=1}^{k}\frac{\mu_i}{T}dN_i} \tag{1.46}$$

Also from definition (1.33) we have for the density of states

$$\Omega(U, V, \{N_k\}) \sim e^{S/k_B} \tag{1.47}$$

We consider small deviations from the maximum of Ω at $\overline{U}, \overline{V}, \{\overline{N}_k\}$. Let's introduce a $k+2$ components vector

$$\boldsymbol{\alpha} = \Big(U - \overline{U}, V - \overline{V}, \{N_k\} - \{\overline{N}_k\}\Big) \tag{1.48}$$

If we expand Ω near its maximum we can write

$$\Omega = A\exp\bigg(\frac{S(\overline{U}, \overline{V}, \{\overline{N}_k\})}{k_B} - \frac{g_{ij}}{2k_B}\alpha_i\alpha_j + \mathcal{O}(\boldsymbol{\alpha}^3)\bigg) \tag{1.49}$$

where g_{ij} is a symmetric positive defined matrix. Via the normalization condition

$$\int d\alpha_1 \int d\alpha_2 \int \cdots \int d\alpha_{k+2}\, \Omega = 1 \tag{1.50}$$

the Gaussian integral is straight forward and gives

$$A = e^{-\frac{\overline{S}}{k_B}}\left(\frac{\det \boldsymbol{g}}{(2\pi k_B)^{k+2}}\right)^{\frac{1}{2}} \tag{1.51}$$

Defining the generalized thermodynamics forces as

$$\boxed{X_i \equiv \left(\frac{\partial S(\boldsymbol{\alpha})}{\partial \alpha_i}\right)_{\alpha_i \neq \alpha_j} = -g_{ij}\alpha_j} \tag{1.52}$$

where $S(\boldsymbol{\alpha}) = S(0) - \frac{1}{2} g_{ij}\alpha_i\alpha_j$ and

$$\boxed{g_{ij} = -\left(\frac{\partial}{\partial \alpha_j}\right)_{\alpha_k \neq \alpha_j} \left(\frac{\partial}{\partial \alpha_i}\right)_{\alpha_l \neq \alpha_i} S(\boldsymbol{\alpha})} \tag{1.53}$$

we have the following relations for $i = 1 \dots k$

$$\alpha_1 = U - \overline{U} \qquad X_1 = \frac{1}{T} \tag{1.54}$$

$$\alpha_2 = V - \overline{V} \qquad X_2 = \frac{p}{T} \tag{1.55}$$

$$\alpha_{i+2} = \{N_i\} - \{\overline{N}_i\} \qquad X_{i+2} = -\frac{\mu_i}{T} \tag{1.56}$$

The forces X_i are responsible for pushing the system into the equilibrium. Let's calculate the fluctuations of the $\boldsymbol{\alpha}$ vector away from equilibrium by introducing the displacement α_i^0. Shifting the integration variables we want to evaluate

$$\begin{aligned} \langle \alpha_n \rangle &= A \prod_p \int \alpha_n \exp\left(\frac{\overline{S}}{k_B} - \frac{g_{ij}}{2k_B}(\alpha_i - \alpha_i^0)(\alpha_j - \alpha_j^0) \right) d\alpha_p \\ &= A \prod_p \int (\alpha_n + \alpha_n^0) \exp\left(\frac{\overline{S}}{k_B} - \frac{g_{ij}}{2k_B}\alpha_i\alpha_j \right) d\alpha_p \end{aligned} \tag{1.57}$$

If we now differentiate with respect to α_l^0 both sides of the equation, using the normalization condition (1.50) we get

$$\begin{aligned} \delta_{nl} &= \frac{\partial}{\partial \alpha_l^0} A \prod_p \int \alpha_n \exp\left(\frac{\overline{S}}{k_B} - \frac{g_{ij}}{2k_B}(\alpha_i - \alpha_i^0)(\alpha_j - \alpha_j^0) \right) d\alpha_p \\ &= A \prod_p \int \alpha_n \frac{g_{lj}(\alpha_j - \alpha_j^0)}{k_B} \exp\left(\frac{\overline{S}}{k_B} - \frac{g_{ij}}{2k_B}(\alpha_i - \alpha_i^0)(\alpha_j - \alpha_j^0) \right) d\alpha_p \end{aligned} \tag{1.58}$$

So for $\alpha_j^0 = 0$, using (1.52) it follows that

$$k_B \delta_{nl} = \langle \alpha_n g_{lj} \alpha_j \rangle = -\langle \alpha_n X_l \rangle \tag{1.59}$$

$$g_{mn} k_B \delta_{nl} = -g_{mn} \langle \alpha_n X_l \rangle = \langle X_m X_l \rangle = k_B g_{ml} \tag{1.60}$$

We can summarize the important results as

$$\boxed{\langle \alpha_i \alpha_j \rangle = k_B (g^{-1})_{ij}} \tag{1.61}$$

$$\boxed{\langle \alpha_i X_j \rangle = -k_B \delta_{ij}} \tag{1.62}$$

$$\boxed{\langle X_i X_j \rangle = k_B g_{ij}} \tag{1.63}$$

Now suppose we set $\Delta N = 0$ and we just examine the stability with respect to inhomogeneities in energy and volume. A general symmetric 2×2 matrix and its inverse may be written as

$$\boldsymbol{g} = \begin{pmatrix} a & b \\ b & c \end{pmatrix} \tag{1.64}$$

$$\boldsymbol{g}^{-1} = \frac{\operatorname{adj}(\boldsymbol{g})}{\det(\boldsymbol{g})} = \frac{1}{ac - b^2} \begin{pmatrix} c & -b \\ -b & a \end{pmatrix} \tag{1.65}$$

The conjugate variables elements of the matrix g_{ij} are

$$\begin{aligned} a &= -\left(\frac{\partial}{\partial U}\right)_{V,N} \left(\frac{\partial}{\partial U}\right)_{V,N} S(\boldsymbol{\alpha}) \\ &= -\left(\frac{\partial T^{-1}}{\partial U}\right)_{V,N} \\ &= -\left(\frac{\partial U}{\partial T^{-1}}\right)_{V,N}^{-1} \\ &= -\left(\frac{\partial T}{\partial T^{-1}}\right) \left(\frac{\partial U}{\partial T}\right)_{V,N}^{-1} \\ &= \frac{1}{T^2 C_V} \end{aligned} \tag{1.66}$$

$$\begin{aligned} b &= -\left(\frac{\partial}{\partial V}\right)_{U,N} \left(\frac{\partial}{\partial U}\right)_{V,N} S(\boldsymbol{\alpha}) \\ &= -\left(\frac{\partial T^{-1}}{\partial V}\right)_{U,N} \\ &= -\left(\frac{\partial T^{-1}}{\partial T}\right) \left(\frac{\partial T}{\partial V}\right)_{U,N} \\ &= \frac{1}{T^2} \left(\frac{\partial T}{\partial V}\right)_{U,N} \end{aligned} \tag{1.67}$$

To calculate the term $(\partial T/\partial V)$ we can use the differential expression for the volume

$$dV = \left(\frac{\partial V}{\partial U}\right)_{T,N} dU + \left(\frac{\partial V}{\partial T}\right)_{U,N} dT + \left(\frac{\partial V}{\partial N}\right)_{U,T} dN \tag{1.68}$$

$$\Rightarrow \quad \left(\frac{\partial U}{\partial T}\right)_{V,N} = -\frac{(\partial V/\partial T)_{U,N}}{(\partial V/\partial U)_{T,N}} \tag{1.69}$$

$$\Rightarrow \quad \left(\frac{\partial V}{\partial T}\right)_{U,N} = -\left(\frac{\partial U}{\partial T}\right)_{V,N}\left(\frac{\partial V}{\partial U}\right)_{T,N} \tag{1.70}$$

But from equations (1.2), (1.14) and (1.21) we know that

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_{T,N} &= -p + T\left(\frac{\partial S}{\partial V}\right)_{T,N} \\ &= -p + T\left(\frac{\partial p}{\partial T}\right)_{V,N} \\ &= -p + T\frac{\alpha_P}{\kappa_T} \end{aligned} \tag{1.71}$$

and using (1.69), equation(1.70) becomes

$$\left(\frac{\partial V}{\partial T}\right)_{U,N} = \frac{C_V}{p - T\frac{\alpha_P}{\kappa_T}} \tag{1.72}$$

Substituting in (1.67) gives

$$b = \frac{p - T\frac{\alpha_P}{\kappa_T}}{C_V T^2} \tag{1.73}$$

For the last conjugate variable we use (1.4) and obtain

$$\begin{aligned} c &= -\left(\frac{\partial}{\partial V}\right)_{U,N}\left(\frac{\partial}{\partial V}\right)_{U,N} S(\boldsymbol{\alpha}) \\ &= -\left(\frac{\partial (p/T)}{\partial V}\right)_{U,N} \\ &= -p\left(\frac{\partial T^{-1}}{\partial V}\right)_{U,N} - \frac{1}{T}\left(\frac{\partial p}{\partial V}\right)_{U,N} \end{aligned} \tag{1.74}$$

In our case N is constant and we can reformulate (1.2) and (1.21) as

$$dU = C_V dT + \left(T\frac{\alpha_P}{\kappa_T} - p\right)dV \quad \Rightarrow \quad dT = \frac{1}{\alpha_P V}dV + \frac{\kappa_T}{\alpha_P}dP \tag{1.75}$$

$$dV = -V\kappa_T dp + V\alpha_P dT \tag{1.76}$$

from which it follows

$$dU = \frac{C_V\kappa_T}{\alpha_P}dp + \left(T\frac{\alpha_P}{\kappa_T} - p + \frac{C_V}{\alpha_P V}\right)dV \tag{1.77}$$

$$\left(\frac{\partial p}{\partial V}\right)_{U,N} = -\left(T\frac{\alpha_P}{\kappa_T} - p + \frac{C_V}{\alpha_P V}\right)\frac{\alpha_P}{\kappa_T C_V} \tag{1.78}$$

$$\begin{aligned}\left(\frac{\partial (p/T)}{\partial V}\right)_{U,N} &= \frac{p}{C_V T^2}\left(T\frac{\alpha_P}{\kappa_T} - p\right) - \left(T\frac{\alpha_P}{\kappa_T} - p + \frac{C_V}{\alpha_P V}\right)\frac{\alpha_P}{T\kappa_T C_V} \\ &= -\frac{1}{\kappa_T V T} - \left(p - \frac{\alpha_P T}{\kappa_T}\right)^2 \frac{1}{C_V T^2}\end{aligned} \tag{1.79}$$

If we define now from (1.65) the inverse element of the matrix as

$$\boldsymbol{g}^{-1} \equiv \begin{pmatrix} a' & b' \\ b' & c' \end{pmatrix} \tag{1.80}$$

we have

$$a' = \left(p - \frac{\alpha_P T}{\kappa_T}\right)^2 \kappa_T V T + C_V T^2 \tag{1.81}$$

$$b' = \kappa_T V T \left(T\frac{\alpha_P}{\kappa_T} - p\right) \tag{1.82}$$

$$c' = \kappa_T V T \tag{1.83}$$

The first term in the a' component comes in because of the coupling of the volume fluctuations that we have in real thermodynamics systems while the second term, proportional to the square of the temperature, is what we usually have in standard thermodynamics. We see that the fluctuations are coupled

$$\left\langle (U - \overline{U})^2 \right\rangle = k_B\left[\left(p - \frac{\alpha_P T}{\kappa_T}\right)^2 \kappa_T V T + C_V T^2\right] \tag{1.84}$$

$$\left\langle (V - \overline{V})^2 \right\rangle = k_B \kappa_T V T \tag{1.85}$$

$$\left\langle (U - \overline{U})(V - \overline{V}) \right\rangle = k_B \kappa_T V T \left(T\frac{\alpha_P}{\kappa_T} - p\right) \tag{1.86}$$

1.4. Systematic expansion

We can expand the entropy near its maximum $\overline{S} = S(\alpha_i = \overline{\alpha}_i)$, where the first derivative vanishes, as

$$S = \overline{S} - \frac{1}{2}\alpha_i\alpha_j g_{ij} - \frac{1}{6}\alpha_i\alpha_j\alpha_k g_{ijk} + \dots \tag{1.87}$$

where

$$g_{ij} \sim \frac{1}{N}, \quad g_{ijk} = -\frac{\partial^3 S}{\partial U \partial V \partial N} \sim \frac{1}{N^2} \tag{1.88}$$

which follows from the results just found in the previous section for the matrix elements a, b and c. Here S can be considered as an action that gather fluctuations away from $\overline{S}$. Since S is extensive also $\overline{S} \sim N$ and $\alpha_i\alpha_j g_{ij} \sim N$. After an action rescaling the entropy (1.87) can be written as

$$S = N\left(\widetilde{S} - \frac{1}{2}\widetilde{\alpha}_i\widetilde{\alpha}_j\widetilde{g}_{ij} - \frac{1}{6}\widetilde{\alpha}_i\widetilde{\alpha}_j\widetilde{\alpha}_k\widetilde{g}_{ijk} + \dots\right) \tag{1.89}$$

where

$$\widetilde{\alpha}_i = \frac{\alpha_i}{N} \tag{1.90}$$

$$\widetilde{g}_{ij} = N g_{ij} \tag{1.91}$$

$$\widetilde{g}_{ijk} = N^2 g_{ijk} \tag{1.92}$$

For the fluctuations of the rescaled variables $\widetilde{\alpha}$ we have

$$\left\langle \widetilde{\alpha}^2 \right\rangle = \frac{\displaystyle\int \widetilde{\alpha}^2 \exp\left\{ N\left(\widetilde{S} - \tfrac{1}{2}\widetilde{\alpha}^2\widetilde{g}_2 - \tfrac{1}{6}\widetilde{\alpha}^3\widetilde{g}_3 + \dots \right)\right\} d\widetilde{\alpha}}{\displaystyle\int \exp\left\{ N\left(\widetilde{S} - \tfrac{1}{2}\widetilde{\alpha}^2\widetilde{g}_2 - \tfrac{1}{6}\widetilde{\alpha}^3\widetilde{g}_3 + \dots \right)\right\} d\widetilde{\alpha}} \tag{1.93}$$

Rescaling back the expectation value with $\sqrt{N}\widetilde{\alpha} = \alpha'$ we get

$$\left\langle \widetilde{\alpha}^2 \right\rangle = \frac{\displaystyle\int \tfrac{\alpha'^2}{N} \exp\left\{ - \tfrac{1}{2}\alpha'^2\widetilde{g}_2 - \tfrac{1}{6}\tfrac{\alpha'^3}{\sqrt{N}}\widetilde{g}_3 + \dots \right\} d\alpha'}{\displaystyle\int \exp\left\{ - \tfrac{1}{2}\alpha'^2\widetilde{g}_2 - \tfrac{1}{6}\tfrac{\alpha'^3}{\sqrt{N}}\widetilde{g}_3 + \dots \right\} d\alpha'} = \frac{1}{N}\left\langle \alpha'^2 \right\rangle \tag{1.94}$$

and

$$\left\langle \alpha'^2 \right\rangle = \frac{\displaystyle\int \alpha'^2 \exp\left\{ -\tfrac{1}{2}\alpha'^2 \widetilde{g}_2 - \tfrac{1}{6}\tfrac{\alpha'^3}{\sqrt{N}}\widetilde{g}_3 + \dots \right\} d\alpha'}{\displaystyle\int \exp\left\{ -\tfrac{1}{2}\alpha'^2 \widetilde{g}_2 - \tfrac{1}{6}\tfrac{\alpha'^3}{\sqrt{N}}\widetilde{g}_3 + \dots \right\} d\alpha'} = \widetilde{g}_2^{-1} + \mathcal{O}(\frac{1}{N}) \tag{1.95}$$

so that

$$\left\langle \alpha'^2 \right\rangle = N \left\langle \widetilde{\alpha}^2 \right\rangle = \frac{1}{N} \left\langle \alpha^2 \right\rangle = \widetilde{g}_2^{-1} \tag{1.96}$$

From (1.88) and (1.91) we can finally states that the fluctuations are extensive

$$\left\langle \alpha^2 \right\rangle = N \, \widetilde{g}_2^{-1} \tag{1.97}$$

In analogy with this derivation if we look at energy-particles coupling where $\Delta V = 0$, we find for a general symmetric 2×2 matrix the conjugate variables

$$a = -\left(\frac{\partial}{\partial U}\right)\left(\frac{\partial}{\partial U}\right)_{V,N} S(\boldsymbol{\alpha}) = \frac{1}{C_V T^2} \tag{1.98}$$

$$b = -\left(\frac{\partial}{\partial N}\right)_{V,U}\left(\frac{\partial}{\partial U}\right)_{V,N} S(\boldsymbol{\alpha}) = -\left(\frac{\partial T^{-1}}{\partial N}\right)_{V,U} = \frac{1}{T^2}\left(\frac{\partial T}{\partial N}\right)_{V,U} \tag{1.99}$$

To calculate $(\partial T/\partial N)$ we use that the internal energy is an extensive quantity

$$U(V,T,N) = N \; u(T, V/N) = N \; u(T,v) \tag{1.100}$$

$$\begin{aligned} \Rightarrow \quad \left(\frac{\partial U}{\partial N}\right)_{V,T} &= u + N\left(\frac{\partial u}{\partial v}\right)\left(\frac{\partial v}{\partial N}\right)_T \\ &= u - \frac{V}{N}\left(\frac{\partial u}{\partial v}\right)_T \\ &= u - v\left(\frac{\partial u}{\partial v}\right)_T \end{aligned} \tag{1.101}$$

The differential form of the internal energy $U(V,T,N)$ becomes

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial V}\right)_{T,N} dV + \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial N}\right)_{T,V} dN \\ &= \left(\frac{\partial u}{\partial v}\right)_T dV + N\left(\frac{\partial u}{\partial T}\right)_V dT + \left[u - v\left(\frac{\partial u}{\partial v}\right)\right]_T dN \\ &= \left(T\frac{\alpha_P}{\kappa_T} - p\right) dV + C_V dT + \frac{1}{N}\left(U + pV - \frac{\alpha_P TV}{\kappa_T}\right) dN \end{aligned} \tag{1.102}$$

where in the last derivation we have used (1.71). From this it follows

$$\left(\frac{\partial T}{\partial N}\right)_{V,U} = \frac{1}{NC_V}\left(\frac{\alpha_P TV}{\kappa_T} - U - pV\right) \tag{1.103}$$

$$\Rightarrow \quad b = \frac{1}{NT^2 C_V}\left(\frac{\alpha_P TV}{\kappa_T} - U - pV\right) \tag{1.104}$$

For the last conjugate variable we have to evaluate

$$c = -\left(\frac{\partial}{\partial N}\right)_{V,U}\left(\frac{\partial}{\partial N}\right)_{V,U} S(\alpha) = \left(\frac{\partial}{\partial N}\right)_{V,U}\frac{\mu}{T} \tag{1.105}$$

Using the Gibbs-Duhem relation (1.9) and equation (1.21) we can write

$$N d\mu = V dp - S dT = V\left(-\frac{dV}{V\kappa_T} + \frac{\alpha_P}{\kappa_T} dT + \frac{dN}{N\kappa_T}\right) - S dT \tag{1.106}$$

and inserting (1.102) in the previous equation and using (1.103) one gets after few manipulations

$$c = \frac{\left(U + pV - \frac{\alpha_P TV}{\kappa_T}\right)^2}{C_V N^2 T^2} + \frac{V}{N^2 \kappa_T T} \tag{1.107}$$

Finally we can express the fluctuations in particles number and temperature. With the same methods used in the previous section using (1.61), (1.63), (1.62) and (1.65), after some derivations gives

$$\left\langle (N - \overline{N})^2 \right\rangle = \frac{k_B \kappa_T T N^2}{V} \tag{1.108}$$

$$\left\langle \left(\frac{1}{T} - \frac{1}{\overline{T}}\right)^2 \right\rangle = \frac{k_B}{C_V T^2} \tag{1.109}$$

$$\langle \Delta N \Delta T \rangle = 0 \tag{1.110}$$

Chapter 2

Balance Equations

A systematic macroscopic scheme for the description of non-equilibrium processes makes it necessary to formulate the laws of thermodynamics for systems of which the properties are continuous functions of space and time, i.e. a field, to obtain a local formulation of the law of conservation of energy. Also local momentum and mass densities may change in time so that we need local formulations of the laws of conservation of momentum and mass.

2.1. Mass conservation

We look at a k-component system described by the continuous density $\rho^i(\boldsymbol{r},t)$ with $i = 1 \dots k$ denoting the component. The density $\rho^i(\boldsymbol{r},t)$ results from a suitable local averaging over the microscopic density operator in a classical fashion and

$$\rho^i(\boldsymbol{r},t) = \sum_{j=1}^{N} m^i \delta(\boldsymbol{r} - \boldsymbol{r}^{i,j}) \tag{2.1}$$

tells us where the mass is located. The rate of change of the mass of component i within a given volume V is

$$\frac{d}{dt}\int_V \rho^i(\boldsymbol{r},t)dV = \int_V \frac{\partial}{\partial t}\rho^i(\boldsymbol{r},t)dV \tag{2.2}$$

where $\rho^i(r,t)$ is the density of the i component. This quantity is equal to the material flow of component i into the volume V through its surface S, plus the total production of i in chemical reactions which occur inside V

$$\frac{d}{dt}m = \int_V \frac{\partial \rho^i}{\partial t}dV = -\int_S \rho^i v^i_j dS_j + \sum_{l=1}^{r}\int_V \nu^{il}k^l dV \tag{2.3}$$

where the integral over the surface S is the flux of component i over the same surface and $v^i_j(r,t)$ its velocity, while $\nu^{il}k^l$ is the production of i per unit volume in the l chemical reaction for a total of r reactions. The quantity ν^{il} divided by the molecular mass of component i is proportional to the stoichiometric coefficient of i in the l reaction. The quantity $k^l(r,t)$ is the chemical reaction rate of the l reaction with dimensions kg/m^3s. As an example for the auto disintegration of water we have the two reactions

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (l=1) \tag{2.4}$$

$$H_2O + H_3O^+ \rightleftharpoons H_5O_2^+ \qquad (l=2) \tag{2.5}$$

Then we have for the stoichiometric coefficient

$$\nu^{11} = -2m_{H_2O}, \quad \nu^{21} = +m_{H_3O+}, \quad \nu^{31} = +m_{OH-} \tag{2.6}$$

$$\nu^{12} = -m_{H_2O}, \quad \nu^{22} = +m_{H_3O+}, \quad \nu^{42} = +m_{H_5O_2+} \tag{2.7}$$

where the sign is chosen to be + if the element is produced or − if it is destroyed. Since mass is conserved in each chemical reaction we have

$$\sum_{i=1}^{k} \nu^{il} = 0 \tag{2.8}$$

and since the volume V is arbitrary, using Gauss law for the integral over S in equation (2.3) gives

$$\frac{\partial}{\partial t}\rho^i = -\nabla_j \rho^i v^i_j + \sum_{l=1}^{r} \nu^{il} k^l \tag{2.9}$$

After summing over all the k components and using (2.8) we obtain the law of conservation of mass

$$\boxed{\frac{\partial \rho}{\partial t} = -\nabla_j \rho v_j} \tag{2.10}$$

with the barycentric velocity weighted over all components defined as

$$v_j = \frac{\sum_i \rho^i v^i_j}{\rho} \tag{2.11}$$

The conservation of mass (2.10) expresses the fact that the total mass is conserved, i.e. that the total mass in any volume element of the system can only change if matter flows into (or out of) the volume element. We introduce the barycentric substantial time derivative

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + v_j \nabla_j \tag{2.12}$$

and the j component of the diffusion flow current of substance i with respect to the barycentric motion

$$J_j^i = \rho^i (v_j^i - v_j) \tag{2.13}$$

From this definition it follows that for a one component system $J_j^i = 0$ and from equation (2.11) it is also

$$\sum_i J_j^i = 0 \tag{2.14}$$

With the barycentric derivative (2.12) and diffusion flow (2.13) we can write using equation (2.9)

$$\begin{aligned}
\frac{d\rho^i}{dt} &= \frac{\partial}{\partial t}\rho^i + v_j \nabla_j \rho^i \\
&= -\nabla_j \rho^i v_j^i + \sum_{l=1}^{r} \nu^{il} k^l + v_j \nabla_j \rho^i \\
&= -\nabla_j \rho^i v_j^i + \sum_{l=1}^{r} \nu^{il} k^l + v_j \nabla_j \rho^i + \nabla_j \rho^i (v_j^i - v_j) - \nabla_j J_j^i \\
&= \sum_{l=1}^{r} \nu^{il} k^l - \rho^i \nabla_j v_j - \nabla_j J_j^i
\end{aligned} \tag{2.15}$$

If we now sum over all the k components, using (2.8) and (2.14), we obtain a reformulation of the conservation of mass (2.10) with the barycentric time derivative

$$\boxed{\frac{d\rho}{dt} = -\rho \nabla_j v_j} \tag{2.16}$$

2.2. Linear momentum conservation

We define the stress vector $\boldsymbol{T}$ which acts on the surface S of the volume V with normal surface component $T_\perp = (p\hat{\boldsymbol{n}})\hat{\boldsymbol{n}}$ and tangential component $T_\parallel = p - (p\hat{\boldsymbol{n}})\hat{\boldsymbol{n}}$, where $\hat{\boldsymbol{n}}$ is a unit vector normal to the surface S. Then the equation of motion of the system, with F_i force per unit mass, can be written as

$$\int_V \rho \frac{dv_i}{dt} dV = \int_V \sum_l \rho^l F_i^l dV + \int_S T_i dS \tag{2.17}$$

In terms of the stress tensor σ_{ij} we have $T_i = \sigma_{ij} n_j$ so that using Gauss law we obtain

$$\int_S T_i dS = \int_S \sigma_{ij} n_j dS = \int_S \sigma_{ij} dS_j = \int_V \nabla_j \sigma_{ij} dV \tag{2.18}$$

Substituting this expression into the equation of motion (2.17), since the volume V of integration is arbitrary, we obtain a continuum version of Noether theorem

$$\rho \frac{dv_i}{dt} = \sum_l \rho^l F_i^l + \nabla_j \sigma_{ij} \tag{2.19}$$

Now using the definition of the barycentric derivative (2.12) we have

$$\begin{aligned} \rho \frac{dv_i}{dt} &= \rho \frac{\partial v_i}{\partial t} + \rho v_j \nabla_j v_i \\ &= \frac{\partial \rho v_i}{\partial t} - v_i \frac{\partial \rho}{\partial t} + \nabla_j \rho v_i v_j - v_i \nabla_j \rho v_j \end{aligned} \tag{2.20}$$

and since the mass is conserved by equation (2.10) the second and the last term of this last expression cancel out to give

$$\rho \frac{dv_i}{dt} = \frac{\partial \rho v_i}{\partial t} + \nabla_j (\rho v_i v_j) \tag{2.21}$$

Combining this last equation with (2.19) we finally find the balance equation for the linear momentum

$$\boxed{\frac{\partial \rho v_i}{\partial t} + \nabla_j (\rho v_i v_j - \sigma_{ij}) = \sum_l \rho^l F_i^l} \tag{2.22}$$

where on the left hand side the first term is the momentum density and the second a momentum flow with a convective plus a stress part, while the quantity on the right hand side expresses the source of momentum given by the force per mass F_i.

2.3. Angular momentum conservation

The angular momentum $\boldsymbol{L}$ is defined as

$$\boldsymbol{L} = \boldsymbol{r} \times m\boldsymbol{v} \tag{2.23}$$

or in components with the Levi-Civita tensor

$$L_i = \epsilon_{ijk} r_j m v_k \tag{2.24}$$

Multiplying equation (2.22) for $(\epsilon_{lki} r_k)$ gives

$$\epsilon_{lki} r_k \frac{\partial \rho v_i}{\partial t} + \epsilon_{lki} r_k \nabla_j (\rho v_i v_j - \sigma_{ij}) = \epsilon_{lki} r_k \sum_m \rho^m F_i^m \equiv M_l \tag{2.25}$$

where we defined M_l the mass weighted torque density. Rewriting the first term of this equation as

$$\epsilon_{lki} r_k \frac{\partial \rho v_i}{\partial t} = \frac{\partial}{\partial t}(\epsilon_{lki} r_k \rho v_i) - \rho v_i \frac{\partial}{\partial t} \epsilon_{lki} r_k \tag{2.26}$$

and since the time derivative of the Levi-Civita tensor vanish so that

$$\rho v_i \frac{\partial}{\partial t} \epsilon_{lki} r_k = \rho v_i \epsilon_{lki} v_k = \rho (v \times v)_l \equiv 0 \tag{2.27}$$

equation (2.25), using $\nabla_j r_k = \delta_{kj}$, becomes

$$\begin{aligned} \frac{\partial}{\partial t}(\epsilon_{lki} r_k \rho v_i) + \nabla_j \epsilon_{lki} r_k (\rho v_i v_j - \sigma_{ij}) &= M_l + \epsilon_{lki} (\rho v_i v_j - \sigma_{ij}) \delta_{kj} \\ &= M_l + \epsilon_{lki} (\rho v_i v_k - \sigma_{ik}) \\ &= M_l - \epsilon_{lki} \sigma_{ik} \end{aligned} \tag{2.28}$$

where in the last passage we have used again (2.27). The final result is the balance equation for angular momentum

$$\boxed{\frac{\partial}{\partial t}(\epsilon_{lki} r_k \rho v_i) + \nabla_j \epsilon_{lki} r_k (\rho v_i v_j - \sigma_{ij}) = M_l - \epsilon_{lki} \sigma_{ik}} \tag{2.29}$$

Here the first term is the angular momentum density, the second the respective flux and on the right hand side we have the torque. When the force momentum vanishes $\boldsymbol{M} = 0$ and the angular momentum is conserved, then from this last result one gets $\epsilon_{lki} \sigma_{ik} = 0$. This implies that the stress tensor is symmetric $\sigma_{ik} = \sigma_{ki}$. There are some exceptions to this last argument, for example systems where the angular momentum is also stored internally (spin angular momentum).

2.4. Energy balance equation

We start by multiplying the velocity for the linear momentum balance equation (2.22)

$$v_i \frac{\partial \rho v_i}{\partial t} + v_i \nabla_j (\rho v_i v_j - \sigma_{ij}) = \sum_l v_i \rho^l F_i^l \tag{2.30}$$

Now summing up this two identities

$$\frac{\partial}{\partial t} \rho \frac{v_i^2}{2} = v_i \frac{\partial \rho v_i}{\partial t} - \frac{v_i^2}{2} \frac{\partial \rho}{\partial t} \tag{2.31}$$

$$\nabla_j v_j \rho \frac{v_i^2}{2} = v_i \nabla_j \rho v_i v_j - \frac{v_i^2}{2} \nabla_j \rho v_j \tag{2.32}$$

simply obtained by applying the rule for derivative of a product, and using the conservation of mass (2.10), we get from (2.30) the kinetic energy balance equation

$$\boxed{\frac{\partial}{\partial t} \rho \frac{v_i^2}{2} + \nabla_j \left(\frac{v_i^2}{2} v_j \rho - v_i \sigma_{ij} \right) = \sum_l v_i \rho^l F_i^l - \sigma_{ij} \nabla_j v_i} \tag{2.33}$$

In analogy with the previous balance equations the first term is the density of kinetic energy while the second is the correspondent flux density (Poynting vector).

Now we want to consider the case of a force per mass related to a potential ψ as

$$F_i^l(r,t) = -\nabla_i \psi^l(r,t) \tag{2.34}$$

We can then write the first term on the right hand side of (2.33) as

$$\sum_l v_i \rho^l F_i^l = -\sum_l v_i \rho^l \nabla_i \psi^l = -\sum_l \nabla_i v_i \rho^l \psi^l + \sum_l \psi^l \nabla_i v_i \rho^l \tag{2.35}$$

By defining the potential energy density $\rho\psi \equiv \sum_l \rho^l \psi^l$ and using (2.13) and (2.9) we get

$$\begin{aligned} \sum_l v_i \rho^l F_i^l &= -\nabla_i v_i \rho \psi + \sum_l \psi^l \nabla_i (\rho^l v_i^l - J_i^l) \\ &= -\nabla_i v_i \rho \psi + \sum_l \psi^l \Big(-\frac{\partial}{\partial t} \rho^l + \sum_m^r \nu^{lm} k^m\Big) - \sum_l \psi^l \nabla_i J_i^l \\ &= -\nabla_i v_i \rho \psi - \frac{\partial}{\partial t} \psi \rho + \sum_l \rho^l \frac{\partial \psi^l}{\partial t} - \sum_l \psi^l \nabla_i J_i^l \end{aligned} \tag{2.36}$$

having assumed the potential energy to be conserved in the chemical reaction so that $\sum_l \psi^l \nu^{lm} = 0$. If we now insert

$$-\sum_l \psi^l \nabla_i J_i^l = -\nabla_i \sum_l \psi^l J_i^l + \sum_l J_i^l \nabla_i \psi^l = -\nabla_i \sum_l \psi^l J_i^l - \sum_l J_i^l F_i^l \tag{2.37}$$

in (2.36) and then this back into (2.33) we finally get the balance equation for the kinetic plus local potential energy

$$\boxed{\begin{aligned} &\frac{\partial}{\partial t}\left(\rho \frac{v_i^2}{2} + \rho\psi\right) + \nabla_j \left[v_j \left(\rho \frac{v_i^2}{2} + \rho\psi\right) + \sum_l \psi^l J_j^l - v_i \sigma_{ij} \right] \\ &\qquad = -\sum_l J_i^l F_i^l + \sum_l \rho^l \frac{\partial \psi^l}{\partial t} - \sigma_{ij} \nabla_j v_i \end{aligned}} \tag{2.38}$$

The first term is the kinetic plus potential energy density, while for the term between square brackets there is the convective and the non convective flux respectively. From this equation we see that the total (kinetic plus potential) energy is not conserved since there are terms different from zero on the right hand side. We need also to include the internal energy to get the balance equation for the total energy density, resulting in the concept of heat. To see this we define the internal energy density $u(r,t)$ via the total energy density

$$e(r,t) = \frac{v_i^2}{2} + \psi + u \tag{2.39}$$

is defined as conserved so that

$$\frac{d}{dt} \int_V \rho e \, dV = \int_V \frac{\partial \rho e}{\partial t} dV = -\int_S J^e dS \tag{2.40}$$

which gives using Gauss law

$$\frac{\partial \rho e}{\partial t} = -\nabla_j J_j^e \tag{2.41}$$

The internal energy $u(r,t)$ is microscopically due to the thermal motion of particles which doesn't contribute to the macroscopic velocity $v(r,t)$. For the j component of the total energy flux we add to the term between square brackets in (2.38) the internal energy and the heat flux J^q to have

$$\begin{aligned} J_j^e &= v_j \left(\rho \frac{v_i^2}{2} + \rho\psi + \rho u\right) + \sum_l \psi^l J_j^l - v_i \sigma_{ij} + J_j^q \\ &= v_j \rho e + \sum_l \psi^l J_j^l - v_i \sigma_{ij} + J_j^q \end{aligned} \tag{2.42}$$

Now (2.38) can be written with no source on the right hand side in terms of the total energy density

$$\frac{\partial}{\partial t}\left(\rho\frac{v_i^2}{2}+\rho\psi+\rho u\right)+\nabla_j\left[v_j\left(\rho\frac{v_i^2}{2}+\rho\psi+\rho u\right)+\sum_l\psi^l J_j^l - v_i\sigma_{ij}+J_j^q\right]=0 \tag{2.43}$$

And subtracting from this (2.38) we find the balance equation for the internal energy

$$\boxed{\frac{\partial}{\partial t}(\rho u)+\nabla_j(v_j\rho u+J_j^q)=\sum_l J_i^l F_i^l-\sum_l\rho^l\frac{\partial\psi^l}{\partial t}+\sigma_{ij}\nabla_j v_i} \tag{2.44}$$

From this equation we see that the internal energy density is not conserved even when the local potential energy is constant.

