QSM - Lecture Notes

Part I. Thermodynamics

1 Equilibrium Thermodynamics.

The (thermodynamical) Universe $\mathcal{U} = \{\Gamma_1, ..., \Gamma_k\}$ is a set of systems Γ_i.
Each System Γ_i is a set of equilibrium states and is a convex subset of $\mathbb{R}^n$. The elements Γ_i (the states) will be denoted by X. Typically the components (coordinates) of a state $X = (V, U, N)$ will represent here the volume (V), the energy (U) and the amount of chemical substance (N) [e.g. number of atoms or molecules] present in the system.
More generally the state may have more components representing e.g. additional mechanical variables, additional conserved quantities etc.
Universe is assumed to be closed under at least the following operations
1) Dilation (scaling by a factor λ): $\Gamma \to \lambda\Gamma$
2) Composite systems: $\Gamma_1, \Gamma_1 \to \Gamma_1 \times \Gamma_2$.
3) Removal of (physical) constraints $V_1, V_2 \to V = V_1 + V_2$ ($V = V_1 = V_2$, etc.)

1.1 Adiabatic Accessibility.

On the set of states we define preorder (transitive, but not necessarily antisymmetric) relation $X \prec Y$, read as "Y is accessible form X" and satisfying comparison hypothesis i.e.
If $X \prec Z$ and $Y \prec Z$ then $X \prec Y$ or $Y \prec X$ (the order is total on '$\prec$-connected' components of Γ)

1.2 Entropy.

It is assumed that there exists a function $S : \Gamma \to \mathbb{R}$ for each system Γ in the universe $\mathcal{U}$ satisfying the following properties
1) concavity, continuity, and differentiability
2) homogeneity of degree 1 i.e.

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

3) additivity. If $\Gamma = \Gamma_1 \times \Gamma_2$ then $S = S_1 + S_2$
4) Second law of thermodynamics.
If $X \prec Y$ then $S(X) \leq S(Y)$. If $X \prec Y$ but $Y \not\prec X$ then $S(X) < S(Y)$
(the entropy difference measures the irreversibility of the process)
5) First law of thermodynamics (conservation of energy)
In order to state the first low we first state the assumption that $S = S(V, U, N)$ must be strictly increasing in U i.e. $\frac{\partial S}{\partial U} > 0$. Thus S can be inverted w.r.t. U: $U = U(V, S, N)$.

Now we define field (intensive) variables

$$\begin{aligned} T &= \frac{\partial U}{\partial S} && \text{temperature} \\ -p &= \frac{\partial U}{\partial V} && \text{pressure} \\ \mu &= \frac{\partial U}{\partial N} && \text{chemical potential} \end{aligned}$$

Having a curve $\tau \mapsto (V(\tau), U(\tau), N(\tau))$ in a state space we can compute

$$\frac{dU}{d\tau} = -p\frac{dV}{d\tau} + T\frac{dS}{d\tau} + \mu\frac{dN}{d\tau}$$

This gives the first law

$$dU = -pdV + TdS + \mu dN$$

Which is sometimes written as

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

1.3 Interpretation of the first law

Assuming that N is const we see form the above that the energy is exchanged between systems according to the formula

$$\Delta U = \Delta Q - W$$

Which can be read as "Change of energy = exchange of heat - work done by a system"
The work of a mechanical system is given by

$$W = -\int pdV$$

or

$$W = Fd = (F/A)Ad = p\Delta V$$

where p stands for (mechanical) pressure F-force d-displacement and A-area. The entropy function S is chosen in such a way that thermodynamical pressure coincides with mechanical one.

1.4 Euler equation and Gibbs-Duhem identity

Using the homogeneity of order one of S, computing the derivative

$$\frac{d}{d\lambda}U(\lambda V, \lambda S, \lambda N)$$

and evaluating it at $\lambda = 1$ yields the following Euler equation (for energy)

$$U = -pV + TS + \mu N \tag{1}$$

Equivalent form for entropy follows immediately

$$S = \frac{U}{T} + V\frac{p}{T} - N\frac{\mu}{T} \tag{2}$$

Differentiating (1)

