Lecture 1 (Provisional)

Daniele Roselli[1]

[1] *Università degli studi di Firenze and INFN Sezione di Firenze, Via G. Sansone 1, I-50019 Sesto Fiorentino (Florence), Italy*

NON-EQUILIBRIUM RELATIVISTIC STATISTICAL MECHANICS

In statistical mechanics we often want to describe a macroscopic system whose microscopic state is not known. From the quantum-mechanical point of view, this means that we do not know which vector in the Hilbert space represents the actual state of the system. We therefore describe the system as a statistical mixture of possible microscopic states: the number w_i is the probability that the system is in the state $|\psi_i\rangle$.

The state is then described by a matrix, built out of the microscopic states, called the *density operator* or *statistical operator*:

$$\widehat{\rho} = \sum_{i=1}^{N} w_i |\psi_i\rangle\langle\psi_i| \ . \tag{1}$$

Since the coefficients w_i are classical probabilities, the density operator is normalized accordingly:

$$\sum_{i=1}^{N} w_i = 1 \implies \mathrm{Tr}\widehat{\rho} = 1 \ , \tag{2}$$

where the trace Tr denotes the sum over a complete set of states. The amount of missing information about the microscopic state of the system is quantified by the Von Neumann, or information, entropy:

$$S = -\mathrm{Tr}(\widehat{\rho}\ln\widehat{\rho}) = -\sum_{i=1}^{N} w_i \ln w_i \ . \tag{3}$$

For a genuine statistical mixture the entropy is positive, while its minimum value, $S = 0$, is reached only when one state has probability one and all the others have probability zero. Because of the normalization condition, this can happen for one state only. In that case,

$$\widehat{\rho} = |\psi_i\rangle\langle\psi_i| \equiv \widehat{\mathrm{P}}_{\psi_i} \ , \tag{4}$$

so the density operator reduces to the projector onto the microscopic state $|\psi_i\rangle$. This is the case of maximal information: the precise microscopic state of the system is known. Given that a statistical operator is built in terms of the states, (1), it then follows that in Heisenberg picture, where the states are fixed, the density operator must be stationary, i.e. it must solve:

$$\frac{\mathrm{d}\widehat{\rho}}{\mathrm{d}t} = 0 \ , \tag{5}$$

also known as Liouville equation.

The expectation value of an observable $\widehat{O}$ in a statistical state is obtained by averaging the quantum expectation value over all possible microscopic states, weighted by their probabilities:

$$\langle\widehat{O}\rangle = \sum_{i=1}^{N} w_i \langle\psi_i|\widehat{O}|\psi_i\rangle = \mathrm{Tr}\left(\widehat{\rho}\,\widehat{O}\right) \ . \tag{6}$$

We now want to connect this statistical description with a thermodynamic one. Consider a macroscopic system made of a very large number N of microscopic constituents, each of them in a state $|\phi_k\rangle$. A possible microscopic state of the full system may be written schematically as

$$|\psi_i\rangle = \bigotimes_{k=1}^{N} |\phi_k\rangle \ .$$

In principle, each possible combination of the states $|\phi_k\rangle$ gives a different microscopic state of the whole system. For macroscopic N, however, this information is completely inaccessible in practice.

Let us assume that the system is in contact with a much larger environment, with which it can exchange energy, momentum and particles. When the system equilibrates with the environment, the total entropy is maximized, in agreement with the second law of thermodynamics. In a thermodynamic description, the state of the system is characterized only by a finite set of macroscopic observables $\widehat{A}_i$, whose expectation values are fixed. One could impose exact values of the conserved quantities, as in a microcanonical description, but here we are interested in the situation where the system can exchange these quantities with the surroundings. Therefore they are fixed only on average.

The thermodynamic state is then defined as the statistical state that maximizes the entropy subject to the constraints of fixed average observables and normalized density operator. In other words, one maximizes

$$F[\,\widehat{\rho}\,] \equiv -\mathrm{Tr}(\widehat{\rho}\ln\widehat{\rho}) + c\,(\mathrm{Tr}\widehat{\rho}-1) + \sum_i \lambda_i \left(\mathrm{Tr}(\widehat{\rho}\,\widehat{A}_i) - \langle\widehat{A}_i\rangle\right) \,. \tag{7}$$

The quantities λ_i and c are Lagrange multipliers. They implement, respectively, the constraints on the average values of the observables and on the normalization of the density operator. The general solution is

$$\widehat{\rho} = \frac{1}{Z}\exp\left(-\sum_i \lambda_i \widehat{A}_i\right) \,. \tag{8}$$

A familiar example is obtained when the relevant macroscopic quantities are the energy and the total number of particles. This gives the usual *grand-canonical density operator*:

$$\widehat{\rho} = \frac{1}{Z}\exp\left(-\beta\widehat{H} + \zeta\widehat{Q}\right) \,, \tag{9}$$

where the two Lagrange multipliers are identified with the inverse temperature $\beta = 1/T$ and the reduced chemical potential $\zeta = \mu/T$. Their physical interpretation follows by comparing the maximum-entropy construction with the ordinary thermodynamic relation between entropy, energy and conserved charge: the multiplier conjugate to the energy is the inverse temperature, while the multiplier conjugate to the charge is the chemical potential divided by the temperature.

The operator in (9) is suitable for a non-relativistic formulation, but it is not written in a manifestly covariant form: the Hamiltonian $\widehat{H}$ is the time component of the four-momentum and is not a Lorentz scalar. To construct the relativistic density operator it is better to use a covariant formulation from the beginning. This is also the most natural starting point for the later extension to non-equilibrium situations.

A macroscopic system is effectively described in terms of a set of *macroscopic observables*. In order to be associated with the system as a whole, these observables must be *global*: they must be defined over the entire system. In relativity, global observables are naturally written as integrals of conserved local currents. If a current $J^{\mu\mu_1\cdots}$ is conserved,

$$\partial_\mu J^{\mu\mu_1\cdots} = 0 \,, \tag{10}$$

then its integral over a spacelike hypersurface is independent of the choice of hypersurface:

$$\int_\Sigma \mathrm{d}\Sigma_\mu \, J^{\mu\mu_1\cdots} \equiv Q^{\mu_1\cdots} \;\forall\,\Sigma \,. \tag{11}$$

This is the covariant version of the statement that a global charge is obtained by integrating the corresponding density over space. If the current is conserved, the charge is independent of the time parameter in any inertial reference frame.

The two currents that will be relevant for us are the stress-energy tensor and the baryon current. In a quantum system they are promoted to operators on the Hilbert space and satisfy the conservation equations

$$\partial_\mu \widehat{T}^{\mu\nu} = 0 \,, \quad \partial_\mu \widehat{j}^{\,\mu}_{\mathrm{B}} = 0 \,. \tag{12}$$

Therefore their integrals over an arbitrary spacelike hypersurface are well-defined and correspond, respectively, to the total four-momentum and the total baryon number:

$$\widehat{P}^\nu = \int_\Sigma \mathrm{d}\Sigma_\mu \widehat{T}^{\mu\nu} \,, \qquad \widehat{Q}_{\mathrm{B}} = \int_\Sigma \mathrm{d}\Sigma_\mu \widehat{j}^{\,\mu}_{\mathrm{B}} \,. \tag{13}$$

From the stress-energy tensor one can also construct the conserved Lorentz generators, which include angular momentum and boosts:

$$\widehat{J}^{\nu\lambda} = \int_\Sigma \mathrm{d}\Sigma_\mu \left(\widehat{T}^{\mu\lambda} x^\nu - \widehat{T}^{\mu\nu} x^\lambda \right) \ . \tag{14}$$

Note that the integrand has vanishing divergence due to (12). Hence, for symmetric stress-energy tensor, the conservation of the angular momentum does not introduce another Lagrange multiplier in the maximization and thus no other independent thermodynamic field appears.