In the case of a liquid we can always split the stress tensor into two parts

$$\sigma_{ij}=-p\delta_{ij}+R_{ij} \tag{2.45}$$

where p is the hydrostatic pressure which is merely the pressure in a fluid at rest and R_{ij} is called the deviatoric stress that express a distortion from the mean normal stress tensor. Now looking at the left hand side of (2.44) and using the conservation of mass (2.10) and the barycentric derivative (2.12) we can write

$$\begin{aligned}\frac{\partial}{\partial t}(\rho u)+\nabla_j(v_j\rho u+J_j^q)&=\rho\frac{\partial u}{\partial t}+u\frac{\partial\rho}{\partial t}+v_j\rho\nabla_j u+u\nabla_j v_j\rho+\nabla_j J_j^q\\&=\rho\frac{du}{dt}+\nabla_j J_j^q\end{aligned} \tag{2.46}$$

and substituting in the right hand side of (2.44) the expression for the stress tensor (2.45) we obtain

$$\rho\frac{du}{dt}+\nabla_j J_j^q=\sum_l J_i^l F_i^l-\sum_l\rho^l\frac{\partial\psi^l}{\partial t}-p\nabla_i v_i+R_{ij}\nabla_j v_i \tag{2.47}$$

Now defining the heat added per unit of mass dq as

$$\rho\frac{dq}{dt}+\nabla_j J_j^q=0 \tag{2.48}$$

and substituting in (2.47) we have

$$\rho\frac{du}{dt}=\rho\frac{dq}{dt}+\sum_l J_i^l F_i^l-\sum_l\rho^l\frac{\partial\psi^l}{\partial t}-p\nabla_i v_i+R_{ij}\nabla_j v_i \tag{2.49}$$

$$\frac{du}{dt} = \frac{dq}{dt} + \frac{1}{\rho}\sum_l J_i^l F_i^l - \frac{1}{\rho}\sum_l \rho^l \frac{\partial \psi^l}{\partial t} - \frac{p}{\rho}\nabla_i v_i + \frac{R_{ij}}{\rho}\nabla_j v_i \tag{2.50}$$

Now plugging this identity

$$\frac{d}{dt}\frac{1}{\rho} = -\frac{1}{\rho^2}\frac{d\rho}{dt} \quad \Rightarrow \quad \frac{d\rho}{dt} = -\rho^2 \frac{d}{dt}\frac{1}{\rho} \tag{2.51}$$

in (2.16) gives

$$\rho \frac{d}{dt}\frac{1}{\rho} = \nabla_j v_j \tag{2.52}$$

and substituting this in (2.50) we finally find the first law of thermodynamics in the form

$$\boxed{\frac{du}{dt} = \frac{dq}{dt} + \frac{1}{\rho}\sum_l J_i^l F_i^l - \frac{1}{\rho}\sum_l \rho^l \frac{\partial \psi^l}{\partial t} - p\frac{d}{dt}\frac{1}{\rho} + \frac{R_{ij}}{\rho}\nabla_j v_i} \tag{2.53}$$

Comparing with (1.22) we note that within this derivation the infinitesimal amounts of heat supplied to the system dq/dt becomes a true differential.

2.5. Entropy balance equation

For any macroscopic system we can introduce the state variable entropy with the following properties. Its change dS can be written as the sum of two terms

$$dS = d_e S + d_i S \tag{2.54}$$

where the subscripts stand for external change (entropy supplied to the system from the surrounding) and internal change (entropy produced inside the system). From the second law of thermodynamics for reversible (equilibrium) transformations $d_i S = 0$ and for irreversible transformations $d_i S \geq 0$. On the other hand for an adiabatic insulated system with no exchange of heat and matter with the surrounding $d_e S = 0$, so that from (2.54) it follows $dS \geq 0$. For a closed system which can exchange heat with its surrounding the Carnot-Clausius theorem tells us

$$d_e S = \frac{\delta Q}{T} \tag{2.55}$$

where δQ is the supplied heat to the system by its surrounding at temperature T. Then for a closed system at the equilibrium from (2.54) it follows the second law of thermodynamics

$$dS \geq \frac{\delta Q}{T} \tag{2.56}$$

For an open system which can exchange heat and matter with the surrounding (non-equilibrium processes) the Carnot-Clausius theorem (2.55) doesn't apply and (2.56) in general is not true, while the general expression (2.54) remains valid. We define the entropy per unit mass s, the entropy flux outside the boundary $\boldsymbol{J}^s$, and the entropy production per unit volume and unit time σ as

$$S = \int_V \rho s \; dV \tag{2.57}$$

$$\frac{d_e S}{dt} = -\int_\Omega (\boldsymbol{J}^s + \rho s \boldsymbol{v}) \; d\boldsymbol{\Omega} \tag{2.58}$$

$$\frac{d_i S}{dt} = \int_V \sigma \; dV \tag{2.59}$$

Here $\rho s \boldsymbol{v}$ is the convective term which represents the entropy relative to the material moving outside the boundary $\boldsymbol{\Omega}$. We note that since (2.59) must hold for an arbitrary volume and $d_i S \geq 0$ it must be also

$$\sigma \geq 0 \tag{2.60}$$

We'll keep the notation for the entropy production always with no indices to distinguish it from the stress tensor.

Using Gauss law and (2.54) to combine the last three equations we have

$$\int_V \left(\frac{\partial}{\partial t} \rho s + \nabla_i (J_i^s + \rho s v_i) - \sigma \right) dV = 0 \tag{2.61}$$

which implies

$$\frac{\partial}{\partial t} \rho s + \nabla_i (J_i^s + \rho s v_i) = \sigma \tag{2.62}$$

Now using the conservation of mass (2.10) and the barycentric derivative (2.12)

$$\begin{aligned}\frac{\partial}{\partial t}\rho s+\nabla_i\rho s v_i &= \rho\frac{\partial s}{\partial t}+s\frac{\partial\rho}{\partial t}+s\nabla_i\rho v_i+\rho v_i\nabla_i s\\ &= \rho\frac{\partial s}{\partial t}+\rho v_i\nabla_i s\\ &= \rho\left(\frac{\partial}{\partial t}+v_i\nabla_i\right)s\\ &= \rho\frac{ds}{dt}\end{aligned}\tag{2.63}$$

and we rewrite (2.62) as

$$\rho\frac{ds}{dt}=-\nabla_i J_i^s+\sigma\tag{2.64}$$

To relate the balance equations found in the previous sections to the rate of change of entropy it's useful to define the specific quantities

Specific Quantities
These specific quantities as defined here do not depend on space any more, e.g. S does not depend on space, because it is the total entropy and it's the same for M. In principle one could talk about small volume elements large enough that thermodynamics makes sense but small enough to be regarded as points and space and redefine the specific quantities using these small volume elements. Reference: Risken

$$s=\frac{S}{M},\quad u=\frac{U}{M},\quad v=\frac{V}{M}=\frac{1}{\rho},\quad c^l=\frac{M^l}{M}=\frac{\rho^l}{\rho}\tag{2.65}$$

where M is the total mass of the system and M^l is the total mass of component l. To avoid confusion with the specific volume v for the velocity v_i we will always keep the tensor index unless otherwise specified.

The Gibbs relation of thermodynamics in equilibrium expresses the total differential of S as

$$TdS=dU+pdV-\sum_l\mu^l dM^l\tag{2.66}$$

which can be divided by $M=\sum_l M^l$ to give, using (2.65)

$$Tds=du+pdv-\sum_l\mu^l dc^l\tag{2.67}$$

where p is the equilibrium pressure and μ^l the chemical potential of component l. If we assume that even if our system is not in equilibrium within small mass elements a state of local equilibrium exists, along the trajectory we have

$$T\frac{ds}{dt} = \frac{du}{dt} + p\frac{dv}{dt} - \sum_l \mu^l \frac{dc^l}{dt} \tag{2.68}$$

where d/dt is the barycentric derivative (2.12). The hypothesis of local equilibrium made here are justified by the validity of the following conclusions. Multiplying for ρ equation (2.53) and using the definition of specific volume (2.65) and heat added per mass (2.48) we have

$$\begin{aligned}\rho\frac{du}{dt} &= \rho\frac{dq}{dt} + \sum_l J_i^l F_i^l - \sum_l \rho^l \frac{\partial \psi^l}{\partial t} - \rho p\frac{dv}{dt} + R_{ij}\nabla_j v_i \\ &= -\nabla_j J_j^q + \sum_l J_i^l F_i^l - \rho p\frac{dv}{dt} + R_{ij}\nabla_j v_i \end{aligned} \tag{2.69}$$

where in the last line we have also assumed the case $\dot{\psi} =$ of a constant potential. Now using (2.15), (2.16) and (2.65) we can write

$$\begin{aligned}\rho\frac{dc^l}{dt} &= \rho\frac{d}{dt}\frac{\rho^l}{\rho} \\ &= -\frac{\rho^l}{\rho}\frac{d\rho}{dt} + \frac{d\rho^l}{dt} \\ &= \rho^l\nabla_j v_j - \rho^l \nabla_j v_j - \nabla_j J_j^l + \sum_j^r \nu^{lj} k^j \\ &= -\nabla_j J_j^l + \sum_j^r \nu^{lj} k^j \end{aligned} \tag{2.70}$$

Multiplying (2.68) for ρ/T and using (2.69) and (2.70) we find

$$\begin{aligned}\rho\frac{ds}{dt} &= -\frac{1}{T}\nabla_j J_j^q + \frac{1}{T}\sum_l J_i^l F_i^l - \frac{1}{T}\rho p\frac{dv}{dt} + \frac{1}{T}R_{ij}\nabla_j v_i + \frac{\rho}{T}p\frac{dv}{dt} - \frac{\rho}{T}\sum_l \mu^l \frac{dc^l}{dt} \\ &= -\frac{1}{T}\nabla_j J_j^q + \frac{1}{T}\sum_l J_i^l F_i^l + \frac{1}{T}R_{ij}\nabla_j v_i + \frac{1}{T}\sum_l \mu^l \nabla_j J_j^l - \frac{1}{T}\sum_l \mu^l \sum_j \nu^{lj} k^j \end{aligned} \tag{2.71}$$

Introducing the so-called chemical affinities of the reactions $j = 1 \dots r$, proportional to their strength, as

$$A^j = \sum_l \mu^l \nu^{lj} \tag{2.72}$$

we can rewrite equation (2.71) in the form

$$\begin{aligned}\rho\frac{ds}{dt} &= -\frac{1}{T}\nabla_j J_j^q + \frac{1}{T}\sum_l J_i^l F_i^l + \frac{1}{T}R_{ij}\nabla_j v_i + \frac{1}{T}\sum_l \mu^l \nabla_j J_j^l - \frac{1}{T}\sum_j A^j k^j \\ &= -\nabla_j\left(\frac{J_j^q}{T} - \sum_l \frac{\mu^l}{T} J_j^l\right) - J_j^q\frac{\nabla_j T}{T^2} - \sum_l J_j^l\left(\nabla_j\frac{\mu^l}{T} - \frac{F_i^l}{T}\right) + \frac{1}{T}R_{ij}\nabla_j v_i - \frac{1}{T}\sum_j A^j k^j\end{aligned} \tag{2.73}$$

From comparison with (2.64) it follows that the entropy flux outside the boundary is

$$\boxed{J_j^s = \frac{J_j^q}{T} - \sum_l \frac{\mu^l}{T} J_j^l} \tag{2.74}$$

and the entropy production

$$\boxed{\sigma = -J_j^q\frac{\nabla_j T}{T^2} - \sum_l J_j^l\left(\nabla_j\frac{\mu^l}{T} - \frac{F_i^l}{T}\right) + \frac{1}{T}R_{ij}\nabla_j v_i - \frac{1}{T}\sum_j A^j k^j} \tag{2.75}$$

From (2.74) we see that the entropy flux $\boldsymbol{J}^s$ consists of two parts, the reduced heat flow $\boldsymbol{J}^q/T$ and the diffusion flow of matter $\boldsymbol{J}^l$. For the entropy production we have four different contributions:

1. Heat conduction ($\boldsymbol{J}^q$)
2. Diffusion ($\boldsymbol{J}^l$)
3. Viscous fluxes ($\boldsymbol{R}$)
4. Chemical reactions (k^j)

Chapter 3

Onsager Relations

In thermodynamic equilibrium, i.e. when all thermodynamic forces vanish, the entropy production is zero. Thus, we also expect the fluxes to vanish. In many cases the fluxes depend linearly on thermodynamic forces, e.g. the heat flux or the diffusional flux. From these linear laws, one can derive symmetry relations, called Onsager relations.

3.1. Formulation of Onsager relations

For usual systems without magnetic fields time reversal symmetry holds, i.e. the equations of motion are symmetric in time and if all velocities are inverted, all trajectories are followed backward in time. If we consider an adiabatically isolated system, there are only two type of fields. Those, which are invariant under velocity inversion or 'even' in the velocities (energy, concentration etc.), denoted by $A_1, \ldots, A_n$, and those which change their sign under velocity inversion or 'uneven' (velocity itself, momentum etc.), denoted by $B_1, \ldots, B_n$. The deviations from their equilibrium values A_i^0, B_i^0 are defined by

$$\alpha_i = A_i - A_i^0; \quad i = 1, \ldots, n \tag{3.1}$$

$$\beta_i = B_i - B_i^0; \quad i = 1, \ldots, n \tag{3.2}$$

At equilibrium, the entropy has a maximum and the state variables α_i, β_i are zero by definition. For the deviation ΔS of the entropy from its equilibrium value we can approximate

$$\Delta S = -\tfrac{1}{2} g_{ik} \alpha_i \alpha_k - \tfrac{1}{2} h_{ik} \beta_i \beta_k \ , \tag{3.3}$$

where $\boldsymbol{g}, \boldsymbol{h}$ are positive defined matrices and for vanishing magnetic fields, there is no $\alpha\beta$ cross term, since the entropy is even in the velocities.

We can assume a linear law for the time evolution of α and β

$$\frac{\mathrm{d}\alpha_i}{\mathrm{d}t} = -M_{ik}^{\alpha\alpha} \alpha_k - M_{ik}^{\alpha\beta} \beta_k \tag{3.4}$$

$$\frac{\mathrm{d}\beta_i}{\mathrm{d}t} = -M_{ik}^{\beta\beta} \beta_k - M_{ik}^{\beta\alpha} \alpha_k \tag{3.5}$$

and define thermodynamic forces in analogy with (1.52) as

$$\boxed{\begin{aligned} X_i &= \frac{\partial \Delta S}{\partial \alpha_i} = -g_{ik}\alpha_k \quad \Rightarrow \quad \alpha_i = -(g^{-1})_{ik}X_k \qquad (3.6)\\ Y_i &= \frac{\partial \Delta S}{\partial \beta_i} = -h_{ik}\beta_k \quad \Rightarrow \quad \beta_i = -(h^{-1})_{ik}Y_k \qquad (3.7)\end{aligned}}$$

Inserting (3.6) and (3.7) into (3.4) and (3.5), we obtain

$$\boxed{\begin{aligned} \frac{\mathrm{d}\alpha_i}{\mathrm{d}t} &= L^{\alpha\alpha}_{ik}X_k + L^{\alpha\beta}_{ik}Y_k \equiv J_i \qquad (3.8)\\ \frac{\mathrm{d}\beta_i}{\mathrm{d}t} &= L^{\beta\beta}_{ik}Y_k + L^{\beta\alpha}_{ik}X_k \equiv I_i\ , \qquad (3.9)\end{aligned}}$$

where the L matrices are given by

$$L^{\alpha\alpha}_{ik} = M^{\alpha\alpha}_{il}(g^{-1})_{lk} \tag{3.10}$$

and we have defined the thermodynamic fluxes J_i and I_i. The Onsager reciprocal relations state that

$$\boxed{\begin{aligned} L^{\alpha\alpha}_{ik} &= L^{\alpha\alpha}_{ki} \qquad (3.11)\\ L^{\beta\beta}_{ik} &= L^{\beta\beta}_{ki} \qquad (3.12)\\ L^{\alpha\beta}_{ik} &= -L^{\beta\alpha}_{ki}\ . \qquad (3.13)\end{aligned}}$$

This relations are valid only if no external magnetic field is present since the Lorentz force is proportional to the vector product of the particles velocity with the field.
We now consider the time derivative of the entropy, i.e. the entropy production, for which using equations (3.6) to (3.9) gives

$$\boxed{\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\Delta S &= -g_{ik}\alpha_k\frac{\mathrm{d}\alpha_i}{\mathrm{d}t} - h_{ik}\beta_k\frac{\mathrm{d}\beta_i}{\mathrm{d}t}\\ &= X_iJ_i + Y_iI_i\\ &= L^{\alpha\alpha}_{ik}X_iX_k + L^{\beta\beta}_{ik}Y_iY_k\ . \qquad (3.14)\end{aligned}}$$

where in the last line, we have used the third Onsager relation (3.13) in order to eliminate the XY-coupling term. We see from this last result that the entropy production is quadratic in the forces.

3.2. Thermohydrodynamics

To make exemplary use of the Onsager relations, we consider a hydrodynamic system. Without external forces $F_i = \psi = 0$, the linear momentum balance equation (2.19), using (2.45), gives

$$\rho \frac{\mathrm{d}v_i}{\mathrm{d}t} = \nabla_j \sigma_{ij} = -\nabla_i p + \nabla_j R_{ij} \ . \tag{3.15}$$

Setting $F_i = \psi = 0$ also in (2.47) gives for the internal energy

$$\rho \frac{\mathrm{d}u}{\mathrm{d}t} = -\nabla_i J_i^q - p \nabla_i v_i + R_{ij} \nabla_j v_i \tag{3.16}$$

For the entropy production (2.75) with no diffusion and chemical reactions we have

$$\sigma = -J_j^q \frac{\nabla_j T}{T^2} + \frac{1}{T} R_{ij} \nabla_j v_i \tag{3.17}$$

According to Onsager the phenomenological equation for the heat flux reads

$$J_j^q = -L^{qq} \frac{\nabla_j T}{T^2} \tag{3.18}$$

The differential form of Fourier law also states that

$$J_j^q = -\lambda \nabla_j T \tag{3.19}$$

so that

$$\frac{L^{qq}}{T^2} = \lambda \tag{3.20}$$

with λ is the heat conductivity. For fluids the off diagonal matrix of the stress tensor can be written in terms of two different viscosities η and η' as

$$R_{ij} = \eta(\nabla_i v_j + \nabla_j v_i) + \eta' \delta_{ij} \nabla_k v_k \tag{3.21}$$

which is clearly symmetric. Since every tensor can be decomposed into a a sum of a symmetric and antisymmetric part we also have

$$\nabla_j v_i = \tfrac{1}{2}(\nabla_j v_i + \nabla_i v_j) + \tfrac{1}{2}(\nabla_j v_i - \nabla_i v_j) \tag{3.22}$$

and its contraction with the symmetric tensor (3.21) gives

$$R_{ij} \nabla_j v_i = \tfrac{\eta}{2}(\nabla_i v_j + \nabla_j v_i)(\nabla_i v_j + \nabla_j v_i) + \eta' (\nabla_k v_k)^2 \geq 0 \tag{3.23}$$

Since there is no cross term between $\nabla_j T$ and $\nabla_i v_j$ because they have different symmetry (Curie Principle), substituting in (3.17) equations (3.19) and (3.23) gives

$$\sigma = \frac{\lambda}{T^2} (\nabla T)^2 + \frac{\eta}{2T} (\nabla_i v_j + \nabla_j v_i)^2 + \frac{\eta'}{T} (\nabla_k v_k)^2 \geq 0 \tag{3.24}$$

Inserting (3.21) into (3.15), (3.19) and (3.23) into (3.16), we can rewrite (3.15) and (3.16) together with the conservation of mass (2.16) as five equations

$$\boxed{\begin{aligned}\rho\frac{\mathrm{d}v_i}{\mathrm{d}t} &= -\nabla_i p + \eta\Delta v_i + (\eta+\eta')\nabla_j\nabla_i v_j && (3.25)\\ \frac{\mathrm{d}\rho}{\mathrm{d}t} &= -\rho\nabla_j v_j && (3.26)\\ \rho\frac{\mathrm{d}u}{\mathrm{d}t} &= \lambda\Delta T - p\nabla_i v_i + \frac{\eta}{2}(\nabla_i v_j + \nabla_j v_i)^2 + \eta'(\nabla_k v_k)^2 && (3.27)\end{aligned}}$$

in the seven unknowns $\boldsymbol{v}, \rho, T, u$ and p (given λ, η and η'). Thus we need the equation of state to generate two more equations

$$\boxed{\begin{aligned}U(V,T,N) &\Rightarrow u(\rho,T) && (3.28)\\ p(V,T,N) &\Rightarrow p(\rho,T) && (3.29)\end{aligned}}$$

which together with (3.25), (3.26) and (3.27) represent the basic equations of thermohydrodynamics.
Non equilibrium statistical mechanics can be divided into 3 major subjects

1. Thermohydrodynamics
2. Stochastics
3. Boltzmann equation

The subject of Thermohydrodynamics itself can be grouped into 4 major fields

1. Hydrodynamics, where the internal energy u is unimportant
2. Thermostatics, where there is no dynamic transport
3. Heat conduction
4. Diffusion equation

Some important approximations include the isothermal approximation, where $p(\rho,T) \to p(\rho)$, which results into a decoupling of the equations and the vanishing velocity field $\boldsymbol{v} = 0$, which from (3.16) leads to Fourier law $\rho\dot{u} = \lambda\Delta T$.

3.3. Microscopic derivation

We consider an adiabatically insulated system, i.e. a microcanonical ensemble. In equilibrium, the probability density of N particles is given by

$$\rho = \rho(\boldsymbol{q}^N, \boldsymbol{p}^N) = \begin{cases}\rho_0 & E \in [E, E + \mathrm{d}E]\\ 0 & \text{otherwise}\end{cases} \tag{3.30}$$

where ρ_0 is determined by the normalization condition

$$\int \mathrm{d}\boldsymbol{q}^N \mathrm{d}\boldsymbol{p}^N \rho(\boldsymbol{q}^N, \boldsymbol{p}^N) = 1 \ . \tag{3.31}$$

Using (3.30), we can explicitly calculate (3.31) as an integral over ρ_0 and restrict the integration volume to states with energies in the given interval $[E, E + \mathrm{d}E]$. This leads directly to an expression for the inverse of the probability density

$$\frac{1}{\rho_0} = \int_{E,E+\mathrm{d}E} \mathrm{d}\boldsymbol{q}^N \mathrm{d}\boldsymbol{p}^N = \Omega(E) \ , \tag{3.32}$$

where $\Omega(E)$ denotes the accessible phase space volume of the energy shell defined by the considered interval. Macroscopically our system is described by a set of extensive variables A_i, such as mass, energy, electric charge etc.. We can view each A_i as component of the vector

$$\boldsymbol{A} = \boldsymbol{A}(\boldsymbol{q}^N, \boldsymbol{p}^N) \ . \tag{3.33}$$

The probability to find the system in a state $\boldsymbol{A}(\boldsymbol{q}^N, \boldsymbol{p}^N)$, that fulfills $\boldsymbol{A}(\boldsymbol{q}^N, \boldsymbol{p}^N) \in [\boldsymbol{A}, \boldsymbol{A} + \mathrm{d}\boldsymbol{A}]$ is given by

$$f(\boldsymbol{A})\mathrm{d}\boldsymbol{A} = \int_{\boldsymbol{A},\boldsymbol{A}+\mathrm{d}\boldsymbol{A}} \mathrm{d}\boldsymbol{q}^N \mathrm{d}\boldsymbol{p}^N \rho(\boldsymbol{q}^N, \boldsymbol{p}^N) \tag{3.34}$$

$$= \rho_0 \int_{\substack{E,E+\mathrm{d}E \\ \boldsymbol{A},\boldsymbol{A}+\mathrm{d}\boldsymbol{A}}} \mathrm{d}\boldsymbol{q}^N \mathrm{d}\boldsymbol{p}^N = \frac{\Omega(\boldsymbol{A}, E)}{\Omega(E)} \tag{3.35}$$

where in the last line we have used (3.32) and $\Omega(\boldsymbol{A}, E)$ is the volume in phase space containing the points with energy $[E, E+\mathrm{d}E]$ and $[\boldsymbol{A}, \boldsymbol{A}+\mathrm{d}\boldsymbol{A}]$ and $f(\boldsymbol{A})$ the distribution function for the state $\boldsymbol{A}$. If we assume $f(\boldsymbol{A})$ to be Gaussian we can write

$$f(\boldsymbol{A}) = C \exp\left(- \frac{g_{ij}}{2k_B}(A_i - \langle A_i \rangle)(A_j - \langle A_j \rangle) \right) \tag{3.36}$$

where g_{ij} are the elements of a symmetric positive defined matrix. Then the fluctuations $\alpha_i = A_i - \langle A_i \rangle$ follow the equilibrium distribution

$$f(\boldsymbol{\alpha}) = C \exp\left\{ - \frac{g_{ij}}{2k_B} \alpha_i \alpha_j \right\} \ . \tag{3.37}$$

and

$$\langle A_i \rangle = \int \mathrm{d}\boldsymbol{A} \ f(\boldsymbol{A}) A_i \ . \tag{3.38}$$

Then from (3.34) the normalization condition

$$\int f(\boldsymbol{\alpha}) \ \mathrm{d}\boldsymbol{\alpha} = 1 \tag{3.39}$$

gives

$$C = \left(\frac{\det \boldsymbol{g}}{(2\pi k_B)^n} \right)^{1/2} \tag{3.40}$$

Now we define in analogy with (1.52) the forces

$$\boxed{X_i \equiv k_B \frac{\partial \ln f}{\partial \alpha_i} = -g_{ik}\alpha_k} \tag{3.41}$$

As for (1.62) we have the following relations

$$\begin{aligned}
\langle \alpha_i X_j \rangle &= -\langle \alpha_i g_{jk} \alpha_k \rangle \\
&= \int \alpha_i X_j f(\boldsymbol{\alpha})\, \mathrm{d}\boldsymbol{\alpha} \\
&= k_B \int \alpha_i \frac{\partial f}{\partial \alpha_j} \mathrm{d}\boldsymbol{\alpha} \\
&= -k_B \int f \frac{\partial \alpha_i}{\partial \alpha_j} \mathrm{d}\boldsymbol{\alpha} \\
&= -k_B \delta_{ij}
\end{aligned} \tag{3.42}$$

Then we obtain an expression equivalent to (1.61) for the correlation function

$$\boxed{\langle \alpha_i \alpha_j \rangle = k_B (g^{-1})_{ij}} \tag{3.43}$$

We now consider the joint distribution function

$$f(\boldsymbol{\alpha}, \boldsymbol{\alpha}', \tau) \tag{3.44}$$

for which

$$f(\boldsymbol{\alpha}, \boldsymbol{\alpha}', \tau) \mathrm{d}\boldsymbol{\alpha} \mathrm{d}\boldsymbol{\alpha}' \tag{3.45}$$

is by definition the joint (product) probability that the system is initially in a state $\boldsymbol{\alpha}$ and after a time τ in a state $\boldsymbol{\alpha}'$. Therefore, we first consider the conditional probability in phase space

$$P(\boldsymbol{q}^N, \boldsymbol{p}^N | \boldsymbol{q}'^N \boldsymbol{p}'^N; \tau) = P(\boldsymbol{\alpha}|\boldsymbol{\alpha}'; \tau) \tag{3.46}$$

to find the system in a state $\boldsymbol{q}'^N, \boldsymbol{p}'^N$, when it was in a state $\boldsymbol{q}^N, \boldsymbol{p}^N$ a time interval τ before. The conditional probability obeys the normalization relation

$$\int \mathrm{d}\boldsymbol{\alpha}' P(\boldsymbol{\alpha}|\boldsymbol{\alpha}'; \tau) = \int_{E, E+\mathrm{d}E} \mathrm{d}\boldsymbol{\alpha}' P(\boldsymbol{\alpha}|\boldsymbol{\alpha}'; \tau) = 1 \;, \tag{3.47}$$

which states, that the probability to find a particle in any state of the accessible phase space volume after some time τ is unity independently of the initial starting point, and also that all phase spec trajectories remain inside the considered interval. With the conditional probability distribution, we can describe propagation in time of the probability density as

$$\rho(\boldsymbol{\alpha}';\tau) = \int \mathrm{d}\boldsymbol{\alpha}\ \rho(\boldsymbol{\alpha};0)P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) \tag{3.48}$$

and since we have a micro canonical ensemble with a stationary distribution

$$\rho(\boldsymbol{\alpha};\tau) = \rho(\boldsymbol{\alpha};0) = \rho_0 \tag{3.49}$$

equation (3.48) gives

$$\int \mathrm{d}\boldsymbol{\alpha}\ P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) = 1\ . \tag{3.50}$$

The equations of motions for a conservative system (no friction) are invariant under time reversal transformation

$$\tau \to -\tau, \qquad \boldsymbol{q}^N \to \boldsymbol{q}^N, \qquad \boldsymbol{p}^N \to -\boldsymbol{p}^N \tag{3.51}$$

Therefore, the conditional probability obeys the following relation

$$P(\boldsymbol{q}^N,\boldsymbol{p}^N|\boldsymbol{q}'^N,\boldsymbol{p}'^N;\tau) = P(\boldsymbol{q}^N,-\boldsymbol{p}^N|\boldsymbol{q}'^N,-\boldsymbol{p}'^N;-\tau) \tag{3.52}$$

and as a consequence of causality in the equation of motion it must be also

$$P(\boldsymbol{q}^N,-p^N|\boldsymbol{q}'^N,-p'^N;-\tau) = P(\boldsymbol{q}'^N,-\boldsymbol{p}'^N|\boldsymbol{q}^N,-\boldsymbol{p}^N;\tau)\ . \tag{3.53}$$

so that

$$\boxed{P(\boldsymbol{q}^N,\boldsymbol{p}^N|\boldsymbol{q}'^N,\boldsymbol{p}'^N;\tau) = P(\boldsymbol{q}'^N,-\boldsymbol{p}'^N|\boldsymbol{q}^N,-\boldsymbol{p}^N;\tau)} \tag{3.54}$$

which expresses that if we reverse the momenta at a certain time, the particles will retrace their former path.