$$dU = SdT + TdS - pdV - Vdp + \mu dN + Nd\mu$$

and combining it with the first law we get Gibbs-Duhem identity

$$SdT - Vdp + Nd\mu = 0$$

Similarly starting from (2) we have

$$Ud(1/T) + Vd(p/T) - Nd(\mu/T) = 0$$

1.5 Heat capacities and other thermodynamical variables

Heat capacity at constant volume - c_V

$$c_V = \frac{1}{N}(\frac{dQ}{dT})_V$$

Heat capacity at constant pressure - c_p

$$c_p = \frac{1}{N}(\frac{dQ}{dT})_p$$

Coefficient of thermal expansion - α

$$\alpha = \frac{1}{V}(\frac{dV}{dT})_p$$

Isothermal compressibilty - κ_T

$$\kappa_T = -\frac{1}{V}(\frac{dV}{dp})_T$$

1.6 Example (Boyle): Monatomic Ideal Gas

Empirical laws

$$\begin{aligned} pV &= NRT, \\ U &= \frac{3}{2}NRT, \end{aligned}$$

where R is the universal gas const.
Entropy

$$S = U\frac{1}{T} + V\frac{p}{T} - N\frac{\mu}{T}$$

Here

$$\frac{1}{T} = \frac{3NR}{2U} p = \frac{2U}{3V}$$

Now since N is kept fixed the first law yields

$$dS = \frac{1}{T}dU + \frac{p}{T}dV = \frac{3NR}{2U}dU + \frac{NR}{V}dV$$

Choosing reference state (fiducial point) (V_0, U_0, N_0) and integrating we get

$$S = S_0 + \frac{3}{2} NR \ln \frac{U}{U_0} + NR \ln \frac{V}{V_0}$$

To compute c_V we note that for const V $dQ = TdS = dU$.

$$c_V = \frac{1}{N}\frac{dQ}{dT} = \frac{1}{N}\frac{dU}{dT} = \frac{3}{2}R$$

For c_p we use $dQ = TdS = dU + pdV$ to get

$$c_p = \frac{3}{2}R + p(\frac{dV}{dT})_p = \frac{5}{2}R = c_v + R$$

More generally we have

$$c_p - c_V = \frac{TV}{N}\frac{\alpha^2}{\kappa_T^2}$$

Where α and κ_T can also be computed explicitly

$$\begin{aligned} \alpha &= \frac{1}{V}\frac{NR}{p} = \frac{1}{T} \\ \kappa_T &= -\frac{1}{V} NRT(-1/p^2) = \frac{1}{p} \end{aligned}$$

We can now give an example of irreversible processes i.e. such that the entropy increase is strictly positive. Consider Thermal expansion or in general heating.

$$(\frac{dS}{dT})_V = \frac{1}{T}(\frac{dU}{dT})_V = Nc_V\frac{1}{T} > 0$$

2 Composite Systems

We define the entropy of a composite system $\Gamma = \Gamma_1 \times \Gamma_2$ by means of variational principles.

2.1 Maximum Entropy Principle.

States of Γ are defined as functions $Z(X, Y)$, for $X \in \Gamma_1$ and $Y \in \Gamma_2$. The entropy is defined by

$$S(Z_0) = \max_{X,Y: Z_0 = Z(X,Y)} S_1(X) + S_2(Y).$$

Example.
Assume the state of Γ_1 is characterized by (V_1, U_1, N_1) and this of Γ_2 by (V_2, U_2, N_2). Now we remove one physical constraint, namely, we allow energy to be exchanged. The energy U of a composite system will now be given by $U = U_1 + U_2$. The entropy is then

$$S(V_1, V_1, U, N_1, N_2) = \max_{U_1, U_2: U_1 + U_2 = U} S_1(V_1, U_1, N_1) + S_2(V_2, U_2, N_2).$$

Proposition. If S_1 and S_2 are entropy functions then so is S.
We prove below concativity of S restricting ourselves to the case considered in the example.