We can now repeat the maximum-entropy construction in a covariant form. The entropy is maximized at fixed average values of the conserved currents on a spacelike hypersurface $\Sigma(\tau)$:

$$F[\widehat{\rho}, \Sigma] = -\mathrm{Tr}(\widehat{\rho} \ln \widehat{\rho}) + c\,(\mathrm{Tr}\widehat{\rho} - 1) + \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left\{ \beta_\nu \left[\mathrm{Tr}\left(\widehat{\rho} \widehat{T}^{\mu\nu} \right) - \langle \widehat{T}^{\mu\nu} \rangle \right] - \zeta \left[\mathrm{Tr}\left(\widehat{\rho} \widehat{j}^\mu_{\mathrm{B}} \right) - \langle \widehat{j}^\mu_{\mathrm{B}} \rangle \right] \right\} \ . \tag{15}$$

The constraint on the total angular momentum is redundant once the stress-energy tensor is assumed to be symmetric, because the Lorentz generators are then already determined by the stress-energy tensor.

The corresponding solution is

$$\widehat{\rho} = \frac{1}{Z} \exp\left[- \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left(\widehat{T}^{\mu\nu} \beta_\nu - \widehat{j}^\mu_{\mathrm{B}} \zeta \right) \right] \ , \tag{16}$$

where the matching with the thermodynamic equilibrium relations tells us that β_μ and ζ have now the physical meaning of four-temperature and reduced chemical potential:

$$\beta_\mu = \frac{u_\mu}{T} \ , \qquad \zeta = \frac{\mu}{T} \ . \tag{17}$$

The vector field u^μ represents the four-velocity of the fluid, $u^2 = 1$, while T is the proper temperature, i.e. the temperature measured by a thermomether comoving with the system. Note that in this framework the fundamental quantity is the four-temperature whereas the four-velocity is a derived quantity:

$$u_\mu(x) \equiv \frac{\beta_\mu(x)}{\sqrt{\beta^2(x)}} \ . \tag{18}$$

This can be derived from the definition of entropy:

$$\begin{aligned} S = -\mathrm{Tr}(\widehat{\rho} \ln \widehat{\rho}) &= -\mathrm{Tr}\left[\widehat{\rho} \left(-\ln Z + \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu (\widehat{T}^{\mu\nu} \beta_\nu - \widehat{j}^\mu \zeta) \right) \right] \\ &= \ln Z + \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left(\langle \widehat{T}^{\mu\nu} \rangle \beta_\nu - \langle \widehat{j}^\mu \rangle \zeta \right) \ , \end{aligned}$$

and assuming that the thermodynamic field are constant implies:

$$S = \ln Z + \beta_\nu \langle \widehat{P}^\nu \rangle - \zeta \langle \widehat{Q} \rangle \ .$$

Comparing with the classical expression:

$$TS = \ln Z + u \cdot P - \mu Q \ , \tag{19}$$

then leads to the identification (17).

At this stage the operator (16) seems to depend on the hypersurface Σ. In true thermodynamic equilibrium, however, the statistical operator must be independent of the hypersurface used in the maximization. This is equivalent to requiring the integrand to be divergenceless:

$$\nabla_\mu \left(\widehat{T}^{\mu\nu} \beta_\nu - \widehat{j}^\mu \zeta \right) = \widehat{T}^{\mu\nu} \nabla_\mu \beta_\nu - \widehat{j}^\mu \nabla_\mu \zeta = 0 \ .$$

For this condition to hold independently of the particular state of the system, the four-temperature field must be a Killing vector and the reduced chemical potential to be covariantly conserved. If we consider the case of Minkowski space-time in cartesian coordinates then $\nabla \to \partial$ and the equilibrium correction turns out to be ((see exercise **??**)):

$$\partial_\mu \beta_\nu + \partial_\nu \beta_\mu \ = \ 0 \ , \implies \beta_\mu = b_\mu + \varpi_{\mu\nu} x^\nu \ , \tag{20}$$

$$\partial_\mu \zeta \ = \ 0 \ , \implies \zeta = \text{const.} \tag{21}$$

where b_μ is a constant four-vector, while $\varpi_{\mu\nu}$ is a constant antisymmetric tensor called *thermal vorticity*.

Thus, global equilibrium can be characterized geometrically: the four-temperature is a Killing vector, and the reduced chemical potential is constant. Using these conditions in (16), the dependence on the hypersurface disappears, as expected:

$$b_\nu \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \widehat{T}^{\mu\nu} - \frac{1}{2}\varpi_{\nu\lambda} \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left(\widehat{T}^{\mu\lambda} x^\nu - \widehat{T}^{\mu\nu} x^\lambda\right) - \zeta \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \, \widehat{j}^\mu_{\mathrm{B}} = b \cdot \widehat{P} - \frac{1}{2}\varpi : \widehat{J} - \zeta \widehat{Q}_{\mathrm{B}} \ .$$

We then obtain the most general global-equilibrium operator:

$$\widehat{\rho}_{\mathrm{GE}} = \frac{1}{Z_{\mathrm{GE}}} \exp\left(-b \cdot \widehat{P} + \frac{1}{2}\varpi : \widehat{J} + \zeta \widehat{Q}\right) \ . \tag{22}$$

In general this state is neither homogeneous nor isotropic.

The usual grand-canonical result is recovered in the special case of vanishing thermal vorticity. In that case,

$$\widehat{\rho}_{\mathrm{GE}} = \frac{1}{Z} \exp\left(-\beta \cdot \widehat{P} + \zeta \widehat{Q}\right) \tag{23}$$

which reduces to (9) in the local rest frame, since $\widehat{P}^0 = \widehat{H}$. This state is usually called *homogeneous global equilibrium*. It is invariant under spatial translations and rotations. However, it is not the most general equilibrium state allowed by relativity. A non-vanishing thermal vorticity allows global equilibrium configurations that are inhomogeneous or anisotropic. In such cases, the temperature measured by comoving observers can vary in space, as happens for instance in rotating or accelerated equilibrium. This is the relativistic content of the Tolman–Ehrenfest law.

A. Non-equilibrium density operator

The previous discussion led to the construction of the global equilibrium density operator. We now want to move one step further and describe a system which is not in global equilibrium, but which is still close enough to equilibrium that a thermodynamic language remains meaningful locally.

Local equilibrium, despite its name, is not true thermodynamic equilibrium. It is a special kind of non-equilibrium state in which thermodynamic variables can be assigned locally. Classically, one may think of a system whose temperature, chemical potential and velocity vary from point to point. The system as a whole is not in equilibrium, but if we look at a sufficiently small region, these quantities are approximately constant and a local thermodynamic description can be used.

This picture relies on a separation of scales. On the one hand, there is the microscopic scale over which the local state is established, for instance the mean free path or the relaxation scale. On the other hand, there is the macroscopic scale over which the thermodynamic fields vary appreciably. Local equilibrium is meaningful only when these two scales are well separated. In that case, each small fluid cell can be described by thermodynamic variables, even though the system as a whole is evolving out of equilibrium.

The question is how to formulate this idea covariantly. Away from global equilibrium, it is no longer useful to characterize the state only in terms of global conserved quantities. For example, although the total energy of an isolated system is conserved, the local energy density and the local momentum density vary in space and time. What remains naturally defined are the local conserved currents.