As we are interested in the joint distribution $f(\boldsymbol{\alpha},\boldsymbol{\alpha}',\tau)$ as a function of the $\boldsymbol{\alpha}$ variables, we consider the connection between the distribution function f, the conditional probability P and the probability density ρ. The joint probability for the microcanonical ensemble for the states $\boldsymbol{\alpha}$ and $\boldsymbol{\alpha}'$ is given by the integrand in (3.48). Using (3.49) we express the joint probability as

$$\begin{aligned} f(\boldsymbol{\alpha},\boldsymbol{\alpha}',\tau)\mathrm{d}\boldsymbol{\alpha}\mathrm{d}\boldsymbol{\alpha}' &= \iint_{\substack{\boldsymbol{\alpha},\boldsymbol{\alpha}+\mathrm{d}\boldsymbol{\alpha}\\ \boldsymbol{\alpha}',\boldsymbol{\alpha}'+\mathrm{d}\boldsymbol{\alpha}'}} \mathrm{d}\boldsymbol{\alpha}\mathrm{d}\boldsymbol{\alpha}'\ \rho(\boldsymbol{\alpha})\,P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) \\ &= \rho_o \iint_{\substack{\boldsymbol{\alpha},\boldsymbol{\alpha}+\mathrm{d}\boldsymbol{\alpha}\\ \boldsymbol{\alpha}',\boldsymbol{\alpha}'+\mathrm{d}\boldsymbol{\alpha}'\\ E,E+\mathrm{d}E}} \mathrm{d}\boldsymbol{\alpha}\mathrm{d}\boldsymbol{\alpha}'\ P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) \end{aligned} \tag{3.55}$$

from which it follows immediately that $f(\boldsymbol{\alpha},\boldsymbol{\alpha}',\tau)\mathrm{d}\boldsymbol{\alpha}\mathrm{d}\boldsymbol{\alpha}'$ is stationary since it is just a function of the time interval τ and not of some initial time t. By replacing $\boldsymbol{A}$ with $\boldsymbol{\alpha}$ in equation (3.34), and using (3.47) we find from last equation

$$\int f(\boldsymbol{\alpha},\boldsymbol{\alpha}',\tau)\mathrm{d}\boldsymbol{\alpha}' = f(\boldsymbol{\alpha}) \tag{3.56}$$

$$\int f(\boldsymbol{\alpha},\boldsymbol{\alpha}',\tau)\mathrm{d}\boldsymbol{\alpha} = f(\boldsymbol{\alpha}') \tag{3.57}$$

and defining the conditional probability density for the microcanonical ensemble as

$$P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau)\mathrm{d}\boldsymbol{\alpha}' \equiv \frac{f(\boldsymbol{\alpha},\boldsymbol{\alpha}';\tau)\mathrm{d}\boldsymbol{\alpha}\mathrm{d}\boldsymbol{\alpha}'}{f(\boldsymbol{\alpha})\mathrm{d}\boldsymbol{\alpha}} \tag{3.58}$$

we obtain from (3.32), (3.35) and (3.55)

$$\begin{aligned} P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau)\mathrm{d}\boldsymbol{\alpha}' &= \frac{1}{\rho_0\ \Omega(\boldsymbol{\alpha},E)} f(\boldsymbol{\alpha},\boldsymbol{\alpha}';\tau)\mathrm{d}\boldsymbol{\alpha}\mathrm{d}\boldsymbol{\alpha}' \\ &= \frac{1}{\Omega(\boldsymbol{\alpha},E)} \iint_{\substack{\boldsymbol{\alpha},\boldsymbol{\alpha}+\mathrm{d}\boldsymbol{\alpha}\\ \boldsymbol{\alpha}',\boldsymbol{\alpha}'+\mathrm{d}\boldsymbol{\alpha}'\\ E,E+\mathrm{d}E}} \mathrm{d}\boldsymbol{\alpha}\,\mathrm{d}\boldsymbol{\alpha}'\,P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) \end{aligned} \tag{3.59}$$

from which we see that also the conditional probability is stationary. We can now state from the last results some important properties of the conditional probability

1. $P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) \geq 0$
2. $P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';0) = \delta(\boldsymbol{\alpha}-\boldsymbol{\alpha}')$
3. $\int \mathrm{d}\boldsymbol{\alpha}'\ P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) = 1$
4. $\int \mathrm{d}\boldsymbol{\alpha} f(\boldsymbol{\alpha})P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) = f(\boldsymbol{\alpha}')$

The fifth relation describes the **detailed balance**, meaning that in equilibrium each process is balanced by its reversed process

$$\boxed{f(\boldsymbol{\alpha})P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) = f(\boldsymbol{\alpha}')P(\boldsymbol{\alpha}'|\boldsymbol{\alpha};\tau)} \tag{3.60}$$

This is an important observation and will be proven in the following. By using equation (3.32) (3.35) and (3.59) we obtain

$$f(\boldsymbol{\alpha})P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) = \rho_0 \int_{\boldsymbol{\alpha}} \mathrm{d}\boldsymbol{q}^N \mathrm{d}\boldsymbol{p}^N \int_{\boldsymbol{\alpha}'} P(\boldsymbol{q}^N,\boldsymbol{p}^N|\boldsymbol{q}'^N,\boldsymbol{p}'^N;\tau) \tag{3.61}$$

Using equation (3.54) we find

$$\begin{aligned} f(\boldsymbol{\alpha})P(\boldsymbol{\alpha}|\boldsymbol{\alpha}';\tau) =&\rho_0 \int_{\boldsymbol{\alpha}} \mathrm{d}\boldsymbol{q}^N \mathrm{d}\boldsymbol{p}^N \int_{\boldsymbol{\alpha}'} P(\boldsymbol{q}^N,\boldsymbol{p}^N|\boldsymbol{q}'^N,\boldsymbol{p}'^N;\tau) \\ =&\rho_0 \int_{\boldsymbol{\alpha}} \mathrm{d}\boldsymbol{q}^N \mathrm{d}\boldsymbol{p}^N \int_{\boldsymbol{\alpha}'} P(\boldsymbol{q}'^N,-\boldsymbol{p}'^N|\boldsymbol{q}^N,-\boldsymbol{p}^N;\tau) \\ =&f(\boldsymbol{\alpha}')P(\boldsymbol{\alpha}'|\boldsymbol{\alpha};\tau) \end{aligned}$$

where we have used that the $\boldsymbol{\alpha}$ variables are by definition invariant under the transformation $(\boldsymbol{q}^N, \boldsymbol{p}^N) \to (\boldsymbol{q}^N, -\boldsymbol{p}^N)$.
Next we consider the expectation value of the $\boldsymbol{\alpha}$ variables

$$\langle \alpha_i(t) \rangle_{\alpha_i^0} , \qquad \text{with } \langle \alpha_i(0) \rangle \equiv \alpha_i^0 . \tag{3.62}$$

We assume, that $(\alpha_i^0)^2 \gg k_B (g^{-1})_{ii}$, i.e. we are looking at deviations from equilibrium larger then the equilibrium fluctuations given by (3.43). A phenomenological approach to describe the time evolution of the expectation value is given by (3.4) for the $\boldsymbol{\alpha}$ variables

$$\frac{\mathrm{d} \langle \alpha_i(t) \rangle_{\alpha_i^0}}{\mathrm{d}t} = -M_{ik} \langle \alpha_k(t) \rangle_{\alpha_k^0} , \tag{3.63}$$

where

$$\langle \alpha_i(t) \rangle_{\alpha_i^0} = \int \mathrm{d}\boldsymbol{\alpha}\, P(\boldsymbol{\alpha}^0|\boldsymbol{\alpha}, t) \alpha_i \tag{3.64}$$

If the matrix M_{ik} is independent of time, we obtain the formal solution

$$\langle \boldsymbol{\alpha}(t) \rangle_{\alpha^0} = e^{-Mt} \boldsymbol{\alpha}^0 \tag{3.65}$$

with

$$e^{-\boldsymbol{M}t} \equiv \sum_{n=0}^{\infty} \frac{(-\boldsymbol{M}t)^n}{n!} = 1 - \boldsymbol{M}t + \tfrac{1}{2} \boldsymbol{M}\boldsymbol{M}t^2 + \dots \tag{3.66}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} e^{-\boldsymbol{M}t} = -\boldsymbol{M} e^{-\boldsymbol{M}t} \tag{3.67}$$

Multiply by $\boldsymbol{\alpha}^0 f(\boldsymbol{\alpha}^0)$ and integrate over $\boldsymbol{\alpha}^0$ equation (3.64), using (3.65), gives

$$\int \mathrm{d}\boldsymbol{\alpha}^0 \boldsymbol{\alpha}^0 f(\boldsymbol{\alpha}^0) \langle \boldsymbol{\alpha}(t) \rangle_{\boldsymbol{\alpha}^0} = \iint \mathrm{d}\boldsymbol{\alpha}^0 \mathrm{d}\boldsymbol{\alpha}\ \boldsymbol{\alpha}^0 f(\boldsymbol{\alpha}^0) P(\boldsymbol{\alpha}^0|\boldsymbol{\alpha}, t) \boldsymbol{\alpha} \tag{3.68}$$

$$= \int \mathrm{d}\boldsymbol{\alpha}^0 \boldsymbol{\alpha}^0 f(\boldsymbol{\alpha}^0) e^{-Mt} \boldsymbol{\alpha}^0 \tag{3.69}$$

If we swap $\boldsymbol{\alpha}$ and $\boldsymbol{\alpha}^0$ and assuming that we are in equilibrium where the detailed balance relation (3.60) is valid, we can write

$$\iint \mathrm{d}\boldsymbol{\alpha}^0 \mathrm{d}\boldsymbol{\alpha} f(\boldsymbol{\alpha}^0) \boldsymbol{\alpha}^0 \boldsymbol{\alpha} P(\boldsymbol{\alpha}^0|\boldsymbol{\alpha}, t) = \iint \mathrm{d}\boldsymbol{\alpha} \mathrm{d}\boldsymbol{\alpha}^0 f(\boldsymbol{\alpha}^0) \boldsymbol{\alpha} \boldsymbol{\alpha}^0 P(\boldsymbol{\alpha}^0|\boldsymbol{\alpha}, t) \tag{3.70}$$

i.e. we have a symmetric matrix. Thus combining (3.69) and (3.70) yields

$$\begin{aligned} \int \mathrm{d}\boldsymbol{\alpha}^0 \boldsymbol{\alpha}^0 f(\boldsymbol{\alpha}^0) e^{-Mt} \boldsymbol{\alpha}^0 &= \iint \mathrm{d}\boldsymbol{\alpha}^0 \mathrm{d}\boldsymbol{\alpha} f(\boldsymbol{\alpha}^0) \boldsymbol{\alpha}^0 \boldsymbol{\alpha} P(\boldsymbol{\alpha}^0|\boldsymbol{\alpha}, t) \\ &= \iint \mathrm{d}\boldsymbol{\alpha} \mathrm{d}\boldsymbol{\alpha}^0 f(\boldsymbol{\alpha}^0) \boldsymbol{\alpha} \boldsymbol{\alpha}^0 P(\boldsymbol{\alpha}^0|\boldsymbol{\alpha}, t) \\ &= \int \mathrm{d}\boldsymbol{\alpha}^0 f(\boldsymbol{\alpha}^0) \left(e^{-Mt} \boldsymbol{\alpha}^0 \right) \boldsymbol{\alpha}^0 . \end{aligned} \tag{3.71}$$

We define the matrix

$$B_{ij} = \left(e^{-Mt}\right)_{ij} \tag{3.72}$$

and rewrite the previous equation in components as

$$\int \mathrm{d}\boldsymbol{\alpha}^0 \alpha_k^0 f(\boldsymbol{\alpha}^0) B_{ij} \alpha_j^0 = \int \mathrm{d}\boldsymbol{\alpha}^0 f(\boldsymbol{\alpha}^0) B_{kj} \alpha_j^0 \alpha_i^0 \ . \tag{3.73}$$

which gives, using (3.43)

$$g_{kj}^{-1} B_{ij} = g_{ji}^{-1} B_{kj} \ . \tag{3.74}$$

Using the useful relation

$$\left(e^{\boldsymbol{M}}\right)^T = e^{(\boldsymbol{M}^T)} \ , \tag{3.75}$$

where ^{T} denotes the matrix transposition $A_{ij}^T = A_{ji}$, from (3.74) we have

$$\boldsymbol{g}^{-1}\boldsymbol{B}^T = \boldsymbol{B}\boldsymbol{g}^{-1} \ . \tag{3.76}$$

Using the series representation of the matrix exponential $\boldsymbol{B} = e^{\boldsymbol{M}t}$, we can compare the left and right hand side in every order of t and conclude that

$$\boldsymbol{g}^{-1}\boldsymbol{M}^T = \boldsymbol{M}\boldsymbol{g}^{-1} \, . \tag{3.77}$$

We further use, that $\boldsymbol{g}$ is symmetric and thus also its inverse is symmetric. From (3.10) we can verify the first Onsager relation (3.11) easily by looking at (3.77)

$$\boldsymbol{L} = \boldsymbol{M}\boldsymbol{g}^{-1} = \boldsymbol{g}^{-1}\boldsymbol{M}^T = (\boldsymbol{g}^{-1})^T\boldsymbol{M}^T = \left(\boldsymbol{M}\boldsymbol{g}^{-1}\right)^T = \boldsymbol{L}^T \ . \tag{3.78}$$

The proof for the other Onsager relations can be found in the original works by Onsager $L.Onsager, PhysRev37, 405(1931); 382265(1931)$.

3.4. Curie principle and coupling effects

Curie Principle.
This is not really clear yet and it could just be left out.

Every tensor T_{ij} can be decomposed according to

$$T_{ij} = \frac{1}{3}\delta_{ij}T_{ll} + T_{ij}^A + T_{ij}^S \ , \tag{3.79}$$

where we used Einstein notation and thus $T_l l$ is nothing but the trace of the tensor and $T^{A/S}$ are the antisymmetric and symmetric components respectively. The symmetric part has five components and the antisymmetric part, which is traceless, has three components.

COMMENT: check on number of components

The general expression for the entropy production is

$$\sigma = J^S X^S + J_i^P X_i^P + J_i^a X_i^a + J_{ij}^S X_{ij}^S \tag{3.80}$$

where $J^S X^S$ is a scalar and represents the chemical reactions $\nabla_i V_i$, $J_i^P X_i^P$ is a polar vector and represents the heat flux, $J_i^a X_i^a$ is an axial vector and represents shear stress and rotation and $J_{ij}^S X_{ij}^S$ is a symmetric tensor representing viscosity. One can show that for an isotropic system it is

$$J^S = L^{SS} X^S \tag{3.81}$$

$$J_i^P = L^{PP} X_i^P \tag{3.82}$$

$$J_i^a = L^{aa} X_i^a \tag{3.83}$$

$$J_{ij}^S = (L^{SS})^T X_{ij}^S \tag{3.84}$$

These quantities are all scalars and there is coupling between different terms of the same symmetry!

$$\sigma = L^{SS} X_S^2 \geq 0 \tag{3.85}$$

$$+ L^{PP} X_i^{P2} \geq 0 \tag{3.86}$$

$$+ L^{aa} X_i^{a2} \geq 0 \tag{3.87}$$

$$+ (L^{SS})^T X_{ij}^{S2} \geq 0 \tag{3.88}$$

We now want to consider heat flux or diffusion as an example. Therefore, we consider a system without chemical reaction at rest $\boldsymbol{v} = 0$, $\boldsymbol{F}^l = 0$. The entropy production is then given by

$$\sigma(\boldsymbol{r}, t) = -J_i^q \frac{\nabla_i T}{T^2} - \sum_{l=1}^{k} J_i^l \nabla_i \frac{\mu^l}{T} \tag{3.89}$$

As the system in total is at rest, we have $\sum_{l=1}^k J_i^l = \sum_{l=1}^k \rho^l (v_i^l - v_i) = 0$, thus we can add $\sum_{l=1}^k J_i^l \nabla_i \frac{\mu^k}{T} = 0$ and eq. (3.89) becomes

$$\begin{aligned} \sigma(\boldsymbol{r}, t) &= -J_i^q \frac{\nabla_i T}{T^2} - \sum_{l=1}^{k} J_i^l \nabla_i \left(\frac{\mu^l}{T} - \frac{\mu^k}{T} \right) \\ &= -J_i^q \frac{\nabla_i T}{T^2} - \sum_{l=1}^{k-1} J_i^l \nabla_i \left(\frac{\mu^l}{T} - \frac{\mu^k}{T} \right) \end{aligned} \tag{3.90}$$

By comparing (3.90) with the relations in (3.14) we obtain

$$J_i^q = -L^{qq} \frac{\nabla_i T}{T^2} - \sum_{l=1}^{k-1} L^{ql} \nabla_i \left(\frac{\mu^l}{T} - \frac{\mu^k}{T} \right) \tag{3.91}$$

$$J_i^l = -L^{ql} \frac{\nabla_i T}{T^2} - \sum_{m=1}^{k-1} L^{lm} \nabla_i \left(\frac{\mu^l}{T} - \frac{\mu^k}{T} \right) \tag{3.92}$$

According to Onsager we have $L^{ql} = L^{lq}$, $L^{lm} = L^{ml}$.

3.5. Stationarity and stability

Stationary states are characterized by a constant value of the $\boldsymbol{\alpha}$ variables, although it is not required that $\boldsymbol{\alpha} = 0$ since we want to consider both equilibrium and non equilibrium stationarity states. We want to proof that stationary states are characterized by a minimum in the entropy production. Let's consider a fluid at equilibrium where equation (2.19), using (3.21), reads

$$\begin{aligned} 0 = \rho \frac{dv_i}{dt} &= \sum_l \rho^l F_i^l + \nabla_j \sigma_{ij} \\ &= \sum_l \rho^l F_i^l - \nabla_i p + \eta \Delta v_i + (\eta + \eta') \nabla_j \nabla_i v_j \end{aligned} \tag{3.93}$$

which is just equation (3.25) with $F_i \neq 0$. If we assume the velocity constant in space the last equation gives the condition of mechanical equilibrium for a k-component fluid

$$\sum_l \rho^l F_i^l = \nabla_i p \tag{3.94}$$

Now consider a one component system with temperature fixed at the surface for boundary condition. The phenomenological equation for the heat flux (3.18) is

$$J_j^q = -L^{qq} \frac{\nabla_j T}{T^2} \tag{3.95}$$

for which the entropy production (3.17) with the velocity constant in space becomes

$$\sigma = -J_j^q \frac{\nabla_j T}{T^2} = L^{qq} \left(\frac{\nabla_j T}{T^2} \right)^2 \tag{3.96}$$

Assuming $L^{qq} = \text{const}$, the total entropy production Σ in the system (2.59) is then given by

$$\Sigma \equiv \frac{d_i S}{dt} = \int_V \sigma \; dV = \int_V L^{qq} \left(\frac{\nabla_j T}{T^2} \right)^2 \; dV \tag{3.97}$$

To find the temperature profile $T(\boldsymbol{r})$ for which $\Sigma[T(\boldsymbol{r})]$ is extremal we have to evaluate the functional derivative

$$\begin{aligned} \frac{\delta \Sigma[T(\boldsymbol{r})]}{\delta T(\tilde{\boldsymbol{r}})} &\equiv \lim_{\epsilon \to 0} \frac{\Sigma[T(\boldsymbol{r}) + \epsilon \delta(\boldsymbol{r} - \tilde{\boldsymbol{r}})] - \Sigma[T(\boldsymbol{r})]}{\epsilon} \\ &= \lim_{\epsilon \to 0} \int_V \frac{L^{qq} \nabla_j \nabla_j}{\epsilon T^4} \left\{ [T(\boldsymbol{r}) + \epsilon \delta(\boldsymbol{r} - \tilde{\boldsymbol{r}})]^2 - [T(\boldsymbol{r})]^2 \right\} \; dV \\ &= \int_V \frac{L^{qq}}{T^4} \nabla_j \nabla_j \left\{ 2T(\boldsymbol{r}) \delta(\boldsymbol{r} - \tilde{\boldsymbol{r}}) \right\} \; dV \end{aligned} \tag{3.98}$$

and since for boundary condition the temperature is constant at the surface this gives

$$\begin{aligned}\frac{\delta\Sigma[T(\boldsymbol{r})]}{\delta T(\tilde{\boldsymbol{r}})} &= -\int_V \frac{2L^{qq}}{T^4}\nabla_j\nabla_j T(\boldsymbol{r})\delta(\boldsymbol{r}-\tilde{\boldsymbol{r}})\ dV \\ &= -2L^{qq}\frac{1}{T^4}\nabla_j\nabla_j T(\tilde{\boldsymbol{r}}) \end{aligned} \tag{3.99}$$

Imposing $\Sigma[T(\boldsymbol{r})] = 0$ it must be

$$L^{qq}\frac{1}{T^4}\nabla_j\nabla_j T(\tilde{\boldsymbol{r}}) = 0 \quad \Rightarrow \quad \nabla_j J_j^q = 0 \tag{3.100}$$

In terms of energy balance, equation (2.47) with constant potential reads

$$\rho\frac{du}{dt} = -\nabla_j J_j^q - p\nabla_j v_i + R_{ij}\nabla_j v_i \tag{3.101}$$

which for constant velocity and with the condition for extremal entropy production $\nabla_j J_j^q = 0$ gives

$$0 = \frac{du}{dt} = \frac{\partial T}{\partial t}\left(\frac{\partial u}{\partial T}\right)_V = C_V\frac{\partial T}{\partial t} \quad \Rightarrow \quad \frac{\partial T}{\partial t} = 0 \tag{3.102}$$

Then the total entropy production Σ is extremal for the stationarity of the temperature and since $\sigma \geq 0$ this must be a minimum with respect to the entropy production. We show now how stationary states are stable with respect to small perturbations $\delta T(\boldsymbol{r})$. The time derivative of the total entropy production (3.97) is

$$\begin{aligned}\frac{\partial\Sigma}{\partial t} &= \frac{\partial}{\partial t}\int_V L^{qq}\left(\frac{\nabla_j T}{T^2}\right)^2 dV \\ &= \frac{\partial}{\partial t}\int_V L^{qq}\left(\nabla_j\frac{1}{T}\right)^2 dV \\ &= 2\int_V L^{qq}\left(\nabla_j\frac{1}{T}\right)\left(\nabla_j\frac{\partial}{\partial t}\frac{1}{T}\right) dV \\ &= 2\int_V J_j^q\nabla_j\frac{\partial}{\partial t}\frac{1}{T}\ dV \\ &= 2\int_S J_j^q\frac{\partial}{\partial t}\frac{1}{T}\ dS_j - 2\int_V\frac{\partial}{\partial t}\frac{1}{T}\nabla_j J_j^q\ dV \\ &= -2\int_V\frac{\partial}{\partial t}\frac{1}{T}\nabla_j J_j^q\ dV \end{aligned} \tag{3.103}$$

since the integral over the surface vanishes as the temperature is fixed there. From (3.101) with constant velocity we have

$$\nabla_j J_j^q = -\rho \frac{du}{dt} = -\rho C_V \frac{\partial T}{\partial t} \tag{3.104}$$

so that the total entropy production time derivative becomes

$$\begin{aligned}\frac{\partial \Sigma}{\partial t} &= -2 \int_V \frac{\partial}{\partial t} \frac{1}{T} \left(-\rho C_V \frac{\partial T}{\partial t} \right) dV \\ &= -2 \int_V \frac{\rho C_V}{T^2} \left(\frac{\partial T}{\partial t} \right)^2 dV \leq 0 \end{aligned} \tag{3.105}$$

Then the entropy production in the total volume V can only decrease in time

$$\frac{\partial \Sigma}{\partial t} \leq 0 \tag{3.106}$$

A stationary state, for which Σ is minimal, is also a stable state. Non stationary states with $\Sigma > \Sigma_{min}$ evolve into the minimum and small perturbations decay.

Chapter 4

Response Functions

4.1. Time correlation function

The time correlation function $C_{ij}(\tau)$ has characteristic properties, that can be derived from the detailed balance relation. It is defined via

$$\boxed{C_{ij}(\tau) = \langle \alpha_i(t+\tau)\alpha_j(t)\rangle = \iint \mathrm{d}\boldsymbol{\alpha}_0 \mathrm{d}\boldsymbol{\alpha}\ \alpha_j^0 f(\boldsymbol{\alpha}^0) P(\boldsymbol{\alpha}^0|\boldsymbol{\alpha};\tau)\alpha_i\ .} \tag{4.1}$$

Using the detailed balance (3.60)

$$f(\boldsymbol{\alpha}^0) P(\boldsymbol{\alpha}^0|\boldsymbol{\alpha};\tau) = f(\boldsymbol{\alpha}) P(\boldsymbol{\alpha}|\boldsymbol{\alpha}^0;\tau)\ , \tag{4.2}$$

we obtain for the correlation function (4.1)

$$\begin{aligned} C_{ij}(\tau) &= \iint \mathrm{d}\boldsymbol{\alpha}_0 \mathrm{d}\boldsymbol{\alpha}\ \alpha_j^0 f(\boldsymbol{\alpha}) P(\boldsymbol{\alpha}|\boldsymbol{\alpha}^0;\tau)\alpha_i \\ &= \langle \alpha_i(t)\alpha_j(t+\tau)\rangle = \langle \alpha_i(t-\tau)\alpha_j(t)\rangle\ . \end{aligned} \tag{4.3}$$

Therefore, we obtain the time and index symmetry relation for $C_{ij}(\tau)$

$$\boxed{\begin{aligned} &C_{ij}(\tau) = C_{ij}(-\tau)\ , && (4.4) \\ &C_{ij}(\tau) = C_{ji}(-\tau) = C_{ji}(\tau)\ . && (4.5) \end{aligned}}$$

In order to express the correlation function in terms of the matrices $\boldsymbol{g}$ and $\boldsymbol{M}$ defined in Chapter 3, we consider the correlation function at equal times

$$\begin{aligned} C_{ij}(0) = k_B(g^{-1})_{ij} &= \iint \mathrm{d}\boldsymbol{\alpha}^0 \mathrm{d}\boldsymbol{\alpha}\ \alpha_j^0 f(\boldsymbol{\alpha}^0) \underbrace{P(\boldsymbol{\alpha}^0|\boldsymbol{\alpha};0)}_{\delta(\boldsymbol{\alpha}^0-\boldsymbol{\alpha})} \alpha_i \\ &= \int \mathrm{d}\boldsymbol{\alpha}^0 \alpha_j^0 \alpha_i^0 f(\boldsymbol{\alpha}^0) \end{aligned} \tag{4.6}$$

and the time evolution of the expectation value for an even variable α_i starting from a non-equilibrium state $\boldsymbol{\alpha}^0$

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t} \langle \alpha_i(t) \rangle_{\boldsymbol{\alpha}^0} = -M_{ik} \langle \alpha_k(t) \rangle_{\boldsymbol{\alpha}^0} \\ \Rightarrow \quad &\langle \alpha_i(t) \rangle_{\boldsymbol{\alpha}^0} = e^{-Mt}{}_{ik} \alpha_k^0 = \int \mathrm{d}\boldsymbol{\alpha}\ \alpha_i P(\boldsymbol{\alpha}^0 | \boldsymbol{\alpha}, t) \ . \end{aligned} \tag{4.7}$$

Using the two relations (4.6) and (4.7), we find

$$\begin{aligned} C_{ij}(\tau) = \langle \alpha_i(t+\tau)\alpha_j(t) \rangle &= \iint \mathrm{d}\boldsymbol{\alpha}_0 \mathrm{d}\boldsymbol{\alpha}\ \alpha_j^0 f(\boldsymbol{\alpha}^0) P(\boldsymbol{\alpha}^0 | \boldsymbol{\alpha}; \tau) \alpha_i \\ &= \int \mathrm{d}\boldsymbol{\alpha}_0\ \alpha_j^0 f(\boldsymbol{\alpha}^0) (e^{-M\tau})_{ik} \alpha_k^0 = (e^{-M\tau})_{ik} k_B (g^{-1})_{jk} \ . \end{aligned} \tag{4.8}$$

$$\Rightarrow \quad \boxed{C_{ij}(\tau) = (e^{-M\tau})_{ik} k_B (g^{-1})_{jk}} \tag{4.9}$$

4.2. Causality and Kramers-Kronig relation

We consider the response of a system to a set of external forces F_j, that is induced via the response function $K_{ij}(t)$ according to

$$\boxed{\langle \alpha_i(t) \rangle = \int_{-\infty}^{\infty} \mathrm{d}t' K_{ij}(t-t') F_j(t') \ ,} \tag{4.10}$$

by applying to changes of variables $t' \to t' + t$ and $t' \to -t'$, we obtain

$$\langle \alpha_i(t) \rangle = \int_{-\infty}^{\infty} \mathrm{d}t' K_{ij}(-t') F_j(t'+t) = \int_{-\infty}^{\infty} \mathrm{d}t' K_{ij}(t') F_j(t-t') \ . \tag{4.11}$$

The matrix K_{ij} is real and causality imposes the following property

$$\boxed{K_{ij}(t-t') = 0 \ ; \quad t < t' \qquad \text{or} \qquad K_{ij}(t) = 0 \ ; \quad t < 0 \ .} \tag{4.12}$$

Now we consider the Fourier transform of an expectation value

$$\langle \alpha_i(t) \rangle = \frac{1}{2\pi} \int \mathrm{d}\omega\ \langle \tilde{\alpha}_i(\omega) \rangle \, e^{-i\omega t} \tag{4.13}$$

$$\begin{aligned} &= \iiint \mathrm{d}t' \mathrm{d}\omega \mathrm{d}\omega'\ \frac{1}{2\pi} e^{-i\omega(t-t')} \tilde{K}_{ij}(\omega) \frac{1}{2\pi} e^{-i\omega' t'} \tilde{F}_j(\omega') \\ &= \iint \mathrm{d}\omega \mathrm{d}\omega'\ \delta(\omega' - \omega) \tilde{K}_{ij}(\omega) \frac{1}{2\pi} e^{-i\omega t} \tilde{F}_j(\omega') \\ &= \frac{1}{2\pi} \int \mathrm{d}\omega\ e^{-i\omega t} \tilde{K}_{ij}(\omega) \tilde{F}_j(\omega) \ , \end{aligned} \tag{4.14}$$

$$\Rightarrow \qquad \boxed{\langle \tilde{\alpha}_i(\omega) \rangle = \tilde{K}_{ij}(\omega) \tilde{F}_j(\omega)\ .} \tag{4.15}$$

The response function in frequency space $\tilde{K}_{ij}(\omega)$ is given by

$$\tilde{K}_{ij}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t\ e^{i\omega t} K_{ij}(t) = \int_{0}^{\infty} \mathrm{d}t\ e^{i\omega t} K_{ij}(t)\ , \tag{4.16}$$

where the second equal sign follows directly from the principle of causality (4.12).

We assume, that $\tilde{K}_{ij}(0)$ is finite, which makes sense as for a constant force $F_j(t) = \bar{F}_j$, the response should be finite

$$\langle \alpha_i(t) \rangle = \bar{F}_j \int_{-\infty}^{\infty} \mathrm{d}t'\ K_{ij}(t - t') = \bar{F}_j \int_{0}^{\infty} \mathrm{d}t'\ K_{ij}(t') \tag{4.17}$$

$$\Rightarrow \qquad \langle \bar{\alpha}_i \rangle = \bar{F}_j \tilde{K}_{ij}(0)\ . \tag{4.18}$$

Now we introduce the analytic continuation of the Fourier transformed response function in the upper half of the complex plane $\tilde{K}_{ij}(z)$, where $z = \omega + i\epsilon$ and $\epsilon \geq 0$

$$\tilde{K}_{ij}(z) = \int_{0}^{\infty} \mathrm{d}t\ K(t) e^{itz} = \int_{0}^{\infty} \mathrm{d}t\ K(t) e^{it\omega} e^{-\epsilon t} \tag{4.19}$$

should converge for $\tilde{K}_{ij}(\omega)$ convergent (causality), which means, that there are no poles in the upper complex plane.

It is useful to note, that

$$\tilde{K}_{ij}(\omega) = \tilde{K}_{ij}(-\omega)\ , \tag{4.20}$$

where * denotes complex conjugation. This fact directly follows from the property, that $K_{ij}(t)$ is real:

$$\tilde{K}^*_{ij}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t\ e^{i\omega t} K_{ij}(t) = \int \mathrm{d}t\ \left[\cos(\omega t) + i \sin(\omega t)\right] \tag{4.21}$$

$$\tilde{K}_{ij}(-\omega) = \int \mathrm{d}t\ \left[\cos(\omega t) - i \sin(\omega t)\right] = \tilde{K}_{ij}(\omega)^*\ . \tag{4.22}$$

Causality will also yield a relation between the real and the imaginary part. To this end, we consider the function

$$f_{ij}(z) = \frac{\tilde{K}_{ij}(z)}{z - u}\ , \qquad u \in \mathbb{R} \tag{4.23}$$

and its contour integral along C'. As there are no poles within the area enclosed by C' it follows that the integral vanishes

$$\oint_{C'} f_{ij}(z) \mathrm{d}z = \oint_{C'} \frac{\tilde{K}_{ij}(z)}{z - u} \mathrm{d}z = 0\ . \tag{4.24}$$

We can also split the path C' into four contributions

$$\begin{aligned}\oint_{C'} f_{ij}(z)\mathrm{d}z = &\int_{-R}^{u-r} \frac{\tilde{K}_{ij}(\omega)}{\omega-u}\mathrm{d}\omega + \int_{u+r}^{R} \frac{\tilde{K}_{ij}(\omega)}{\omega-u}\mathrm{d}\omega \\ &+ \int_{\pi}^{0} ire^{i\Phi}\frac{\tilde{K}_{ij}(u+re^{i\Phi})}{u+re^{i\Phi}-u}\mathrm{d}\Phi + \int_{0}^{\pi} iRe^{i\Phi}\frac{\tilde{K}_{ij}(Re^{i\Phi})}{Re^{i\Phi}-u}\mathrm{d}\Phi\end{aligned} \tag{4.25}$$

The last contribution vanishes for a quickly enough decaying function $\tilde{K}_{ij}$. We consider the Cauchy principal value

$$\mathcal{P}\int_{-\infty}^{\infty} \frac{\tilde{K}_{ij}(\omega)}{\omega-u}\mathrm{d}\omega = \lim_{r\to 0}\left[\int_{-\infty}^{u-r} \frac{\tilde{K}_{ij}(\omega)}{\omega-u}\mathrm{d}\omega + \int_{u+r}^{\infty} \frac{\tilde{K}_{ij}(\omega)}{\omega-u}\mathrm{d}\omega\right] \tag{4.26}$$

and use equation (4.25) to obtain

$$\mathcal{P}\int_{-\infty}^{\infty} \frac{\tilde{K}_{ij}(\omega)}{\omega-u}\mathrm{d}\omega = -\lim_{r\to 0}\int_{\pi}^{0} i\tilde{K}_{ij}(u+re^{i\Phi})\mathrm{d}\Phi = i\pi\tilde{K}_{ij}(\omega)\ , \tag{4.27}$$

$$\tilde{K}_{ij}(u) = \frac{1}{i\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\tilde{K}_{ij}(\omega)}{\omega-u}\mathrm{d}\omega\ . \tag{4.28}$$

We decompose $\tilde{K}$ into its real and imaginary part

$$\boxed{\tilde{K}_{ij}(\omega) = \tilde{K}'_{ij}(\omega) + i\tilde{K}''_{ij}(\omega)} \tag{4.29}$$

and apply equation (4.28)

$$\begin{aligned}\tilde{K}'_{ij}(u) + i\tilde{K}''_{ij}(u) &= \frac{1}{i\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\tilde{K}_{ij}(\omega)}{\omega-u}\mathrm{d}\omega & (4.30)\\ &= \frac{1}{i\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\tilde{K}'_{ij}(\omega)}{\omega-u}\mathrm{d}\omega + \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\tilde{K}''_{ij}(\omega)}{\omega-u}\mathrm{d}\omega\ . & (4.31)\end{aligned}$$

By comparison of the real and imaginary contributions we obtain the following two relations, which are called Kramers-Kronig (KK) relation and imply, that the response function is already completely described by either its real or imaginary component.

$$\boxed{\begin{aligned}\tilde{K}'_{ij}(u) &= \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\tilde{K}''_{ij}(\omega)}{\omega-u}\mathrm{d}\omega\ , \\ \tilde{K}''_{ij}(u) &= -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty} \frac{\tilde{K}'_{ij}(\omega)}{\omega-u}\mathrm{d}\omega\ .\end{aligned}} \qquad \begin{aligned}(4.32)\\(4.33)\end{aligned}$$

An alternative way to derive the KK-relation is as follows: From the relation (4.20) it is clear that

$$K'(\omega) - iK''(\omega) = K'(-\omega) + iK''(-\omega) \tag{4.34}$$

and thus

$$\boxed{\begin{array}{ll} K'(\omega) = K'(-\omega) & \text{even function} \\ K''(\omega) = -K''(\omega) & \text{uneven function} \end{array}} \tag{4.35, 4.36}$$

$$\tilde{K}'_{ij}(u) = \frac{1}{\pi}\mathcal{P}\int_0^\infty \mathrm{d}\omega \left(\frac{\tilde{K}''_{ij}(\omega)}{\omega - u} + \frac{\tilde{K}''_{ij}(\omega)}{-\omega - u}\right) \sim \frac{K''(\omega)2\omega}{\omega^2 - u^2} \tag{4.37}$$

$$\tilde{K}''_{ij}(u) = -\frac{1}{\pi}\mathcal{P}\int_0^\infty \mathrm{d}\omega \left(\frac{\tilde{K}'_{ij}(\omega)}{\omega - u} + \frac{\tilde{K}'_{ij}(\omega)}{-\omega - u}\right) \sim \frac{K'(\omega)2u}{\omega^2 - u^2} \tag{4.38}$$

4.3. Example – The harmonic oscillator

The equation of motion for a damped and driven harmonic oscillator states

$$\boxed{m\ddot{x} = -kx - \gamma\dot{x} + F_{ext}(t)\ .} \tag{4.39}$$

The solution for the not driven case is

$$x(t) = Ae^{-\zeta\omega_0 t}\sin(\sqrt{1-\zeta^2}\omega_0 t + \phi)\ , \tag{4.40}$$

where $\omega_0 = \sqrt{\frac{k}{m}}$ is the undamped frequency and the damping ratio is given by

$$\zeta = \frac{\gamma}{2\sqrt{mk}} = \frac{\gamma/k}{2\sqrt{m/k}} = \frac{\tau_\gamma}{2\tau_k}$$

For a sinusoidal force

$$F_{ext} = F_0\cos(\omega t) = \mathrm{Re}[F_0 e^{i\omega t}] \tag{4.41}$$

we make the ansatz $x(t) = x_0 e^{i\omega t}$ for a stationary solution. Inserted into the equation of motion we obtain

$$-m\omega^2 x_0 e^{i\omega t} = -kx_0 e^{i\omega t} - \gamma i\omega e^{i\omega t} + F_0 e^{i\omega t}$$

$$\boxed{x_0 = F_0 K(\omega) = \frac{F_0}{k + i\gamma\omega - m\omega^2}}$$

Harmonic Oscillator Response.
I calculated x_0 by the definition $x(t) = \int K(t-t')F(t')\mathrm{d}t' = x_0 e^{i\omega t}$ and $F(t) = F_0 e^{i\omega t}$ which resulted in a different result, i.e. $x_0 = F_0 K^*(\omega)$, this would replace $-i\gamma\omega$ by $+i\gamma\omega$ in the following, which would then also result in two positive Lorentzians for zero mas limit for K' and K"

The last equation follows from (4.15).

$$K(\omega) = \frac{k - m\omega^2 - i\gamma\omega}{(k - m\omega^2 + i\gamma\omega)(k - m\omega^2 - i\gamma\omega)} = \frac{k - m\omega^2 - i\gamma\omega}{(k - m\omega^2)^2 + \gamma^2\omega^2}$$

The real and imaginary parts of K are

$$K'(\omega) = \frac{k - m\omega^2}{(k - m\omega^2)^2 + \gamma^2\omega^2} \,, \qquad K''(\omega) = \frac{-\gamma\omega}{(k - m\omega^2)^2 + \gamma^2\omega^2}$$

Assume F_0 real, then the real part of the equation is important.

$$\begin{aligned} x(t) &= \mathrm{Re}\left[F_0 K(\omega) e^{i\omega t}\right] \\ &= \mathrm{Re}\left[F_0(K'(\omega) + iK''(\omega))(\cos(\omega t) + i\sin(\omega t))\right] \\ &= \underbrace{F_0 K'(\omega)\cos(\omega t)}_{\text{inphase response}} - \underbrace{F_0 K''(\omega)\sin(\omega t)}_{\text{out-of-phase response}} \end{aligned}$$

$$|K(\omega)| = \sqrt{K'^2 + K''^2} = \left[(k - m\omega^2)^2 + \gamma\omega^2\right]^{-1/2}$$

SOME NICE PICTURES

The resonance frequency can be defined by

$$\frac{\partial |k|}{\partial(\omega^2)} = 0 \qquad \Rightarrow \qquad \omega*^2 = \omega_0^2(1 - 2\zeta^2) \;.$$

In case of a massless particle, the response function reduces to a Lorentz curve

$$K'(\omega) = \frac{k}{k^2 + \gamma^2\omega^2} \,, \qquad K''(\omega) = \frac{\gamma\omega}{k^2 + \gamma^2\omega^2}$$

Now we consider the work done on the system.