We write $S(U) = S(V_1, V_1, U, N_1, N_2)$. Take $U = tv + (1-t)w$, $S(v) = S_1(v_1) + S_2(v_2)$ and $S(w) = S_1(w_1) + S_2(w_2)$. Define $U_1 = tv_1 + (1-t)w_1$ and $U_2 = tv_2 + (1-t)w_2$. then

$$\begin{aligned} S(U) &\geq S_1(U_1) + S_2(U_2) = S_1(tv_1 + (1-t)w_1) + S_2(tv_2 + (1-t)w_2) \\ &\geq tS_1(v_1) + (1-t)S_1(w_1) + tS_2(v_2) + (1-t)S_2(w_2) = tS(v) + (1-t)S(w) \end{aligned}$$

The physical interpretation of maximum entropy principle can be obtained by using differentiability of S_1 and S_2 and expressing maximum in terms of their derivatives.

$$0 = \frac{\partial}{\partial v}[S_1(v) + S_2(U-v)] = \frac{\partial}{\partial U_1} S_1(v) - \frac{\partial}{\partial U_2} S_2(U-v) = \frac{1}{T(v)} - \frac{1}{T(U-v)}$$

This implies $T(v) = T(U-v)$ i.e. the equilibrium state for composite system is achieved when the temperatures of both systems involved are equal. Same equilibrium conditions can be derived for other variables e.g.

$$V = V_1 + V_2 \to p_1 = p_2$$

$$N = N_1 + N_2 \to \mu_1 = \mu_2$$

The variational law for composite systems can also be formulated in terms of minimal energy condition.

2.2 Minimal Energy Principle.

Assuming that the entropy S of a composite system is already defined by maximum principle we show that the energy has to obey the following minimum principle.

$$U(V_1, V_1, S, N_1, N_2) = \min_{U_1, U_2 : S_1 + S_2 = S} U_1(V_1, S_1, N_1) + U_2(V_2, S_2, N_2)$$

Indeed, suppose there exist $\tilde{S}_1$ and $\tilde{S}_2$ such that $S = \tilde{S}_1 + \tilde{S}_2$ and $U_1(\tilde{S}_1) + U_2(\tilde{S}_2) < U(S)$. Then increasing at least one of $\tilde{S}_1$, $\tilde{S}_2$ we can find $\tilde{\tilde{S}}_1$ and $\tilde{\tilde{S}}_2$ such that $U_1(\tilde{\tilde{S}}_1) + U_2(\tilde{\tilde{S}}_2) = U(S)$ and $S < \tilde{S}_1 + \tilde{S}_2$. This contradicts the fact that U is strictly increasing in S.

3 Legendre transform.

$\Gamma \subset \mathbb{R}^n$ - convex domain. $f : \Gamma \mapsto \mathbb{R}^n \cup \{+\infty\}$ -convex function. WLOG we can assume $\Gamma = \mathbb{R}^n$ by extending f to $+\infty$ outside of Γ and defining the essential domain of f by $\{x \in \mathbb{R}^n : f(x) < +\infty\}$.
Now for any $f : \Gamma \mapsto \mathbb{R}^n \cup \{+\infty\}$ we define its Legendre transform $f^* : \Gamma \mapsto \mathbb{R}^n \cup \{+\infty\}$ by

$$f^*(y) = \sup_{x \in \mathbb{R}^n} \{\langle y, x\rangle - f(x)\}$$

It can be proved that f^* is convex.
Define

$$epi(f) = \{y = x, t \in \Gamma \times \mathbb{R} : f(x) \leq t\}$$

We have
1) If f has convex essential domain then f is convex iff epi(f) is convex.

2) f is lower-semicontinuous iff $epi(f)$ is closed
3) If f is convex then f is upper-semicontinuous, and hence if moreover $epi(f)$ is closed then f is continuous.
We denote by $\overline{co}(A)$ the closed convex hall of A.
Proposition. For any $f : \mathbb{R}^n \mapsto \mathbb{R}^n \cup \{+\infty\}$ we have $epi(f^{**}) = \overline{co}(epi(f))$

3.1 Free energy.

The Helmholtz free energy F can be described as a Legendre transform of energy U w.r.t. entropy S.

$$F(T) = [U - TS](S^*),$$

with $T = \frac{\partial U}{\partial S}$. That is

$$F(T) = \inf_S (U(S) - TS).$$

F is additive at constant T,

$$F(V_1, V_2, T, N_1, N_2) = F_1(V_1, T, N_1) + F_2(V_2, T, N_2).$$

4 Nonequilibrium Thermodynamics

4.1 Fluctuactions

We consider a system Γ coupled to a reservoir kept at a given equilibrium state. We denote by $\Gamma_\lambda = \lambda\Gamma_1$ the rescaled system. It will be referred to as a system of the size λ (e.g. V (N) may be kept const. and then λV_1 (λN_1) determines the size of the system for given reference value V_1 (N_1)).
The extensive variables describing the state of Γ will be denoted by X,Y, where X corresponds to fluctuating variables and Y to truly constant variables. The intensive variables will be denoted by f. Since we are only interested here in fluctuations we will use the shortcut notation $S(X) = S(X,Y)$. Thus we have

$$\begin{aligned} S(\lambda X) &= \lambda S(X), \\ \frac{\partial S}{\partial X} &= f. \end{aligned}$$

