Open quantum system driven out of equilibrium: Lindblad-equation approach

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1 Introduction

1. Hamiltonian of system+environment

$$H(t) = H_S(t) + H_{SE} + H_E \tag{1}$$

   where time-dependence is considered only in $H_S(t)$.

2. The density matrix (DM) of total system
   For pure state

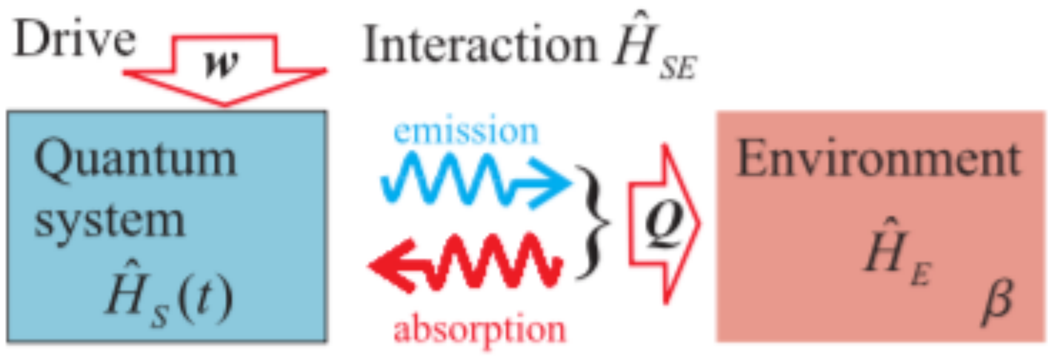
$$\rho = |\Psi\rangle\langle\Psi| \quad \text{and} \quad \rho(t)^2 = I$$

   For mixed state

$$\rho = \sum_\alpha p_\alpha^2 |\alpha\rangle\langle\alpha|$$

   Time-evolution of DM:

$$\rho(t) = U(t,0)\rho(0)U^\dagger(t) \tag{2}$$



where

$$U(t,0) = \overleftarrow{T} e^{-i\int_0^t d\tau H(\tau)}, \; U^\dagger = \overrightarrow{T} e^{+i\int_0^t d\tau H(\tau)}$$

where the time-ordered product of $A(t_1), B(t_2), C(t_3)$ for $t_1 < t_2 < t_3$ is defined as $\overleftarrow{T}(ABC) = C(t_3)B(t_2)A(t_1)$ and $\overrightarrow{T}(ABC\cdots) = A(t_1)B(t_2)C(t_3)$. One has the time-evolution equation for DM

$$d_t\rho = -i[H,\rho] \tag{3}$$

where $\hbar = 1$ is used for simplicity.

3. The time-average
For single operator $A(t)$,

$$\langle A(t)\rangle = \mathrm{Tr}\rho(t)A(t) \tag{4}$$

Write a time-evolution superoperator: $\mathcal{V}(t,0)(\cdot) = U(t,0)(\cdot)U^\dagger(t,0)$.

$$\rho(t) = \mathcal{V}(t,0)\rho(0)$$

The correlation functions at different times:

$$\langle A(t_3)B(t_2)C(t_1)\rangle = TrA(t_3)\mathcal{V}(t_3,t_2)B(t_2)\mathcal{V}(t_2,t_1)C(t_1)\rho(t_1) \tag{5}$$

A simplest two-time correlation function:

$$\langle A(t)B(0)\rangle = \mathrm{Tr}A(t)U(t,0)B(0)\rho(0)U^\dagger(t,0) \tag{6}$$

4. Von-Neumann entropy:

$$S = -\mathrm{Tr}\rho\ln\rho \tag{7}$$

Time-invariance of von-Neumann entropy:

$$S = -\mathrm{Tr}[\rho(t)\ln\rho(t)] = -\mathrm{Tr}[\rho(0)\ln\rho(0)], \tag{8}$$

which can be shown by using $\ln\rho = \ln(I + (\rho - I)) = (\rho - I) - (1/2)(\rho - I)^2 + (1/3)(\rho - I)^3 - \cdots$ and $\rho(t) = U(t,0)\rho(0)U^\dagger(t,0)$.
For pure state, $S = 0$, which can be shown by using $\rho^2 = 1$. The von-Neumann entropy of the total system is time-invariant.