For the pure in-phase motion, i.e. $K'' = 0$, $F(t) = F_0\cos(\omega t)$, the equation of motion is just

$$x(t) = \cos(\omega t) F_0 K'(\omega)$$

and the work done is fully recovered in one cycle

$$\boxed{W = F_0 x_0 = F_0^2 K'(\omega) \;.}$$

Power:

$$\boxed{P = \frac{W}{T} = F_0^2 \frac{K'(\omega)\omega}{2\pi} \qquad K' : \text{storage modulus}}$$

For the out-of-phase contribution, i.e. $K''(\omega) \neq 0$, the external force does perform work on the system

$$F(t) = F_0\cos(\omega t), \quad x(t)F_0[K'\cos(\omega t) - K''\cos(\omega t)$$

$$W = \int_{\text{cycle}} F(x)\,\mathrm{d}x = \int_0^T F(t)\frac{\mathrm{d}x}{\mathrm{d}t}\,\mathrm{d}t$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = F_0\left[-K'\omega\sin(\omega t) - K''\omega\cos(\omega t)\right]$$

$$\boxed{W = F_0^2\omega \int_0^\tau \cos(\omega t)\left[-K'\sin(\omega t) - K''\cos(\omega t)\right] = F_0^2\omega K''(\omega)\frac{\tau}{2}}$$

Here W refers to the net work in one cycle. The adsorption power is given by

$$\boxed{P = W/\tau = -F_0^2\frac{\omega K''(\omega)}{2} \geq 0;, \qquad K'' : \text{ loss modulus}}$$

4.4. Fluctuation-Dissipation theorem

In the following we want to find a relation between $C(t)$ and $K(t)$. To this end, we consider a step force

$$F_j(t) = \begin{cases} \bar{F}_j & \text{for } t < 0 \\ 0 & \text{for } t > 0 \end{cases} .$$

The response for $t \geq 0$ is

$$\langle \alpha_i(t)\rangle = \int \mathrm{d}\boldsymbol{\alpha}^0 \; \langle \alpha_i(t)\rangle_{\boldsymbol{\alpha}^0} f(\boldsymbol{\alpha}^0, \boldsymbol{F}) \;, \tag{4.42}$$

where $f(\boldsymbol{\alpha}, \boldsymbol{F})$ is the stationary distribution function in presence of a constant force $\boldsymbol{F}$ and $\langle \alpha_i(t)\rangle_{\boldsymbol{\alpha}^0}$ is the conditional probability without external force for going from $\boldsymbol{\alpha}^0$ to $\alpha_i(t)$ in time t

$$\langle \alpha_i(t)\rangle_{\boldsymbol{\alpha}^0} = \int \mathrm{d}\alpha \; \alpha_i P(\boldsymbol{\alpha}^0|\boldsymbol{\alpha}; t) = (e^{-Mt})_{ik}\alpha_k^0 \;. \tag{4.43}$$

Inserting (4.43) into (4.42) yields

$$\langle \alpha_i(t)\rangle = (e^{-Mt})_{ik} \int \mathrm{d}\boldsymbol{\alpha}^0 \; f(\boldsymbol{\alpha}^0, \boldsymbol{F})\alpha_k^0 = (e^{-Mt})_{ik}\langle \alpha_k(0)\rangle \;, \tag{4.44}$$

We can also express the expectation value of α in terms of the response function $K(t)$

$$\langle \alpha_i(t)\rangle = \int_{-\infty}^t \mathrm{d}t' \; K_{ij}(t-t')F_j(t') \tag{4.45}$$

$$\begin{aligned}
\text{for } t = 0 : \langle \alpha_i(0)\rangle &= \bar{F}_j \int_{-\infty}^0 \mathrm{d}t' \; K_{ij}(-t') \\
&= \bar{F}_j \int_0^\infty K_{ij}(t')\mathrm{d}t' = \bar{F}_j \tilde{K}_{ij}(0) && (4.46) \\
\text{for } t > 0 : \langle \alpha_i(t)\rangle &= \bar{F}_j \int_{-\infty}^0 \mathrm{d}t' \; K_{ij}(t-t') = \bar{F}_j \int_t^\infty \mathrm{d}t'' \; K_{ij}(t'') && (4.47)
\end{aligned}$$

Inserting (4.46) and (4.47) into (4.44), we obtain

$$\langle \alpha_i(t)\rangle = (e^{-Mt})_{ik}\bar{F}_j\tilde{K}_{kl}(0) = \bar{F}_j \int_t^\infty \mathrm{d}t'' \; K_{ij}(t'') \tag{4.48}$$

and conclude

$$(e^{-Mt})_{ik} = (\tilde{K}^{-1})_{jk}(0) \int_t^\infty \mathrm{d}t' \; K_{ij}(t') \; . \tag{4.49}$$

Remembering equation (4.9), we use (4.49) and arrive at a preform of the fluctuation dissipation theorem

$$\begin{aligned} C_{ij}(t) &= \langle \alpha_i(t)\alpha_j(0)\rangle = (e^{-Mt})_{ik} k_B (g^{-1})_{jk} \\ C_{ij}(t) &= k_B (g^{-1})_{jk} (\tilde{K}^{-1})_{jk}(0) \int_t^\infty \mathrm{d}t' \; K_{ij}(t') \; . \end{aligned} \tag{4.50}$$

In order to make the last result completely meaningful, we derive a relation between g and $\tilde{K}^{-1}(0)$ from statistical mechanics. Therefore, we look at the partition function

$$Z(T) = \int \mathcal{D}\boldsymbol{a} \; e^{-\beta H(\boldsymbol{a}) + \boldsymbol{a}\cdot F\beta} \; , \tag{4.51}$$

where $\mathcal{D} = \int_{-\infty}^{\infty} \mathrm{d}\alpha_1 \int_{-\infty}^{\infty} \mathrm{d}\alpha_2 \ldots$ denotes the integration over all α variables. The statistical expectation values is given by

$$\langle \alpha_i \rangle = \frac{1}{Z} \int \mathcal{D}\boldsymbol{a} \; \alpha_i e^{-\beta H + \boldsymbol{\alpha}\cdot\boldsymbol{F}\beta} = \frac{\partial \ln Z}{\partial \beta \bar{F}_i} \equiv \tilde{K}_{ij}(0)\bar{F}_j \; , \tag{4.52}$$

where $\tilde{K}_{ij}(0)$ is nothing but the generalized susceptibility. The statistical fluctuation is given by

$$\begin{aligned} \frac{\partial \langle \alpha_i \rangle}{\partial \bar{F}_l \beta} &= \frac{1}{Z} \int \mathcal{D}\boldsymbol{a} \; \alpha_i \alpha_l e^{-\beta H + \boldsymbol{\alpha}\cdot\boldsymbol{F}\beta} - \frac{1}{Z} \int \mathcal{D}\boldsymbol{a} \; \alpha_i e^{-\beta H + \boldsymbol{\alpha}\cdot\boldsymbol{F}\beta} \frac{1}{Z} \int \mathcal{D}\boldsymbol{a} \; \alpha_l e^{-\beta H + \boldsymbol{\alpha}\cdot\boldsymbol{F}\beta} \\ &= \langle \alpha_i \alpha_l \rangle - \langle \alpha_i \rangle \langle \alpha_l \rangle = k_B (g^{-1})_{il} \; , \end{aligned} \tag{4.53}$$

but also by

$$\frac{\partial \langle \alpha_i \rangle}{\partial \bar{F}_l \beta} = \tilde{K}_{il}(0) k_B T \; . \tag{4.54}$$

Combining (4.53) and (4.54) yields

$$(g^{-1})_{il} = \tilde{K}_{il}(0) T \; , \tag{4.55}$$

which is referred to as the static limit of the fluctuation dissipation theorem.

Inserting (4.55) into (4.50), we find the fluctuation-dissipation theorem for $t \geq 0$

$$\boxed{\begin{aligned} C_{ij}(t) &= k_B T \int_t^\infty \mathrm{d}t' \; K_{ij}(t') \\ \frac{\mathrm{d}C_{ij}(t)}{\mathrm{d}t} &= -k_B T K_{ij}(t) \end{aligned}} \qquad \begin{aligned} &(4.56) \\ &(4.57) \end{aligned}$$

To obtain a similar result for the Fourier transforms of C and K, we make some notes on the correlation function:

$C_{ij}(t)$ is even in time, thus its Fourier transform $\tilde{C}_{ij}(\omega)$ is real. Likewise its time derivative $\dot{C}_{ij}(t)$ is uneven in time and its Fourier transform $\tilde{\dot{C}}_{ij}(\omega)$ is purely imaginary. We can further derive a simple relation between $\tilde{C}_{ij}(\omega)$ and $\tilde{\dot{C}}_{ij}(\omega)$ by directly performing the Fourier transform and taking time derivatives

$$\begin{aligned} C_{ij}(t) &= \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi}\, \tilde{C}_{ij}(\omega) e^{-i\omega t} \\ \dot{C}_{ij}(t) &= \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi}\, (-i\omega)\tilde{C}_{ij}(\omega) e^{-i\omega t} \\ \Rightarrow \quad \tilde{\dot{C}}_{ij}(\omega) &= -i\omega \tilde{C}_{ij}(\omega) \; . \end{aligned} \tag{4.58}$$

Using relation (4.16) and the explicit expression for $\dot{C}_{ij}(t)$

$$\dot{C}_{ij}(t) = \begin{cases} -k_B T K_{ij}(t), & \text{for } t > 0 \\ k_B T K_{ij}(-t), & \text{for } t < 0 \end{cases} \; , \tag{4.59}$$

it follows that

$$\boxed{\begin{aligned} \tilde{\dot{C}}_{ij}(\omega) &= -2ik_B T \tilde{K}''_{ij}(\omega) \\ \tilde{K}''_{ij}(\omega) &= \frac{\omega}{2k_B T}\tilde{C}_{ij}(\omega) \; , \end{aligned}} \tag{4.60}$$

where we have used (4.58) to get to the last equation.

Chapter 5

Stochastics

5.1. Brownian motion and Langevin equations

The theory of Brownian motion is the simplest way to approach the dynamics of the of non-equilibrium systems. The fundamental equation is the Langevin equation in which we have frictional forces and random forces coexisting. The connection between this two forces is given by the fluctuation-dissipation theorem. The random motion of a particle immersed in a fluid is called Brownian motion, but the theory of Brownian motion has been extended to systems were the particle becomes a collective property of a macroscopic system. We consider the motion of a spherical particle of mass m, radius r in a one dimensional fluid with viscosity η. Then the equation of motion is by Newton

$$m\frac{dv}{dt} = F_{tot}(t) \tag{5.1}$$

where $F_{tot}(t)$ is the total instantaneous force on the particle at time t due to the interaction with the surrounding medium. If we know the position in time of the particles of the surrounding medium then this force would be a known function of time so that it would not be random at all. From the phenomenological point of view this force is a frictional term so that $F = -\zeta v$ proportional to the velocity of the particle. If this was the only contribution then

$$m\frac{dv}{dt} = -\zeta v \tag{5.2}$$

with the frictional coefficient given by the Stokes law

$$\zeta = 6\pi\eta r \tag{5.3}$$

The solution of the differential equation (5.2) is given by

$$v(t) = v(0)e^{-\zeta t/m} \tag{5.4}$$

which decays to zero for $t \longrightarrow \infty$. However since the velocity of the particle at thermal equilibrium has to be according to the equipartition theorem

$$\boxed{\left\langle v^2 \right\rangle_{eq} = \frac{k_B T}{m}} \tag{5.5}$$

the actual velocity cannot remain at zero. It follows that an extra term in the total force must be added. This is a random force $\delta F(t)$, so that the equation of motion becomes the Langevin equation for a Brownian particle

$$\boxed{m\frac{dv}{dt} = -\zeta v + \delta F(t)} \tag{5.6}$$

The first is the systematic part or friction and the second is the fluctuating part or noise. Since the force during an impact with the surrounding cannot vary with extreme rapidity over the time of any infinitesimal time interval, the first two moments of the noise averaged over an infinitesimal amount of time are given by

$$\boxed{\langle \delta F(t) \rangle = 0 \quad \langle \delta F(t) \delta F(t') \rangle = 2B\delta(t - t')} \tag{5.7}$$

Here the constant B gives the strength of the fluctuating force with Gaussian distribution determined by this moments. The Langevin equation (5.6) has the solution

$$\boxed{v(t) = v(0)e^{-\zeta t/m} + \int_0^t dt' e^{-\zeta(t-t')/m} \frac{\delta F(t')}{m}} \tag{5.8}$$

where the first term is just equation (5.4) giving the exponential decay due to friction and the second term gives the extra velocity produced by the random noise. If we now square this equation we get the three terms

$$v^2(0)e^{-2\zeta t/m} \tag{5.9}$$

$$2v(0) \int_0^t dt' e^{-\zeta(t-t')/m} \frac{\delta F(t')}{m} e^{-\zeta t/m} \tag{5.10}$$

$$\int_0^t dt' e^{-\zeta(t-t')/m} \int_0^t dt'' e^{-\zeta(t-t'')/m} \frac{\delta F(t') \delta F(t'')}{m^2} \tag{5.11}$$

so that taking the average and using (5.7) gives the mean squared velocity

$$\langle v^2(t) \rangle = v^2(0)e^{-2\zeta t/m} + \frac{B}{\zeta m}(1 - e^{-2\zeta t/m}) \tag{5.12}$$

Taking the limit $t \longrightarrow \infty$ and using (5.5) we find the relation that connects the strength of the fluctuating force B to the magnitude ζ of the friction

$$\boxed{B = \zeta k_B T} \tag{5.13}$$

which is a simplest derivation of the fluctuation-dissipation theorem.

5.2. Velocity correlation function

Equilibrium statistical mechanics is based on the idea of statistical ensemble. In non equilibrium statistical mechanics since there is no unique partition function this quantities are replaced by time correlation functions which appear whenever we analyze the statistical behavior of some time-dependent quantity $A(t)$ measured over a long time. Defining the fluctuation $\delta A(t) = A(t) - \langle A \rangle$, the time averaged product of two fluctuations at different times is then given by the time correlation function of δA as

$$\boxed{C(t) = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau ds\ \delta A(s) \delta A(t+s)} \tag{5.14}$$

We can use the Langevin equation (5.6) and the fluctuation-dissipation theorem (5.13) to express several time correlation functions. The velocity correlation function can be obtained from the long time average

$$\langle v(t) v(t') \rangle_t = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau ds\ v(t+s) v(t'+s) \tag{5.15}$$

where $\langle \ldots \rangle_t$ means that the average is taken over long time. Assuming the initial time in the infinite past, in equation (5.8) we only need to keep the second term. So shifting the variable of integration $t - t' \to u$ we have

$$\begin{aligned} v(t) &= \int_{-\infty}^t dt' e^{-\zeta(t-t')/m} \frac{\delta F(t')}{m} \\ &= \int_0^\infty du\ e^{-\zeta u/m} \frac{\delta F(t-u)}{m} \end{aligned} \tag{5.16}$$

Then the velocity correlation function (5.15) is

$$\begin{aligned}
\langle v(t)v(t')\rangle_t &= \int_0^\infty du \int_0^\infty du' e^{-\zeta(u+u')/m} \frac{1}{\tau} \int_0^\tau ds\ \frac{1}{m^2} \delta F(t-u+s) \delta F(t'-u+s) \\
&= \int_0^\infty du \int_0^\infty du' e^{-\zeta(u+u')/m} ds\ \frac{1}{m^2} 2B\delta(t-u-t'+u') \\
&= \int_0^\infty du\ e^{-\zeta(2u+|t'-t|)/m} \frac{2B}{m^2}
\end{aligned}$$

$$\Rightarrow \quad \boxed{\langle v(t)v(t')\rangle_t = \frac{B}{m\zeta} e^{-\zeta|t'-t|/m}} \tag{5.17}$$

where the product of two random force factor has been replaced by its average. In the end using the fluctuation-dissipation theorem (5.13) we find the expression for the velocity correlation function

$$\langle v(t)v(t')\rangle_t = \frac{k_B T}{m} e^{-\zeta|t'-t|/m} \tag{5.18}$$

The same result is obtained calculating the equilibrium ensemble average $\langle \ldots \rangle_{eq}$ instead of the long time average $\langle \ldots \rangle_t$. For the equilibrium ensemble we average over the noise equation (5.8) to get

$$\langle v(t)\rangle_{noise} = v(0) e^{-\zeta t/m} \tag{5.19}$$

and multiplying for $v(0)$ and averaging over the initial velocity we find

$$\langle v(t)v(0)\rangle_{eq} = \frac{k_B T}{m} e^{-\zeta t/m} \tag{5.20}$$

which is the same result obtained in (5.18) since this last equation as the Langevin equation is valid only for $t > 0$.

5.3. Mean squared displacement

An easy way to show the connection between the time correlation function for the velocity and the self diffusion coefficient D which appears in Einstein equation is to start with the one dimensional diffusion equation for the concentration $c(x,t)$ of a particle. This is nothing but a continuity equation with the assumption that the current flux of concentration $J(x,t)$ is proportional to the gradient of the concentration itself by the factor D so that $J(x,t) = -D\ \partial c/\partial x$ and then

$$\frac{\partial}{\partial t} c(x,t) = -\frac{\partial}{\partial x} J(x,t) = D \frac{\partial^2}{\partial x^2} c(x,t) \tag{5.21}$$

The mean squared displacement at time t is then found by multiplying this equation by x^2 and integrating over x. We assume, that the distribution is initially localized. The time derivative of the mean squared displacement is

$$\begin{aligned}\frac{\partial}{\partial t}\left\langle x^2\right\rangle &= \frac{\partial}{\partial t}\int dx\ x^2 c(x,t)\\ &= \int dx\ x^2 \frac{\partial}{\partial t} c(x,t)\\ &= D\int dx\ x^2 \frac{\partial^2}{\partial x^2} c(x,t)\\ &= -2D\int dx\ x \frac{\partial}{\partial x} c(x,t)\\ &= 2D\int dx\ c(x,t)\\ &= 2D \end{aligned} \tag{5.22}$$

since the concentration is normalized to unity $\int dx\ c(x,t) = 1$. Integrating over time (5.22) gives Einstein equation for diffusion in one dimension

$$\boxed{\left\langle [x(t)-x(0)]^2\right\rangle = 2Dt} \tag{5.23}$$

But since the net displacement of the particle's position during the interval t is given by

$$x(t)-x(0) = \int_0^t dt' v(t') \tag{5.24}$$

taking the average of (5.8) and using (5.7) we find two terms contributing to $\langle [x(t)-x(0)]^2\rangle$ which are

$$\int_0^t dt' \int_0^t dt'' \left\langle v^2(0) e^{-\zeta(t'+t'')/m}\right\rangle \tag{5.25}$$

$$\int_0^t dt' \int_0^t dt'' \int_0^t d\tau' \int_0^t d\tau'' e^{-\zeta(t'-\tau')/m} e^{-\zeta(t''-\tau'')/m} \frac{2B\delta(\tau'-\tau'')}{m^2} \tag{5.26}$$

Then using (5.18) and the same integrals done in the previous section the average of the mean square displacement becomes

$$\left\langle [x(t)-x(0)]^2\right\rangle = 2\frac{k_B T}{\zeta}\left[t - \frac{m}{\zeta} + \frac{m}{\zeta} e^{-\zeta t/m}\right] \tag{5.27}$$

So for long times the effect of the noise is dominant and the mean squared displacement increases linearly with time

$$\boxed{\left\langle [x(t)-x(0)]^2 \right\rangle \sim 2\frac{k_B T}{\zeta} t \,, \qquad \text{for} \quad t \gg m/\zeta} \tag{5.28}$$

while for short times the exponential in (5.27) can be expanded to give

$$\boxed{\left\langle [x(t)-x(0)]^2 \right\rangle \sim \frac{k_B T}{m} t^2 \,, \qquad \text{for} \quad t \ll m/\zeta} \tag{5.29}$$

Using Stokes law (5.3) and Einstein equation (5.23), from (5.28) we find the Einstein-Stokes formula for the ballistic motion

$$\boxed{D = \frac{k_B T}{\zeta} = \frac{k_B T}{6\pi\eta r}} \tag{5.30}$$

Equating the mean squared displacement for long and short times (5.28) and (5.29), we identify the critical time after which the ballistic regime take place scaling as

$$t^* = \frac{2m}{\zeta} \sim \frac{m}{\zeta} \tag{5.31}$$

Using (5.24) we can write the mean squared displacement as

$$\left\langle [x(t)-x(0)]^2 \right\rangle = \int_0^t d\tau \int_0^t d\tau' \left\langle v(\tau) v(\tau') \right\rangle \tag{5.32}$$

and using the time-translational invariance, the time derivative of this quantity is then

$$\begin{aligned} \frac{d}{dt} \left\langle [x(t)-x(0)]^2 \right\rangle &= 2 \int_0^t d\tau \left\langle v(t) v(\tau) \right\rangle \\ &= 2 \int_0^t d\tau \left\langle v(t-\tau) v(0) \right\rangle \\ &= 2 \int_0^t d\tau \left\langle v(\tau) v(0) \right\rangle \end{aligned} \tag{5.33}$$

where in the last passage we have just changed the integration variable switching the sign. We see that now then time t appears only in the integral domain. From comparison with equation (5.23), we obtain, that the diffusion coefficient is given by

$$\boxed{D = \int_0^t d\tau \, \langle v(\tau) v(0) \rangle} \tag{5.34}$$

The general form of the fluctuation-dissipation theorem (4.57) tells us that the correlation function $C(t)$ is linked to the response function $K(t)$ as

$$\frac{dC(t)}{dt} = -k_B T K(t) \tag{5.35}$$

We wish to find the connection between the diffusion and the fluctuation-dissipation theorem. If for a state variable α we have the position $x(t)$ in one dimension then for the force $F(t)$ we have

$$\begin{aligned} x(t) &= \int dt' K(t-t') F(t') \\ &= \int dt' K(t') F(t-t') \end{aligned} \tag{5.36}$$

$$v(t) = \frac{dx(t)}{dt} = \int dt' \frac{dK(t-t')}{dt} F(t') \tag{5.37}$$

But since $-v(t)\zeta = F(t)$ for the response function it must be

Minus Sign. what we already talked about: the minus sign in the definition of the friction force here, causes a wrong sign in the fluc-dis-t later.

$$\frac{dK(t)}{dt} = -\frac{\delta(t)}{\zeta} \tag{5.38}$$

$$K(t) = -\frac{\Theta(t)}{\zeta} \tag{5.39}$$

and the position expectation value (5.36) becomes

$$x(t) = -\frac{1}{\zeta} \int_0^\infty dt' F(t-t') \tag{5.40}$$

The correlation function for the position at initial time and general time t is

$$C(t) = \langle x(0) x(t) \rangle \tag{5.41}$$

and since $\langle x^2(0) \rangle$ and $\langle x^2(t) \rangle$ are both constant if averaged over a long time, we can write the mean square displacement time derivative, using (5.23), as

$$\begin{aligned}\frac{d}{dt}\left\langle [x(t)-x(0)]^2\right\rangle &= -2\frac{d}{dt}\left\langle x(0)x(t)\right\rangle \\ &= -2\frac{d}{dt}C(t) \\ &= 2D\end{aligned} \tag{5.42}$$

From this equation using (5.35) and (5.39) we find the relation connecting diffusion and the fluctuation-dissipation theorem

$$\boxed{D = -\frac{d}{dt}C(t) = k_B T K(t) = \frac{k_B T}{\zeta}\ .} \tag{5.43}$$

5.4. Langevin equation for many variables

We consider a set of dynamical variables $\{a_1, a_2, \dots\}$ and the corresponding first order linear Langevin equation

$$\boxed{\frac{da_j}{dt} = \Theta_{jk} a_k + \delta F_j(t)} \tag{5.44}$$

in which the entries of the matrix Θ_{jk} depend on whether the variables a_j represent the position or the momentum and $\delta F_j(t)$ are the random forces. As for the one variable case the strength of the noise is given by

$$\langle \delta F_j(t)\rangle = 0, \qquad \langle \delta F_j(t)\delta F_k(t')\rangle = 2B_{jk}\delta(t-t') \tag{5.45}$$

The matrix Θ_{jk} can be diagonalized by a unitary transformation. The eigenvector relative to a vanishing eigenvalue of this matrix corresponds to a dynamical constant of motion, i.e. the equilibrium condition. If we assume that all this quantities have been removed from the set $\{a_1, a_2, \dots\}$, for a system that reaches equilibrium in the limit $t \to \infty$ all the eigenvalues have negative real part but can also have an imaginary part. So the solution of equation (5.44) is given by

$$\boxed{a_j(t) = \left(e^{\Theta t}\right)_{jk} a_k(0) + \int_0^t dt'\ \left(e^{\Theta(t-t')}\right)_{jk} \delta F_k(t')\ .} \tag{5.46}$$

We can neglect the first therm for long times since it decays to zero. Then using (5.45) for the second moment we have

$$\begin{aligned}
\langle a_j(t)a_i(t)\rangle &= \int_0^t dt' \int_0^t dt'' \left(e^{\Theta(t-t')}\right)_{jk} \left(e^{\Theta(t-t'')}\right)_{il} \langle \delta F_k(t')\delta F_l(t'')\rangle \\
&= \int_0^t dt' \int_0^t dt'' \left(e^{\Theta(t-t')}\right)_{jk} \left(e^{\Theta(t-t'')}\right)_{il} 2B_{kl}\delta(t'-t'') \\
&= \int_0^t dt' \left(e^{\Theta(t-t')}\right)_{jk} \left(e^{\Theta(t-t')}\right)_{il} 2B_{kl} \\
&= \int_0^t dt' \left(e^{\Theta(t-t')}\right)_{jk} 2B_{kl} \left(e^{\Theta^T(t-t')}\right)_{li} ,
\end{aligned} \tag{5.47}$$

where ^{T} denotes the matrix transpose and we used that, for an arbitrary matrix A it is

$$\left(e^{A}\right)^T = e^{A^T} . \tag{5.48}$$

For large times, we obtain

$$\langle a_j a_i\rangle_{eq} = \langle a_j(\infty)a_i(\infty)\rangle = \int_0^\infty dt \left(e^{\Theta t}\right)_{jk} 2B_{kl}\left(e^{\Theta^T t}\right)_{li} \equiv M_{ji} \tag{5.49}$$

where M_{ji} denotes the equilibrium value for the second moment. Since $\langle a_j a_i\rangle = \langle a_i a_j\rangle$ the matrix $M_{ji} = M_{ij}$ must be symmetric.
Consider now the quantity constructed to be symmetric in $\{n, i\}$

$$\begin{aligned}
\Theta_{nj}M_{ji} + \Theta_{ij}M_{jn} &= \Theta_{nj}M_{ji} + M_{nj}\Theta^T_{ji} \\
&= \int_0^\infty dt\ \Theta_{nj} \left(e^{\Theta t}\right)_{jk} 2B_{kl}\left(e^{\Theta^T t}\right)_{li} + \int_0^\infty dt \left(e^{\Theta t}\right)_{nk} 2B_{kl}\left(e^{\Theta^T t}\right)_{lj}\Theta^T_{ji} \\
&= \int_0^\infty dt \frac{d}{dt} \left(e^{\Theta t}\right)_{nk} 2B_{kl}\left(e^{\Theta^T t}\right)_{li} \\
&= (2e^{\Theta t}Be^{\Theta^T t})_{t=\infty} - 2B \\
&= -2B
\end{aligned} \tag{5.50}$$

where in the last line we have used that the eigenvalues of $\boldsymbol{\Theta}$ have negative real parts. The last result is another derivation of the fluctuation-dissipation theorem

$$\boxed{\mathbf{\Theta M} + \mathbf{M\Theta}^T = -2\mathbf{B}} \tag{5.51}$$

We note that since both $\boldsymbol{B}$ and $\boldsymbol{M}$ are defined as second moments they are symmetric while Θ is not and can be divided in two parts

$$\boxed{\Theta_{ij} = i\Omega_{ij} - K_{ij}} \tag{5.52}$$

with properties

$$\mathbf{KM} = (\mathbf{KM})^T = \mathbf{MK}^T \tag{5.53}$$

$$i\mathbf{\Omega M} = -i(\mathbf{\Omega M})^T = -i\mathbf{M\Omega}^T \tag{5.54}$$

From this last two relations and (5.52) it follows

$$\boxed{\mathbf{B} = \mathbf{KM} = \mathbf{MK}^T} \tag{5.55}$$

In equation (5.52) the first term represents the oscillatory motion and the quantity **KM** is real and symmetric and describes the decaying motion connected with the Onsager reciprocal relations. To construct the $\mathbf{\Theta}$ matrix we note that

$$\mathbf{M}^{-1}(i\mathbf{\Omega} - \mathbf{K})\mathbf{M} = -\mathbf{K}^T - i\mathbf{\Omega}^T \tag{5.56}$$

$$\mathbf{M}^{-1}\mathbf{\Theta M} + \mathbf{\Theta}^T = -\mathbf{K}^T - i\mathbf{\Omega}^T + i\mathbf{\Omega}^T - \mathbf{K}^T = -2\mathbf{K}^T \tag{5.57}$$

$$\mathbf{M}^{-1}\mathbf{\Theta M} - \mathbf{\Theta}^T = -\mathbf{K}^T - i\mathbf{\Omega}^T - i\mathbf{\Omega}^T + \mathbf{K}^T = -2i\mathbf{\Omega}^T \tag{5.58}$$

As an example we consider the Brownian motion of a harmonic oscillator with equations of motion given by (5.44)

$$\frac{dx}{dt} = \frac{p}{m} \tag{5.59}$$

$$\frac{dp}{dt} = -\zeta\frac{p}{m} - m\omega^2 x + \delta F_p(t) \tag{5.60}$$

The dynamical variables vector, the force matrix and second moment matrix are given by

$$\mathbf{a} = \begin{pmatrix} x \\ p \end{pmatrix} \tag{5.61}$$

$$\mathbf{F} = \begin{pmatrix} 0 \\ \delta F_p \end{pmatrix} \tag{5.62}$$

$$\mathbf{M} = \begin{pmatrix} \langle x^2 \rangle & 0 \\ 0 & \langle p^2 \rangle \end{pmatrix} = \begin{pmatrix} k_B T/m\omega^2 & 0 \\ 0 & mk_B T \end{pmatrix} \tag{5.63}$$

where the vanishing off diagonal entries of the second moment matrix assures no coupling between position and momentum. Comparing equation (5.44) with (5.59) and (5.60) one finds for the $\mathbf{\Theta}$ matrix

$$\mathbf{\Theta} = \begin{pmatrix} 0 & 1/m \\ -m\omega^2 & -\zeta/m \end{pmatrix} \tag{5.64}$$

$$\mathbf{\Theta}^T = \begin{pmatrix} 0 & -m\omega^2 \\ 1/m & -\zeta/m \end{pmatrix} \tag{5.65}$$

$$\mathbf{M}^{-1}\mathbf{\Theta}\mathbf{M} = \begin{pmatrix} 0 & m\omega^2 \\ -1/m & -\zeta/m \end{pmatrix} \tag{5.66}$$

$$\mathbf{M}^{-1}\mathbf{\Theta}\mathbf{M} + \mathbf{\Theta}^T = 2\begin{pmatrix} 0 & 0 \\ 0 & -\zeta/m \end{pmatrix} \tag{5.67}$$

$$\mathbf{M}^{-1}\mathbf{\Theta}\mathbf{M} - \mathbf{\Theta}^T = 2\begin{pmatrix} 0 & m\omega^2 \\ -1/m & 0 \end{pmatrix} \tag{5.68}$$

Comparing this last two equations with (5.57) and (5.58) we find

$$\mathbf{K}^T = \mathbf{K} = \begin{pmatrix} 0 & 0 \\ 0 & \zeta/m \end{pmatrix} \tag{5.69}$$

$$i\mathbf{\Omega}^T = \begin{pmatrix} 0 & -m\omega^2 \\ 1/m & 0 \end{pmatrix} \tag{5.70}$$

$$i\mathbf{\Omega} = \begin{pmatrix} 0 & 1/m \\ -m\omega^2 & 0 \end{pmatrix} \tag{5.71}$$

and the general result (5.13) of the fluctuation-dissipation theorem is verified

$$\mathbf{B} = \mathbf{K}\mathbf{M} = \begin{pmatrix} 0 & 0 \\ 0 & \zeta/m \end{pmatrix} \begin{pmatrix} \langle x^2 \rangle & 0 \\ 0 & \langle p^2 \rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & \langle p^2 \rangle \zeta/m \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & \zeta k_B T \end{pmatrix} \tag{5.72}$$

5.5. Non Markovian Langevin equations

In theory of probability given $X_0, \dots X_n$, if the conditional distribution of X_{n+1} depends only on X_n, the model assumes the Markov property or memoryless property. In this contest of non-equilibrium statistical mechanics it is used to indicate that the friction at time t is proportional to the velocity at the same time and that the noise is white delta correlated. The term white noise means that the Fourier transform of the correlation function of the noise is independent of frequency since B is constant

$$\langle \delta F(t) \delta F(t') \rangle = 2B \; \delta(t-t') = \int \frac{d\omega}{2\pi} \; 2B \; e^{-i\omega t} \tag{5.73}$$

Generally real problems are not Markovian, the friction at time t depends on the history of the velocity at earlier times, i.e. it has a memory. We can replace the friction coefficient ζ with a memory function $K(t)$ so that

$$-\zeta v(t) \longrightarrow -\int_{-\infty}^{t} ds \; K(t-s) v(s) = -\int_{0}^{\infty} ds \; K(s) v(t-s) \tag{5.74}$$