Therefore, on a point x of a given space-like hypersurface Σ, with future-directed unit normal vector $\hat{n}$, one introduces local thermodynamic fields $\beta(x)$ and $\zeta(x)$ and defines an operator $\widehat{\rho}_{\mathrm{LE}}$ which reproduces the local state on that hypersurface:

$$\begin{aligned} \hat{n}_\mu \mathrm{Tr}\left(\widehat{\rho}_{\mathrm{LE}} \, \widehat{T}^{\mu\nu}(x)\right)[\beta,\zeta,\hat{n}] &\equiv \hat{n}_\mu \langle \widehat{T}^{\mu\nu}(x)\rangle_{\mathrm{LE}} = \hat{n}_\mu \langle \widehat{T}^{\mu\nu}(x)\rangle \ , \\ \hat{n}_\mu \mathrm{Tr}\left(\widehat{\rho}_{\mathrm{LE}} \, \widehat{j}^{\mu}(x)\right)[\beta,\zeta,\hat{n}] &\equiv \hat{n}_\mu \langle \widehat{j}^{\mu}(x)\rangle_{\mathrm{LE}} = \hat{n}_\mu \langle \widehat{j}^{\mu}(x)\rangle \ . \end{aligned} \tag{24}$$

This operator is obtained by maximizing the entropy, in close analogy with the construction of the global equilibrium operator, but now with the local constraints above. i.e. the local equilibrium opeator is the operator maximizing the following functional:

$$\begin{aligned} F[\,\widehat{\rho}, \Sigma(\tau)\,] = &-\mathrm{Tr}(\widehat{\rho}_{\mathrm{LE}} \ln \widehat{\rho}_{\mathrm{LE}}) + c\,[\mathrm{Tr}(\widehat{\rho}_{\mathrm{LE}}) - 1] \\ &+ \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left\{\beta_\mu \left[\mathrm{Tr}(\widehat{\rho}_{\mathrm{LE}} \, \widehat{T}^{\mu\nu}) - \langle \widehat{T}^{\mu\nu}\rangle_{\mathrm{LE}}\right] - \zeta \left[\mathrm{Tr}(\widehat{\rho}_{\mathrm{LE}} \, \widehat{j}^{\mu}) - \langle \widehat{j}^{\mu}\rangle_{\mathrm{LE}}\right]\right\} \ , \end{aligned} \tag{25}$$

which is formally the same as (15). The general solution is given by:

$$\widehat{\rho}_{\rm LE} = \frac{1}{Z_{\rm LE}} \exp\left[- \int_\Sigma {\rm d}\Sigma_\mu \left(\widehat{T}^{\mu\nu}\beta_\nu - \widehat{j}^\mu \zeta \right) \right] \ . \tag{26}$$

This is usually called the *local equilibrium operator*. The quantities on the right-hand side of (24) are the true non-equilibrium expectation values, whereas the expressions on the left-hand side are computed with the local equilibrium operator. The square brackets emphasize that these local-equilibrium expectation values are functionals of the thermodynamic fields and of the chosen hypersurface.

The reason why the matching conditions involve the projections along $\hat{n}_\mu$ is not primarily that information cannot propagate along a space-like hypersurface. Rather, it is a consequence of the maximum-entropy construction on a chosen hypersurface: the local constraints are imposed on the densities measured by the observer normal to Σ. In this sense, $\widehat{\rho}_{\rm LE}$ is a pseudo-equilibrium operator adapted to the hypersurface Σ. It reproduces the local densities fixed by the matching conditions, but it does not describe a stationary equilibrium state.

The name "local equilibrium density operator" can therefore be slightly misleading. The operator $\widehat{\rho}_{\rm LE}$ is constructed to reproduce the local state on a given hypersurface, but it is not stationary in the Heisenberg picture. In particular, it does not satisfy the Liouville equation (5). The reason is that, out of global equilibrium, the fields β and ζ do not satisfy the global-equilibrium conditions, and the operator explicitly depends on the hypersurface on which the entropy maximization is performed.

Let us now assume that the system is in local thermodynamic equilibrium on an initial hypersurface $\Sigma_0 \equiv \Sigma(\tau_0)$. The operator

$$\widehat{\rho} \equiv \widehat{\rho}_{\rm LE}(\tau_0) = \frac{1}{Z} \exp\left[- \int_{\Sigma_0} {\rm d}\Sigma_\mu \left(\widehat{T}^{\mu\nu}\beta_\nu - \widehat{j}^\mu \zeta \right) \right] \tag{27}$$

then describes the state of the system on Σ_0. Since it is defined once and for all from the initial data, it is the statistical operator used to compute non-equilibrium expectation values. In the Heisenberg picture, the state is fixed, while the operators carry the time dependence.

To express the same operator in terms of fields on a later hypersurface $\Sigma(\tau)$, we apply Gauss' theorem to the space-time region Ω enclosed between Σ_0 and $\Sigma(\tau)$. Using the conservation equations for $\widehat{T}^{\mu\nu}$ and $\widehat{j}^\mu$, one obtains

$$\widehat{\rho} = \frac{1}{Z} \exp\left[- \int_{\Sigma(\tau)} {\rm d}\Sigma_\mu (\widehat{T}^{\mu\nu}\beta_\nu - \widehat{j}^\mu \zeta) + \int_\Omega {\rm d}\Omega \left(\widehat{T}^{\mu\nu}\partial_\mu\beta_\nu - \widehat{j}^\mu \partial_\mu \zeta \right) \right] \ . \tag{28}$$

The first term has the same structure as the local equilibrium operator on the final hypersurface. The second term depends on the space-time history between Σ_0 and $\Sigma(\tau)$ and is controlled by gradients of the thermodynamic fields. It is this term which contains the dissipative departure from local equilibrium.

B. Linear response theory

Once the non-equilibrium state has been defined, the main goal is to compute expectation values of observables in that state. This is generally difficult, especially when dissipation is important, because dissipative effects depend on the microscopic interactions of the system.

However, if the system is close to local equilibrium, the gradients of the thermodynamic fields are small on the relevant microscopic scales. This makes it possible to treat the non-equilibrium part perturbatively. Starting from the non-equilibrium operator above, we write

$$\widehat{\rho} = \frac{1}{Z} \exp\left(\widehat{\mathcal{E}} + \widehat{\mathcal{D}} \right) \ , \qquad Z = {\rm Tr}\left[\exp\left(\widehat{\mathcal{E}} + \widehat{\mathcal{D}} \right) \right] \ , \tag{29}$$

where $\widehat{\mathcal{E}}$ is the local-equilibrium part and $\widehat{\mathcal{D}}$ is the dissipative part:

$$\begin{aligned} \widehat{\mathcal{E}} &= - \int_\Sigma {\rm d}\Sigma_\mu \left(\widehat{T}^{\mu\nu}\beta_\nu - \widehat{j}^\mu \zeta \right) \ , \\ \widehat{\mathcal{D}} &= \int_\Omega {\rm d}\Omega \left(\widehat{T}^{\mu\nu}\partial_\mu\beta_\nu - \widehat{j}^\mu \partial_\mu \zeta \right) \ . \end{aligned} \tag{30}$$

The operator $\widehat{\mathcal{D}}$ is proportional to gradients of the thermodynamic fields. It is therefore natural, in the regime of slowly varying fields, to regard it as a small correction to $\widehat{\mathcal{E}}$ and expand the density operator in powers of $\widehat{\mathcal{D}}$.

The useful identity is the Kubo identity, which follows from the Baker–Campbell–Hausdorff formula:

$$\mathrm{e}^{\widehat{\mathcal{E}}+\widehat{\mathcal{D}}} = \mathrm{e}^{\widehat{\mathcal{E}}} + \left(\int_0^1 \mathrm{d}z\, \mathrm{e}^{z(\widehat{\mathcal{E}}+\widehat{\mathcal{D}})}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}}\right) \mathrm{e}^{\widehat{\mathcal{E}}} \,. \tag{31}$$

At first order in $\widehat{\mathcal{D}}$ this becomes

$$\mathrm{e}^{\widehat{\mathcal{E}}+\widehat{\mathcal{D}}} \simeq \mathrm{e}^{\widehat{\mathcal{E}}} + \left(\int_0^1 \mathrm{d}z\, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}}\right) \mathrm{e}^{\widehat{\mathcal{E}}} \,. \tag{32}$$

The same expansion can be applied to the normalization factor:

$$\begin{aligned} Z = \mathrm{Tr}\left(\mathrm{e}^{\widehat{\mathcal{E}}+\widehat{\mathcal{D}}}\right) &\simeq \mathrm{Tr}\left[\mathrm{e}^{\widehat{\mathcal{E}}} + \left(\int_0^1 \mathrm{d}z\, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}}\right) \mathrm{e}^{\widehat{\mathcal{E}}}\right] \\ &= \mathrm{Tr}(\mathrm{e}^{\widehat{\mathcal{E}}}) + \mathrm{Tr}\left[\left(\int_0^1 \mathrm{d}z\, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}}\right) \mathrm{e}^{\widehat{\mathcal{E}}}\right] \\ &\equiv Z_{\mathrm{LE}} + Z_{\mathrm{LE}} \int_0^1 \mathrm{d}z\, \mathrm{Tr}\left[\frac{\mathrm{e}^{\widehat{\mathcal{E}}}}{Z_{\mathrm{LE}}}\, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}}\right] \,. \end{aligned}$$