The considerations presented below do not apply, strictly speaking, to finite systems but are valid in the sense of asymptotic approximation ($\lambda \to \infty$).
Assume that Γ is initially at equilibrium and is slightly perturbed form it due to its interactions with the reservoir. If S denotes the entropy of Γ at equilibrium then due to the max entropy principle the change of entropy ΔS caused by fluctuation is negative.
The main hypothesis is then that the probability P of finding the system in the perturbed state satisfies the following proportionality relation

$$P \sim e^{k_B^{-1}\Delta S},$$

where $k_B = \frac{R}{N_A}$ denotes the Boltzmann constant (R- is the universal gas const. and N_A is Avogadro Number).

We define the associated density function, as a function of X, for system of size λ

$$W_\lambda(X,f) = \frac{1}{Z_\lambda(f)} e^{k_B^{-1}(S(X)-f\cdot X)} \tag{3}$$

where f parametrizes W_λ w.r.t. equilibrium states, and X represents fluctuating variables. For simplicity we take $k_B = 1$. $Z_\lambda(f)$ is a normalizing const given by

$$Z_\lambda(f) = \int_{\Gamma_\lambda} d^n X e^{k_B^{-1}(S(X)-f\cdot X)} = \int_{\Gamma_\lambda} d^n X e^{k_B^{-1}(S(X)-f\cdot X)}$$

To simplify the computations we will usually take $k_B = 1$.

4.1.1 Asymptotics of $Z_\lambda(f)$

In this section We prove that

$$Z_\lambda(f) \approx e^{\lambda \tilde{s}(f)},$$

where

$$\tilde{s}(f) = \max_{x\in\Gamma_1}\{S(x) - f\cdot x\}.$$

That is we are going to show that

$$\lim_{\lambda\to\infty} \frac{1}{\lambda} \ln Z_\lambda = \tilde{s}(f)$$

To this end we put $X = \lambda x$ where $X \in \Gamma_\lambda$ and $x \in \Gamma_1$.

$$\lim_{\lambda\to\infty} \frac{1}{\lambda} \ln \lambda^n \int_{\Gamma_1} dx e^{S(\lambda x)-f\cdot(\lambda x)} = \lim_{\lambda\to\infty} \frac{1}{\lambda} \ln \lambda^n + \lim_{\lambda\to\infty} \frac{1}{\lambda} \ln \int_{\Gamma_1} dx e^{\lambda(S(x)-f\cdot x)} =$$
$$\lim_{\lambda\to\infty} \frac{1}{\lambda} \ln e^{\lambda \tilde{s}(f)} \int_{\Gamma_1} dx e^{\lambda(S(x)-f\cdot x-\tilde{s}(f))} = \tilde{s}(f) + \lim_{\lambda\to\infty} \frac{1}{\lambda} \ln \int_{\Gamma_1} dx e^{\lambda(S(x)-f\cdot x-\tilde{s}(f))}$$

Now since $S(x) - f\cdot x - \tilde{s}(f)) \leq 0$ we can take any fixed $\lambda_0 > 0$ and get the following estimate valid for all $\lambda \geq \lambda_0$

$$0 \leq \lim_{\lambda\to\infty} \frac{1}{\lambda} \ln \int_{\Gamma_1} dx e^{\lambda(S(x)-f\cdot x-\tilde{s}(f))} \leq \lim_{\lambda\to\infty} \frac{1}{\lambda} \ln \int_{\Gamma_1} dx e^{\lambda_0(S(x)-f\cdot x-\tilde{s}(f))} = 0$$

Thus finally

$$\lim_{\lambda\to\infty} \frac{1}{\lambda} \ln Z_\lambda = \tilde{s}(f)$$

4.1.2 The interpretation of $\tilde{s}$ in terms of Legendre transform.

As we know the entropy function S is concave and hence $-S$ is convex. One can apply the Legendre transform to $-S$ and get

$$(-S)^*(y) = \max_x\{y\cdot x - (-S(x))\} = \max_x\{S(x) + y\cdot x\} = \tilde{s}(-y)$$