Accordingly the fluctuation-dissipation theorem must be modified and the noise becomes colored. A simple example of a memory (non Markovian) behavior of the system is given by the harmonic oscillator, arising when the momentum is eliminated. The equations of motion are again (5.59) and (5.60) with solution given by (5.46)

$$p(t) = e^{-\zeta(t-t_0)/m} \; p(t_0) + \int_{t_0}^{t} dt' \; e^{-\zeta(t-t')/m} \Big(\delta F_p(t') - m\omega^2 x(t') \Big) \tag{5.75}$$

By sending $t_0 \longrightarrow -\infty$ and setting $s = t - t'$ we can write

$$\boxed{p(t) = \int_{0}^{\infty} ds \; e^{-\zeta s/m} \Big(\delta F_p(t-s) - m\omega^2 x(t-s) \Big)} \tag{5.76}$$

and substituting this back into (5.59) we find

$$\boxed{\begin{aligned} \frac{dx(t)}{dt} &= \frac{1}{m} \int_{0}^{\infty} ds \; e^{-\zeta s/m} \Big(\delta F_p(t-s) - m\omega^2 x(t-s) \Big) \\ &= \delta F_x(t) - \int_{0}^{\infty} ds \; K(s) \; x(t-s) \end{aligned}} \tag{5.77}$$

where the memory function and the new random force acting on the position with the ${}_x$ subscript, given by

$$\boxed{K(s) = \omega^2 e^{-\zeta s/m}} \tag{5.78}$$

$$\boxed{\delta F_x(t) = \frac{1}{m}\int_0^\infty ds\; e^{-\zeta s/m}\;\delta F_p(t-s)} \tag{5.79}$$

From the equipartition theorem at equilibrium the second moment of x is

$$\boxed{\left\langle x^2\right\rangle_{eq} = \frac{k_B T}{m\omega^2}} \tag{5.80}$$

For the second moment of the new random force using (5.73) and (5.13) we have

$$\begin{aligned}\langle \delta F_x(t)\delta F_x(t')\rangle &= \frac{1}{m^2}\int_0^\infty ds\; e^{-\zeta s/m}\int_0^\infty ds'\; e^{-\zeta s'/m}\,\langle \delta F_p(t-s)\delta F_p(t'-s')\rangle \\ &= 2\frac{\zeta k_B T}{m^2}\int_0^\infty ds\; e^{-\zeta s/m}\int_0^\infty ds'\; e^{-\zeta s'/m}\delta(t-s-t'+s')\end{aligned} \tag{5.81}$$

We can distinguish two cases:

I $\boxed{t-t'\geq 0} \implies s = t-t'+s'$

$$\begin{aligned}\langle \delta F_x(t)\delta F_x(t')\rangle &\sim \int_0^\infty ds'\; e^{-\zeta s'/m}\; e^{-\zeta(t-t'+s')/m} \\ &= e^{-\zeta(t-t')/m}\int_0^\infty ds'\; e^{-\zeta 2s'/m}\end{aligned} \tag{5.82}$$

II $\boxed{t-t'\leq 0} \implies s' = t'-t+s$

$$\begin{aligned}\langle \delta F_x(t)\delta F_x(t')\rangle &\sim \int_0^\infty ds\; e^{-\zeta s/m}\; e^{-\zeta(t'-t+s)/m} \\ &= e^{-\zeta(t'-t)/m}\int_0^\infty ds\; e^{-\zeta 2s/m}\end{aligned} \tag{5.83}$$

So with both cases using (5.80) and (5.78) we find

$$\begin{aligned}\langle \delta F_x(t)\delta F_x(t')\rangle &= \frac{2k_B T\zeta}{m^2}e^{-\zeta|t-t'|/m}\int_0^\infty ds\; e^{-\zeta 2s/m} \\ &= \frac{k_B T}{m}e^{-\zeta|t-t'|/m} \\ &= \left\langle x^2\right\rangle_{eq} K(|t-t'|)\end{aligned} \tag{5.84}$$

We remark that since we could distinguish two different cases this already implied a non analyticity of the function. This last result is a non Markovian version of the fluctuation-dissipation theorem where the correlation function of the new noise is proportional to the memory function of the new friction

$$\boxed{\langle \delta F_x(t)\delta F_x(t')\rangle = \left\langle x^2\right\rangle_{eq} K(|t-t'|) \equiv C_{Fx}(t-t')} \tag{5.85}$$

If we are interested in the spectrum of $C_{Fx}(t-t')$ we can take the Fourier transform

$$\begin{aligned}
\tilde{C}_{Fx}(\omega) &= \int_{-\infty}^{\infty} dt\ \frac{k_B T}{m} e^{-\zeta|t|/m} e^{i\omega t} \\
&= \frac{k_B T}{m}\left\{\int_{-\infty}^{0} dt\ e^{\zeta t/m + i\omega t} + \int_{0}^{\infty} dt\ e^{-\zeta t/m + i\omega t}\right\} \\
&= \frac{k_B T}{m}\left\{\int_{0}^{\infty} dt\ e^{-\zeta t/m - i\omega t} + \int_{0}^{\infty} dt\ e^{-\zeta t/m + i\omega t}\right\} \\
&= \frac{k_B T}{m}\left\{\frac{1}{\frac{\zeta}{m} + i\omega} + \frac{1}{\frac{\zeta}{m} - i\omega}\right\} \\
&= \frac{k_B T}{m} \frac{2\frac{\zeta}{m}}{\frac{\zeta}{m}^2 + \omega^2}
\end{aligned} \tag{5.86}$$

$$\Rightarrow \qquad \boxed{\tilde{C}_{Fx}(\omega) = \frac{2k_B T}{m} \frac{\frac{\zeta}{m}}{\frac{\zeta}{m}^2 + \omega^2}\ .} \tag{5.87}$$

This spectrum is not white as before since it is not constant but has a term involving the frequency ω. However in the limit of small mass (large friction) and long time limit (small frequency) the spectrum becomes white again

$$\boxed{\lim_{\omega\to 0} \tilde{C}_{Fx}(\omega) = \frac{2k_B T}{\zeta}} \tag{5.88}$$

Doing the inverse Fourier transform of this last result we obtain

$$\boxed{C_{Fx}(t-t') = \frac{2k_B T}{\zeta}\delta(t-t')} \tag{5.89}$$

and using (5.85) for the memory function $K(t)$ we find the expression

$$K(t) = \frac{C_{Fx}(t)}{\left\langle x^2\right\rangle_{eq}} = 2\frac{m\omega^2}{\zeta}\delta(t)\frac{1}{2} = \frac{m\omega^2}{\zeta}\delta(t) \tag{5.90}$$

corresponding to Markovian friction. We had to add a factor $\frac{1}{2}$, because K is only non-zero on the positive t-axis and we have to take care of this asymmetry also for the delta-function. Equations (5.77) and (5.85) then become

$$\frac{dx(t)}{dt} = \delta F_x(t) - \frac{m\omega^2}{\zeta}x(t) \tag{5.91}$$

$$\langle \delta F_x(t)\delta F_x(t')\rangle = \frac{2k_BT}{\zeta}\delta(t-t') \tag{5.92}$$

Quite generally eliminating variables from a Markovian system of equations leads to memory effects and non Markovian equations. Conversely if memory decays exponentially in time, non Markovian Langevin equation can be made Markovian by introducing coupled variables. As a short derivation of the one dimensional Langevin equation for the harmonic oscillator by taking the limit of small mass of (5.60) we get

$$\frac{dp}{dt} = -\zeta\frac{dx}{dt} - m\omega^2 x + \delta F_p(t) = m\frac{d^2x}{dx^2} = 0 \tag{5.93}$$

$$\Rightarrow \quad \zeta\frac{dx}{dt} = -m\omega^2 x + \delta F_p(t) \tag{5.94}$$

This equation is of the same form of (5.6) with the substitutions

$$\zeta \longrightarrow m\omega^2 \tag{5.95}$$

$$m \longrightarrow \zeta \tag{5.96}$$

$$v(t) \longrightarrow x(t) \tag{5.97}$$

In analogy with the derivation for the Markovian Langevin equation we have

$$\left\langle x^2 \right\rangle_{eq} = \frac{B}{\zeta m\omega^2} \tag{5.98}$$

and from the equipartition theorem it must be

$$\left\langle x^2 \right\rangle_{eq} = \frac{k_BT}{m\omega^2} \tag{5.99}$$

Equating this last two gives the noise strength as found before with the fluctuation dissipation theorem

$$\boxed{B = \zeta k_BT} \tag{5.100}$$

5.6. Projection and partition in phase-space

We now see the Liouville equation from which in principle Langevin equations can be derived. A microscopic state is completely described classically by $6N$ variables (p^{3N}, q^{3N}) governed by Hamilton's equations

$$\boxed{\dot{q}_i = \frac{\partial H(\boldsymbol{p}, \boldsymbol{q})}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H(\boldsymbol{p}, \boldsymbol{q})}{\partial q_i}} \tag{5.101}$$

This set of first order differential equations determines the trajectory in the phase space with the initial time condition. As an example the one-dimensional harmonic oscillator is subjected to the Hamiltonian

$$H(\boldsymbol{p}, \boldsymbol{q}) = \frac{\boldsymbol{p}^2}{2m} + \frac{m\omega^2 \boldsymbol{q}^2}{2} \tag{5.102}$$

leading to the differential equations

$$\dot{q}_i = \frac{p_i}{m}, \qquad \dot{p}_i = -m\omega^2 q_i \tag{5.103}$$

for which the solutions are

$$q_i(t) = q_0 \cos(\omega(t - t_0)) + \frac{p_0}{m\omega} \sin(\omega(t - t_0)) \tag{5.104}$$

$$p_i(t) = -m\omega q_0 \sin(\omega(t - t_0)) + p_0 \cos(\omega(t - t_0)) \tag{5.105}$$

The expectation values of physical observable follows from the phase space density $\rho(\boldsymbol{p}, \boldsymbol{q}, t)$ with the normalization condition

$$\int \mathrm{d}\boldsymbol{p}\mathrm{d}\boldsymbol{q}\ \rho(\boldsymbol{p}, \boldsymbol{q}, t) = 1 \qquad \forall t \tag{5.106}$$

Generally whenever an integral of a quantity $A(t)$ over an entire domain is constant we have a conservation law of the form

$$\frac{\partial A}{\partial t} + \nabla(\boldsymbol{v}A) = 0 \tag{5.107}$$

where $\boldsymbol{v}$ is the velocity,$A\boldsymbol{v}$ is a flux and there is the correspondence with the $6N$ dimensional vectors

$$\nabla = \left(\frac{\partial}{\partial p_i}, \frac{\partial}{\partial q_i} \right) \tag{5.108}$$

$$\boldsymbol{v} = \left(\frac{\partial p_i}{\partial t}, \frac{\partial q_i}{\partial t} \right) \tag{5.109}$$

So for the phase space density we have

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial p_i} \left(\frac{\partial p_i}{\partial t} \rho \right) + \frac{\partial}{\partial q_i} \left(\frac{\partial q_i}{\partial t} \rho \right) = 0 \tag{5.110}$$

which by using Hamilton equations (5.101) becomes

$$\frac{\partial \rho}{\partial t} - \frac{\partial}{\partial p_i} \left(\frac{\partial H}{\partial q_i} \rho \right) + \frac{\partial}{\partial q_i} \left(\frac{\partial H}{\partial p_i} \rho \right) = 0 \tag{5.111}$$

Since for the second derivatives we have

$$\frac{\partial^2 H}{\partial p_i \partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} \tag{5.112}$$

this terms cancel out in (5.111) and we obtain

$$\frac{\partial \rho}{\partial t} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} + \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} = 0 \tag{5.113}$$

$$\boxed{\frac{\partial \rho(\boldsymbol{p}, \boldsymbol{q}, t)}{\partial t} + \boldsymbol{L} \rho(\boldsymbol{p}, \boldsymbol{q}, t) = 0} \tag{5.114}$$

where we have defined the Liouville operator

$$\boxed{\boldsymbol{L} \equiv \frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i}} \tag{5.115}$$

The formal solution of (5.114) is given by

$$\boxed{\rho(\boldsymbol{p}, \boldsymbol{q}, t) = e^{-\boldsymbol{L} t} \rho(\boldsymbol{p}, \boldsymbol{q}, 0)} \tag{5.116}$$

The Liouville operator has the formal properties:

I L **is anti-self-adjoint operator:**

$$
\begin{aligned}
LA\rho &= \left(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i}\right)A\rho \\
&= \left(\frac{\partial}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial}{\partial p_i}\frac{\partial H}{\partial q_i}\right)A\rho \\
&= \left(\frac{\partial}{\partial q_i}\dot{q}_i + \frac{\partial}{\partial p_i}\dot{p}_i\right)A\rho
\end{aligned} \tag{5.117}
$$

Comparing (5.107) with (5.114) and integrating over the phase-space volume $\mathrm{d}V = \mathrm{d}\boldsymbol{p}\mathrm{d}\boldsymbol{q}$ we have

$$
\int_V \mathrm{d}V\ \boldsymbol{L}A\rho = \int_V \mathrm{d}V\ \nabla \boldsymbol{v}A\rho = \oint_{S(V)} \mathrm{d}\boldsymbol{S}\ \boldsymbol{v}A\rho \tag{5.118}
$$

Since typically the system is confined to a finite region in the phase space, the density vanishes at the boundary thus

$$
\int_V \mathrm{d}V\ \boldsymbol{L}A\rho = 0 \tag{5.119}
$$

Also because $\boldsymbol{L}$ contains first derivatives we can write

$$
\boldsymbol{L}A\rho = \rho\boldsymbol{L}A + A\boldsymbol{L}\rho \tag{5.120}
$$

and insert into (5.119) to get

$$
\boxed{\int_V \mathrm{d}V\ A\boldsymbol{L}\rho = -\int_V \mathrm{d}V\ \rho\boldsymbol{L}A} \tag{5.121}
$$

i.e. $\boldsymbol{L}$ is anti-self-adjoint in phase-space.

II **Dynamical evolution:**
Assuming the time dependance to be only implicit we have for a generic dynamical variable

$$
A(\boldsymbol{p}, \boldsymbol{q}, t) = A(\boldsymbol{p}(t), \boldsymbol{q}(t)) \equiv A(t) \tag{5.122}
$$

$$A(\boldsymbol{p},\boldsymbol{q},t=0)\equiv A \tag{5.123}$$

The initial rate of change with time is calculated from

$$\begin{aligned}\left(\frac{\partial A(\boldsymbol{p},\boldsymbol{q},t)}{\partial t}\right)_{t=0} &= \frac{\partial A}{\partial q_i}\left(\frac{\partial q_i}{\partial t}\right)_{t=0}+\frac{\partial A}{\partial p_i}\left(\frac{\partial p_i}{\partial t}\right)_{t=0}\\ &= \left(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i}-\frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i}\right)A\\ &= \boldsymbol{L}A\end{aligned} \tag{5.124}$$

This can be generalized easily to n^{th} order derivatives as

$$\boxed{\left(\frac{\partial^n A(\boldsymbol{p},\boldsymbol{q},t)}{\partial t^n}\right)_{t=0}=\boldsymbol{L}^n A} \tag{5.125}$$

Then the time dependent dynamical variables can be expanded in Taylor's series

$$\begin{aligned}A(\boldsymbol{p},\boldsymbol{q},t) &= \sum_{n=0}^{\infty}\frac{t^n}{n!}\left(\frac{\partial^n A(\boldsymbol{p},\boldsymbol{q},t)}{\partial t^n}\right)_{t=0}\\ &= \sum_{n=0}^{\infty}\frac{t^n}{n!}\boldsymbol{L}^n A\\ &= e^{\boldsymbol{L}t}A\end{aligned} \tag{5.126}$$

which is the solution of the differential operator equation

$$\frac{\partial}{\partial t}A(\boldsymbol{p},\boldsymbol{q},t)-\boldsymbol{L}A(\boldsymbol{p},\boldsymbol{q},t)=0 \tag{5.127}$$

So in analogy with quantum mechanics we can view the Liouville equation (5.114) for the distribution function ρ as in the Schroedinger picture and the Liouville equation (5.127) for the dynamical variable $A(t)$ as in the Heisemberg picture. The operator $\exp(\boldsymbol{L}t)$ moves the dynamical variables along a trajectory in phase space as a propagator and has the properties

$$e^{\boldsymbol{L}t}A(\boldsymbol{p},\boldsymbol{q},0)=e^{\boldsymbol{L}t}A=A(e^{\boldsymbol{L}t}\boldsymbol{p},e^{\boldsymbol{L}t}\boldsymbol{q},0) \tag{5.128}$$

$$e^{\boldsymbol{L}t}AB = (e^{\boldsymbol{L}t}A)(e^{\boldsymbol{L}t}B) \tag{5.129}$$

The expectation value of a dynamical variable over the phase space at time t is given by

$$\begin{aligned} \langle A(t) \rangle &= \int_V \mathrm{d}V \; A\rho(\boldsymbol{p}, \boldsymbol{q}, t) \\ &= \int_V \mathrm{d}V \; Ae^{-\boldsymbol{L}t}\rho(\boldsymbol{p}, \boldsymbol{q}, 0) \end{aligned} \tag{5.130}$$

but also equivalently by

$$\begin{aligned} \langle A(t) \rangle &= \int_V \mathrm{d}V \; A(\boldsymbol{p}, \boldsymbol{q}, t)\rho(\boldsymbol{p}, \boldsymbol{q}, 0) \\ &= \int_V \mathrm{d}V \; \rho(\boldsymbol{p}, \boldsymbol{q}, 0)e^{\boldsymbol{L}t}A \end{aligned} \tag{5.131}$$

since from (5.121) the Liouville operator is anti-self-adjoint.

At this point we want to find the matrix form of the Liouville equation since we found that for a dynamical variable is linear. We define the scalar product of two dynamical variables

$$\left\langle A, B^\dagger \right\rangle_{eq} = \int_V \mathrm{d}V \; \rho_{eq} AB^\dagger \tag{5.132}$$

where ρ_{eq} is the equilibrium density distribution. Taking the compete and orthonormal set of functions $\{\phi_n\}$ in the phase space, with $\left\langle \phi_j \phi_k^\dagger \right\rangle = \delta_{jk}$ the matrix form of the dynamical variable is

$$A(\boldsymbol{p}, \boldsymbol{q}, t) = \sum_m a_m(t)\phi_m(\boldsymbol{p}, \boldsymbol{q}) \tag{5.133}$$

with

$$a_m(t) = \left\langle A(\boldsymbol{p}, \boldsymbol{q}, t), \phi_m^\dagger(\boldsymbol{p}, \boldsymbol{q}) \right\rangle \tag{5.134}$$

Inserting (5.133) into the Liouville equation (5.127) we have

$$\sum_m \dot{a}_m(t)\phi_m(\boldsymbol{p}, \boldsymbol{q}) = \sum_m a_m(t)\boldsymbol{L}\phi_m(\boldsymbol{p}, \boldsymbol{q}) \tag{5.135}$$

From completeness of the set of functions we can integrate over the equilibrium distribution to get

$$\dot{a}_m(t) = \sum_m a_m(t) L_{mn} \phi_m(\boldsymbol{p}, \boldsymbol{q}) \tag{5.136}$$

with

$$L_{mn} = \int \mathrm{d}V \; \rho_{eq} \boldsymbol{L} \phi_n^\dagger = \left\langle \boldsymbol{L} \phi_n^\dagger \right\rangle \tag{5.137}$$

Usually we are only interested in a subset of variables. For example we might have

$$\boxed{\frac{\partial}{\partial t} \begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} a_1(t) \\ a_2(t) \end{pmatrix}} \tag{5.138}$$

of which the $a_1(t)$ variables are the relevant, while the $a_1(t)$ variables are irrelevant. We have

$$\dot{a}_2(t) = L_{22} a_2(t) + L_{21} a_1(t) \tag{5.139}$$

$$a_2(t) = e^{L_{22} t} a_2(0) + \int_0^t ds e^{L_{22}(t-s)} L_{21} a_1(s) \tag{5.140}$$

$$\boxed{\begin{aligned} \dot{a}_1(t) &= L_{11} a_1(t) + L_{12} a_2(t) \\ &= L_{11} a_1(t) + \underbrace{L_{12} \int_0^t ds e^{L_{22}(t-s)} L_{21} a_1(s)}_{\text{non markovian friction}} + \underbrace{L_{12} e^{L_{22} t} a_2(0)}_{\text{noise term}} \end{aligned}} \tag{5.141}$$

As mentioned before eliminating the variable $a_2(t)$from a Markovian system of equations leads to memory effects and non Markovian equations,.This can be seen from the non Markovian friction term, here dependent on the history of $a_1(t)$.

Chapter 6

Fokker-Planck Equations

6.1. Motivation and derivation from Langevin equation

Linear Langevin equations can be solved exactly, while nonlinear ones are very hard to treat analytically. We consider the general case

$$\dot{x}(t) = \frac{p(t)}{m} \qquad \dot{p}(t) = -\zeta \frac{p}{m} - U'(x) + \delta F_p(t) \tag{6.1}$$

where the nonlinear terms are contained in the spatial derivative of the potential. In the linear case, the equations for $\langle x \rangle$ and $\langle p \rangle$ only involve the first moment of each. In the nonlinear case let us consider the typical example of a periodic potential

$$U(x) = U_0 \cos(x) \tag{6.2}$$

$$U'(x) = -U_0 \sin(x) = -U_0 (x - \frac{1}{6} x^3 + \dots) \tag{6.3}$$

The average $\langle U'(x) \rangle$ contains higher moments of x

$$\langle U'(x) \rangle = U_0 (- \langle x \rangle + \frac{1}{6} \langle x^3 \rangle - \dots) \tag{6.4}$$

so that

$$U'(\langle x \rangle) = U_0 (- \langle x \rangle + \frac{1}{6} \langle x \rangle^3 - \dots) \neq \langle U'(x) \rangle \tag{6.5}$$

One obtains coupled equations for the moments $\langle x^n \rangle$, which are difficult to solve or even not solvable often.

In the following, we consider the nonlinear Langevin equation for the N dynamical variables $\{a_1, \dots, a_N\}$ in the form

$$\frac{\mathrm{d}a_j(t)}{\mathrm{d}t} = h_j(\boldsymbol{a}) + \delta F_j(t) \,, \tag{6.6}$$

where in general h_j is some nonlinear given function of the dynamical variables $\{a_1, \ldots, a_N\}$, but without memory. The random force $\delta\boldsymbol{F}(t)$ obeys the usual relations (5.45) for a Gaussian distribution with delta correlated second moment. Instead of fluctuating, stochastic trajectories $a_j(t)$, we are now interested in the probability distribution $f(\boldsymbol{a}, t)$ averaged over the noise $\delta\boldsymbol{F}(t)$. As the phase space density $f(\boldsymbol{a}, t)$ is conserved at all times the normalization condition holds

$$\int \mathrm{d}\boldsymbol{a} f(\boldsymbol{a}, t) = 1 \tag{6.7}$$

so that the time derivative of $f(\boldsymbol{a}, t)$ is balanced by a the divergence of a flux in the form of a conservation equation

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial a_j}\left(\frac{\partial a_j}{\partial t} f\right) = 0 \tag{6.8}$$

Plugging (6.6) into (6.8) yields

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial a_j}\Big(h_j(\boldsymbol{a})f + \delta F_j(t) f\Big) = -Lf - \frac{\partial}{\partial a_j}\delta F_j(t) f \tag{6.9}$$

where the operator

$$L = \frac{\partial}{\partial a_j} h_j(\boldsymbol{a}) \tag{6.10}$$

is the analogue of the Liouville operator but acting on any function $f(\boldsymbol{a}, t)$. The formal solution of equation (6.9) is of the form

$$f(\boldsymbol{a}, t) = e^{-tL} f(\boldsymbol{a}, 0) - \int_0^t \mathrm{d}s\, e^{-(t-s)L} \frac{\partial}{\partial a_j} \delta F_j(s) f(\boldsymbol{a}, s) \tag{6.11}$$

where $f(\boldsymbol{a}, t)$ depends on the noise $\delta\boldsymbol{F}(s)$ only for times s earlier than t. Plugging (6.11) back into (6.9), we obtain a series expansion for $f(\boldsymbol{a}, t)$ in powers of the noise

$$\begin{aligned} \frac{\partial f(\boldsymbol{a}, t)}{\partial t} &= -Lf(\boldsymbol{a}, t) - \frac{\partial}{\partial a_j}\delta F_j(t) e^{-tL} f(\boldsymbol{a}, 0) \\ &\quad + \frac{\partial}{\partial a_j}\delta F_j(t) \int_0^t \mathrm{d}s\ e^{-(t-s)L}\frac{\partial}{\partial a_k}\delta F_k(s) f(\boldsymbol{a}, s) \end{aligned} \tag{6.12}$$

where $f(\boldsymbol{a}, s)$ still implicitly depends on the noise $\delta\boldsymbol{F}(s)$ at time $s < t$. Iteratively inserting (6.11) into (6.12), one generates higher order terms in $\delta\boldsymbol{F}$. The average over the noise can be performed exactly and gives

$$\frac{\partial \langle f(\boldsymbol{a}, t)\rangle}{\partial t} \tag{6.13}$$

$$= -L\langle f(\boldsymbol{a}, t)\rangle + \frac{\partial}{\partial a_j}\int_0^t \mathrm{d}s e^{-(t-s)L}\langle \delta F_j(t)\delta F_k(s)\rangle \frac{\partial}{\partial a_k}\langle f(\boldsymbol{a}, s)\rangle \tag{6.14}$$

$$= -L\langle f(\boldsymbol{a}, t)\rangle + \frac{\partial}{\partial a_j} B_{jk} \frac{\partial}{\partial a_k}\langle f(\boldsymbol{a}, t)\rangle\ , \tag{6.15}$$

FP derivation
we still want to do this more explicitly and more clear, when we also have written something abut gaussian integrals in the appendix.

since $\langle \delta F_j(t) f(\boldsymbol{a},0)\rangle = f(\boldsymbol{a},0)\langle \delta F_j(t)\rangle = 0$ and higher order terms in $\delta\boldsymbol{F}$ do not generate additional terms because the noise is Gaussian and has all vanishing cumulants higher than the second. Overall, we obtain the Fokker-Planck equation for the noise averaged distribution function $\langle f(\boldsymbol{a},t)\rangle$

$$\frac{\partial}{\partial t}\langle f(\boldsymbol{a},t)\rangle = -\frac{\partial}{\partial a_j} h_j(\boldsymbol{a})\langle f(\boldsymbol{a},t)\rangle + \underbrace{\frac{\partial}{\partial a_j} B_{jk}\frac{\partial}{\partial a_k}\langle f(\boldsymbol{a},t)\rangle}_{\text{noise}} \; . \tag{6.16}$$

which we rewrite changing our notation $\langle f\rangle \to f$ from this point forward

$$\boxed{\frac{\partial}{\partial t} f(\boldsymbol{a},t) = -\frac{\partial}{\partial a_j} h_j(\boldsymbol{a}) f(\boldsymbol{a},t) + \frac{\partial}{\partial a_j} B_{jk}\frac{\partial}{\partial a_k} f(\boldsymbol{a},t)} \tag{6.17}$$

As an examples we consider a particle in an external potential $U(x)$ with equations of motion

$$\dot{x}(t) = \frac{p(t)}{m} \; , \qquad \dot{p}(t) = -U'(x) - \zeta\frac{p}{m} + \delta F(t) \tag{6.18}$$

and delta correlated random force given by the fluctuation dissipation theorem (5.13)

$$\langle \delta F_j(t)\delta F_l(t')\rangle = 2\zeta k_B T\delta(t-t') \; . \tag{6.19}$$

The quantities defined above are then given by

$$\boldsymbol{a} = \begin{pmatrix} x(t) \\ p(t)\end{pmatrix} \quad \boldsymbol{h} = \begin{pmatrix} p(t)/m \\ -U'(x) - \zeta p(t)/m\end{pmatrix} \tag{6.20}$$

$$\delta\boldsymbol{F} = \begin{pmatrix} 0 \\ \delta F_p\end{pmatrix} \quad B = \begin{pmatrix} 0 & 0 \\ 0 & \zeta k_B T\end{pmatrix} \tag{6.21}$$

The Fokker Planck (FP) equation for $f = f(x,p,t)$ reads

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial x}\frac{p}{m} f + \frac{\partial}{\partial p}\left(U'(x) + \zeta\frac{p}{m}\right) f + \zeta k_B T\frac{\partial^2 f}{\partial p^2} \tag{6.22}$$

Without friction the FP equation reduces to the standard Liouville equation for the phase space density ρ of a system with Hamiltonian $H = p^2/2m + U(q)$

$$L = \frac{\partial H}{\partial p}\frac{\partial}{\partial q} - \frac{\partial H}{\partial q}\frac{\partial}{\partial p} = \frac{\partial}{\partial q}\frac{p}{m} - \frac{\partial}{\partial p}U'(q) \tag{6.23}$$

$$\frac{\partial \rho}{\partial t} = -L\rho = -\frac{\partial}{\partial q}\frac{p}{m}\rho + \frac{\partial}{\partial p}U'(q)\rho \tag{6.24}$$

as we can see by setting $f=\rho$ and $\zeta=0$ in (6.22).
One stationary solution of the FP equation is given by $f_{eq}=e^{-H/k_BT}/Z$, where $Z=\int \mathrm{d}x\mathrm{d}p\, e^{-\beta H(x,p)}$ is the partition function. We find indeed for $f=f_{eq}$ in (6.22)

$$\begin{aligned}
\frac{\partial f_{eq}}{\partial t} &= -\frac{p}{m}\frac{\partial f}{\partial x}+U'(x)\frac{\partial f}{\partial p}+\frac{\zeta}{m}f+\zeta\frac{p}{m}\frac{\partial f}{\partial p}+\zeta k_BT\frac{\partial^2 f}{\partial p^2}\bigg|_{f=f_{eq}}\\
&=\left[\frac{p}{m}\beta\frac{\partial H}{\partial x}-U'(x)\beta\frac{\partial H}{\partial p}+\frac{\zeta}{m}-\zeta\beta\frac{p}{m}\frac{\partial H}{\partial p}-\zeta\frac{\partial^2 H}{\partial p^2}+\zeta\beta\left(\frac{\partial H}{\partial p}\right)^2\right]f_{eq}\\
&=\left[\frac{p}{m}\beta U'(x)-U'(x)\beta\frac{p}{m}+\frac{\zeta}{m}-\zeta\beta\frac{p}{m}\frac{\partial H}{\partial p}-\frac{\zeta}{m}+\zeta\beta\left(\frac{\partial H}{\partial p}\right)^2\right]f_{eq}\\
&=\left[-\zeta\beta\frac{p}{m}\frac{\partial H}{\partial p}+\zeta\beta\left(\frac{\partial H}{\partial p}\right)^2\right]f_{eq}\\
&=0
\end{aligned} \tag{6.25}$$

Now we introduce the operator notation

$$\frac{\partial}{\partial t}f(\boldsymbol{a},t)=\mathcal{D}f(\boldsymbol{a},t)\ , \tag{6.26}$$

where $\mathcal{D}$ is the Fokker-Planck operator

$$\mathcal{D}\equiv-\frac{\partial}{\partial a_j}h_j(\boldsymbol{a})+\frac{\partial}{\partial a_j}B_{jk}\frac{\partial}{\partial a_k} \tag{6.27}$$

composed by the Liouville operator and a stochastic part. The formal solution of (6.26) reads

$$f(\boldsymbol{a},t)=e^{\mathcal{D}t}f(\boldsymbol{a},0)\,. \tag{6.28}$$

The expectation value of an arbitrary function $\Phi(\boldsymbol{a})$ in a Schroedinger-picture like way is given by

$$\langle\Phi(\boldsymbol{a})\rangle=\int \mathrm{d}\boldsymbol{a}\,\Phi(\boldsymbol{a})f(\boldsymbol{a},t)=\int \mathrm{d}\boldsymbol{a}\,\Phi(\boldsymbol{a})e^{\mathcal{D}t}f(\boldsymbol{a},0)\ . \tag{6.29}$$

We can define the adjoint operator $D^\dagger$ via

$$\int \mathrm{d}\boldsymbol{a}\,\Phi(\boldsymbol{a})\mathcal{D}\Psi(\boldsymbol{a})=\int \mathrm{d}\boldsymbol{a}\,\Psi(\boldsymbol{a})\mathcal{D}^\dagger\Phi(\boldsymbol{a}) \tag{6.30}$$

and obtain with an integration by parts, using (6.27)

$$\mathcal{D}^\dagger=h_j(\boldsymbol{a})\frac{\partial}{\partial a_j}+\frac{\partial}{\partial a_j}B_{jk}\frac{\partial}{\partial a_k}\ . \tag{6.31}$$

Thus, we can also express the expectation value in a Heisenberg-picture like way where the average is taken over the initial distribution

$$\langle\Phi(\boldsymbol{a})\rangle=\int \mathrm{d}\boldsymbol{a}\,f(\boldsymbol{a},0)e^{\mathcal{D}^\dagger t}\Phi(\boldsymbol{a})=\int \mathrm{d}\boldsymbol{a}\,f(\boldsymbol{a},0)\Phi(\boldsymbol{a},t)\ . \tag{6.32}$$

where the time evolution of the dynamical function is given by

$$\Phi(\boldsymbol{a},t) = e^{\mathcal{D}^\dagger t}\Phi(\boldsymbol{a}) \quad \text{with} \quad \Phi(\boldsymbol{a},0) = \Phi(\boldsymbol{a}) \tag{6.33}$$

The equation of motion for the time dependent variable becomes

$$\boxed{\frac{\partial \Phi(\boldsymbol{a},t)}{\partial t} = \left[h_j(\boldsymbol{a})\frac{\partial}{\partial a_j} + \frac{\partial}{\partial a_j}B_{jk}\frac{\partial}{\partial a_k}\right]\Phi(\boldsymbol{a},t)} \tag{6.34}$$

We note that solving a FP equation for f or for an arbitrary function Φ is equally difficult.

6.2. Smulochowski equation

We now consider the same general system as in the previous section, but assume, that the inertia term $m\ddot{x}(t)$ is negligible, thus equation (6.1) gives

$$\dot{x}(t) = -\frac{1}{\zeta}U'(x) + \frac{1}{\zeta}\delta F_p(t) \tag{6.35}$$

and absorbing the friction in the noise

$$\dot{x}(t) = -\frac{1}{\zeta}U'(x) + \delta F_x(t) \tag{6.36}$$

Comparing with (6.6) and using (5.45) for $\delta F_p = \zeta \delta F_x$, with (5.13) gives

$$a(t) = x(t)\,, \quad h = -\frac{U'(x)}{\zeta}\,, \quad B_{jk} = B = \frac{k_B T}{\zeta} \tag{6.37}$$

from which the FP equation (6.17) becomes the Smulochowski (SM) equation

$$\boxed{\begin{aligned}\frac{\partial f(x,t)}{\partial t} &= \frac{\partial}{\partial x}\frac{U'(x)}{\zeta}f(x,t) + \frac{\partial^2}{\partial x^2}\frac{k_B T}{\zeta}f(x,t)\\ &= \frac{k_B T}{\zeta}\frac{\partial}{\partial x}e^{-U/k_B T}\frac{\partial}{\partial x}e^{U/k_B T}f\\ &= D\frac{\partial}{\partial x}e^{-U/k_B T}\frac{\partial}{\partial x}e^{U/k_B T}f\end{aligned}} \tag{6.38}$$

which describe diffusion in an external potential with the diffusion coefficient $D = k_B T/\zeta = B$. Again, we notice, that the FP equilibrium solution $f_{eq} = e^{-U/k_B T}/Z$ is a stationary solution, but there exist also further stationary solutions, that are not stationary solutions of the full FP equation.