5. Reduced DM

$$\rho_S = \mathrm{Tr}_\mathrm{E}\rho, \quad \rho_\mathrm{E} = \mathrm{Tr}_\mathrm{S}\rho \tag{9}$$

For large reservoir, it is assumed

$$\rho_E = \frac{e^{-\beta H_E}}{Z_E} \tag{10}$$

The system von-Neumann entropy $S_S = -\mathrm{Tr}\rho_\mathrm{S}\ln\rho_\mathrm{S}$ is not time-invariant. Is it involved in thermodynamic second law? $d_tS_S + \beta Q \geq 0$?.

6. Open classical system: a colloidal particle immersed in a liquid reservoir

$$H = H_S(\mathbf{x}, \mathbf{p}, t) + H_{SE}(\mathbf{x}, \{\mathbf{X}_i\}) + H_E(\{\mathbf{X}_i, \mathbf{P}_i\})$$

where $i = 1, \ldots, N$ for $N \to \infty$.

$$H_{SE} = \sum_{i=1}^{N} V_i(|\mathbf{x} - \mathbf{X}_i|) \tag{11}$$

Energy relations by interpreting heat as energy transfer or work done by interaction force:

$$\begin{aligned} d_t H_E &= \underbrace{-\sum_i \partial_{\mathbf{X}_i} V_i \cdot \dot{\mathbf{X}}_i}_{\dot{Q}_E \text{ heat absorption rate into bath}} = \sum_i \partial_{\mathbf{x}} V_i \cdot \mathbf{X}_i \\ d_t H_S &= \underbrace{\partial_t H}_{\dot{W}} - \underbrace{\sum_i \partial_{\mathbf{x}} V_i \cdot \dot{\mathbf{x}}}_{\dot{Q}_S \text{ heat dissipation rate out of system}} \end{aligned} \tag{12}$$

Note $Q_E \neq Q_S$!
First law for system and reservoir:

$$\begin{aligned} d_t H_E &= \dot{Q}_E \\ d_t H_S &= \partial_t H - (d_t \sum_i V_i \underbrace{- \sum_i \partial_{\mathbf{X}_i} V_i \cdot \dot{\mathbf{X}}_i}_{d_t H_E}) = \partial_t H_S - d_t(H_E + H_{SE}) \end{aligned} \tag{13}$$

$$= \dot{W} - \dot{Q}_S \tag{14}$$

which gives

$$d_t(H_S + H_E + H_{SE}) = \dot{W} (= \partial_t H_s) \tag{15}$$

7. Fluctuation theorem (FT) for work for closed quantum system provided that $\rho(0) = Z_0^{-1} e^{-\beta(H_S(0)+H_E+H_{SE})} = Z_0^{-1} e^{-\beta H(0)}$

$$\langle e^{-\beta(W-\Delta F)} \rangle = 1 \text{ (Jarzynski identity or integral FT (IFT))} \tag{16}$$

$$\frac{P_F(W)}{P_R(-W)} = e^{\beta(W-\Delta F)} \text{ (detailed FT (DFT))} \tag{17}$$

The work can be found from two-time projection measurement:
Using $H(t)|\alpha(t) = E_\alpha(t)|\alpha(t)\rangle$ and $H(0)|\gamma(0) = E_\gamma(0)|\gamma(0)\rangle$,

$$\begin{aligned} \langle W \rangle &= \mathrm{Tr}[H(t)\rho(t) - H(0)\rho(0)] \\ &= \mathrm{Tr}[H(t)|\alpha(t)\rangle\langle\alpha(t)|\mathcal{V}(t,0)\rho(0) - \mathcal{V}(t,0)H(0)|\gamma(0)\rangle\langle\gamma(0)|\rho(0)] \end{aligned}$$

$$
\begin{aligned}
&= \sum_{\alpha(t)} E_\alpha(t)\langle\alpha(t)| \underbrace{\mathcal{V}(t,0)\rho(0)}_{U(t,0)\rho(0)U^\dagger(t,0)} |\alpha(t)\rangle \\
&\quad - \sum_{\alpha(t),\gamma(0)} E_\gamma(0)\langle\alpha(t)| \underbrace{\mathcal{V}(t,0)|\gamma(0)\rangle\langle\gamma(0)|\rho(0)}_{U(t,0)|\gamma(0)\rangle\langle\gamma(0)|\rho(0)U^\dagger(t,0)} |\alpha(t)\rangle \\
&= \sum_{\alpha(t),\gamma(0)} (E_\alpha(t) - E_\gamma(0)) \underbrace{\underbrace{|\langle\alpha(t)|U(t,0)|\gamma(0)\rangle|^2 \frac{e^{-\beta E_\gamma(0)}}{Z_0}}_{P[\alpha(t),\gamma(0)]}}_{\text{transition prob}} \qquad (18)
\end{aligned}
$$