Using the fact that Legendre transform is involutive

$$\begin{aligned}(-S)(x) &= (-S)^{**}(x) = \max_y\{y\cdot x - (-S)^*(y)\} = \max_y\{y\cdot x - \tilde{s}(-y)\} \\ &= \max_{-y}\{-y\cdot x - \tilde{s}(y)\} = \max_y\{-y\cdot x - \tilde{s}(y)\}\end{aligned}$$

Hence

$$S(x) = \min_y \{y \cdot x + \tilde{s}(y)\} = \min_f \{\tilde{s}(f) + f \cdot x\}$$

Denoting by $f^* = (f_1^*, ..., f_n^*)$ the minimizer of $\tilde{s}(f) + f \cdot x$ and by $x^* = (x_1^*, ..., x_n^*)$ the maximizer of $S(x) - f \cdot x$ we get

$$\begin{aligned} S(x) &= \tilde{s}(f^*) + f^* \cdot x \\ \tilde{s}(f) &= S(x^*) - f \cdot x^* \\ S(x^*) &= \tilde{s}(f^*) + f^* \cdot x^* \end{aligned}$$

In particular

$$\frac{\partial S}{\partial x_i}(x) = f_i^*(x), \qquad \frac{\partial \tilde{s}}{\partial f_i}(f) = -x_i^*(f) \tag{4}$$

4.1.3 Expectation.

Taking the derivatives of both sides of

$$\frac{1}{\lambda} \ln Z_\lambda \to \tilde{s}(f)$$

yields

$$\frac{\partial}{\partial f_i} \frac{1}{\lambda} \ln Z_\lambda \to \frac{\partial}{\partial f_i} \tilde{s}(f).$$

Now

$$\frac{\partial}{\partial f_i} \frac{1}{\lambda} \ln Z_\lambda = \frac{1}{\lambda} \frac{1}{Z_\lambda} \frac{\partial}{\partial f_i} \int_{\Gamma_\lambda} dX e^{S(X) - f \cdot X} = \frac{1}{\lambda} \frac{1}{Z_\lambda} \int_{\Gamma_\lambda} dX (-X_i) e^{S(X) - f \cdot X} = -\frac{1}{\lambda} \mathbb{E}_\lambda(X_i),$$

Where $\mathbb{E}_\lambda$ denotes the expectation w.r.t. density W_λ. Thus

$$\lim_{\lambda \to \infty} \frac{1}{\lambda} \mathbb{E}_\lambda(X_i) = x_i^*(f)$$

4.1.4 Covariance.

First we introduce the following approximation to $W_\lambda(X, f)$

$$\tilde{W}_\lambda(X, f) := e^{k_B^{-1}(S(X) - f \cdot X - \lambda \tilde{s}(f))}. \tag{5}$$

The fact that $\tilde{W}_\lambda \approx W_\lambda$ for large λ follows form the asymptotics of Z_λ. Indeed

$$W_\lambda(X, f) = e^{k_B^{-1}(S(X) - f \cdot X - \ln(Z_\lambda(f)))} = e^{k_B^{-1} \lambda (S(x) - f \cdot x - (1/\lambda) \ln(Z_\lambda(f))} \approx e^{k_B^{-1} \lambda (S(x) - f \cdot x - \tilde{s}(f))} = \tilde{W}_\lambda(X, f).$$

Now we compute the covariance. To this end we first note that

$$\frac{\partial}{\partial f_j} \frac{1}{\lambda} \mathbb{E}_\lambda(X_i) = \frac{\partial}{\partial f_j} x_i^*(f) = -\frac{\partial^2}{\partial f_i \partial f_j} \tilde{s}(f).$$

Now

$$\begin{aligned} \frac{\partial}{\partial f_i} \frac{1}{\lambda} \mathbb{E}_\lambda(X_i) &= -\frac{1}{\lambda} \int_{\Gamma_\lambda} dX X_i \frac{\partial}{\partial f_j} \tilde{W}_\lambda(X, f) = -\frac{1}{\lambda} \int_{\Gamma_\lambda} dX X_i \lambda (x_j + \frac{\partial \tilde{s}}{\partial f_j}) \tilde{W}_\lambda(X, f) \\ &= -\frac{1}{\lambda} \int_{\Gamma_\lambda} dX X_i (X_j - \lambda x_j^*) \tilde{W}_\lambda(X, f) \approx -\frac{1}{\lambda} \mathbb{E}_\lambda(X_i - \mathbb{E}_\lambda(X_i))(X_j - \mathbb{E}_\lambda(X_j)) = cov(X_i, X_j) \end{aligned}$$