Here $Z_{\mathrm{LE}} = \mathrm{Tr}(\exp(\widehat{\mathcal{E}}))$, and the operator $\exp(\widehat{\mathcal{E}})/Z_{\mathrm{LE}}$ is precisely the local equilibrium operator. Therefore

$$\mathrm{Tr}\left[\frac{\mathrm{e}^{\widehat{\mathcal{E}}}}{Z_{\mathrm{LE}}}\, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}}\right] \equiv \left\langle \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}} \right\rangle_{\mathrm{LE}} \,.$$

The partition function of the full operator is then approximated by

$$Z \simeq Z_{\mathrm{LE}} \left(1 + \int_0^1 \mathrm{d}z\, \left\langle \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}} \right\rangle_{\mathrm{LE}}\right) \,. \tag{33}$$

Using this result in the expression for $\widehat{\rho}$ and expanding the denominator to first order gives

$$\begin{aligned} \widehat{\rho} &\simeq \frac{\mathrm{e}^{\widehat{\mathcal{E}}} + \left(\int_0^1 \mathrm{d}z\, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}}\right) \mathrm{e}^{\widehat{\mathcal{E}}}}{Z_{\mathrm{LE}} \left(1 + \int_0^1 \mathrm{d}z\, \left\langle \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}} \right\rangle_{\mathrm{LE}}\right)} \\ &\simeq \left[\mathrm{e}^{\widehat{\mathcal{E}}} + \left(\int_0^1 \mathrm{d}z\, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}}\right) \mathrm{e}^{\widehat{\mathcal{E}}}\right] \frac{1}{Z_{\mathrm{LE}}} \left[1 - \int_0^1 \mathrm{d}z\, \left\langle \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}} \right\rangle_{\mathrm{LE}}\right] \\ &\simeq \frac{\mathrm{e}^{\widehat{\mathcal{E}}}}{Z_{\mathrm{LE}}} + \int_0^1 \mathrm{d}z\, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}}\, \frac{\mathrm{e}^{\widehat{\mathcal{E}}}}{Z_{\mathrm{LE}}} - \frac{\mathrm{e}^{\widehat{\mathcal{E}}}}{Z_{\mathrm{LE}}} \int_0^1 \mathrm{d}z\, \left\langle \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}} \right\rangle_{\mathrm{LE}} \,. \end{aligned}$$

Thus

$$\widehat{\rho} \simeq \widehat{\rho}_{\mathrm{LE}} + \int_0^1 \mathrm{d}z\, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}}\, \widehat{\rho}_{\mathrm{LE}} - \widehat{\rho}_{\mathrm{LE}} \int_0^1 \mathrm{d}z\, \left\langle \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}} \right\rangle_{\mathrm{LE}} \,. \tag{34}$$

With this approximate density operator, the non-equilibrium expectation value of an observable $\widehat{O}(x)$ becomes

$$\langle \widehat{O}(x) \rangle \simeq \langle \widehat{O}(x) \rangle_{\mathrm{LE}} + \int_0^1 \mathrm{d}z\, \left\langle \widehat{O}(x)\, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}} \right\rangle_{\mathrm{LE}} - \langle \widehat{O}(x) \rangle_{\mathrm{LE}} \int_0^1 \mathrm{d}z\, \left\langle \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}} \right\rangle_{\mathrm{LE}} \,.$$

For two observables $\widehat{O}_1$ and $\widehat{O}_2$, we define the connected local-equilibrium expectation value by

$$\langle \widehat{O}_1 \,, \widehat{O}_2 \rangle_{c,\mathrm{LE}} \equiv \langle \widehat{O}_1 \widehat{O}_2 \rangle_{\mathrm{LE}} - \langle \widehat{O}_1 \rangle_{\mathrm{LE}} \langle \widehat{O}_2 \rangle_{\mathrm{LE}} \,. \tag{35}$$

Therefore the expectation value can be written compactly as

$$\langle \widehat{O}(x) \rangle \simeq \langle \widehat{O}(x) \rangle_{\mathrm{LE}} + \int_0^1 \mathrm{d}z\, \left\langle \widehat{O}(x) \,, \mathrm{e}^{z\widehat{\mathcal{E}}}\, \widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}} \right\rangle_{c,\mathrm{LE}} \,. \tag{36}$$

This is already an important simplification: a non-equilibrium expectation value has been reduced, at linear order in gradients, to a local-equilibrium expectation value plus a connected correlator computed in local equilibrium.

We can simplify further. Since gradients are the quantities that drive the system away from global equilibrium, the expectation value of a local observable at x should be dominated by the homogeneous equilibrium state defined by the local values $\beta(x)$ and $\zeta(x)$. The dependence on the variation of the thermodynamic fields around x can then be treated perturbatively.

We therefore write

$$\begin{aligned}\Delta\beta_\nu(y,x) = \beta_\nu(y) - \beta_\nu(x) &= \sum_{n=1}^{\infty} \frac{1}{n!} \left[\prod_{j=1}^{n} \left(y^{\lambda_j} - x^{\lambda_j}\right) \partial^y_{\lambda_j} \right] \beta_\nu(y) \Big|_{y=x} \,, \\ \Delta\zeta(y,x) = \zeta(y) - \zeta(x) &= \sum_{n=1}^{\infty} \frac{1}{n!} \left[\prod_{j=1}^{n} \left(y^{\lambda_j} - x^{\lambda_j}\right) \partial^y_{\lambda_j} \right] \zeta(y) \Big|_{y=x} \,.\end{aligned} \tag{37}$$

In this way $\beta_\nu(y) = \beta_\nu(x) + \Delta\beta_\nu(y,x)$ and $\zeta(y) = \zeta(x) + \Delta\zeta(y,x)$, so that

$$\begin{aligned}-\int_\Sigma \mathrm{d}\Sigma_\mu(y) \left(\widehat{T}^{\mu\nu}(y)\beta_\nu(y) - \widehat{j}^\mu(y)\zeta(y)\right) &= -\beta_\nu(x) \int_\Sigma \mathrm{d}\Sigma_\mu(y) \widehat{T}^{\mu\nu}(y) + \zeta(x) \int_\Sigma \mathrm{d}\Sigma_\mu(y) \widehat{j}^\mu(y) \\ &\quad - \int_\Sigma \mathrm{d}\Sigma_\mu(y) \left(\widehat{T}^{\mu\nu}(y)\Delta\beta_\nu(y,x) - \widehat{j}^\mu(y)\Delta\zeta(y,x)\right) \\ &\equiv -\beta(x)\cdot\widehat{P} + \zeta(x)\widehat{Q} + \Delta\widehat{\mathcal{E}} \,.\end{aligned}$$

Equivalently,

$$\Delta\widehat{\mathcal{E}} \equiv -\int_\Sigma \mathrm{d}\Sigma_\mu(y) \left(\widehat{T}^{\mu\nu}(y)\Delta\beta_\nu(y,x) - \widehat{j}^\mu(y)\Delta\zeta(y,x)\right) \,. \tag{38}$$

The local equilibrium operator can therefore be separated as

$$\widehat{\rho}_{\mathrm{LE}} = \frac{1}{Z_{\mathrm{LE}}} \exp\left(\widehat{\mathcal{E}}_{\mathrm{GE}} + \Delta\widehat{\mathcal{E}}\right) \,, \qquad Z_{\mathrm{LE}} = \mathrm{Tr}\left[\exp\left(\widehat{\mathcal{E}}_{\mathrm{GE}} + \Delta\widehat{\mathcal{E}}\right)\right] \,, \tag{39}$$

where

$$\widehat{\mathcal{E}}_{\mathrm{GE}} \equiv -\beta(x)\cdot\widehat{P} + \zeta(x)\widehat{Q} \tag{40}$$

is the homogeneous global-equilibrium operator constructed from the local values of the thermodynamic fields at the same space-time point x where the observable is evaluated. The correction $\Delta\widehat{\mathcal{E}}$ contains the spatial variation of the thermodynamic fields around x and can be treated perturbatively. At first order,

$$\langle\widehat{O}(x)\rangle_{\mathrm{LE}} \simeq \langle\widehat{O}(x)\rangle_{\mathrm{GE}} + \int_0^1 \mathrm{d}z \left\langle \widehat{O}(x) \,, \mathrm{e}^{z\widehat{\mathcal{E}}_{\mathrm{GE}}} \,\Delta\widehat{\mathcal{E}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}_{\mathrm{GE}}} \right\rangle_{c,\mathrm{GE}} \,. \tag{41}$$