Next, we consider a more intuitive derivation of the SM equation in terms of a continuity equation

$$\frac{\partial f(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x}\,, \tag{6.39}$$

where the flux J is given by

$$J(x,t) = -\frac{1}{\zeta}U'(x)f - D\frac{\partial}{\partial x}f\,. \tag{6.40}$$

consisting of a force contribution and a diffusive contribution. If we define the function $g(x,t)$

$$f = \sqrt{f_{eq}}g = \frac{e^{-U/2k_BT}}{\sqrt{Z}}g\,. \tag{6.41}$$

and insert into (6.39), using (6.40), we obtain

$$\begin{aligned}
e^{-U/2k_BT}\frac{\partial g}{\partial t} =& \frac{1}{\zeta}\frac{\partial}{\partial x}U'e^{-U/2k_BT}g + D\frac{\partial^2}{\partial x^2}e^{-U/2k_BT}g \\
=& \frac{1}{\zeta}U''e^{-U/2k_BT}g - \frac{1}{\zeta 2k_BT}U'^2e^{-U/2k_BT} + \frac{1}{\zeta}U'e^{-U/2k_BT}g' \\
& + D\frac{\partial}{\partial x}\left(-\frac{U'}{2k_BT}e^{-U/2k_BT}g + e^{-U/2k_BT}g'\right) \\
=& \frac{1}{\zeta}U''e^{-U/2k_BT}g - \frac{1}{\zeta 2k_BT}U'^2e^{-U/2k_BT} + \frac{1}{\zeta}U'e^{-U/2k_BT}g' \\
& + D\left(-\frac{U''}{2k_BT}e^{-U}2k_BTg + \frac{U'^2}{4k_BT^2}e^{-U/2k_BT}g\right. \\
& \left. -\frac{U'}{2k_BT}e^{-U/2k_BT}g' - \frac{U'}{2k_BT}e^{-U/2k_BT}g' + e^{-U/2k_BT}g''\right) \\
=& \frac{U''}{2\zeta}e^{-U/2k_BT}g - \frac{U'^2}{4\zeta k_BT}e^{-U/2k_BT}g + \frac{k_BT}{\zeta}e^{-U}2k_BTg''\,.
\end{aligned}$$

Thus

$$\boxed{\begin{aligned}
\frac{\partial g}{\partial t} &= D\left[\frac{1}{2k_BT}U'' - \frac{U'^2}{4(k_BT)^2} + \frac{\partial^2}{\partial x^2}\right]g \\
&= -D\left[-\frac{\partial^2}{\partial x^2} + U_{eff}\right]g
\end{aligned}} \tag{6.42}$$

where the effective potential is given by

$$U_{eff} = -\frac{1}{2k_BT}U'' + \left(\frac{U'}{2k_BT}\right)^2\,. \tag{6.43}$$

We recognize, that equation (6.42) is nothing but a usual Schroedinger equation, that has real eigenvalues and eigenfunctions and that therefore a large set of quantum mechanical tools can be used for this particular FP equation.

6.3. Kramers problem

We are interested in the rate, with which a particle subject to Brownian motion passes a potential barrier. This process is important in e.g. molecule dissociation or protein folding. From B the probability to go to A or C are equal, if we neglect inertia.

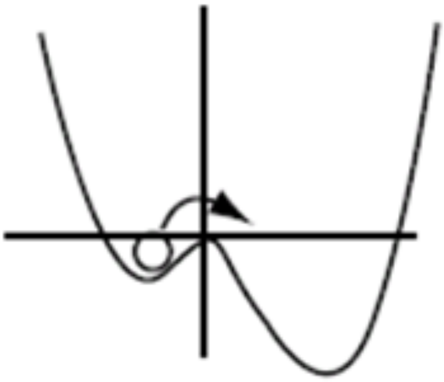

Figure 6.1.: First well (A) with position x_1, potential barrier (B) with position x_2 and second well (C)

When we start at A, with which rate does a particle come to point C? To treat this problem we will use the SM equation as the full FP equation is too difficult.

$$\frac{\partial f}{\partial t} = D\frac{\partial}{\partial x}e^{-U/k_BT}\frac{\partial}{\partial x}e^{U/k_BT}f \tag{6.44}$$

We treat this problem with a stationary solution $\dot{f} = 0$ with the assumption for the flux (6.40)

$$J = -De^{-\tilde{U}}\frac{\partial}{\partial x}e^{\tilde{U}}f = \text{const.} \neq 0 \, , \tag{6.45}$$

where we introduced $\tilde{U} = U/k_BT$ for the sake of brevity. Rearranging eq (6.45) yields

$$\frac{Je^{\tilde{U}}}{D} = -\frac{\partial}{\partial x}e^{\tilde{U}}f \quad \Rightarrow \quad \int_{x_1}^{x_2} \mathrm{d}x\,\frac{Je^{\tilde{U}}}{D} = -\left[e^{\tilde{U}}f\right]_{x_1}^{x_2} \tag{6.46}$$

or since J and D are assumed constant

$$\frac{J}{D} = \frac{-e^{\tilde{U}(x_2)}f(x_2) + e^{\tilde{U}(x_1)}f(x_1)}{\int_{x_1}^{x_2}\mathrm{d}x\,e^{\tilde{U}}} \, . \tag{6.47}$$

We assume an adsorbing boundary condition at x_2 meaning that $f(x_2) = 0$ and no particle can get to x_2 from the right. Thus,

$$\frac{J}{D} = \frac{e^{\tilde{U}(x_1)}f(x_1)}{\int_{x_1}^{x_2}\mathrm{d}x\,e^{\tilde{U}}} \, . \tag{6.48}$$

For a high barrier, we can expand $\tilde{U}$ near the maximum in x_2

$$\tilde{U} = \tilde{U}_2 - \frac{\tilde{U}_2''}{2}(x_2 - x)^2 \, , \tag{6.49}$$

where $\tilde{U}_2 = \tilde{U}(x_2)$ and $\tilde{U}_2'' \geq 0$, and thus

$$\begin{aligned}\int_{x_1}^{x_2} \mathrm{d}x\, e^{\tilde{U}} &= e^{\tilde{U}_2} \int_{x_1}^{x_2} \mathrm{d}x\, e^{-\frac{\tilde{U}_2''}{2}(x_2-x)^2} \\ \simeq \frac{1}{2} e^{\tilde{U}_2} \int_{-\infty}^{\infty} \mathrm{d}x\, e^{-\frac{\tilde{U}_2''}{2}(x_2-x)^2} &= \frac{1}{2} e^{\tilde{U}_2} \sqrt{\frac{2\pi}{\tilde{U}_2''}} = e^{\tilde{U}_2} \sqrt{\frac{\pi}{2\tilde{U}_2''}}\end{aligned}$$

With this approximation, equation (6.48) reads

$$J = D e^{-(\tilde{U}_2 - \tilde{U}_1)} \sqrt{\frac{2\tilde{U}_2''}{\pi}} f(x_1) \tag{6.50}$$

so that the flux depends exponentially on the potential difference and also on the curvature $\tilde{U}_2''$ of the barrier. We assume, that $f(x_1)$ is given by the equilibrium distribution

$$f(x_1) = \frac{e^{-\tilde{U}(x_1)}}{\int_{x_0}^{x_2} \mathrm{d}x\, e^{-\tilde{U}(x)}} \,. \tag{6.51}$$

This is justified because

$$J = -D e^{-\tilde{U}} \frac{\partial}{\partial x} e^{\tilde{U}} f$$

and thus

$$\frac{\partial}{\partial x} f e^{\tilde{U}} = -\frac{J}{D} e^{\tilde{U}} \,,$$

which means, that for $e^{\tilde{U}}$ small, also $\frac{\partial}{\partial x} f e^{\tilde{U}}$ is small.

We can also expand the potential around x_1

$$\tilde{U}(x) \simeq \tilde{U}_1 + \frac{\tilde{U}_1''}{2}(x - x_1)^2 \tag{6.52}$$

and insert this into (6.51), yielding

$$f(x_1) \simeq \frac{1}{\int_{x_0}^{x_2} \mathrm{d}x\, e^{-\frac{\tilde{U}_1''}{2}(x-x_1)^2}} \sim \sqrt{\frac{\tilde{U}_1''}{2\pi}} \tag{6.53}$$

Finally we obtain for the flux

$$\boxed{J = \frac{D\sqrt{\tilde{U}_1''\tilde{U}_2''}}{\pi} e^{-\Delta\tilde{U}} = \frac{D\sqrt{U_1''U_2''}}{\pi k_B T} e^{-\Delta U/k_B T}} \tag{6.54}$$

where $\Delta U = U_2 - U_1$. So for the rate of crossing the barrier $\kappa = J/2$ (i.e. the rate to go from A to C), using $D = k_B T/\zeta$ we find

$$\boxed{\kappa = \frac{\sqrt{U_1''U_2''}}{2\pi\zeta} e^{-\Delta U/k_B T}}, \tag{6.55}$$

6.4. Mean first-passage time

We consider the Smulochowski equation

$$\frac{\partial f(x,t)}{\partial t} = \mathcal{D} f(x,t) \tag{6.56}$$

with

$$\mathcal{D} = D \frac{\partial}{\partial x} e^{-\tilde{U}} \frac{\partial}{\partial x} e^{\tilde{U}} \tag{6.57}$$

and look at the Green's function $G(x,t;x_0,t_0)$ that is defined via

$$\left(\frac{\partial}{\partial t} - \mathcal{D} \right) G(x,t;x_0,t_0) = \delta(x-x_0)\delta(t-t_0) \tag{6.58}$$

Statement:

$$f(x,t) = \int \mathrm{d}\tilde{x}\, f_0(\tilde{x}) G(x,t;\tilde{x},t_0) \tag{6.59}$$

solves the SM eq. where

$$f(x,t_0) = f_0(x)\ . \tag{6.60}$$

First we proof (6.59)

$$\begin{aligned}
\left(\frac{\partial}{\partial t} - \mathcal{D} \right) f &= \left(\frac{\partial}{\partial t} - \mathcal{D} \right) \int \mathrm{d}\tilde{x}\, f_0(\tilde{x}) G(x,t;\tilde{x},t_0) && (6.61)\\
&= \int \mathrm{d}\tilde{x}\, f_0(\tilde{x}) \left(\frac{\partial}{\partial t} - \mathcal{D} \right) G(x,t;\tilde{x},t_0) && (6.62)\\
&= \int \mathrm{d}\tilde{x} f_0(\tilde{x}) \delta(x-\tilde{x})\delta(t-t_0) && (6.63)\\
&= f_0(x)\delta(t-t_0) && (6.64)
\end{aligned}$$

Thus f is a solution for all times $t \neq t_0$.
Now we proof (6.60), where we use that

$$\mathcal{D} f = -\frac{\partial}{\partial x} J(x,t) \tag{6.65}$$

and integrate (6.58) over space

$$\int_{x_0-\epsilon}^{x_0+\epsilon} \mathrm{d}x\, \delta(x-x_0)\delta(t-t_0) = \delta(t-t_0) = \frac{\partial}{\partial t} \int \mathrm{d}x\, G + J(x+\epsilon,t) - J(x-\epsilon,t)$$

For $\epsilon \to \infty$, the flux J vanishes and we find

$$\int \mathrm{d}x\, G = \theta(t-t_0)\ , \tag{6.66}$$

which corresponds to a particle being created at $t = t_0$. If we integrate over time, we find

$$\int_{t_0-\epsilon}^{t_0+\epsilon} \delta(x-x_0)\delta(t-t_0) = \delta(x-x_0) = G(x,t_0+\epsilon;x_0,t_0) + \int_{t_0-\epsilon}^{t_0+\epsilon} \mathrm{d}t \,\frac{\partial}{\partial x} J(x,t_0+\epsilon)$$

Here we used that $G = 0$ for $t < t_0$. Again, we use that in the limit $\epsilon \to 0$, the flux vanishes and thus $G(x,t_0+\epsilon;x_0,t_0) = \delta(x-x_0)$, which can be inserted into (6.59) and yields

$$f(x,t_0) = \lim_{\epsilon\to 0} f(x,t_0+\epsilon) = \lim_{\epsilon\to 0}\int \mathrm{d}\tilde{x}\, f_0(\tilde{x})G(x,t_0+\epsilon;\tilde{x},t_0) \tag{6.67}$$

$$= \int \mathrm{d}\tilde{x}\, f_0(\tilde{x})\delta(x-\tilde{x}) = f_0(x) \tag{6.68}$$

We consider the initial value problem

$$f(x,t) = e^{\mathcal{D}(t-t_0)} f_0(x) = \int \mathrm{d}\tilde{x}\, e^{\mathcal{D}(t-t_0)}\delta(x-\tilde{x}) f_0(\tilde{x}) \tag{6.69}$$

$$f(x,t) = \int \mathrm{d}\tilde{x}\, G(x,t;\tilde{x},t_0) f_0(\tilde{x}) \tag{6.70}$$

and conclude

$$G(x,t;x_0,t_0) = \begin{cases} e^{\mathcal{D}(t-t_0)}\delta(x-x_0) & \text{for } t > t_0 \\ 0 & \text{for } t < t_0 \end{cases} \tag{6.71}$$

$$= \theta(t-t_0) e^{\mathcal{D}(t-t_0)}\delta(x-x_0) \tag{6.72}$$

From this we conclude

$$\frac{\partial}{\partial t} G = \delta(t-t_0) e^{\mathcal{D}(t-t_0)}\delta(x-x_0) + \mathcal{D}\theta(t-t_0) e^{D(t-t_0)}\delta(x-x_0) \tag{6.73}$$

and thus

$$\left(\frac{\partial}{\partial t} - \mathcal{D}\right) G = \delta(t-t_0)\delta(x-x_0) \tag{6.74}$$

and we find $G = 0$ for $t < t_0$.

We consider a stochastic motion in the space of variables $\boldsymbol{a}, \boldsymbol{a}(t)$ and start at $t = 0$ at point $\boldsymbol{a}_0$. The space V shall be restricted by a surface ∂V. The first passage time, is the time when the trajectory reaches the surface ∂V for the first time. For many realizations, there exists a first-passage time (FPT) distribution and we are interested in the mean FPT.

The motion of the distribution obeys the FP equation. When we consider all trajectories, that are still inside the volume V, we have to eliminate trajectories that 'touched' ∂V, i.e. we have adsorbing boundary conditions $f(\boldsymbol{a},t)|_{\partial V} = 0$. We consider the initial value problem

$$f_{a_0}(\boldsymbol{a},t) = e^{\mathcal{D}t}\delta(\boldsymbol{a}-\boldsymbol{a}_0) \tag{6.75}$$

The fraction of trajectories still in V, that can be interpreted as a kind of survival probability is given by

$$\boxed{S_{\boldsymbol{a}_0}(t) = \int_V \mathrm{d}\boldsymbol{a}\, f_{\boldsymbol{a}_0}(\boldsymbol{a}, t)} \tag{6.76}$$

and vanishes for large times $t \to \infty$. The amount of trajectories leaving the volume V in a time interval $\mathrm{d}t$ is given by $S(t) - S(t + \mathrm{d}t)$. We define the FPT distribution via

$$\rho_{\mathrm{FP}}(\boldsymbol{a}_0, t) = S_{\boldsymbol{a}_0}(t) - S_{\boldsymbol{a}_0}(t + \mathrm{d}t) \tag{6.77}$$

or

$$\boxed{\rho_{\mathrm{FP}}(\boldsymbol{a}_0, t) = -\frac{\mathrm{d}S_{\boldsymbol{a}_0}(t)}{\mathrm{d}t}\ .} \tag{6.78}$$

The mean FPT τ is the first moment of ρ and the n-th moment is given by

$$T_n^{\mathrm{FP}}(\boldsymbol{a}_0) = \int_0^\infty \mathrm{d}t\, t^n \rho_{\mathrm{FP}}(\boldsymbol{a}_0, t) = -\int \mathrm{d}t\, t^n \frac{\partial}{\partial t} \int_V \mathrm{d}\boldsymbol{a} f_{\boldsymbol{a}_0}(\boldsymbol{a}, t) \tag{6.79}$$

$$= -\int_V \mathrm{d}\boldsymbol{a} \int \mathrm{d}t\, t^n \frac{\partial f_{\boldsymbol{a}_0}(\boldsymbol{a}, t)}{\partial t} \tag{6.80}$$

The mean first passage time can thus be calculated via

$$\boxed{\begin{aligned} \tau(\boldsymbol{a}_0) = T_1^{\mathrm{FP}}(\boldsymbol{a}_0) &= \int_0^\infty \mathrm{d}t\, t \rho_{\mathrm{FP}}(\boldsymbol{a}_0, t) = -\int_0^\infty \mathrm{d}t\, t \frac{\mathrm{d}S_{\boldsymbol{a}_0}(t)}{\mathrm{d}t} && (6.81) \\ &= -tS_{\boldsymbol{a}_0}(t)|_0^\infty + \int_0^\infty \mathrm{d}t S_{\boldsymbol{a}_0}(t) && (6.82) \end{aligned}}$$

We find that for the first addend

$$\lim_{t\to\infty} tS_{\boldsymbol{a}_0}(t) = \lim_{t\to\infty} \int_V \mathrm{d}\boldsymbol{a}\, t f_{\boldsymbol{a}_0}(\boldsymbol{a}, t) = \lim_{t\to\infty} \int_V \mathrm{d}\boldsymbol{a}\, t e^{\mathcal{D}t} \delta(\boldsymbol{a} - \boldsymbol{a}_0) = 0 \tag{6.83}$$

as it decays exponentially. Thus, we obtain

$$\tau(\boldsymbol{a}_0) = \int_0^\infty \mathrm{d}t \int_V \mathrm{d}\boldsymbol{a}\, e^{\mathcal{D}t} \delta(\boldsymbol{a} - \boldsymbol{a}_0) = \int \mathrm{d}t \int_V \delta(\boldsymbol{a} - \boldsymbol{a}_0) e^{\mathcal{D}^\dagger t} 1 \tag{6.84}$$

We perform the space integration, $\mathcal{D}_{\boldsymbol{a}_0}$ then denotes the operator $\mathcal{D}$ acting on $\boldsymbol{a}_0$

$$\boxed{\tau(\boldsymbol{a}_0) = \int_0^\infty e^{\mathcal{D}^\dagger_{\boldsymbol{a}_0}} 1} \tag{6.85}$$

or

$$\mathcal{D}^\dagger_{\boldsymbol{a}_0} \tau(\boldsymbol{a}_0) = \int_0^\infty \mathcal{D}^\dagger_{\boldsymbol{a}_0} e^{\mathcal{D}^\dagger_{\boldsymbol{a}_0} t} 1 = \int_0^\infty \mathrm{d}t\, \frac{\mathrm{d}}{\mathrm{d}t} e^{\mathcal{D}^\dagger t} 1 \tag{6.86}$$

$$= e^{\mathcal{D}^\dagger t} 1|_0^\infty = -1\ , \tag{6.87}$$

as $e^{\mathcal{D}^\dagger t} \to 0$ for $t \to \infty$, because $t\mathcal{D}^\dagger 1 = 0$. So we conclude, that

$$\mathcal{D}^\dagger \tau(\boldsymbol{a}_0) = -1 \tag{6.88}$$

and

$$\tau(\boldsymbol{a}_0) = 0 \tag{6.89}$$

for $\boldsymbol{a}_0$ on ∂V, i.e. a initial point on the surface immediately leaves the system. From the Smulochowski equation we obtain

$$\frac{\partial f(x,t)}{\partial t} = \mathcal{D} f(x,t) \tag{6.90}$$

we derive a differential equation for the mean first-passage time

$$\mathcal{D}^\dagger \tau(x_1) = -1 \ , \quad \text{with } \tau = 0 \quad \text{for } x \in \partial V \ . \tag{6.91}$$

The mean first-passage time τ obeys the adjoined FP/SM equation

$$\frac{\partial f}{\partial t} = \mathcal{D} f = D \frac{\partial}{\partial x} e^{-\tilde{U}} \frac{\partial}{\partial x} e^{\tilde{U}} f = \left(D \frac{\partial}{\partial x} \tilde{U}' + D \frac{\partial^2}{\partial x^2} \right) f \ , \tag{6.92}$$

with $\tilde{U} = U/k_B T$ and D diffusion constant.

$$\mathcal{D}^\dagger \tau(x) = \left(D\tilde{U}' \frac{\partial}{\partial x} + D \frac{\partial^2}{\partial x^2} \right) \tau(x) = D e^{\tilde{U}} \frac{\partial}{\partial x} e^{-\tilde{U}} \frac{\partial}{\partial x} \tau(x) = -1 \tag{6.93}$$

Consider starting point x with $x_0 < x < x_2$ reflecting boundary condition at x_0 , i.e. flux is zero, barrier at x_2: maximum of energy landscape. From eq. (6.93), we obtain

$$\frac{\partial}{\partial x} e^{-\tilde{U}} \frac{\partial}{\partial x} \tau(x) = \frac{e^{-\tilde{U}}}{D} \tag{6.94}$$

$$\int_{x_0}^{x} \mathrm{d}\tilde{x} \, \frac{\partial}{\partial x} e^{-\tilde{U}} \frac{\partial}{\partial x} \tau(\tilde{x}) = -\int_{x_0}^{x} \frac{\mathrm{d}\tilde{x}}{D} e^{-\tilde{U}(\tilde{x})} \tag{6.95}$$

$$e^{-\tilde{U}(\tilde{x})} \frac{\partial}{\partial x} \tau(\tilde{x})|_{x_0}^{x} = e^{-\tilde{U}(x)} \frac{\partial}{\partial x} \tau(x) = -\int_{x_0}^{x} \frac{\mathrm{d}\tilde{x}}{D} e^{-\tilde{U}(\tilde{x})} \tag{6.96}$$

since $\tilde{U}(x_0) = \infty$.

$$\int_{x}^{x_2} \mathrm{d}\tilde{x}' \frac{\partial}{\partial \tilde{x}'} \tau(\tilde{x}') = -\int_{x}^{x_2} e^{\tilde{U}(\tilde{x}')} \int_{x_0}^{\tilde{x}'} \frac{\mathrm{d}\tilde{x}}{D} e^{-\tilde{U}(\tilde{x})} = \tau(\tilde{x}')|_{x}^{x_2} \tag{6.97}$$

$$\tau(x) = \int_{x}^{x_2} \mathrm{d}\tilde{x}' \, e^{\tilde{U}(\tilde{x}')} \int_{x_0}^{\tilde{x}} e^{-\tilde{U}(\tilde{x})} \tag{6.98}$$

The last result is an exact expression for τ. We now rederive the Kramers expression from this result. Therefore, we start at the minimum $x = x_1$

$$\tau(x_1) = \int_{x_1}^{x_2} \mathrm{d}\tilde{x}' \, e^{\tilde{U}(\tilde{x}')} \int_{x_0}^{\tilde{x}'} \frac{\mathrm{d}\tilde{x}}{D} \, e^{-\tilde{U}(\tilde{x})} = \int_{x_1}^{x_2} \mathrm{d}\tilde{x}' e^{\tilde{U}(\tilde{x}')} I(\tilde{x}') \sim e^{\tilde{U}(\tilde{x}') + \ln I(\tilde{x}')} \tag{6.99}$$

Expand around the maximum in the integral at $\tilde{x}' = x_2$

$$\ln I(\tilde{x}') = \ln I(x_2) + \ldots \tag{6.100}$$

Leading term:

$$\tau = \int_{x_1}^{x_2} \mathrm{d}\tilde{x}'\, e^{\tilde{U}(\tilde{x}')} \int_{x_0}^{x_2} \frac{\mathrm{d}\tilde{x}}{D}\, e^{-\tilde{U}(\tilde{x})}$$

This approximation works well as long as $\Delta\tilde{U} \gg 1$.

$$\begin{aligned}
\tau &\simeq \int_{x_1}^{x_2} \mathrm{d}\tilde{x}'\, e^{\tilde{U}(\tilde{x}')} \int_{-\infty}^{\infty} \frac{\mathrm{d}\tilde{x}}{D}\, e^{-\tilde{U}(\tilde{x})} && (6.101)\\
&\simeq \int_{x_1}^{x_2} \mathrm{d}\tilde{x}'\, e^{\tilde{U}(\tilde{x}')} \int_{-\infty}^{\infty} \frac{\mathrm{d}\tilde{x}}{D}\, e^{-\tilde{U}_1 - \tilde{U}_1''(\tilde{x}-x_1)^2/2} && (6.102)\\
&\simeq \int_{-\infty}^{x_2} \mathrm{d}\tilde{x}'\, e^{\tilde{U}_2 - \tilde{U}_2''(\tilde{x}'-x_2)^2} \sqrt{\frac{2\pi}{\tilde{U}_1''}}\frac{1}{D} e^{-\tilde{U}_1} && (6.103)\\
&\simeq \frac{1}{2} e^{\tilde{U}_2} \sqrt{\frac{2\pi}{\tilde{U}_2''}}\frac{1}{D}\sqrt{\frac{2\pi}{\tilde{U}_1''}} e^{-\tilde{U}_1} && (6.104)
\end{aligned}$$

$$\boxed{\tau(x_1) = \frac{1}{D} e^{(U_2-U_1)/k_BT} \frac{\pi k_B T}{\sqrt{U_1'' U_2''}} = J^{-1}} \tag{6.105}$$

The particle flux in the Kramers approximation corresponds to the frequency of particles reaching the barrier top, inverse mean-first passage time $K = J/2$.

Next, we will discuss the kinetic invariance of the FP equation We allow for the diffusion coefficient to depend on the position

$$\frac{\partial}{\partial t} f(x,t) = \frac{\partial}{\partial x} D(x) e^{-\beta U} \frac{\partial}{\partial x} e^{\beta U} f(x,t) \tag{6.106}$$

The stationary meandistribution is given by

$$\langle f(x) \rangle = \lim_{T\to\infty} \int_0^T \frac{\mathrm{d}t}{T} f(x,t) \equiv e^{-\beta U} \tag{6.107}$$

$$\int_{x_1}^{x_2} \mathrm{d}x\, e^{-\beta U(x)} = Z \quad \text{(partition function)} \tag{6.108}$$

We define the rescaled time independent coordinate $\tilde{x}(x)$

$$\frac{\partial}{\partial x} = \frac{\partial \tilde{x}(x)}{\partial x} \frac{\partial}{\partial \tilde{x}} = \tilde{x}' \frac{\partial}{\partial \tilde{x}} = \tilde{x}'(\tilde{x}) \frac{\partial}{\partial \tilde{x}}\ . \tag{6.109}$$

Further we define $f = \tilde{f}\tilde{x}'$ and insert this into (6.106)

$$\tilde{x}' \frac{\partial \tilde{f}}{\partial t} = \tilde{x}' \frac{\partial}{\partial \tilde{x}} D e^{-\beta U} \tilde{x}' \frac{\partial}{\partial \tilde{x}} e^{\beta U} \tilde{x}' \tilde{f} \tag{6.110}$$

and thus

$$\frac{\partial \tilde f}{\partial t} = \frac{\partial}{\partial \tilde x} D e^{-\beta U}\tilde x' \frac{\partial}{\partial \tilde x} e^{\beta U}\tilde x' \tilde f \,. \tag{6.111}$$

Defining $e^{\beta U}\tilde x' = e^{\beta \tilde U}$ with $\beta\tilde U = \beta U + \ln \tilde x'$ and $\tilde F = (\tilde x')^2 D$, we find

$$\boxed{\frac{\partial \tilde f}{\partial t} = \frac{\partial}{\partial \tilde x}\tilde D e^{-\beta\tilde U}\frac{\partial}{\partial \tilde x} e^{\beta\tilde U}\tilde f \,.} \tag{6.112}$$

We conclude, that the FP equation is invariant under the transformation we just made and notice, that the function $D(x)$ can be transformed into a constant via the right gauge

$$\tilde D(\tilde x) \overset{!}{=} \tilde D_0 \to \tilde x' = (\tilde D_0/D(x))^{1/2} \tag{6.113}$$

$$\beta\tilde U = \beta U + \frac{1}{2}\ln(\tilde D_0/D(x)) \tag{6.114}$$

The partition function stays invariant per definition

$$Z = \int_{x_1}^{x_2} \mathrm{d}x\, e^{-\beta U(x)} = \int_{\tilde x(x_1)}^{\tilde x(x_2)} \mathrm{d}\tilde x\, \frac{e^{-\beta U(\tilde x)}}{\mathrm{d}\tilde x/\mathrm{d}x} = \int \mathrm{d}\tilde x\, e^{-\beta U - \ln \tilde x'} = \int \mathrm{d}\tilde x\, e^{-\beta \tilde U(\tilde x)} \,.$$

Thus we can shift the diffusive effects into the free energy landscape and vice versa.

6.5. Master equations

We start with the single variable Smulochowski (SM) equation

$$\begin{aligned} \frac{\partial}{\partial t} f(x,t) &= \frac{\partial}{\partial x} D(x) e^{-\tilde U(x)} \frac{\partial}{\partial x} e^{\tilde U(x)} f(x,t) \qquad (6.115)\\ &= \frac{\partial}{\partial x}\left[D(x)\frac{\partial}{\partial x} f + D(x) f \frac{\partial}{\partial x}\tilde U\right] \,, \qquad (6.116) \end{aligned}$$

where $D(x)$ is a more general, position dependent diffusion constant. We now consider discretized spatial coordinates, where we introduce

$$x_{n+1} - x_n = d, \quad f(x,t) \to f_n(t), \quad \tilde U(x) \to \tilde U_n, \quad D(x) \to D_n \,.$$

To discretize the spatial derivatives consistently, we consider the first spatial derivative $\frac{\partial g}{\partial x}$ as being the difference of $g_{n+1/2} = (g_{n+1} + f_n)/2$ and $g_{n-1/2} = (g_n - g_{n-1})/2$ divided by d. Here $\frac{\partial g}{\partial x}$ corresponds to the right hand side of equation (6.115). With this we arrive at

$$\begin{aligned} \frac{\mathrm{d} f_n(t)}{\mathrm{d}t} =& \left[\frac{D_{n+1} + D_n}{2} e^{-(\tilde U_{n+1} + \tilde U_n)/2}\left(f_{n+1} e^{\tilde U_{n+1}} - f_n e^{\tilde U_n}\right)/d \right.\\ & \left. - \frac{D_n + D_{n-1}}{2} e^{-(\tilde U_n + \tilde U_{n-1})/2}\left(f_n e^{\tilde U_n} - f_{n-1} e^{\tilde U_{n-1}}\right)/d\right]/d \\ =& \frac{D_{n+1} + D_n}{2d^2}\left[e^{-(\tilde U_n - \tilde U_{n+1})/2} f_{n+1} - e^{-(\tilde U_{n+1} - \tilde U_n)/2} f_n\right] \\ & + \frac{D_{n-1} + D_n}{2d^2}\left[e^{-(\tilde U_n - \tilde U_{n-1})/2} f_{n-1} - e^{-(\tilde U_{n-1} - \tilde U_n)/2} f_n\right] \end{aligned}$$

By elimination of spatial derivatives, we arrive at the discrete Master equation. The general formulation of a Master equation is given by

$$\boxed{\frac{\mathrm{d}f_m(t)}{\mathrm{d}t} = \sum_{n\neq m} W_{mn} f_n(t) - \sum_{n} W_{nm} f_m(t)\ ,} \tag{6.117}$$

with the transition rates where the W_{mn} represent growth rates, while the W_{nm} represent loss rates, and are given by Fermi golden rule. The formulation above is reffered to as the gain/loss formulation. An alternative formulation also called matrix or operator formulation is

$$\boxed{\frac{\mathrm{d}f_m(t)}{\mathrm{d}t} = \sum_{n} D_{mn} f_n(t)}, \tag{6.118}$$

with

$$D_{mn} = W_{mn}(1-\delta_{mn}) - \delta_{mn}\sum_k W_{kn}\ , \tag{6.119}$$

where D_{mn} is called transition rate matrix. To verify this result, we insert (6.119) into (6.118)

$$\begin{aligned} \frac{\mathrm{d}f_m(t)}{\mathrm{d}t} &= \sum_n \left(W_{mn}(1-\delta_{mn}) - \delta_{mn}\sum_k W_{kn} \right) f_n(t) & (6.120)\\ &= \sum_{n\neq m} W_{mn} f_n(t) - \sum_k W_{km} f_m(t) & (6.121) \end{aligned}$$

If the probability is conserved, we obtain the relation

$$\boxed{\sum_m D_{mn} = 0\ .} \tag{6.122}$$

Properties of Master equations:

1. discrete set of states
2. system characterized by occupation/state probabilities $f_n(t)$
3. rate equation characterized transition rate matrix W_{mn}: rate for reaction from n to m, which is not necessarily symmetric, rates are non-negative
4. matrix has at least one eigenvalue that is zero, all other eigenvalues have negative real component (decay to equilibrium)
5. expectation value $\langle A(t)\rangle = \sum_m A_m f_m(t)$

To interpret the last property, we consider the formal solution of the Master equation (6.118)

$$f_m(t) = \left(e^{t\mathcal{D}}\right)_{mn} f_n(0) \tag{6.123}$$

and notice the following relations:

- negative eigenvalue $\lambda \leq 0$: approach to equilibrium
- eigenvector with $\lambda = 0$: equilibrium state
- multiple eigenvalue $\lambda = 0$ (two states, which 'do not talk to each other'): no ergodic system, usually not possible to be derived from 'usual' Hamiltonians

Note, that the Master equation is more general than the Fokker-Planck equation. The FP equation is in fact a tridiagonal Master equation.

6.6. Chapman Kolmogorov equation

We consider a probability distribution $f(x,t)$ and a joint probability distribution $f(x_1,t_1;x_2,t_2;\ldots$ e.g. the joint probability distribution for a particle-tracking experiment. We can perform some reduction

$$f(x_1,t_1) = \int \mathrm{d}x_2 f(x_1,t_1;x_2,t_2) \ , \tag{6.124}$$

With the normalization condition:

$$\int \mathrm{d}x_1\, f(x_1,t_1) = 1 \ . \tag{6.125}$$

the conditional probability distribution $f(x_1,t_1|x_2,t_2)$ denotes the probability to find a particle at position x_2 at time t_2 under the condition, that it has been or will be at position x_1 at time t_1 with the formal definition given by

$$f(x_1,t_1)f(x_1,t_1|x_2,t_2) = f(x_1,t_1;x_2,t_2) \ . \tag{6.126}$$

Combining equation (6.124) and (6.126) we obtain

$$\int \mathrm{d}x_1\, f(x_1,t_1)f(x_1,t_1|x_2,t_2) = f(x_2,t_2) \ . \tag{6.127}$$

From the last equation we see, that the conditional probability ca be viewed as a transition probability. We are now able to reformulate the Markov assumption for times $t_1 < t_2 < t_3$

$$\boxed{f(x_1,t_1;x_2,t_2;x_3,t_3) = f(x_1,t_1)f(x_1,t_1|x_2,t_2)f(x_2,t_2|x_3,t_3) \ ,} \tag{6.128}$$

which states, that the state at time t_3 only depends on the state at time t_2 and not on all previous states, here t_1. Therefore, this factorization is possible. Markov processes are defined by just two functions $f(x,t)$ and $f(x_1,t_1|x_2,t_2)$. If we integrate equation (6.128) over x_2 we obtain

$$f(x_1,t_1;x_3,t_3) = f(x_1,t_1) \int \mathrm{d}x_2\, f(x_1,t_1|x_2,t_2)f(x_2,t_2|x_3,t_3) \ . \tag{6.129}$$

and using equation (6.126) we have derived the Chapman Kolmogorov equation

$$\boxed{f(x_1,t_1|x_3,t_3) = \int \mathrm{d}x_2\, f(x_1,t_1|x_2,t_2) f(x_2,t_2|x_3,t_3)\ ,} \tag{6.130}$$

which states, that the transition from position x_1 to x_3 can be broken into two independent processes.