Hence we arrived at the following formula

$$\frac{\partial}{\partial f_j}\mathbb{E}_\lambda(X_i) \approx cov(X_i, X_j) \approx -\lambda\frac{\partial^2}{\partial f_i \partial f_j}\tilde{s}(f)$$

Example.
Taking $X_i = U$ we can compute the variance σ_U^2

$$\sigma_U^2 \approx -\frac{\partial U}{\partial(1/T)} = -\frac{\partial U}{\partial T}\frac{\partial T}{\partial(1/T)} = T^2(\frac{\partial U}{\partial T})_{V,N} = VT^2 c_V$$

4.2 Fluxes and Entropy production rate

For a large system Γ not in equilibrium we consider local 'equilibrium' regions the states of which will now depend on the position x of the region within set Γ as well as on the time and will be described by local denisties:
$s(x,t)$-entropy density
$u(x,t)$-energy density
$n(x,t)$-particle denisy
The time evolution of the denisites are represented in terms of corresponding fluxes or currents. The currents are representing thermodynamic forces and are given as gradients of theromodynamic potentials.

$$\begin{aligned} \frac{\partial u}{\partial t} &= -div J_u \\ \frac{\partial n}{\partial t} &= -div J_n \\ \frac{\partial s}{\partial t} &= -div J_s + \sigma \end{aligned}$$

In the last equation $-div J_s$ corresponds to conservative entropy flow while $\sigma \geq 0$ represents the entropy production rate.
Strictly speaking when σ is positive then even the local system is not trurly in equilibrium (since the equilibrum states already correspond to maximal entropy) but the changes are supposed to be small enough so that one can treat the local system approximately as in equilibrium.
Denoting by f filed variable conjugate to x we have

$$J_x = L\nabla f$$

For example in case $x = u$ we get Fourier's law

$$J_u = L_u \nabla\frac{1}{T}$$

similarly for $x = n$ we obtain Fick's law

$$J_u = L_n \nabla\frac{-\mu}{T}.$$

Here the relation is linear. In general L can be a function of f. The independence of L on f assumed here may be justified by the fact that we are not too far from the equilibrium.
Generalization of the above laws as given by Kelvin and Rayleight goes in the direction of allowing the currents to depend on field variables not necessary conjuagte to them, which results in "non-conjugate flows/forces" described by one relation

$$J_x = L\nabla f = LX,$$

where L is a matrix and $X_i = \nabla f_i$. In case of diagonal L we recover previous relations.
The goal of this section is to prove the follwing fundamental relatons
I. Enropy production rate formula

$$\sigma = \sum_i J_i \cdot X_i$$

We note that the positiveness of σ means that J and X have to be alinged, at least the angle between them must not exceede 90 degree.
II. Onsager Reciprocity Relation (Onsager 1931)

$$L = L^T$$

To derrive I i.e. the enropy production rate formula, we assume that the first law can still be applied in this situatoin. We apply it to a unit volume region of our system (hence v is const.)

$$\begin{aligned} T\frac{\partial s}{\partial t} &= \frac{\partial u}{\partial t} - \mu\frac{\partial u}{\partial t} \\ \frac{\partial s}{\partial t} &= \frac{1}{T}(-divJ_u) + \frac{\mu}{T}divJ_n. \end{aligned}$$

Now using standard formula from vector calculus

$$div(\beta J) = \beta div J + J \cdot \nabla\beta$$

we get

$$\frac{\partial s}{\partial t} = -div(\frac{1}{T}J_u - \frac{\mu}{T}divJ_n) + J_u\nabla(\frac{1}{T}) + J_n\nabla(-\frac{\mu}{T})$$

Using Hodge decomposition we arrive at

$$\begin{aligned} J_s &= \frac{1}{T}J_u - \frac{\mu}{T}divJ_n \\ \sigma &= J_u\nabla(\frac{1}{T}) + J_n\nabla(-\frac{\mu}{T}) = \sum_i J_i \cdot X_i \end{aligned}$$