Substituting this expression into the linear-response formula and keeping only terms that are linear in gradients, namely discarding products such as $\widehat{\mathcal{D}}\Delta\widehat{\mathcal{E}}$, we obtain

$$\langle\widehat{O}(x)\rangle \simeq \langle\widehat{O}(x)\rangle_{\mathrm{GE}} + \int_0^1 \mathrm{d}z \left\langle \widehat{O}(x) \,, \mathrm{e}^{z\widehat{\mathcal{E}}_{\mathrm{GE}}} \,\Delta\widehat{\mathcal{E}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}_{\mathrm{GE}}} \right\rangle_{c,\mathrm{GE}} + \int_0^1 \mathrm{d}z \left\langle \widehat{O}(x) \,, \mathrm{e}^{z\widehat{\mathcal{E}}_{\mathrm{GE}}} \,\widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}_{\mathrm{GE}}} \right\rangle_{c,\mathrm{GE}} \,. \tag{42}$$

Thus, in linear response theory, the non-equilibrium expectation value is reduced to the computation of connected correlators in a homogeneous global-equilibrium state. The local values $\beta(x)$ and $\zeta(x)$ determine the reference equilibrium state, while the gradients of these fields generate the corrections.

It is useful to separate the correction into two contributions. We define the *local-equilibrium* correction and the *dissipative* correction as

$$\begin{aligned}\Delta_{\mathrm{LE}} O(x) &\equiv \int_0^1 \mathrm{d}z \left\langle \widehat{O}(x) \,, \mathrm{e}^{z\widehat{\mathcal{E}}_{\mathrm{GE}}} \,\Delta\widehat{\mathcal{E}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}_{\mathrm{GE}}} \right\rangle_{c,\mathrm{GE}} \,, \\ \Delta_{\mathrm{diss}} O(x) &\equiv \int_0^1 \mathrm{d}z \left\langle \widehat{O}(x) \,, \mathrm{e}^{z\widehat{\mathcal{E}}_{\mathrm{GE}}} \,\widehat{\mathcal{D}}\, \mathrm{e}^{-z\widehat{\mathcal{E}}_{\mathrm{GE}}} \right\rangle_{c,\mathrm{GE}} \,.\end{aligned} \tag{43}$$

Therefore

$$\langle \widehat{O}(x) \rangle \simeq \langle \widehat{O}(x) \rangle_{\rm GE} + \Delta O(x) \ , \tag{44}$$

where the total non-equilibrium correction is

$$\Delta O(x) \equiv \Delta_{\rm LE} O(x) + \Delta_{\rm diss} O(x) \ . \tag{45}$$

C. Entropy Production

The local equilibrium operator, which we remember is not the real quantum state of the system, is obtained by maximizing the entropy with the constraint of that it must reproduce the local thermodynamic state of the system. The entropy is given by:

$$S = -{\rm Tr}(\widehat{\rho}_{\rm LE} \ln \widehat{\rho}_{\rm LE}) \ . \tag{46}$$

Note that being the trace of an operator it must be invariant under local Lorentz transformation and thus is a Lorentz scalar. Also the entropy being a state function may only depend on the internal degrees of freedom of the system and thus cannot depend on the state of motion of it. This is important because some extensions of relativistic thermodynamic assume that the entropy is not a scalar but rather is the time component of a four-vector.

The operator maximizing (46) with the local constraints (24) is again:

$$\widehat{\rho}_{\rm LE}(\tau) = \frac{1}{Z_{\rm LE}} \exp\left[- \int_{\Sigma(\tau)} {\rm d}\Sigma_\mu \left(\widehat{T}^{\mu\nu} \beta_\nu - \widehat{j}^\mu \zeta \right) \right] \ , \quad Z_{\rm LE} = {\rm Tr}\left(\exp\left[- \int_{\Sigma(\tau)} {\rm d}\Sigma_\mu \left(\widehat{T}^{\mu\nu} \beta_\nu - \widehat{j}^\mu \zeta \right) \right] \right) \ . \tag{47}$$

With the above we can then compute the entropy:

$$\begin{aligned} S &= -{\rm Tr}\left\{ \widehat{\rho}_{\rm LE} \left[- \ln Z_{\rm LE} - \int_{\Sigma(\tau)} {\rm d}\Sigma_\mu \left(\widehat{T}^{\mu\nu} \beta_\nu - \widehat{j}^\mu \zeta \right) \right] \right\} \\ &= \ln Z_{\rm LE} {\rm Tr}(\widehat{\rho}_{\rm LE}) + \int_{\Sigma(\tau)} {\rm d}\Sigma_\mu \left[{\rm Tr}(\widehat{\rho}_{\rm LE} \widehat{T}^{\mu\nu}) \beta_\nu - {\rm Tr}(\widehat{\rho}_{\rm LE} \widehat{j}^\mu) \zeta \right] \ , \end{aligned}$$

then using that $\widehat{\rho}_{\rm LE}$ is normalized we obtain:

$$S = \ln Z_{\rm LE} + \int_{\Sigma(\tau)} {\rm d}\Sigma_\mu \left(\langle \widehat{T}^{\mu\nu} \rangle_{\rm LE} \, \beta_\nu - \langle \widehat{j}^\mu \rangle_{\rm LE} \, \zeta \right) \ . \tag{48}$$

Note that being ${\rm d}\Sigma_\mu = {\rm d}\Sigma \, \hat{n}_\mu$, due to the constraints (24) the above can be equivalently written as:

$$S = \ln Z_{\rm LE} + \int_{\Sigma(\tau)} {\rm d}\Sigma_\mu \left(\langle \widehat{T}^{\mu\nu} \rangle \, \beta_\nu - \langle \widehat{j}^\mu \rangle \, \zeta \right) \ . \tag{49}$$

that is we can replace the local equilibrium expectation values with the actual non-equilibrium one.

In order to express the total entropy in a manifest covariant way we introduce the entropy current s^μ defined as:

$$S = \int_\Sigma {\rm d}\Sigma_\mu \, s^\mu \ . \tag{50}$$

The integral is independent from Σ if $\partial_\mu s^\mu = 0$ which is equivalent to have:

$$S\Big|_{\Sigma(\tau)} = S\Big|_{\Sigma(\tau')} \ , \tag{51}$$

i.e. no entropy is produced. This of course is true at global equilibrium. We will see how the fact that $\partial_\mu s^\mu \neq 0$ is related to the dissipative term in the linear expansion. This is ultimately the reason that allows to interpret such term as the dissipative one.

Now in order to be able to define an entropy current s^μ, according to (48) and (49) it is clear that it must exist a field ϕ^μ such that:

$$\ln Z_{\rm LE} = \int_\Sigma {\rm d}\Sigma_\mu \, \phi^\mu \tag{52}$$

where ϕ^μ is a four-vector called *thermodynamic potential current*. With this we have:

$$S = \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left(\phi^\mu + \langle \widehat{T}^{\mu\nu} \rangle \, \beta_\nu - \langle \widehat{j}^\mu \rangle \, \zeta \right) ,$$

which leads to identify:

$$s^\mu = \phi^\mu + \langle \widehat{T}^{\mu\nu} \rangle \beta_\nu - \langle \widehat{j}^\mu \rangle \zeta \, . \tag{53}$$

Note that the entropy current is defined up- to a four-vector L^μ orthogonal to the hypersurface, $L \cdot \hat{n} = 0$.