In a similar way, one can find the generating function for work as

$$
\begin{aligned}
\mathcal{G}_F(\lambda) = \langle e^{-\lambda\beta W}\rangle &= \mathrm{Tr} e^{-\lambda\beta H(t)}\mathcal{V}(t,0)e^{\lambda\beta H(0)}\rho(0) \\
&= \sum_{\alpha(t),\gamma(0)} e^{-\lambda\beta(E_\alpha(t)-E_\gamma(0))} P[\alpha(t),\gamma(0)] \qquad (19)
\end{aligned}
$$

from which one find the moments of work

$$
\frac{\partial^n}{\partial(-\lambda\beta)^n}\mathcal{G}_F(\lambda)\Big|_{\lambda\to 0} = \langle W^n\rangle \qquad (20)
$$

and the probability distribution

$$
P_F(W) = \int \frac{\beta d\lambda}{2\pi i}\mathcal{G}_F(\lambda)e^{\lambda\beta W}. \qquad (21)
$$

The quantum Jarzynski identity (integral fluctuation theorem) can be derived for a special case with $\lambda = \beta$:

$$
\begin{aligned}
\langle e^{-\beta W}\rangle &= \mathrm{Tr}\left[e^{-\beta(H_S(t)+H_E+H_{SE})} U(t,0) \underbrace{e^{\beta(H_S(0)+H_E+H_{SE})}\rho(0)}_{Z_0^{-1}} U^\dagger(t,0) \right] \\
&= \underbrace{\mathrm{Tr}\left[U^\dagger(t,0)Z_t^{-1}e^{-\beta(H_S(t)+H_E+H_{SE})}U(t,0)\right]}_{1} \frac{Z_t}{Z_0} \\
&= \frac{Z_t}{Z_0} \simeq e^{-\Delta\beta F_S(t)}. \qquad (22)
\end{aligned}
$$

In the derivation, usual assumption of product state:

$$
\rho(0) = \frac{e^{-\beta H_S(0)}}{Z_S(0)} \otimes \frac{e^{-\beta H_E}}{Z_E}
$$

is not used. It is more reasonable to assume that the total system is initially in equilibrium rather than the product state, as may be in real experiments.

DFT for work can be derived from the property of $\mathcal{G}_F(1-\lambda)$:

$$\begin{aligned}\mathcal{G}_F(1-\lambda) &= \mathrm{Tr} e^{(\lambda-1)\beta H(t)} U(t,0) e^{-(\lambda-1)\beta H(0)} \rho(0) U^\dagger(t,0) \\ &= \frac{Z_t}{Z_0} \mathrm{Tr} e^{-\lambda H(0)} U^\dagger(t,0) e^{\lambda\beta H(t)} \frac{e^{-\beta H(t)}}{Z_t} U(t,0) \\ &= \frac{Z_t}{Z_0} \mathcal{G}_R(\lambda) \end{aligned} \tag{23}$$

where $\mathcal{G}_R(\lambda)$ is the generating function for work in the time-reversed process. Then the DFT can be found

$$\begin{aligned} P_F(W) &= \int \frac{\beta d\lambda}{2\pi i} \mathcal{G}_F(1-\lambda) e^{(1-\lambda)\beta W} \\ &= \frac{Z_t}{Z_0} e^{\beta W} P_R(-W) = e^{\beta(W-\Delta F)} P_R(-W) \end{aligned} \tag{24}$$

8. Second law for entropy production under the assumption of initial product state:

$$\rho(0) = \rho_S(0) \otimes \frac{e^{-\beta H_E}}{Z_E}$$

Entropy production: $\hat{\Sigma} \equiv \Delta(-\ln \rho_S(t) + \beta H_E)$

$$\Sigma = \langle \hat{\Sigma} \rangle = \mathrm{Tr}[(-\ln \rho(t) + \beta H_E)\rho(t)] - \mathrm{Tr}[(-\ln \rho(0) + \beta H_E)\rho(0)] \geq 0 \tag{25}$$

which is composed of the von-Neumann entropy change of the open system and the heat absorption by the reservoir.