To derive II i.e. Onsager Reciprocity Relation we will assume the so called regression hypothesis

$$\frac{d}{dt}\mathbb{E}(\tilde{X}_i(0)\tilde{X}_j(t))_{|t=0} = \mathbb{E}(\tilde{X}_i(0)(L\tilde{f})_j)$$

where $\tilde{X} = X - \mathbb{E}_\lambda(X)$ is a fluctuation of X around its expectation value $\mathbb{E}_\lambda(X) = \lambda x^*$ taken w.r.t the density $W_\lambda(X, f)$ defined by (3) and $\tilde{f} = f - f^*$.
Moreover we assume that X as a process is stationary in time i.e. for any r

$$\mathbb{E}(X_i(0)X_j(t)) = \mathbb{E}((X_i(0)X_j(r+t))$$

and invariant under the time reversal

$$\mathbb{E}(X_i(0)X_j(t)) = \mathbb{E}(X_i(0)X_j(-t))$$

Under these assumptions we have

Lemma 1

$$A := \mathbb{E}(\tilde{X}_i \tilde{f}_j) = k_B \delta_{ij}$$

Lemma 2

$$(LA)^T = LA^T$$

The above two Lemmas obviously yield symmetricity of L.

Proof of Lemma 1

Recall the definition (5)

$$\tilde{W}_\lambda(X,f) = e^{k_B^{-1}(S(X) - X\cdot f - \lambda \tilde{s}(f))},$$

and the relations (4):

$$\frac{\partial \tilde{s}}{\partial f_i} = -x_i^*, \quad \frac{\partial S}{\partial x_i} = f_i^*,$$

where $x^*(f)$ and $f^*(x)$ are the equilibrium values as a function of f, and the filed variables leading to given equilibrium values, respectively. As $\tilde{f} = f - f^*$, and $\tilde{X} = X - \lambda x^*$, we have

$$\frac{\partial \tilde{W}_\lambda}{\partial X_j} = -k_B^{-1} \tilde{f}_j \tilde{W}_\lambda.$$

By using these relations, and integration by parts, we easily find

$$\mathbb{E}(\tilde{X}_i \tilde{f}_j) = -k_B \int dX \tilde{X}_i \frac{\partial}{\partial X_j} \tilde{W}_\lambda(X,f) = k_B \delta_{ij}.$$

Proof of Lemma 2

Using stationarity (with $r = -t$) and time reversal property we get

$$\mathbb{E}(X_i(0)X_j(t)) = \mathbb{E}(X_i(-t)X_j(0)) = \mathbb{E}(X_i(t)X_j(0))$$

Thus

$$\frac{d}{dt}\mathbb{E}(X_i(0)X_j(t))_{|t=0} = \frac{d}{dt}\mathbb{E}(X_i(t)X_j(0))_{|t=0}$$

Now by regression hypothesis

$$\begin{aligned} \mathbb{E}X_i(0)(L\tilde{f})_j &= \mathbb{E}(L\tilde{f})_i X_j(0) \\ \sum_l L_{jl}\mathbb{E}(X_i(0)\tilde{f}_l) &= \sum_k L_{ik}\mathbb{E}(\tilde{f}_k X_j(0)) \end{aligned}$$

In the limit of small fluctuations $t \to 0$ (note that L is const) the above relation takes the form

$$(LA^T)_{ji} = (LA)_{ij}$$

which completes the proof of Lemma 2.

We end the section on nonequilibrium thermodynamics with a remark regarding the entopy production rate conditioin for nonequilibrium stationary states (NESS) (like a constant heat flow in a rod with two ends fixed into the reservoirs of different temperatures). The basic observation is that in true equilibrum the entropy production shuld achieve its minimal value that is zero.

In NESS with given positive fluxes $J_1, ..., J_k$ with $k \leq n$ the entropy production rate should also achieve its minimal value. Thus we have the following

Proposition (Prigogine ($k = 1$, 1947), de Groot ($k > 2$, 1951))

Assume the stystem is in a NESS with given fluxes $J_1, ..., J_k$ $(k \leq n)$. Then $J_j = 0$ for all $j \geq k$.

Proof We have

$$\sigma = \sum_i X_i fi = \sum_{i,j} X_i L_{ij} X_j \geq 0.$$

In the minimum point, with the constraint $j > k$, we have

$$\frac{\partial}{\partial x_j} \sigma = \sum_l (L_{ij} + L_{ji}) X_j = 2J_j = 0.$$