Now how to prove and derive that ϕ^μ indeed does exist? We start considering the following λ-dependent operator:

$$\widehat{\rho}_{\mathrm{LE}}(\tau; \lambda) \equiv \frac{1}{Z_{\mathrm{LE}}(\lambda)} \exp \left[-\lambda \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left(\widehat{T}^{\mu\nu} \beta_\nu - \widehat{j}^\mu \zeta \right) \right] \tag{54}$$

The above operator is the local equilibrium one with the proper inverse temperature $1/T$ rescaled by λ, that is $1/T \mapsto \lambda/T$ Hence for $\lambda = 1$ the operator is simply the local equilibrium one. Now deriving with respect to λ the logarithm of the partition function:

$$\frac{\partial \ln Z_{\mathrm{LE}}(\lambda)}{\partial \lambda} = - \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left(\langle \widehat{T}^{\mu\nu} \rangle_{\mathrm{LE}}(\lambda) \beta_\nu - \langle \widehat{j}^\mu \rangle_{\mathrm{LE}}(\lambda) \zeta \right)$$

where the local equilibrium expectation values are computed with the rescaled local equilibrium operator. Now integrating both sides in λ between $\lambda = 1$ and λ_0 we get:

$$\ln Z_{\mathrm{LE}} - \ln Z_{\mathrm{LE}}(\lambda_0) = - \int_{\lambda_0}^1 \mathrm{d}\lambda \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left(\langle \widehat{T}^{\mu\nu} \rangle_{\mathrm{LE}}(\lambda) \beta_\nu - \langle \widehat{j}^\mu \rangle_{\mathrm{LE}}(\lambda) \zeta \right) .$$

Now assuming that exists a λ_0 such that $Z_{\mathrm{LE}}(\lambda_0) = 1$ then, changing the order of the integrals, we obtain:

$$\ln Z_{\mathrm{LE}} = \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left[- \int_{\lambda_0}^1 \mathrm{d}\lambda \left(\langle \widehat{T}^{\mu\nu} \rangle_{\mathrm{LE}}(\lambda) \beta_\nu - \langle \widehat{j}^\mu \rangle_{\mathrm{LE}}(\lambda) \zeta \right) \right] ,$$

that is:

$$\phi^\mu \equiv - \int_{\lambda_0}^1 \mathrm{d}\lambda \left(\langle \widehat{T}^{\mu\nu} \rangle_{\mathrm{LE}}(\lambda) \beta_\nu - \langle \widehat{j}^\mu \rangle_{\mathrm{LE}}(\lambda) \zeta \right) .$$

Now the request for the existence of a λ_0 such that $Z_{\mathrm{LE}}(\lambda_0) = 1$ is physically the request of the existence of a reference temperature where the system admits an only possible populated state. Indeed this often happens if one consider $\lambda_0 \to +\infty$ which is equivalent to say that for $T = 0$ only one state, the vacuum, is populated. In this regard we can write the thermodnynamic potential current as:

$$\phi^\mu = \int_0^{+\infty} \mathrm{d}\lambda \left(\langle \widehat{T}^{\mu\nu} \rangle_{\mathrm{LE}}(\lambda) \beta_\nu - \langle \widehat{j}^\mu \rangle_{\mathrm{LE}}(\lambda) \zeta \right) . \tag{55}$$

As said the entropy is constant only on an global equilibrium state. For a system at local thermodynamic equilibrium one should expect:

$$S\Big|_{\Sigma(\tau)} \neq S\Big|_{\Sigma(\tau')} \implies \partial_\mu s^\mu \neq 0 \, .$$

In particular if one consider $\tau' \geq \tau$ then according to the second principle of thermodynamic the entropy must increase and one has an effective entropy production:

$$\frac{\delta S}{\delta \tau} \geq 0 \implies \partial_\mu s^\mu \geq 0 \, . \tag{56}$$

In order to compute the rate of entropy production one has to compute the rate of variation with time of the entropy S. The variation is due to the change in the integration hypersurface which evolves from $\Sigma(\tau)$ to $\Sigma(\tau + \delta\tau)$. The variation of the integral for variation of the integration dominion reads:

$$\frac{\delta S}{\delta \tau} = \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \, \xi^\mu \partial_\nu s^\nu + \int_{\partial\Sigma} \mathrm{d}\sigma_{\mu\nu} s^\mu \xi^\nu \, , \tag{57}$$

where $\mathrm{d}\sigma_{\mu\nu} = -\mathrm{d}\sigma_{\nu\mu}$ is the Area two-form associated with the boundary of Σ and $\xi^\mu = \partial x^\mu/\partial\tau$ is the generator of the displacement of the hypersurface. Note that for comoving foliations $\xi^\mu = u^\mu$. If one assumes that the rate of entropy to be vanishing at infinite then the second term reduces to zero:

$$\frac{\delta S}{\delta\tau} = \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \xi^\mu \partial_\nu s^\nu \ . \tag{58}$$

From its definition the entropy can also be written as:

$$S = \ln Z_{\rm LE} + \int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left(\langle \widehat{T}^{\mu\nu} \rangle \beta_\nu - \langle \widehat{j}^\mu \rangle \zeta \right) \ .$$

Taking the variation with respect to $\delta\tau$ and using again (24) to replace the local equilibrium expectation values with the full non-equilibrium ones:

$$\frac{\delta S}{\delta\tau} = \frac{1}{Z_{\rm LE}} \frac{\delta Z_{\rm LE}}{\delta\tau} + \int_\Sigma \mathrm{d}\Sigma_\mu \, \xi^\mu \left(\langle \widehat{T}^{\nu\lambda} \rangle \partial_\nu \beta_\lambda - \langle \widehat{j}^\nu \rangle \partial_\nu \zeta \right) \ . \tag{59}$$

For the variation of $Z_{\rm LE}$ we start considering the following formula:

$$\delta \, \mathrm{e}^{-\widehat{A}} = -\int_0^1 \mathrm{d}z \, \mathrm{e}^{-z\widehat{A}} \delta\widehat{A} \, \mathrm{e}^{-(1-z)\widehat{A}} \ ,$$

then:

$$\begin{aligned} \delta Z_{\rm LE} &= \mathrm{Tr}\left[\exp\left(-\int_{\Sigma(\tau+\delta\tau)} \mathrm{d}\Sigma \left(\widehat{T}^{\mu\nu} \beta_\nu - \widehat{j}^\mu \zeta \right) \right) \right] - \mathrm{Tr}\left[\exp\left(-\int_{\Sigma(\tau} \mathrm{d}\Sigma_\mu \left(\widehat{T}^{\mu\nu} \beta_\nu - \widehat{j}^\mu \zeta \right) \right) \right] \\ &= \mathrm{Tr}\left\{ \exp\left(-\int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \left(\widehat{T}^{\mu\nu} \beta_\nu - \widehat{j}^\mu \zeta \right) \right) \left[-\int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \, \xi^\mu \left(\widehat{T}^{\nu\lambda} \partial_\nu \beta_\lambda - \widehat{j}^\nu \partial_\nu \zeta \right) \right] \right\} \delta\tau + \mathcal{O}(\delta\tau^2) \ . \end{aligned}$$

Dividing by $Z_{\rm LE}$ and retaining only the $\delta\tau$ term we thus get:

$$\begin{aligned} \frac{1}{Z_{\rm LE}} \frac{\delta Z_{\rm LE}}{\delta\tau} &= -\int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \xi^\mu \, \mathrm{Tr}\left[\widehat{\rho}_{\rm LE} \left(\widehat{T}^{\nu\lambda} \partial_\nu \beta_\lambda - \widehat{j}^\nu \partial_\nu \zeta \right) \right] \\ &= -\int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \, \xi^\mu \left(\langle \widehat{T}^{\nu\lambda} \rangle_{\rm LE} \partial_\nu \beta_\lambda - \langle \widehat{j}^\nu \rangle_{\rm LE} \partial_\nu \zeta \right) \ . \end{aligned}$$