IFT for entropy production:

$$\begin{aligned} \langle e^{-\hat{\Sigma}} \rangle &= \mathrm{Tr} e^{\ln \rho_S(t) - \beta H_E} U(t,0) \underbrace{e^{-\ln \rho_S(0) + \beta H_E} \underbrace{\rho_S(0) Z_E^{-1} e^{-\beta H_E}}_{\rho(0)}}_{Z_E^{-1}} U^\dagger(t,0) \\ &= \mathrm{Tr} U^\dagger(t,0) \rho_S(t) Z_E^{-1} e^{-\beta H_E} U(t,0) = 1 \end{aligned} \tag{26}$$

which gives $\Sigma \geq 0$. Note that $\dot{\Sigma}$ is not necessarily positive! Non-monotonous (oscillatory) behavior of Σ in time can be observed. From a recent work of Esposito et al (NJP **12**, 013013 (2010))

$$\Sigma = D[\rho(t) || \rho_S(t) \otimes \rho_E^{eq}] \geq 0, \qquad \rho_E^{eq} = e^{-\beta H_E}/Z_E \tag{27}$$

where $D[\rho_1 || \rho_2] = \mathrm{Tr}\rho_1(\ln \rho_1 - \ln \rho_2)$ is the relative entropy that is always positive. Σ is measure for distance from the product state.

2 Quantum master equation: the Lindblad (LB) equation

The theoretical results from the perspective of total closed system seem to be plausible, but are useful for applying to experiments or theoretical calculations because it is not tractable to deal with infinite-size reservoir except finite-size numerical calculations. A proper approach is to use the quantum master equation (ME) for ρ_S.

Consider a special form of Hamiltonian that can be applicable to quantum optical systems

$$H_S = \sum_{\epsilon(t)} \epsilon(t)\Pi(\epsilon(t)) + \sum_\alpha h_\alpha(t) S_\alpha, \quad H_{SE} = \sum_\alpha S_\alpha R_\alpha \tag{28}$$

where $\Pi(\epsilon) = |\epsilon\rangle\langle\epsilon|$ is the projection operator. $S_\alpha = S_\alpha^\dagger$ are hermitian operators for system and $R_\alpha = R_\alpha^\dagger$ for bath. Only the system Hamiltonian H_S depends on time such that $\epsilon(t)$ and external field $h_\alpha(t)$ may depend on time t.

For simple examples as follow. One can consider a two-level system (qubit):

$$H_S = \frac{\nu(t)}{2}\sigma_z + \Omega\cos(\omega_d t)\sigma_x \tag{29}$$

where $\sigma_{x,y,z}$ are Pauli matrices. An harmonic oscillator is another example:

$$H_S = \omega(t) a^\dagger a + h(t)(a + a^\dagger) \tag{30}$$

where a and $a^\dagger$ are annihilation and creation operators and the second term describes the dipole interaction with an external field.

2.1 Interaction picture

It is convenient to use the interaction picture.

$$\tilde{\rho}(t) = U_0^\dagger(t,0)\rho(t)U_0(t,0)$$

where

$$U_0(t,0) = \overleftarrow{T}\exp\left[-i\int_0^t d\tau H_S(\tau)\right]e^{-iH_E t}, \; U_0^\dagger(t,0) = \overrightarrow{T}\exp\left[i\int_0^t d\tau H_S(\tau)\right]e^{iH_E t}$$

Time evolution:

$$\begin{aligned} d_t\tilde{\rho} &= iH_0\tilde{\rho} - i\tilde{\rho}H_0 - iU_0^\dagger HU\rho_0U^\dagger U_0 + iU_0^\dagger U\rho_0U^\dagger HU_0 \\ &= -i[\tilde{H}_{SE}, \tilde{\rho}] \end{aligned} \tag{31}$$

where

$$\tilde{H}_{SE} = U_0^\dagger H_{SE} U_0$$

Therefore

$$d_t\tilde{\rho} = -i[\tilde{H}_{SE}(t), \tilde{\rho}(0)] - \int_0^t d\tau \left[\tilde{H}_{SE}(t), \left[\tilde{H}_{SE}(\tau), \tilde{\rho}(\tau)\right]\right] \tag{32}$$