Next, we derive the Master equation from the Chapman Kolmogorov equation. First, we rewrite equation (6.127) with $t_2 = t_1 + \tau$

$$f(x_2, t_1+\tau) = \int \mathrm{d}x_1\, f(x_1,t_1) f(x_1,t_1|x_2,t_1+\tau)\ , \tag{6.131}$$

Since we are interested in small time intervals τ we consider the time derivative of the probability distribution

$$\frac{\mathrm{d}f(x_2,t_1)}{\mathrm{d}t_1} = \frac{f(x_2,t_1+\tau) - f(x_2,t_1)}{\tau} \tag{6.132}$$

= Expanding in τ the second term in the integrand in (6.131), from definition (6.117) we get

$$f(x_1,t_1|x_2,t_1+\tau) = \delta(x_1-x_2) + \tau W(x_1,x_2) - \tau \int \mathrm{d}x\, W(x_1,x)\delta(x_1-x_2)\ , \tag{6.133}$$

The last term is most easily understood as a constraint imposed by normalization

$$\int \mathrm{d}x_2 f(x_1,t_1|x_2,t_1+\tau) = 1\ . \tag{6.134}$$

since

$$\begin{aligned} 1 &= \int \delta(x_1-x_2)\mathrm{d}x_2 + \int \mathrm{d}x_2 \tau W(x_1,x_2) - \int \mathrm{d}x_2 \tau \int \mathrm{d}x\, W(x_1,x)\delta(x_1-x_2) \\ &= 1 + \int \mathrm{d}x_2 \tau W(x_1,x_2) - \int \mathrm{d}x_2 \tau W(x_1,x_2) \end{aligned} \tag{6.135}$$

An alternative way of (6.133) is

$$f(x_1,t_1|x_2,t_1+\tau) = \delta(x_1-x_2)\left(1 - \tau\int \mathrm{d}x\, W(x_1,x)\right) + \tau W(x_1,x_2)\ , \tag{6.136}$$

from which one can see, that the term in brackets can be interpreted as the probability to rest at a position, which is unity minus the probability to move away.
$W(x_1,x_2)$ is the transition rate to go from x_1 to x_2 thus

$$\tau \int \mathrm{d}x\, W(x_1,x) \tag{6.137}$$

is just the probability to move away from position x_1 and

$$1 - \tau \int \mathrm{d}x \, W(x_1, x) \tag{6.138}$$

is the probability to stay. We can now insert the expansion (6.131) into equation (6.132) and using (6.133)

$$\begin{aligned} \frac{\partial f(x_2, t_1)}{\partial t_1} &= \frac{f(x_2, t+\tau) - f(x_2, t_1)}{\tau} && (6.139) \\ &= \int \mathrm{d}x_1 \, f(x_1, t_1) \left(W(x_1, x_2) - \int \mathrm{d}x W(x_1, x) \delta(x_1 - x_2) \right) . && (6.140) \end{aligned}$$

We now perform the x_1 integration in the second term and get

$$\begin{aligned} \frac{\partial f(x_2, t_1)}{\partial t_1} &= \int \mathrm{d}x_1 \, f(x_1, t_1) W(x_1, x_2) - \int \mathrm{d}x \, f(x_2, t_1) W(x_2, x) \\ &= \int \mathrm{d}x_1 \, f(x_1, t_1) W(x_1, x_2) - \int \mathrm{d}x_1 \, f(x_2, t_1) W(x_2, x_1) \\ &= \int \mathrm{d}x_1 \, f(x_1, t_1) W(x_1, x_2) - f(x_2, t_1) W(x_2, x_1) \, . && (6.141) \end{aligned}$$

We have just derived a continuum Master equation in terms of the gain/loss formulation. At this point we can derive the Fokker-Planck equation from the continuous Master equation. To this end, we redefine the transition rates as

$$W(x_1, x_2) = \tilde{W}(x_1, x_2 - x_1) = \tilde{W}(x_1, \xi) \tag{6.142}$$

as we are interested in small space steps $\xi = x_2 - x_1$. We rewrite equation (6.141) changing the integration variable to ξ with $t_1 \longrightarrow t$ as

$$\frac{\partial f(x_2, t)}{\partial t} = \int_{-\infty}^{\infty} \mathrm{d}\xi \, \left[f(x_2 - \xi, t) \tilde{W}(x_2 - \xi, \xi) - f(x_2, t) \tilde{W}(x_2, \xi) \right] . \tag{6.143}$$

We now expand this expression in powers of ξ, keeping the second argument of $\tilde{W}$ fixed we get

$$\begin{aligned} \frac{\partial f(x_2, t)}{\partial t} &= \int_{-\infty}^{\infty} \mathrm{d}\xi \, f(x_2, t) \tilde{W}(x_2, \xi) - \int \mathrm{d}\xi \, \xi \frac{\partial}{\partial x_2} f(x_2, t) \tilde{W}(x_2, \xi) \\ &\quad + \tfrac{1}{2} \int \mathrm{d}\xi \xi^2 \frac{\partial^2}{\partial x_2^2} f(x_2, t) \tilde{W}(x_2, \xi) - \int \mathrm{d}\xi f(x_2, t) \tilde{W}(x_2, \xi) \\ &= - \int \mathrm{d}\xi \, \xi \frac{\partial}{\partial x_2} f(x_2, t) \tilde{W}(x_2, \xi) + \tfrac{1}{2} \int \mathrm{d}\xi \xi^2 \frac{\partial^2}{\partial x_2^2} f(x_2, t) \tilde{W}(x_2, \xi) \\ &= - \frac{\partial}{\partial x_2} \int \mathrm{d}\xi \, \xi f(x_2, t) \tilde{W}(x_2, \xi) + \frac{\partial^2}{\partial x_2^2} \int \mathrm{d}\xi \xi^2 f(x_2, t) \frac{\tilde{W}(x_2, \xi)}{2} \, . && (6.144) \end{aligned}$$

Thus we have obtained the Fokker-Planck equation

$$\boxed{\frac{\partial f(x,t)}{\partial t} = -\frac{\partial}{\partial x} f(x,t)h(x) + \frac{\partial^2}{\partial x^2} f(x,t)B(x)}\,, \tag{6.145}$$

with

$$h(x) = \int \mathrm{d}\xi\, \xi \tilde{W}(x,\xi)\,, \qquad B(x) = \tfrac{1}{2} \int \mathrm{d}\xi\, \xi^2 \tilde{W}(x,\xi)\,. \tag{6.146}$$

Approaching from the Master equation, the functions $h(x)$ and $B(x)$ are respectively the 1^{st} and 2^{nd} moment of the transition rates $\tilde{W}(x,\xi)$. In principle also higher order spatial derivatives and higher moments would appear.
We remark that an expansion in the second argument of $\tilde{W}$

$$\tilde{W}(x_2,\xi) \simeq \tilde{W}(x_2,0) + \xi \tilde{W}'(x_2) + \tfrac{1}{2}\xi^2 \tilde{W}''(x_2) + \ldots \tag{6.147}$$

trivially generates divergences in the moments $h(x)$ and $B(x)$.

6.7. Chemical kinetics

We consider the simplest chemical reaction $A \rightleftharpoons B$, with m molecules of substance A and n molecules of substance B. The total number of molecules is $N = m + n$ constant and the volume is denoted by V. The reaction rates or reaction coefficients are given by k_1 and k_2. In the following we will deal with the 'mean-field' description of a chemical reaction. The concentrations are given by

$$C_A = \frac{m}{V}, \quad C_B = \frac{n}{V} = \frac{(N-m)}{V}\,, \tag{6.148}$$

$$C_0 = C_B + C_A = \frac{N}{V}\,. \tag{6.149}$$

The reaction rates are then given by

$$\begin{aligned} W_{A\to B} &= V k_1 C_A && \text{forward} && (6.150)\\ W_{B\to A} &= V k_2 C_B && \text{backward} && (6.151)\\ &= V k_2 (C_0 - C_A)\,. && && (6.152) \end{aligned}$$

The time derivative of the concentration is given by a Master equation

$$\boxed{\frac{\mathrm{d}C_A}{\mathrm{d}t} = \underbrace{k_2(C_0 - C_A)}_{\text{gain}} - \underbrace{k_1 C_A}_{\text{loss}} = k_2 C_0 - (k_1 + k_2) C_A\,.} \tag{6.153}$$

In equilibrium we have $\dot{C}_A = 0$ and equation (6.153) then implies

$$k_2 C_B = k_1 C_A \quad \Rightarrow \quad C_A^{\mathrm{eq}} = C_0 \frac{k_2}{k_1 + k_2} \tag{6.154}$$

or in other words

$$\boxed{\left.\frac{C_A}{C_B}\right|_{eq} = \frac{k_2}{k_1} = K\ .} \tag{6.155}$$

where K is the equilibrium constant. The formal solution for equation (6.153) is given by

$$C_A(t) = e^{-(k_1+k_2)t}C_A(0) + \int_0^t \mathrm{d}t' e^{-(k_1+k_2)(t-t')}k_2 C_0\ . \tag{6.156}$$

Now we look at an autocatalytic reaction $A + A \rightleftharpoons B + A$. The reaction equation is given by

$$\frac{\mathrm{d}C_A}{\mathrm{d}t} = k_2 C_B C_A - k_1 C_A^2 = k_2(C_0 - C_A)C_A - k_1 C_A^2 \tag{6.157}$$

and in equilibrium $\dot{C}_A = 0$ yields

$$k_2(C_0 - C_A^{eq}) = k_1 C_A^{eq} \quad \Rightarrow \quad C_A^{eq} = C_0 \frac{k_2}{k_1 + k_2}\ . \tag{6.158}$$

Thus, the equilibrium state is the same as in the simple reaction considered above, but we will see, that its dynamics is totally different.

To see, why the dynamics of auto catalytic reactions are important we consider the Lotka-Volterra model, that is used in biology to describe predator-pray models

$$A + X \rightarrow 2X \quad (k_1) \tag{6.159}$$

$$X + Y \rightarrow 2Y \quad (k_2) \tag{6.160}$$

$$Y \rightarrow E \quad (k_3) \tag{6.161}$$

Here A describes the food, X the pray and Y the predator and E describes the 'dead'-state. In the following brackets will denote taking the concentration of X, Y, A. We have

$$[\dot{X}] = k_1[A][X] - k_2[X][Y] \tag{6.162}$$

$$[\dot{Y}] = k_2[Y][X] - k_3[Y]\ . \tag{6.163}$$

In this model, oscillation appear and the frequency depends on the food concentration $[A]$. If we are interested in the question, under what conditions and at what time a species dies out, we realize, that this question can not be answered sufficiently within the framework of mean-field chemistry. Instead, fluctuations have to be taken into account.

Another example invented in the context of chemical reaction (Belousov-Zhabotinsky-Reaction) is the Bruesselator (Prigogine). Compared to the Lotka-Volterra model it shows the additional feature of a limit cycle, meaning reactions described by the Bruesselator show a dynamical complex state independent of the initial condition and $[A]$.

$$A \rightarrow X \tag{6.164}$$

$$2X + Y \rightarrow 3X \tag{6.165}$$

$$B + X \rightarrow Y + D \tag{6.166}$$

$$X \rightarrow E \tag{6.167}$$

Now we turn back to the simple autocatalyitc reaction mentioned above. We will map it to a Master equation. The backward reaction rate is given by

$$W[(m,n)\to(m+1,n-1)] = k_2\frac{m}{V}\frac{n}{V}V \tag{6.168}$$

and the forward reaction rate is

$$W[(m,n)\to(m-1,n+1)] = k_1\frac{m}{V}\frac{m}{V}V\ . \tag{6.169}$$

We assume that at a given time interval only one chemical reaction takes place. The probability to have m molecules of sort A at a time t is denoted by $P_m(t)$. The Master equation then states

$$\begin{aligned}\frac{\mathrm{d}P_m}{\mathrm{d}t} &= W[(m-1,n+1)\to(m,n)]P_{m-1} + W[(m,n)\to(m+1,n-1)]P_m\\ &\quad + W[(m+1,n)\to(m,n+1)]P_{m+1} + W[(m,n)\to(m-1,n+1)]P_m\\ \frac{\mathrm{d}P_m}{\mathrm{d}t} &= \frac{k_2}{V}(m-1)(n+1)P_{m-1} - \frac{k_2}{V}mnP_m \quad \text{forward}\\ &\quad + \frac{k_1}{V}(m+1)^2P_{m+1} - \frac{k_1}{V}m^2P_m \qquad \text{backward}\ .\end{aligned}$$

Rewriting the last equation and using the concentrations $C = m/V$ and $C_0 = N/V$ we obtain

$$\begin{aligned}\frac{\mathrm{d}P_m}{\mathrm{d}t} =& \frac{k_2}{V}(m-1)(N+1-m)P_{m-1} - \left[\frac{k_2}{V}m(N-m) - \frac{k_1}{V}m^2\right]P_m\\ &+ \frac{k_1}{V}(m+1)^2P_{m+1}\\ =&k_2V(C-\frac{1}{V})(C_0+\frac{1}{V}-C)P_{m-1} - \left[k_2VC(C_0-C)+k_1VC^2\right]P_m\\ &+ k_1V(C+\frac{1}{V})^2P_{m+1}\end{aligned} \tag{6.170}$$

Note, that we keep terms in powers of V^{-1}, because we are not only interested in the thermal limit, but also in fluctuations. In order to transform this equation to a FP equation, we introduce the continuum probability distribution $\rho(C,t)$, which is defined via

$$P_{m+1} - P_m \simeq 2\frac{\partial\rho(m,t)}{\partial m} = \frac{2}{V}\frac{\partial\rho(C,t)}{\partial C}\ , \tag{6.171}$$

$$P_{m+1} + P_{m-1} - 2P_m \simeq \frac{1}{V^2}\frac{\partial^2\rho}{\partial C^2}\ . \tag{6.172}$$

Using (6.171) and (6.172) we calculate

$$2P_{m+1} - 2P_m = (P_{m+1} + P_{m-1} - 2P_m) + (P_{m+1} - P_{m-1})\frac{1}{V^2}\rho'' + \frac{2}{V}\rho'$$

$$\Rightarrow \qquad P_{m+1} = \frac{1}{2V^2}\rho'' + \frac{1}{V}\rho' + \rho \tag{6.173}$$

$$P_{m-1} = \frac{1}{2V^2}\rho'' - \frac{1}{V}\rho' + \rho \tag{6.174}$$

Inserting (6.173) and (6.174) into (6.170) we calculate

$$\begin{aligned}\frac{\partial\rho}{\partial t} = &\left[\frac{k_2}{2V}(C-\frac{1}{V})(C_0+\frac{1}{V}-C)+\frac{k_1}{2V}(C+\frac{1}{V})^2\right]\rho'' \\ &+\left[k_1(C+\frac{1}{V})^2 - k_2(C-\frac{1}{V})(C_0+\frac{1}{V}-C)\right]\rho' \\ &+\left[k_2V(C-\frac{1}{V})(C_0+\frac{1}{V}-C) - k_2VC(C_0-C) + k_1V(C+\frac{1}{V})^2 - k_1VC^2\right]\rho\end{aligned}$$

Omitting terms of orders of $O(1/V^2)$, we obtain

$$\begin{aligned}\frac{\partial\rho}{\partial t} =&\frac{1}{2V}\left[k_2C(C_0-C)+k_1C^2\right]\rho'' \\ &+\left[-k_2C(C_0-C)+k_1C^2+\frac{2k_1}{V}C^2-\frac{k_2}{V}(2C-C_0)\right]\rho' \\ &+\left[-\frac{k_2}{V}+k_2(2C-C_0)+\frac{k_1}{V}+2k_1C\right]\rho + O(1/V^2)\end{aligned} \tag{6.175}$$

The final result can be written in the following way

$$\frac{\partial\rho}{\partial t} = -\frac{\partial}{\partial C}\left[k_2C(C_0-C)-k_1C^2\right]\rho + \frac{\partial^2}{\partial C^2}\left[\frac{k_2C(C_0-C)+k_1C^2}{2V}\right]\rho\,. \tag{6.176}$$

Note, that by similarity to the FP equation, we can be sure, that the probability distribution is conserved, which basically means, that we did not do any discretizing mistakes. By comparison to the FP equation

$$\frac{\partial\rho}{\partial t} = -\frac{\partial}{\partial C}h(C)\rho(C,t) + \frac{\partial^2}{\partial C^2}B(C)\rho(C,t) \tag{6.177}$$

we could in principle find $h(C)$ and $B(C)$. The stationary solution $\dot\rho = 0$ we discover for the thermodynamic limit $B(C) \simeq \frac{1}{V} \to 0$, that there is no diffusion in the probability space. I.e. there is no stochastics and the equilibrium solution is given by $h(C) = 0 = k_2C_AC_B - k_1C_A^2$. However, for $B \neq 0$ even the equilibrium is shifted.
Finally, we check, that (6.176) reproduces (6.175). The second addend of (6.176) is

$$\begin{aligned}&\frac{1}{2V}\frac{\partial}{\partial C}\left[(k_2C_0-2k_2C+2k_1C)\rho + \left(k_2C(C_0-C)+k_1C^2\right)\rho'\right] \\ =&\frac{1}{2V}\left[(-2k_2+2k_1)\rho + (k_2C_0-2k_2C+2k_1C)\rho' + (k_2C_0-2k_2C+2k_1C)\rho'\right. \\ &\left.+\left(k_2C(C_0-C)+k_1C^2\right)\rho''\right]\end{aligned} \tag{6.178}$$

while for the first addend of (6.176) we have

$$-\left[k_2C_0 - 2k_1C - 2k_1C\right]\rho - \left[k_1C(C_0 - C) - k_1C(C_0 - C) - k_2C^2\right]\rho' \tag{6.179}$$

Adding both yields

$$\begin{aligned}\frac{\partial\rho}{\partial t} &= (k_2C(C_0 - C) + k_1C^2)\rho'' + \left[-k_2C(C_0 - C) + k_1C^2 + \frac{k_2C_0}{V} - \frac{2k_2C}{V} + \frac{2k_1C}{V}\right]\rho' \\ &\quad + \left[-k_2C_0 + 2k_2C + 2k_1C - \frac{k_2}{V} + \frac{k_2}{V}\right]\rho \end{aligned}\tag{6.180}$$

which is the result stated in (6.175).

Chapter 7

Kinetic Theory

7.1. BBGKY hierarchy

The BBGKY hierarchy named after Bogoliubov, Born, Green, Kirkwood and Yvon is a set of coupled equations describing a many particle system, for which the Hamiltonian equations of motions are valid. In the following this set of equations will be derived.

We consider a classical N-body problem for which the coordinates of the i-th particle is given by the 6-dimensional vector $\boldsymbol{\xi}_i = (\boldsymbol{r}^i, \boldsymbol{p}^i)$ and the coordinates of the total system is given by the $6N$-dimensional vector $\boldsymbol{\xi}$. The probability density of the $6N$-dimensional phase space is given by $\rho(\xi_1, \xi_2, \xi_3, \ldots, \xi_N, t)$. The Hamilton equations of motion read

$$\dot{\boldsymbol{r}}^i = \nabla_{\boldsymbol{p}^i} H_N \ , \tag{7.1}$$

$$\dot{\boldsymbol{p}}^i = -\nabla_{\boldsymbol{r}^i} H_N \ , \tag{7.2}$$

where H_N denotes the Hamiltonian of the full N-particle system. As ρ is a conserved quantity, it obeys the following continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla_{\boldsymbol{\xi}} \cdot (\rho \dot{\boldsymbol{\xi}}) = \frac{\partial \rho}{\partial t} + \dot{\boldsymbol{\xi}} \cdot \nabla_{\xi} \rho + \rho \nabla_{\xi} \cdot \dot{\boldsymbol{\xi}} = 0 \ . \tag{7.3}$$

We note, that the last term cancels using (7.1) and (7.2) and the Schwarz's theorem

$$\nabla_{\xi} \cdot \dot{\boldsymbol{\xi}} = \sum_{i=1}^{N} \left(\frac{\partial \dot{r}^i_j}{\partial r^i_j} + \frac{\partial \dot{p}^i_j}{\partial p^i_j} \right) = \sum_{i=1}^{N} \frac{\partial^2 H_N}{\partial r^i_j \partial p^i_j} - \frac{\partial^2 H_N}{\partial p^i_j \partial r^i_j} = 0 \tag{7.4}$$

thus (7.3) can be rewritten as

$$\begin{aligned} &\frac{\partial \rho}{\partial t} + \sum_{i=1}^{N} \left(\dot{\boldsymbol{r}}^i \cdot \nabla_{\boldsymbol{r}^i} \rho + \dot{\boldsymbol{p}}^i \cdot \nabla_{\boldsymbol{p}^i} \rho \right) \\ =&\frac{\partial \rho}{\partial t} + \sum_{i=1}^{N} \left(\nabla_{\boldsymbol{p}^i} H_N \cdot \nabla_{\boldsymbol{r}^i} \rho - \nabla_{\boldsymbol{r}^i} H_N \cdot \nabla_{\boldsymbol{p}^i} \rho \right) = 0 \ , \end{aligned} \tag{7.5}$$

where we again used (7.1) and (7.2). Introducing the Poisson bracket

$$\{A,B\} = \sum_{i=1}^{N} \left(\nabla_{\boldsymbol{r}^i} A \cdot \nabla_{\boldsymbol{p}^i} B - \nabla_{\boldsymbol{p}^i} A \cdot \nabla_{\boldsymbol{r}^i} B\right) \ , \tag{7.6}$$

we find a very comprehensive version of (7.5)

$$\boxed{\frac{\partial \rho}{\partial t} = \{H_N, \rho\} \ .} \tag{7.7}$$

This equation is known as the Liouville equation and contains all microscopic information.

We are interested in what happens, if we aim at describing the system by a reduced number of particles. Thus, we introduce, the reduced l-particle distribution function defined by

$$\boxed{f_l(\boldsymbol{\xi}_1, \ldots, \boldsymbol{\xi}_l, t) = \int \rho(\boldsymbol{\xi}_1, \ldots, \boldsymbol{\xi}_N, t) \mathrm{d}^6\xi_{l+1} \ldots \mathrm{d}^6\xi_N \ ,} \tag{7.8}$$

where we integrated out $(n-l)$ particles. For further derivations, we specify to a case of N identical particles in an external potential $\Psi(\boldsymbol{r})$ with pairwise interaction $W_{ij} = W(\boldsymbol{r}^i, \boldsymbol{r}^j)$, the Hamiltonian reads

$$H_N = \sum_{i=1}^{N} \left[\frac{\boldsymbol{p}^{i2}}{2m} + \Psi(\boldsymbol{r}^i)\right] + \sum_{1\le i\le j\le N} W_{ij} \tag{7.9}$$

We integrate the Liouville equation over $N-l$ coordinates and use (7.8) and (7.9)

$$\begin{aligned}\frac{\partial f_l}{\partial t} &= \frac{\partial}{\partial t} \int \rho_N(\boldsymbol{\xi}_1, \ldots, \boldsymbol{\xi}_N, t) \mathrm{d}^6\xi_{l+1} \ldots \mathrm{d}^6\xi_N \\ &= \int \left[\left\{\sum_{i=1}^{N} \left(\frac{\boldsymbol{p}^{i2}}{2m} + \Psi(\boldsymbol{r}^i)\right), \rho_N\right\} + \left\{\sum_{1\le i\le j\le N} W_{ij}, \rho_N\right\}\right] \mathrm{d}\xi_{l+1} \ldots \mathrm{d}\xi_N \ .\end{aligned} \tag{7.10}$$

We notice the following useful relation

$$\begin{aligned}&\int \left\{\frac{\boldsymbol{p}^{i2}}{2m} + \Psi(\boldsymbol{r}^i), \rho_N\right\} \mathrm{d}^3r^i \mathrm{d}^3p^i \\ &= \int \left[\nabla_{\boldsymbol{r}^i}\Psi(\boldsymbol{r}^i) \cdot \nabla_{\boldsymbol{p}^i}\rho_N - \frac{\boldsymbol{p}^i}{m} \cdot \nabla_{\boldsymbol{r}^i}\rho_N\right] \mathrm{d}^3r^i \mathrm{d}^3p^i \\ &= \int \nabla_{\boldsymbol{r}^i}\Psi(\boldsymbol{r}^i)\rho_N \mathrm{d}^3r^i \Bigg|_{p^i=-\infty}^{p^i=\infty} - \int \frac{\boldsymbol{p}_i}{m}\rho_N \mathrm{d}^3p^i \Bigg|_{r^i=-\infty}^{r^i=\infty} = 0\end{aligned} \tag{7.11}$$

because ρ_N is normalized and thus has to vanish at the boundary.
*COMMENT: Nicer proof by myself
The phase space density is normalized, i.e.

$$\int \rho \, \mathrm{d}V = 1 \tag{7.12}$$

Thus, we find using Liouville's equation

$$\frac{\partial}{\partial t}\int \rho \,\mathrm{d}V = \int \frac{\partial \rho}{\partial t}\,\mathrm{d}V = \int \{H,\rho\}\,\mathrm{d}V = 0\;. \tag{7.13}$$

*COMMENT over.
In a similar way, we find

$$\int \{W_{ij},\rho_N\}\,\mathrm{d}^6\xi_i \mathrm{d}^6\xi_j = 0\;. \tag{7.14}$$

Thus the potential energy contributes only for particles 1 to l and the interaction energy W_{ij} contributes only if at least one of the indices i, j is not contained in the set $\{l+1,\dots,N\}$. We use this facts and make further use of the symmetry of the interaction $W_{ij}=W_{ji}$. Then, eq. (7.10) becomes

$$\begin{aligned}\frac{\partial f_l}{\partial t} =& \int \left\{\sum_{i=1}^{l}\left(\frac{\boldsymbol{p}^{i2}}{2m}+\Psi(\boldsymbol{r}^i)\right),\rho_N\right\} + \left\{\sum_{1\le i\le j\le l} W_{ij},\rho_N\right\}\mathrm{d}\xi_{l+1}\dots\mathrm{d}\xi_N \\ &+\int \sum_{i=1}^{l}\sum_{j=l+1}^{N}\nabla_{\boldsymbol{r}^i}W_{ij}\cdot\nabla_{\boldsymbol{p}^i}\rho_N\,\mathrm{d}\xi_{l+1}\dots\mathrm{d}\xi_N \\ =& \left\{\sum_{i=1}^{l}\left[\frac{\boldsymbol{p}^{i2}}{2m}+\Psi(\boldsymbol{r}^i)\right]+\sum_{1\le i\le j\le l}W_{ij},f_l\right\} \\ &+(N-l)\int\sum_{i=1}^{l}\nabla_{\boldsymbol{r}^i}W_{i,l+1}\cdot\nabla_{\boldsymbol{p}^i}f_{l+1}\mathrm{d}\xi_{l+1}\end{aligned}$$

For the last step, we used that $\nabla_{\boldsymbol{r}^i}W_{ij}$ does not depend on j, and thus we can perform the sum over j. Also, we performed all the integrals over $\mathrm{d}\xi_{l+2}\dots\mathrm{d}\xi_N$ transforming ρ_N into f_{l+1} by the definition of (7.8). We finally obtain

$$\boxed{\frac{\partial f_l}{\partial t} = \{H_l,f_l\}+(N-l)\int\sum_{i=1}^{l}\nabla_{\boldsymbol{r}^i}W_{i,l+1}\cdot\nabla_{\boldsymbol{p}^i}f_{l+1}\mathrm{d}\xi_{l+1}\;.} \tag{7.15}$$

This is a set of coupled equations referred to as BBGKY hierarchy. Every equation for f_l includes f_{l+1}. Thus, we are faced with the following problem – to calculate f_1 we need f_2, but to calculate f_2, we need f_3 and so on. So far, we have not really made any progress in solving the N-body problem. The strength of the BBGKY hierarchy however, is that it can be approximated in reasonable ways, yielding the Vlasov or the Boltzmann equation.

We consider the first equation for $l=1$ and the corresponding Hamiltonian

$$H_1 = \frac{\boldsymbol{p}^2}{2m}+\Psi(\boldsymbol{r})\;.$$

The first term of eq (7.15) for $l = 1$ is

$$\begin{aligned}\{H_1, f_1\} =&\nabla_{\boldsymbol{r}} H_1 \cdot \nabla_{\boldsymbol{p}} f_1 - \nabla_{\boldsymbol{p}} H_1 \cdot \nabla_{\boldsymbol{r}} f_1 \\ =& - m\boldsymbol{F}(\boldsymbol{r}) \cdot \nabla_{\boldsymbol{p}} f_1 - \frac{\boldsymbol{p}}{m} \cdot \nabla_{\boldsymbol{r}} f_1 \ ,\end{aligned} \tag{7.16}$$

where we used $\nabla_r \Psi(\boldsymbol{r}) = -m\boldsymbol{F}$ as the definition of the potential and the force $\boldsymbol{F}$ and switched to a less cumbersome notation $(\boldsymbol{r}^1, \boldsymbol{p}^1) \to (\boldsymbol{r}, \boldsymbol{p})$ and $(\boldsymbol{r}^2, \boldsymbol{p}^2) \to (\boldsymbol{r}', \boldsymbol{p}')$. Inserting (7.16) into (7.15), we obtain

$$\boxed{\begin{aligned}&\left(\frac{\partial}{\partial t} + \frac{\boldsymbol{p}}{m} \cdot \nabla_r + m\boldsymbol{F}(\boldsymbol{r}) \cdot \nabla_p\right) f_1(\boldsymbol{r}, \boldsymbol{p}, t) \\ =&(N-1) \int \nabla_{\boldsymbol{r}} W(\boldsymbol{r}, \boldsymbol{r}') \cdot \nabla_{\boldsymbol{p}} f_2(\boldsymbol{r}, \boldsymbol{p}, \boldsymbol{r}', \boldsymbol{p}', t) \mathrm{d}^3 r' \mathrm{d}^3 p' \equiv \left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} \ ,\end{aligned}} \tag{7.17}$$

where we defined the collision integral as a function of f_1 and note that for large N, we can approximate $N - 1 \approx N$.