Then plugging the above in (59) we obtain:

$$\frac{\delta S}{\delta\tau} = -\int_{\Sigma(\tau)} \mathrm{d}\Sigma_\mu \, \xi^\mu \left(\langle \widehat{T}^{\nu\lambda} \rangle_{\rm LE} \partial_\nu \beta_\lambda - \langle \widehat{j}^\nu \rangle_{\rm LE} \partial_\nu \zeta \right) + \int_\Sigma \mathrm{d}\Sigma_\mu \, \xi^\mu \left(\langle \widehat{T}^{\nu\lambda} \rangle \partial_\nu \beta_\lambda - \langle \widehat{j}^\nu \rangle \partial_\nu \zeta \right) \ . \tag{60}$$

Combining the above with (58) we thus finally arrive at:

$$\partial_\mu s^\mu = \left(\langle \widehat{T}^{\lambda\nu} \rangle - \langle \widehat{T}^{\lambda\nu} \rangle_{\rm LE} \right) \partial_\lambda \beta_\nu - \left(\langle \widehat{j}^\nu \rangle - \langle \widehat{j}^\nu \rangle_{\rm LE} \right) \partial_\nu \zeta \ . \tag{61}$$

Thus the entropy production is driven by the difference between the full non-equilibrium and the local equilibrium expectation values. If I use linear response theory then:

$$\begin{aligned} \langle \widehat{T}^{\mu\nu} \rangle &\simeq \langle \widehat{T}^{\mu\nu} \rangle_{\rm GE} + \Delta_{\rm LE} T^{\mu\nu} + \Delta_{\rm diss} T^{\mu\nu} \ , \\ \langle \widehat{j}^\mu \rangle &\simeq \langle \widehat{j}^\mu \rangle_{\rm GE} + \Delta_{\rm LE} j^\mu + \Delta_{\rm diss} j^\mu \ , \end{aligned}$$

and thus:

$$\partial_\mu s^\mu = \Delta_{\rm diss} \, T^{\lambda\nu} \partial_\lambda \beta_\nu - \Delta_{\rm diss} \, j^\nu \partial_\nu \zeta \ . \tag{62}$$

It is clear then the terms we interpreted as dissipative are indeed those that drive the entropy rate production.

EXERCISE 1

In this exercise we show that the operator

$$\widehat{\rho} = \frac{1}{Z} \mathrm{e}^{-\lambda \widehat{A}} \tag{63}$$

maximizes the entropy functional under the constraint that the average value $\langle \widehat{A} \rangle$ is fixed.

The functional we have to maximize is

$$F[\,\widehat{\rho}\,] = -\mathrm{Tr}(\widehat{\rho} \ln \widehat{\rho}) - c\,(\mathrm{Tr}\widehat{\rho} - 1) - \lambda \left(\mathrm{Tr}(\widehat{\rho}\,\widehat{A}) - \langle \widehat{A} \rangle \right) \,. \tag{64}$$

Here c and λ are Lagrange multipliers. The first constraint imposes the normalization of the density operator, while the second one fixes the expectation value of $\widehat{A}$:

$$\mathrm{Tr}\widehat{\rho} = 1 \,, \qquad \mathrm{Tr}(\widehat{\rho}\,\widehat{A}) = \langle \widehat{A} \rangle \,.$$

At the maximum, the functional is stationary, namely

$$\frac{\delta F[\,\widehat{\rho}\,]}{\delta \widehat{\rho}} = 0 \,.$$

Let us now introduce the operator

$$\widehat{X} \equiv \widehat{\mathrm{I}} - \widehat{\rho} \,. \tag{65}$$

This rewriting is useful because it allows us to compute the variation of the functional by considering the change

$$\widehat{X} \longrightarrow \widehat{X} + \delta \widehat{X} \,.$$

Since $\widehat{\rho} = \widehat{\mathrm{I}} - \widehat{X}$, this corresponds to

$$\widehat{\rho} \longrightarrow \widehat{\rho} - \delta \widehat{X} \,.$$

In terms of $\widehat{X}$, the functional (64) becomes

$$F[\,\widehat{X}\,] = -\mathrm{Tr}\left[(\widehat{\mathrm{I}} - \widehat{X}) \ln(\widehat{\mathrm{I}} - \widehat{X}) \right] - c \left[\mathrm{Tr}(\widehat{\mathrm{I}} - \widehat{X}) - 1 \right] - \lambda \left[\mathrm{Tr}\left((\widehat{\mathrm{I}} - \widehat{X}) \widehat{A} \right) - \langle \widehat{A} \rangle \right] \,. \tag{66}$$

Equivalently, using the linearity and cyclicity of the trace, the last term can also be written as

$$\mathrm{Tr}\left((\widehat{\mathrm{I}} - \widehat{X}) \widehat{A} \right) = \mathrm{Tr}\widehat{A} - \mathrm{Tr}(\widehat{X}\,\widehat{A}) \,. \tag{67}$$

We now compute the finite difference

$$F[\,\widehat{X} + \delta \widehat{X}\,] - F[\,\widehat{X}\,] \tag{68}$$

to first order in $\delta \widehat{X}$. Explicitly,

$$\begin{aligned} F[\,\widehat{X} + \delta \widehat{X}\,] - F[\,\widehat{X}\,] = & -\mathrm{Tr}\left[(\widehat{\mathrm{I}} - \widehat{X} - \delta \widehat{X}) \ln(\widehat{\mathrm{I}} - \widehat{X} - \delta \widehat{X}) \right] \\ & + \mathrm{Tr}\left[(\widehat{\mathrm{I}} - \widehat{X}) \ln(\widehat{\mathrm{I}} - \widehat{X}) \right] \\ & - c \left[\mathrm{Tr}(\widehat{\mathrm{I}} - \widehat{X} - \delta \widehat{X}) - 1 \right] + c \left[\mathrm{Tr}(\widehat{\mathrm{I}} - \widehat{X}) - 1 \right] \\ & - \lambda \left[\mathrm{Tr}\left((\widehat{\mathrm{I}} - \widehat{X} - \delta \widehat{X}) \widehat{A} \right) - \langle \widehat{A} \rangle \right] \\ & + \lambda \left[\mathrm{Tr}\left((\widehat{\mathrm{I}} - \widehat{X}) \widehat{A} \right) - \langle \widehat{A} \rangle \right] \,. \end{aligned} \tag{69}$$

Let us first consider the entropy term. Up to first order in $\delta\widehat{X}$,

$$
\begin{aligned}
&-\operatorname{Tr}\left[(\widehat{\mathrm{I}}-\widehat{X}-\delta\widehat{X})\ln(\widehat{\mathrm{I}}-\widehat{X}-\delta\widehat{X})\right]+\operatorname{Tr}\left[(\widehat{\mathrm{I}}-\widehat{X})\ln(\widehat{\mathrm{I}}-\widehat{X})\right]\\
&=\operatorname{Tr}\left[\delta\widehat{X}\,\ln(\widehat{\mathrm{I}}-\widehat{X})\right]-\operatorname{Tr}\left\{(\widehat{\mathrm{I}}-\widehat{X})\left[\ln(\widehat{\mathrm{I}}-\widehat{X}-\delta\widehat{X})-\ln(\widehat{\mathrm{I}}-\widehat{X})\right]\right\}+\mathcal{O}(\delta\widehat{X}^2)\,.
\end{aligned}
$$

Therefore

$$
\begin{aligned}
F[\,\widehat{X}+\delta\widehat{X}\,]-F[\,\widehat{X}\,]=\operatorname{Tr}\left[\delta\widehat{X}\,\ln(\widehat{\mathrm{I}}-\widehat{X})\right]-\operatorname{Tr}\left\{(\widehat{\mathrm{I}}-\widehat{X})\left[\ln(\widehat{\mathrm{I}}-\widehat{X}-\delta\widehat{X})-\ln(\widehat{\mathrm{I}}-\widehat{X})\right]\right\}\\
+c\operatorname{Tr}(\delta\widehat{X})+\lambda\operatorname{Tr}(\delta\widehat{X}\,\widehat{A})+\mathcal{O}(\delta\widehat{X}^2)\,.
\end{aligned}
$$