The reduced DM for system $\tilde{\rho}_S(t) = \mathrm{Tr}_E \tilde{\rho}(t)$:

$$\begin{aligned} d_t \tilde{\rho}_S(t) &= -i \underbrace{\mathrm{Tr}_E[\tilde{H}_{SE}(t), \rho_S(0) \otimes \rho_E^{eq}]}_{\text{assumed to zero: } \mathrm{Tr}_E R = 0} \\ &\quad - \int_0^t d\tau \mathrm{Tr}_E[\tilde{H}_{SE}(t), [\tilde{H}_{SE}(\tau), \tilde{\rho}(\tau)]] \end{aligned} \tag{33}$$

Assuming the correlation time τ_E of bath is much smaller than the time scale τ_S of the system, the correlation functions of bath operators decays very fast as $t - \tau \gg \tau_E$. One can then replace $\tilde{\rho}(\tau) \approx \tilde{\rho}(t)$ and extend the lower integral limit to $-\infty$
Further Born-Markov approximation is used for $\tau \sim t$, giving dominant integration:

$$\tilde{\rho}(\tau) \approx \tilde{\rho}_S(t) \otimes \rho_E^{eq} \tag{34}$$

Then we have the master equation:

$$d_t \tilde{\rho}_S(t) = -\int_{-\infty}^t d\tau \mathrm{Tr}_E[\tilde{H}_{SE}(t), [\tilde{H}_{SE}(\tau), \tilde{\rho}_S(t) \otimes \rho_E^{eq}]] \tag{35}$$

2.2 Eigenoperators

We define eigenoperators:

$$S_\alpha(\omega) = \sum_{\epsilon' - \epsilon = \omega} \Pi(\omega) S_\alpha \Pi(\omega'). \tag{36}$$

Note $S_\alpha^\dagger(\omega) = S_\alpha(-\omega)$. We separate H_S into $H_S^0 = \sum_\epsilon \epsilon \Pi(\epsilon)$ and $H_S^{ext} = \sum_\alpha h_\alpha S_\alpha$. Then, we find

$$[H_S^0, S_\alpha(\omega)] = -\omega S_\alpha(\omega), \quad [H_S^0, S_\alpha^\dagger(\omega)] = +\omega S_\alpha^\dagger(\omega) \tag{37}$$

For *time-independent* case, the eigenoperators in the interaction picture are given as

$$e^{iH_S^0 t} S_\alpha(\omega) e^{-iH_S^0 t} = e^{-i\omega t} S_\alpha(\omega) \tag{38}$$

$$e^{iH_S^0 t} S_\alpha^\dagger(\omega) e^{-iH_S^0 t} = e^{+i\omega t} S_\alpha^\dagger(\omega) \tag{39}$$

However, this simple relations cannot be used for *time-dependent* case.

Note

$$S_\alpha = \sum_\omega S_\alpha(\omega) = \sum_\omega S_\alpha^\dagger(\omega). \tag{40}$$

Finally, we find

$$[H_S, S_\alpha(\omega)] = -\omega S_\alpha(\omega) + h_\alpha(t) \ , \quad [H_S, S_\alpha^\dagger(\omega)] = \omega S_\alpha^\dagger(\omega) + h_\alpha(t) \tag{41}$$

2.3 Lindblad equation

First, note

$$H_{SE} = \sum_{\omega,\alpha} S_\alpha(\omega) R_\alpha = \sum_{\omega,\alpha} S_\alpha^\dagger(\omega) R_\alpha \tag{42}$$

The master equation (35) is rewritten as

$$d_t \tilde{\rho}_S(t) = \int_{-\infty}^{t} d\tau \mathrm{Tr}_E\{\tilde{H}_{SE}(\tau)\tilde{\rho}_S(t)\rho_E^{eq}\tilde{H}_{SE}(t) - \tilde{H}_{SE}(t)\tilde{H}_{SE}(\tau)\tilde{\rho}_S(t)\rho_E^{eq}\} + \text{h.c.} \tag{43}$$