7.2. Balance equation from BBGKY equation

Before we continue to treat the N-body problem with the use of the BBGKY hierarchy, we will use it to derive some of the balance equations of chapter from the microscopic picture. To this end, we first make some preliminary considerations concerning relevant densities following from one particle and two particle distribution functions.

$$\boxed{\rho(\boldsymbol{r}, t) = mN \int f_1(\boldsymbol{r}, \boldsymbol{p}, t) \mathrm{d}^3 p \ ,} \tag{7.18}$$

where we assumed, that f is normalized, i.e. $\int f_1 \mathrm{d}^3 r \mathrm{d}^3 p = 1$ and thus $\int \rho(\boldsymbol{r}, t) \mathrm{d}^3 r = Nm$. The velocity field

$$\boxed{\boldsymbol{v}(\boldsymbol{r}, t) = \frac{N}{\rho(\boldsymbol{r}, t)} \int \boldsymbol{p} f_1(\boldsymbol{r}, \boldsymbol{p}, t) \mathrm{d}^3 p \ ,} \tag{7.19}$$

that reduces for a stationary flow with constant velocity

$$f_1(\boldsymbol{r}, \boldsymbol{p}, t) = \frac{1}{V} \delta(\boldsymbol{p} - \boldsymbol{p}_0)$$

and constant density

$$\boldsymbol{\rho}(\boldsymbol{r}, t) = m\frac{N}{V}$$

to

$$\boldsymbol{v}(\boldsymbol{r}, t) = \frac{V}{m} \frac{\boldsymbol{p}_0}{V} = \frac{p_0}{m}$$

as it should be.
The thermal or internal kinetic specific energy density

$$\boxed{\begin{aligned} e^K(\boldsymbol{r},t) &= \frac{N}{\rho(\boldsymbol{r},t)}\int\left(\frac{p^2}{2m}-\frac{1}{2}mv^2(\boldsymbol{r},t)\right)f_1(\boldsymbol{r},\boldsymbol{p},t)\mathrm{d}^3p \\ &= \frac{N}{\rho(\boldsymbol{r},t)}\int\frac{1}{2m}\left(\boldsymbol{p}-m\boldsymbol{v}(\boldsymbol{r},t)\right)^2 f_1(\boldsymbol{r},\boldsymbol{p},t)\mathrm{d}^3p\,, \end{aligned}} \tag{7.20}$$

which is a measure for the width of the velocity distribution or in other words for the strength of the internal momentum fluctuations.
The potential interaction energy density

$$\boxed{e^V(\boldsymbol{r},t) = \frac{1}{2}\frac{N}{\rho(\boldsymbol{r},t)}\int W(r,r')f_2(r,p,r',p',t)\mathrm{d}^3p\,\mathrm{d}^3r'\mathrm{d}^3p'} \tag{7.21}$$

Next, we want to derive the continuity equation for the mass density $\rho(\boldsymbol{r},t)$. To this end, we integrate the first BBGKY equation (7.17) over d^3p and use the approximation $N-1\approx N$

$$\begin{aligned} &\int\frac{\partial}{\partial t}f_1\mathrm{d}^3p+\int\frac{\boldsymbol{p}}{m}\cdot\nabla_{\boldsymbol{r}}f_1\mathrm{d}^3p+m\int\boldsymbol{F}(\boldsymbol{r})\cdot\nabla_{\boldsymbol{p}}f_1(\boldsymbol{r},\boldsymbol{p},t)\mathrm{d}^3p \\ =&N\int\nabla_{\boldsymbol{r}}W(\boldsymbol{r},\boldsymbol{r}')\cdot\nabla_{\boldsymbol{p}}f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p \end{aligned}$$

and multiply by mN

$$\begin{aligned} &\frac{\partial}{\partial t}mN\int f_1\mathrm{d}^3p+\nabla_{\boldsymbol{r}}\cdot N\int\boldsymbol{p}f_1\mathrm{d}^3p+m^2N\int\nabla_{\boldsymbol{p}}\cdot\boldsymbol{F}(\boldsymbol{r})f_1\mathrm{d}^3p \\ &-mN^2\int\nabla_{\boldsymbol{p}}\cdot\nabla_{\boldsymbol{r}}W(\boldsymbol{r},\boldsymbol{r}')f_2\mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p=0 \end{aligned}$$

The last two terms vanish by an argument similar to the one used in the derivation of (7.11) based on the fact, that f_1 and f_2 are normalized. Using relations (7.18) and (7.19), we notice, that we have just derived the well known continuity equation

$$\boxed{\frac{\partial}{\partial t}\rho(\boldsymbol{r},t)+\nabla_r\rho(\boldsymbol{r},t)\boldsymbol{v}(\boldsymbol{r},t)=0\,.} \tag{7.22}$$

To recover the conservation of momentum, we multiply eq. (7.17) by $N\boldsymbol{p}$ and integrate over p, again using the approximation $N\approx N-1$. The equation for the ith component reads

$$\begin{aligned} &\frac{\partial}{\partial t}N\int p_if_1(\boldsymbol{r},\boldsymbol{p},t)\mathrm{d}^3p+\nabla_{r_j}\frac{N}{m}\int p_ip_jf_1\mathrm{d}^3p+mN\int p_iF_j\nabla_{p_j}f_1\mathrm{d}^3p \\ =&N^2\int p_i\nabla_{r_j}W(\boldsymbol{r},\boldsymbol{r}')\nabla_{p_j}f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p\,. \end{aligned} \tag{7.23}$$

With the following side calculations

$$\begin{aligned}&mN\int p_iF_j\nabla_{p_j}f_1\mathrm{d}^3p\\ =&mN\underbrace{\int\nabla_{p_j}(p_iF_jf_1)\mathrm{d}^3p}_{=0}-mN\int f_1F_j\underbrace{\nabla_{p_j}p_i}_{\delta_{ij}}\mathrm{d}^3p\\ =&-mNF_i\int f_1\mathrm{d}^3p=-F_i\rho(\boldsymbol{r},t)\end{aligned}\tag{7.24}$$

we obtain from equation (7.23) by using (7.18) and (7.19) again

$$\begin{aligned}&\frac{\partial}{\partial t}\left(v_i(\boldsymbol{r},t)\rho(\boldsymbol{r},t)\right)+\nabla_{r_j}\frac{N}{m}\int p_ip_jf_1\mathrm{d}^3p\\ &-N^2\int p_i\nabla_{r_j}W(\boldsymbol{r},\boldsymbol{r}')\nabla_{p_j}f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p=F_i\rho(\boldsymbol{r},t)\end{aligned}\tag{7.25}$$

In order to find a more comprehensive expression for (7.25) we multiply the continuity equation by v_i

$$v_i\frac{\partial}{\partial t}\rho+v_i\nabla_{r_j}\rho v_j=0$$

$$v_i\frac{\partial}{\partial t}\rho+\nabla_{r_j}v_i\rho v_j-\rho v_j\nabla_{r_j}v_i=0$$

and subtract it from (7.25)

$$\begin{aligned}&\rho\left(\dot{v}_i+v_j\nabla_{r_j}v_i\right)+\frac{N}{m}\nabla_{r_j}\int\left(p_ip_j-m^2v_iv_j\right)f_1\mathrm{d}^3p\\ &-N^2\int p_i\nabla_{r_j}W(\boldsymbol{r},\boldsymbol{r}')\nabla_{p_j}f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p=F_i\rho(\boldsymbol{r},t)\ .\end{aligned}\tag{7.26}$$

We define the kinetic stress tensor

$$\Pi^K_{ij}(\boldsymbol{r},t)=\frac{N}{m}\int\left(p_ip_j-mv_imv_j\right)f_1\mathrm{d}^3p\tag{7.27}$$

$$=\frac{N}{m}\int(p_i-mv_i)(p_j-mv_j)f_1\mathrm{d}^3p\tag{7.28}$$

and rewrite (7.26) using (7.28)

$$\begin{aligned}&\rho\left(\dot{v}_i+v_j\nabla_{r_j}v_i\right)+\nabla_{r_j}\Pi^K_{ij}(\boldsymbol{r},t)\\ &-N^2\int p_i\nabla_{r_j}W(\boldsymbol{r},\boldsymbol{r}')\nabla_{p_j}f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p=F_i\rho(\boldsymbol{r},t)\ .\end{aligned}\tag{7.29}$$

Next we consider the term involving f_2 in (7.29) and give it a name

$$\Omega_i=-N^2\int p_i\nabla_{r_j}W(\boldsymbol{r},\boldsymbol{r}')\nabla_{p_j}f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p\ .\tag{7.30}$$

So we can shorten (7.29)

$$\rho\left(\dot{v}_i + v_j \nabla_{r_j} v_i\right) + \nabla_{r_j}\Pi^K_{ij}(\boldsymbol{r},t) + \Omega_i = F_i\rho(\boldsymbol{r},t)\ . \tag{7.31}$$

Now, we take a closer look at Ω_i (7.30)

$$\begin{aligned}
\Omega_i =& - N^2 \int p_i \nabla_{r_j} W(\boldsymbol{r},\boldsymbol{r}')\nabla_{p_j} f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p \\
=& - N^2 \underbrace{\int \nabla_{p_j} p_i \nabla_{r_j} W(\boldsymbol{r},\boldsymbol{r}') f_2 \mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p}_{=0} \\
&+ N^2 \int \underbrace{\left(\nabla_{p_j} p_i\right)}_{\delta_{ij}} \nabla_{r_j} W(\boldsymbol{r},\boldsymbol{r}') f_2 \mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p \\
\Omega_i =& N^2 \int \nabla_{r_i} W(\boldsymbol{r},\boldsymbol{r}') f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3r'\mathrm{d}^3p'\mathrm{d}^3p
\end{aligned} \tag{7.32}$$

We define the spatial 2-point distribution function, that will be important later

$$g(\boldsymbol{r},\boldsymbol{r}',t) = \int f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3p\mathrm{d}^3p' \tag{7.33}$$

and find

$$\begin{aligned}
\Omega_i =& N^2 \int g(\boldsymbol{r},\boldsymbol{r}',t)\nabla_{r_i} W(\boldsymbol{r},\boldsymbol{r}')\mathrm{d}^3r' \\
=& N^2 \int g(\tilde{\boldsymbol{r}},\boldsymbol{r}',t)\nabla_{\tilde{r}_i} W(\tilde{\boldsymbol{r}},\boldsymbol{r}')\delta(\tilde{\boldsymbol{r}}-\boldsymbol{r})\mathrm{d}^3\tilde{r}\mathrm{d}^3r'
\end{aligned} \tag{7.34}$$

For a central potential we have $W(\boldsymbol{r},\boldsymbol{r}') = W(|\boldsymbol{r}-\boldsymbol{r}'|)$ and

$$\nabla_{\tilde{r}_i} W(|\tilde{\boldsymbol{r}}-\boldsymbol{r}'|) = -\nabla_{r'_i} W(|\tilde{\boldsymbol{r}}-\boldsymbol{r}'|)\ .$$

Thus, we can rewrite eq (7.34) yielding

$$\Omega_i = \frac{1}{2}N^2 \int g(\tilde{\boldsymbol{r}},\boldsymbol{r}',t)\delta(\tilde{\boldsymbol{r}}-\boldsymbol{r})(\nabla_{\tilde{r}_i} - \nabla_{r'_i})W(|\tilde{\boldsymbol{r}}-\boldsymbol{r}'|)\mathrm{d}^3\tilde{r}\mathrm{d}^3r'\ . \tag{7.35}$$

In the second addend of (7.35) we switch $r' \leftrightarrow \tilde{r}$ and since $g(\tilde{r},r') = g(r',\tilde{r})$, we obtain

$$\Omega_i = \frac{1}{2}N^2 \int g(\tilde{\boldsymbol{r}},\boldsymbol{r}',t)\left[\delta(\tilde{\boldsymbol{r}}-\boldsymbol{r}) - \delta(\boldsymbol{r}'-\boldsymbol{r})\right]\nabla_{\tilde{r}_i} W(|\tilde{\boldsymbol{r}}-\boldsymbol{r}'|)\mathrm{d}^3\tilde{r}\mathrm{d}^3r'\ . \tag{7.36}$$

In the following we will use the subsequent relation

$$\delta(\boldsymbol{r}-\tilde{\boldsymbol{r}})-\delta(\boldsymbol{r}-\boldsymbol{r}') = -\nabla_r\cdot\int_0^1 \mathrm{d}\lambda(\tilde{\boldsymbol{r}}-\boldsymbol{r}')\delta(\boldsymbol{r}-\lambda\tilde{\boldsymbol{r}}-(1-\lambda)\boldsymbol{r}')\delta(\boldsymbol{r}-\boldsymbol{r}'-\lambda(\tilde{\boldsymbol{r}}-\boldsymbol{r}'))\ . \tag{7.37}$$

Proof:

$$
\begin{aligned}
&-\nabla_r \cdot \int_0^1 \mathrm{d}\lambda(\tilde{\boldsymbol{r}}-\boldsymbol{r}')\delta(\boldsymbol{r}-\lambda\tilde{\boldsymbol{r}}-(1-\lambda)\boldsymbol{r}')\delta(\boldsymbol{r}-\boldsymbol{r}'-\lambda(\tilde{\boldsymbol{r}}-\boldsymbol{r}'))\\
=&-\nabla_r \cdot \int_0^1 \mathrm{d}\lambda(\tilde{\boldsymbol{r}}-\boldsymbol{r}')\int \frac{\mathrm{d}^3p}{(2\pi)^3}e^{i\boldsymbol{p}\cdot(\boldsymbol{r}-\boldsymbol{r}')-i\lambda(\tilde{\boldsymbol{r}}-\boldsymbol{r}')\cdot\boldsymbol{p}}\\
=&-\nabla_r \cdot (\tilde{\boldsymbol{r}}-\boldsymbol{r}')\int \frac{\mathrm{d}^3p}{(2\pi)^3}e^{i\boldsymbol{p}\cdot(\boldsymbol{r}-\boldsymbol{r}')}\left|\frac{e^{-i\lambda(\tilde{\boldsymbol{r}}-\boldsymbol{r}')\cdot\boldsymbol{p}}}{-i(\tilde{\boldsymbol{r}}-\boldsymbol{r}')}\right|_0^1\\
=&-\nabla_r \cdot (\tilde{\boldsymbol{r}}-\boldsymbol{r}')\int \frac{\mathrm{d}^3p}{(2\pi)^3}e^{i\boldsymbol{p}\cdot(\boldsymbol{r}-\boldsymbol{r}')}\frac{1-e^{-i(\tilde{\boldsymbol{r}}-\boldsymbol{r}')\cdot\boldsymbol{p}}}{i(\tilde{\boldsymbol{r}}-\boldsymbol{r}')\cdot p}\\
=&\int \frac{\mathrm{d}^3p}{(2\pi)^3}\left(e^{-i\boldsymbol{p}\cdot(\tilde{\boldsymbol{r}}-\boldsymbol{r})}-e^{i\boldsymbol{p}\cdot(\boldsymbol{r}-\boldsymbol{r}')}\right)\\
=&\,\delta(\boldsymbol{r}-\tilde{\boldsymbol{r}})-\delta(\boldsymbol{r}-\boldsymbol{r}')
\end{aligned}
$$

Using this relation, we can write

$$
\begin{aligned}
\Omega_i(\boldsymbol{r},t) &= -\frac{1}{2}N^2\nabla_{r_j}\int_0^1 \mathrm{d}\lambda\int g(\tilde{r},\boldsymbol{r}',t)\left(\tilde{\boldsymbol{r}}_j-\boldsymbol{r}'_j\right)\delta(\boldsymbol{r}-\boldsymbol{r}'-\lambda(\tilde{\boldsymbol{r}}-\boldsymbol{r}'))\nabla_{\tilde{r}_i}W(|\tilde{\boldsymbol{r}}-\boldsymbol{r}'|)\mathrm{d}^3\tilde{r}\mathrm{d}^3r'\\
&= -\frac{1}{2}N^2\nabla_{r_j}\int \mathrm{d}\lambda\int g(\tilde{\boldsymbol{r}}+\boldsymbol{r}',\boldsymbol{r}',t)\tilde{\boldsymbol{r}}_j\delta(\boldsymbol{r}-\boldsymbol{r}'-\lambda\tilde{\boldsymbol{r}})\nabla_{\tilde{r}_i}W(|\tilde{\boldsymbol{r}}|)\mathrm{d}^3\tilde{r}\mathrm{d}^3r'\,.
\end{aligned}
$$

Using the following relation

$$
\int \mathrm{d}^3r f(\boldsymbol{r})\delta(\boldsymbol{r}\lambda-\boldsymbol{r}_0)=\int\frac{\mathrm{d}^3\tilde{r}}{\lambda^3}f(\tilde{\boldsymbol{r}}/\lambda)\delta(\tilde{\boldsymbol{r}}-\boldsymbol{r}_0)=\frac{f(\boldsymbol{r}_0/\lambda)}{\lambda^3} \tag{7.38}
$$

and introducing the interaction component of the stress tensor

$$
\Pi_{ij}^W = -\frac{1}{2}N^2\int \mathrm{d}\lambda\int g(\boldsymbol{r}+(1-\lambda)\tilde{\boldsymbol{r}},\boldsymbol{r}-\lambda\tilde{\boldsymbol{r}},t)\frac{\tilde{r}_j\tilde{r}_i}{|\tilde{r}|}\frac{\mathrm{d}W(|\tilde{r}|)}{\mathrm{d}|\tilde{r}|}\mathrm{d}\tilde{r} \tag{7.39}
$$

we finally obtain

$$
\Omega_i=\nabla_{r_j}\Pi_{ij}^W\ . \tag{7.40}
$$

The stress tensor is decomposed into a kinetic and an interaction component according to

$$
\Pi_{ij}=\Pi_{ij}^K+\Pi_{ij}^W\ , \tag{7.41}
$$

where the kinetic contribution was already introduced in (7.28). Combining (7.29) with (7.40) and (7.41), we finally obtain

$$
\boxed{\rho\left(\dot{v}_i+v_j\nabla_{r_i}v_i\right)+\nabla_{r_j}\Pi_{ij}=F_i\rho} \tag{7.42}
$$

which is an exact relation.

For an isotropic medium we have $g(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = g(|\boldsymbol{r}_1 - \boldsymbol{r}_2|, t)$ and the interaction component of the stress tensor can be rewritten according to

$$\boxed{\Pi^W_{ij} = -\frac{1}{2} N^2 \int g(|\tilde{\boldsymbol{r}}|, t) \frac{\tilde{r}_j \tilde{r}_i}{|\tilde{r}|} \frac{\mathrm{d}W(|\tilde{r}|)}{\mathrm{d}|\tilde{r}|} \mathrm{d}\tilde{r}} \tag{7.43}$$

The term is proportional to N^2 and thus proportional to the density squared. In gases, this quantity is related to collisions, in fluids it describes the coupling between g and the pairing force $-\frac{\mathrm{d}W(r)}{\mathrm{d}r}$, which vanishes for an ideal gas.
The kinetic contribution to Π_{ij}

$$\boxed{\Pi^K_{ij} = \frac{N}{m} \int (p_i - mv_i)(p_j - mv_j) f_1 \mathrm{d}^3 p} \tag{7.44}$$

is proportional to N or to the density.

We consider the hydrostatic pressure

$$p(\boldsymbol{r}, t) = \frac{1}{3} \left(\Pi^K_{ii} + \Pi^W_{ii} \right) \tag{7.45}$$

for an ideal gas, we have

$$p = \frac{1}{3} \frac{N}{m} \int (\boldsymbol{p} - m\boldsymbol{v})^2 f_1 \mathrm{d}^3 p = \frac{2}{3} \rho(\boldsymbol{r}, t) e^K(\boldsymbol{r}, t) , \tag{7.46}$$

where we used (7.18) and (7.20). The phase space distribution function in local equilibrium is given by the Maxwell distribution

$$f_1^{eq}(\boldsymbol{r}, \boldsymbol{p}, t) = \exp\left\{ -\frac{(\boldsymbol{p} - m\boldsymbol{v})^2}{2mk_B T(\boldsymbol{r}, t)} \right\} \left(2\pi m k_B T(\boldsymbol{r}, t)\right)^{-3/2} V^{-1} . \tag{7.47}$$

Using (7.47) to evaluate the internal energy, we obtain

$$\boxed{e^K(\boldsymbol{r}, t) = \frac{3}{2} k_B T(\boldsymbol{r}, t) .} \tag{7.48}$$

Inserting (7.48) into (7.46), we obtain nothing but the ideal gas equation.

$$\boxed{p = \rho k_B T \ .} \tag{7.49}$$

We state without proof, that in a similar way to the derivations above material equations e.g. viscosity or specific heat capacity can derived be from microscopic relation,

7.3. Vlasov equation

The BBGKY equations (7.15) are not exactly solvable, i.e. f_1 can not be calculated. Thus, we consider an approximative approach. We consider the first equation

$$\left(\frac{\partial}{\partial t} + \frac{p_i}{m} \nabla_{r_i} + m F_i \nabla_{p_i} \right) f_1(\boldsymbol{r}, \boldsymbol{p}, t) = \left. \frac{\partial f_1}{\partial t} \right|_{\text{coll}} \tag{7.50}$$

with

$$\left.\frac{\partial f_1}{\partial t}\right|_{\mathrm{coll}} = N\int \left(\nabla_{r_i} W(\boldsymbol{r},\boldsymbol{r}')\right)\nabla_{p_i} f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3r'\mathrm{d}^3p' \tag{7.51}$$

the collision integral. The simplest, mean-field-like approximation is to assume, that the probability density for two particle is nothing, but the product of two single particle probability densities and thus factorizes according to

$$\boxed{f_2(\boldsymbol{r},\boldsymbol{p},\boldsymbol{r}',\boldsymbol{p}',t) = f_1(\boldsymbol{r},\boldsymbol{p},t)f_1(\boldsymbol{r}',\boldsymbol{p}',t)\ .} \tag{7.52}$$

This corresponds to a decoupling of the particles. Using (7.52) in eq (7.50), we obtain for the collision integral

$$\begin{aligned}\left.\frac{\partial f_1}{\partial t}\right|_{\mathrm{coll}} &= N\int \left(\nabla_{r_i} W(\boldsymbol{r},\boldsymbol{r}')\right)\nabla_{p_i} f_1(\boldsymbol{r},\boldsymbol{p},t)f_1(\boldsymbol{r}',\boldsymbol{p}',t)\mathrm{d}^3r'\mathrm{d}^3p' \\ &= \frac{1}{m}\int \left(\nabla_{r_i} W(\boldsymbol{r},\boldsymbol{r}')\right)\nabla_{p_i} f_1(\boldsymbol{r},\boldsymbol{p},t)\rho(\boldsymbol{r}',t)\mathrm{d}^3r' \\ &= \left(\nabla_{p_i} f_1(\boldsymbol{r},\boldsymbol{p},t)\right)\nabla_{r_i}\bar{\Psi}(\boldsymbol{r})\ ,\end{aligned} \tag{7.53}$$

where we have used the definition of the mass density (7.18) in the second line and introduced the mean field potential

$$\boxed{\bar{\Psi}(\boldsymbol{r}) = \frac{1}{m}\int W(\boldsymbol{r},\boldsymbol{r}')\rho(\boldsymbol{r}',t)\mathrm{d}^3r'\ .} \tag{7.54}$$

Using eq (7.53) in (7.50) we obtain the Vlasov kinetic equation (1938)

$$\boxed{\left(\frac{\partial}{\partial t} + \frac{p_i}{m}\nabla_{r_i} + \left(mF_i(r) - \nabla_{r_i}\bar{\Psi}(r)\right)\nabla_{p_i}\right) f_1(\boldsymbol{r},\boldsymbol{p},t) = 0\ .} \tag{7.55}$$

The particles feel only an average potential created by the other particles. This equation in non-linear and reversible, i.e. for time and momentum inversion $t \to -t$, $\boldsymbol{p} \to -\boldsymbol{p}$, we obtain the identical equation for $f_1(\boldsymbol{r}, -\boldsymbol{p}, -t)$. That means, we can describe irreversible phenomena.

7.4. Boltzmann equation and irreversibility

In 1897 Planck stated, that the main question of theoretical physic is to derive the laws for irreversible processes from the Hamilton equations with conservative forces. The problem here is, that the Hamilton equations are invariant under the transformation $t \to -t$ and $\boldsymbol{p} \to -\boldsymbol{p}$ for conservative forces. Planck proposed the 'radiation damping' and wrote 7 papers on this issue between 1895 and 1901, from which important hints concerning the development of quantum mechanics were obtained.

One central point of this discussion is the Boltzmann equation formulated by Boltzmann in 1872. The Boltzmann equation gives an expression for the collision integral based on two-particle scattering. To derive it, we consider the two-body Hamiltonian

$$H_2(\boldsymbol{p},\boldsymbol{r},\boldsymbol{p}',\boldsymbol{r}') = \frac{\boldsymbol{p}^2}{2m} + \frac{\boldsymbol{p}'^2}{2m} + W(|\boldsymbol{r}-\boldsymbol{r}'|) \ . \tag{7.56}$$

We introduce the relative coordinates

$$\Delta\boldsymbol{r} = \boldsymbol{r}-\boldsymbol{r}' \qquad \boldsymbol{R} = \frac{1}{2}(\boldsymbol{r}+\boldsymbol{r}') \tag{7.57}$$

$$\Delta\boldsymbol{p} = \frac{1}{2}(\boldsymbol{p}-\boldsymbol{p}') \qquad \boldsymbol{P} = \boldsymbol{p}+\boldsymbol{p}' \tag{7.58}$$

$$\tag{7.59}$$

and rewrite the Hamiltonian (7.56)

$$H_2 = \frac{\boldsymbol{P}^2}{4m} + \frac{\Delta\boldsymbol{p}^2}{m} + W(|\Delta\boldsymbol{r}|) \ . \tag{7.60}$$

Thus, we have obtained the form of a free particle scattered by a central potential. The scattering process is described by the process $\boldsymbol{p},\boldsymbol{p}' \to \tilde{\boldsymbol{p}},\tilde{\boldsymbol{p}}'$ and

$$\boldsymbol{P} = \tilde{\boldsymbol{P}} \tag{7.61}$$

assures to the conservation of momentum. We define the absolute value of the relative velocity $g = |\boldsymbol{v}-\boldsymbol{v}'|$ by

$$|\Delta\boldsymbol{p}| = |\Delta\tilde{\boldsymbol{p}}| \equiv \frac{m}{2}g \ . \tag{7.62}$$

The angular momentum vector (in laboratory frame) is conserved, because we face a central potential. Its absolute value is given by

$$l = |\Delta\boldsymbol{p}|b \ , \tag{7.63}$$

where b is the distance between the particles trajectory at minus infinity and the parallel line on which the scatterer is located, in this case this corresponds to the coordinate center. If the particle initially moves from left to right, b is measured in the upward direction.
DRAWING
Using classical mechanics, we can derive an equation for the scattering angle Θ. For a derivation we refer to any introductory course on classical mechanics and will only state the final result here. The scattering angle depends on the central potential W, the angular momentum l and the initial velocity. It is given by an integral over the reciprocal radial distance to the scattering object, here the coordinate origin

$$\Theta_0 = \pi - 2\int_0^{\eta^*} \frac{\mathrm{d}\eta}{\left[1-\eta^2-\frac{4}{mg^2}W(b/\eta)\right]^{1/2}} \tag{7.64}$$

The limit of the integration η^* is given by the condition

$$1 - \eta^{*2} - \frac{4}{mg^2} W(b\eta^*) = 0 \; . \tag{7.65}$$

This results from the fact, that the particle can not come closer to the coordinate origin than a certain distance, which is limited by energy conservation, i.e. when the particle has transferred all its kinetic and rotational energy into potential energy.

Now we count the number of collisions. All particles with momentum $\boldsymbol{p}'$ in the volume element $\mathrm{d}^3 r' = 2\pi b \mathrm{d}b g \mathrm{d}t$ will be scattered in the time interval $\mathrm{d}t$. The number of scattering events is thus given by

$$C(\boldsymbol{p}, \boldsymbol{p}' \to \tilde{\boldsymbol{p}}, \tilde{\boldsymbol{p}}') \sim 2\pi g b \, \mathrm{d}b \, \mathrm{d}t \, f_1(\boldsymbol{p}, \boldsymbol{r}, t) f_1(\boldsymbol{p}', \boldsymbol{r}, t) \mathrm{d}^3 p \mathrm{d}^3 p' \; . \tag{7.66}$$

Here we used, that the scattering particles are uncorrelated and thus the two-particle probability density factorizes into a product of one particle probability densities (molecular chaos). The number of collisions of the reverse scattering process is given by

$$C(\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{p}}' \to \boldsymbol{p}, \boldsymbol{p}') \sim 2\pi g b \mathrm{d}b \mathrm{d}t f_1(\tilde{\boldsymbol{p}}, \boldsymbol{r}, t) f_1(\tilde{\boldsymbol{p}}', \boldsymbol{r}, t) \mathrm{d}^3 \tilde{p} \mathrm{d}^3 \tilde{p}' \; . \tag{7.67}$$

With the definition of the scattering cross section

$$\sigma(g, \Theta_0) \sin \Theta_0 \mathrm{d}\Theta_0 = b \mathrm{d}b \; , \tag{7.68}$$

we obtain for the number of particles scattered into the phase space volume $\mathrm{d}^3 p$ per unit time $\mathrm{d}t$ subtracted by the number of particles scattered out of this phase space volume element

$$\begin{aligned} \Delta_{\boldsymbol{p}} =& C(\boldsymbol{p}, \boldsymbol{p}' \to \tilde{\boldsymbol{p}}, \tilde{\boldsymbol{p}}') - C(\boldsymbol{p}, \boldsymbol{p}' \to \tilde{\boldsymbol{p}}, \tilde{\boldsymbol{p}}') \\ \sim& 2\pi g \sigma(g, \Theta_0) \sin \Theta_0 \mathrm{d}\Theta_0 \, \mathrm{d}t \\ & \times \left(f_1(\tilde{\boldsymbol{p}}, \boldsymbol{r}, t) f_1(\tilde{\boldsymbol{p}}', \boldsymbol{r}, t) \mathrm{d}^3 \tilde{p} \mathrm{d}^3 \tilde{p}' - f_1(\boldsymbol{p}, \boldsymbol{r}, t) f_1(\boldsymbol{p}', \boldsymbol{r}, t) \mathrm{d}^3 p \mathrm{d}^3 p' \right) \end{aligned}$$

Thus, we obtain for the rate of change of the phase space density $f(\boldsymbol{p}, \boldsymbol{r}, t)$ per unit time $\mathrm{d}t$ per unit volume $\mathrm{d}^3 p$ due to two-particle scattering the collision integral

$$\boxed{\begin{aligned} \left.\frac{\partial f}{\partial t}\right|_{\text{coll}} =& N \int \mathrm{d}^3 p' \int \mathrm{d}\Theta_0 \sin \Theta_0 \mathrm{d}\alpha g \sigma(\Theta_0, g) \\ & \times \left(f_1(\tilde{\boldsymbol{p}}, \boldsymbol{r}, t) f_1(\widetilde{\boldsymbol{p}'}, \boldsymbol{r}, t) - f_1(\boldsymbol{p}, \boldsymbol{r}, t) f_1(\boldsymbol{p}', \boldsymbol{r}, t) \right) \; , \end{aligned}} \tag{7.69}$$

where $\tilde{\boldsymbol{p}}, \widetilde{\boldsymbol{p}'}$ are functions of $\boldsymbol{p}$ and $\boldsymbol{p}'$ determined by the momentum conservation (7.61) and the conservation of the center of mass momentum (7.62).

7.5. Boltzmann $\mathcal{H}$-theorem

We define the function

$$\boxed{\mathcal{H}(t) = N \int \int \mathrm{d}^3 r \mathrm{d}^3 p f_1(r, p, t) \ln f_1(r, p, t)} \; . \tag{7.70}$$

The Boltzmann $\mathcal{H}$-theorem then states:

$$\boxed{\text{If } f_1 \text{ is governed by the Boltzmann equation, } \mathcal{H} \text{ will decrease in time.}}$$

We will now proof this statement. Thus, we take the time derivative of (7.70)

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} = N \iint \mathrm{d}^3r\mathrm{d}^3p \frac{\partial f_1}{\partial t} \left[\ln f_1 + 1\right] \tag{7.71}$$

and consider the force free Boltzmann equation

$$\begin{aligned}\left(\frac{\partial}{\partial t} + \frac{p_i}{m}\nabla_{r_i}\right) f_1(\boldsymbol{r}, \boldsymbol{p}t) =& N \int \mathrm{d}^3p' \int \mathrm{d}\Theta_0 \sin\Theta_0 \int \mathrm{d}\alpha g\sigma(\Theta_0, g) \\ & \times \left[f_1(\tilde{\boldsymbol{p}}, \boldsymbol{r}, t) f_1(\tilde{\boldsymbol{p}}', \boldsymbol{r}, t) - f_1(\boldsymbol{p}, \boldsymbol{r}, t) f_1(\boldsymbol{p}', \boldsymbol{r}, t)\right]\end{aligned} \tag{7.72}$$

We solve (7.72) for the time derivative of f_1 and insert it into (7.71)

$$\begin{aligned}\frac{\mathcal{H}}{\mathrm{d}t} =& - N \underbrace{\int \mathrm{d}^3r\mathrm{d}^3p \frac{p_i}{m} \nabla r_i f_1 \left[\ln f_1 + 1\right]}_{=0,\text{ normalization of } f_1} \\ & + N^2 \iint \mathrm{d}^3r\mathrm{d}^3p \int \mathrm{d}^3p' \int \mathrm{d}\Omega g\sigma \left[f_1(\tilde{p}, r, t) f_1(\tilde{p}', r, t) - f_1(p, r, t) f_1(p', r, t)\right] \\ & \times \left[\ln f_1(r, p, t) - 1\right]\end{aligned} \tag{7.73}$$

The first term vanishes, because due to normalization f_1 vanishes at the boundaries. We swap p and p'

$$\begin{aligned}\frac{\mathcal{H}}{\mathrm{d}t} =& N^2 \iint \mathrm{d}^3r\mathrm{d}^3p \int \mathrm{d}^3p' \int \mathrm{d}\Omega g\sigma \left[f_1(\tilde{p}, r, t) f_1(\tilde{p}', r, t) - f_1(p, r, t) f_1(p', r, t)\right] \\ & \times \left[\ln f_1(r, p', t) - 1\right]\end{aligned} \tag{7.74}$$

and add (7.73) to (7.74) multiplying by $\frac{1}{2}$

$$\begin{aligned}\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} =& \frac{1}{2}N^2 \int \mathrm{d}^3r\mathrm{d}^3p\mathrm{d}^3p'\mathrm{d}\Omega g\sigma \left[f_1(\tilde{p}, r, t) f_1(\tilde{p}', r, t) - f_1(p, r, t) f_1(p', r, t)\right] \\ & \times \left[\ln f_1(r, p', t) + \ln f_1(r, p, t) - 2\right] .\end{aligned} \tag{7.75}$$

Now we swap $p, p' \to \tilde{p}\tilde{p}'$

$$\begin{aligned}\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} =& \frac{1}{2}N^2 \int \mathrm{d}^3r\mathrm{d}^3\tilde{p}\mathrm{d}^3\tilde{p}'\mathrm{d}\Omega g\sigma \left[f_1(p, r, t) f_1(p', r, t) - f_1(\tilde{p}, r, t) f_1(\tilde{p}', r, t)\right] \\ & \times \left[\ln f_1(r, \tilde{p}', t) + \ln f_1(r, \tilde{p}, t) - 2\right] .\end{aligned}$$

For an elastic scattering event, where relations (7.61) and (7.62) hold, we can replace the integrations $d^3\tilde{p}d^3\tilde{p}'$ by d^3pd^3p'

$$\begin{aligned}\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} =& \frac{1}{2}N^2 \int \mathrm{d}^3r\mathrm{d}^3p\mathrm{d}^3p'\mathrm{d}\Omega g\sigma \left[f_1(p, r, t) f_1(p', r, t) - f_1(\tilde{p}, r, t) f_1(\tilde{p}', r, t)\right] \\ & \times \left[\ln f_1(r, \tilde{p}', t) + \ln f_1(r, \tilde{p}, t) - 2\right] .\end{aligned} \tag{7.76}$$

Now we add (7.75) and (7.76) and divide by $\frac{1}{2}$. We obtain

$$\begin{aligned}\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} =& \frac{N^2}{4} \int \mathrm{d}^3r\mathrm{d}^3p\mathrm{d}^3p'\mathrm{d}\Omega\sigma \left[f_1(\tilde{p},r,t)f_1(\tilde{p}',r,t) - f_1(p,r,t)f_1(p',r,t)\right] \\ & \times \ln \frac{f_1(p,r,t)f_1(p',r,t)}{f_1(\tilde{p},r,t)f_1(\tilde{p}',r,t)} \, . \end{aligned} \tag{7.77}$$

Noting, that

$$(y-x)\ln\frac{x}{y} \leq 0 \quad \forall x,y \in \mathbb{R} \tag{7.78}$$

we realize, that we have proven the $\mathcal{H}$-theorem

$$\boxed{\begin{aligned}\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} =& \frac{N^2}{4} \int \mathrm{d}^3r\mathrm{d}^3p\mathrm{d}^3p'\mathrm{d}\Omega\sigma \left[f_1(\tilde{p},r,t)f_1(\tilde{p}',r,t) - f_1(p,r,t)f_1(p',r,t)\right] \\ & \times \ln \frac{f_1(p,r,t)f_1(p',r,t)}{f_1(\tilde{p},r,t)f_1(\tilde{p}',r,t)} \leq 0 \, . \end{aligned}} \tag{7.79}$$

Boltzmann defined the function

$$S(t) = -k_B\mathcal{H}(t) \tag{7.80}$$

as the entropy and we obtain the second law of thermodynamics from th $\mathcal{H}$-theorem

$$\frac{\mathrm{d}S(t)}{\mathrm{d}t} \geq 0 \, . \tag{7.81}$$

Looking at eq. (7.77) we find a condition for zero entropy production, or zero loss of $\mathcal{H}$

$$\frac{\partial\mathcal{H}}{\partial t} = 0 \Leftrightarrow f_1(\tilde{p})f_1(\tilde{p}') = f_1(p)f_1(p') \tag{7.82}$$

This corresponds to the condition of detailed balance (3.60) in chapter 3, which can be seen by using (7.66) and (7.67).

7.6. Loschmidt argument (1876)

The Hamilton equations are time reversible, when at time t' all velocities are reversed $\boldsymbol{v}^i \to -\boldsymbol{v}^i$, the system goes back to the past. For every trajectory in one direction there is one in the other direction. From this one might follow, that there is no approach to equilibrium.

Solution: Time reversal is not correctly described by the Boltzmann equation, because it is only an approximate equation, that neglects the multi-body correlation of time reversal.

Poincare Wiederkehr (1892) (Zermelo 1896): every insulated, finite, conservative system comes back arbitrarily close to its initial state in a finite time τ_p. however, this does not irreversibility as we observe it, because even for 10 atoms, the recurrence time is $\tau_p/\tau_0 \approx 10^{16}$ and for N atoms it increases exponentially with the number of atoms $\tau_p/\tau_0 \sim C^N$.

Poincare Recurrence.
Look up in book and write down an example

Appendix A

Levi-Civita tensor

Appendix B

Fourier transform

Appendix C

Gaussian processes