We now have to compute the variation of the logarithm. The logarithm of an operator can be formally defined through its Taylor expansion. In particular, for sufficiently small $\widehat{X}$ one has

$$
\ln(\widehat{\mathrm{I}}-\widehat{X})=-\sum_{n=1}^{\infty}\frac{\widehat{X}^n}{n}\,. \tag{70}
$$

Hence:

$$
\begin{aligned}
&\ln(\widehat{\mathrm{I}}-\widehat{X}-\delta\widehat{X})-\ln(\widehat{\mathrm{I}}-\widehat{X})\\
&=-\sum_{n=1}^{\infty}\frac{(\widehat{X}+\delta\widehat{X})^n-\widehat{X}^n}{n}\,.
\end{aligned}
$$

Since, in general, $\widehat{X}$ and $\delta\widehat{X}$ do not commute, we have to keep track of all possible positions of $\delta\widehat{X}$. To first order,

$$
(\widehat{X}+\delta\widehat{X})^n=\widehat{X}^n+\widehat{X}^{n-1}\delta\widehat{X}+\widehat{X}^{n-2}\delta\widehat{X}\,\widehat{X}+\cdots+\delta\widehat{X}\,\widehat{X}^{n-1}+\mathcal{O}(\delta\widehat{X}^2)\,.
$$

Therefore,

$$
\begin{aligned}
&\ln(\widehat{\mathrm{I}}-\widehat{X}-\delta\widehat{X})-\ln(\widehat{\mathrm{I}}-\widehat{X})\\
&=-\sum_{n=1}^{\infty}\frac{\widehat{X}^{n-1}\delta\widehat{X}+\widehat{X}^{n-2}\delta\widehat{X}\,\widehat{X}+\cdots+\delta\widehat{X}\,\widehat{X}^{n-1}}{n}+\mathcal{O}(\delta\widehat{X}^2)\,.
\end{aligned}
$$

Now we plugging this in the variation of the entropy and using the cyclic property of the trace we find that all terms contribute in the same way:

$$
\begin{aligned}
&\operatorname{Tr}\left\{(\widehat{\mathrm{I}}-\widehat{X})\left[\ln(\widehat{\mathrm{I}}-\widehat{X}-\delta\widehat{X})-\ln(\widehat{\mathrm{I}}-\widehat{X})\right]\right\}\\
&=-\operatorname{Tr}\left[(\widehat{\mathrm{I}}-\widehat{X})\delta\widehat{X}\sum_{n=1}^{\infty}\widehat{X}^{n-1}\right]+\mathcal{O}(\delta\widehat{X}^2)\,.
\end{aligned}
$$

Since the sum reduces to a geometric series:

$$
\sum_{n=1}^{\infty}\widehat{X}^{n-1}=(\widehat{\mathrm{I}}-\widehat{X})^{-1}\,, \tag{71}
$$

we obtain

$$
\begin{aligned}
&\operatorname{Tr}\left\{(\widehat{\mathrm{I}}-\widehat{X})\left[\ln(\widehat{\mathrm{I}}-\widehat{X}-\delta\widehat{X})-\ln(\widehat{\mathrm{I}}-\widehat{X})\right]\right\}\\
&=-\operatorname{Tr}\left[(\widehat{\mathrm{I}}-\widehat{X})\delta\widehat{X}(\widehat{\mathrm{I}}-\widehat{X})^{-1}\right]+\mathcal{O}(\delta\widehat{X}^2)\\
&=-\operatorname{Tr}(\delta\widehat{X})+\mathcal{O}(\delta\widehat{X}^2)\,.
\end{aligned}
$$

Therefore the first-order variation of the functional is

$$
F[\,\widehat{X}+\delta\widehat{X}\,]-F[\,\widehat{X}\,]=\operatorname{Tr}\left[\delta\widehat{X}\,\ln(\widehat{\mathrm{I}}-\widehat{X})\right]+\operatorname{Tr}(\delta\widehat{X})+c\operatorname{Tr}(\delta\widehat{X})+\lambda\operatorname{Tr}(\delta\widehat{X}\,\widehat{A})+\mathcal{O}(\delta\widehat{X}^2)\,,
$$

or equivalently:

$$F[\,\widehat{X}+\delta\widehat{X}\,]-F[\,\widehat{X}\,]=\mathrm{Tr}\left\{\delta\widehat{X}\left[\ln(\widehat{\mathrm{I}}-\widehat{X})+\widehat{\mathrm{I}}+c\widehat{\mathrm{I}}+\lambda\widehat{A}\right]\right\}+\mathcal{O}(\delta\widehat{X}^2)\ . \tag{72}$$

We can now rewrite this result in terms of $\widehat{\rho}$ for which

$$\widehat{\rho}=\widehat{\mathrm{I}}-\widehat{X}\implies\delta\widehat{\rho}=-\delta\widehat{X}\ .$$

Then:

$$F[\,\widehat{\rho}+\delta\widehat{\rho}]-F[\,\widehat{\rho}]=-\mathrm{Tr}\left\{\delta\widehat{\rho}\left[\ln\widehat{\rho}+\widehat{\mathrm{I}}+c\widehat{\mathrm{I}}+\lambda\widehat{A}\right]\right\}+\mathcal{O}(\delta\widehat{\rho}^2)\ . \tag{73}$$

At the stationary point, the first-order variation must vanish for arbitrary Hermitian variations $\delta\widehat{\rho}$. Therefore,

$$\ln\widehat{\rho}+\widehat{\mathrm{I}}+c\widehat{\mathrm{I}}+\lambda\widehat{A}=0\ ,$$

which implies

$$\ln\widehat{\rho}=-(1+c)\widehat{\mathrm{I}}-\lambda\widehat{A}\ .$$

Exponentiating both sides, and using the fact that the identity operator commutes with $\widehat{A}$, we obtain

$$\widehat{\rho}=\mathrm{e}^{-(1+c)\widehat{\mathrm{I}}-\lambda\widehat{A}}=\mathrm{e}^{-(1+c)}\mathrm{e}^{-\lambda\widehat{A}}\ . \tag{74}$$

The constant $\mathrm{e}^{-(1+c)}$ is fixed by the normalization condition $\mathrm{Tr}\widehat{\rho}=1$. Therefore,

$$1=\mathrm{Tr}\widehat{\rho}=\mathrm{e}^{-(1+c)}\mathrm{Tr}\left(\mathrm{e}^{-\lambda\widehat{A}}\right)\ .$$

Defining the partition function as

$$Z\equiv\mathrm{Tr}\left(\mathrm{e}^{-\lambda\widehat{A}}\right)\ , \tag{75}$$

and identifying $Z=\mathrm{e}^{-(1+c)}$ we finally obtain:

$$\widehat{\rho}=\frac{1}{Z}\mathrm{e}^{-\lambda\widehat{A}}\ . \tag{76}$$

The Lagrange multiplier λ is fixed by the condition

$$\langle\widehat{A}\rangle=\mathrm{Tr}(\widehat{\rho}\,\widehat{A})\ . \tag{77}$$

In terms of the partition function, this relation can also be written as

$$\langle\widehat{A}\rangle=-\frac{\partial\ln Z}{\partial\lambda}\ . \tag{78}$$

Finally, since the von Neumann entropy is a concave functional of $\widehat{\rho}$ and the constraints are linear in $\widehat{\rho}$, the stationary point found above is the maximum of the entropy under the imposed constraints.

Now lets specialize to the canonical case. Note that, as long as they are commuting, we can simply replace $\widehat{A}$ with any set of operators we want each of one with its own Lagrange multiplier:

$$\widehat{\rho}=\frac{1}{Z}\mathrm{e}^{-\beta\cdot\widehat{P}+\zeta\widehat{Q}}\ ,\qquad Z=\mathrm{Tr}\left(\mathrm{e}^{-\beta\cdot\widehat{P}+\zeta\widehat{Q}}\right)\ .$$

Then is easy to prove that:

$$\langle\widehat{P}^{\nu}\rangle=-\frac{\partial\ln Z}{\partial\beta_\nu}\ ,\qquad\langle\widehat{Q}\rangle=\frac{\partial\ln Z}{\partial\zeta}$$