We can write

$$\tilde{H}_{SE}(\tau) = \sum_{\alpha,\omega} \tilde{S}_\alpha(\tau,\omega)\tilde{R}_\alpha(\tau) \tag{44}$$

$$\tilde{H}_{SE}(t) = \sum_{\beta,\omega'} \tilde{S}_\alpha^\dagger(\tau,\omega')\tilde{R}_\beta(t) \tag{45}$$

where in the interaction picture

$$\tilde{S}_\alpha(\tau,\omega) = \overrightarrow{T} e^{i\int_0^\tau dt' H_S(t')} S_\alpha(\omega) \overleftarrow{T} e^{-i\int_0^\tau dt' H_S(t')} \tag{46}$$

$$\tilde{S}_\beta^\dagger(t,\omega') = \overrightarrow{T} e^{i\int_0^t dt' H_S(t')} S_\beta^\dagger(\omega') \overleftarrow{T} e^{-i\int_0^\tau dt' H_S(t')} \tag{47}$$

$$\tag{48}$$

and

$$\tilde{R}_\alpha(\tau) = e^{iH_E\tau} R_\alpha e^{iH_E\tau}. \tag{49}$$

Using the correlation function for reservoir:

$$\Gamma_{\alpha\beta}(t-\tau) = \mathrm{Tr}_E \tilde{R}_\alpha(\tau)\tilde{R}_\beta(t)\rho_E^{eq} \tag{50}$$

we can find

$$\begin{aligned} d_t\tilde{\rho}_S(t) &= \sum_{\omega,\omega'}\sum_{\alpha,\beta}\int_{-\infty}^{t} d\tau \Gamma_{\alpha\beta}(t-\tau) \\ &\times \left[\tilde{S}_\alpha(\tau,\omega)\tilde{\rho}_S(t)\tilde{S}_\beta^\dagger(t,\omega') - \tilde{S}_\beta^\dagger(t,\omega')\tilde{S}_\alpha(\tau,\omega)\tilde{\rho}_S(t)\right] + \text{h.c.} \end{aligned} \tag{51}$$

Assuming that the integral is only dominant near $\tau = t$, we can write

$$\begin{aligned} \tilde{S}_\alpha(\tau,\omega) &\simeq \overrightarrow{T} e^{i\int_0^t dt' H_S(t')} e^{-i(t-\tau)H_S(t)} S_\alpha(\omega) e^{i(t-\tau)H_S(t)} \overleftarrow{T} e^{i\int_0^t dt' H_S(t')} \\ &\simeq \overrightarrow{T} e^{i\int_0^t dt' H_S(t')} \{S_\alpha(\omega) - i(t-\tau)[H_S(t), S_\alpha(\omega)]\} \overleftarrow{T} e^{i\int_0^t dt' H_S(t')} \\ &\simeq \overrightarrow{T} e^{i\int_0^t dt' H_S(t')} \{S_\alpha(\omega)(1 - i\omega(t-\tau)) - i(t-\tau)h_\alpha(t)\} \overleftarrow{T} e^{i\int_0^t dt' H_S(t')} \\ &\simeq e^{-i\omega(t-\tau)}\tilde{S}_\alpha(t,\omega) - ih_\alpha(t)(t-\tau) \end{aligned} \tag{52}$$

Then we have

$$d_t\tilde{\rho}_S(t) = \sum_{\omega,\omega'}\sum_{\alpha,\beta}\Gamma_{\alpha\beta}(\omega)\left[\tilde{S}_\alpha(t,\omega)\tilde{\rho}_S(t)\tilde{S}_\beta^\dagger(t,\omega') - \tilde{S}_\beta^\dagger(t,\omega')\tilde{S}_\alpha(t,\omega)\tilde{\rho}_S(t)\right] + \text{h.c.} \tag{53}$$

where $h_\alpha(t)$-dependent terms are exactly cancelled and the one-sided Fourier transform is introduced as

$$\Gamma_{\alpha\beta}(\omega) = \int_{-\infty}^{t} d\tau e^{-i\omega(t-\tau)}\Gamma_{\alpha\beta}(t-\tau) = \int_0^\infty ds e^{-i\omega s}\Gamma_{\alpha\beta}(s) \tag{54}$$

Now, the master equation becomes local in time. For time-independent case, equation (39) gives

$$\tilde{S}_\beta^\dagger(t,\omega')\tilde{S}_\alpha(t,\omega) = e^{-i(\omega-\omega')t}S_\beta^\dagger(\omega')S_\alpha(t,\omega). \tag{55}$$

If the relaxation time τ_R is much smaller than system time-scale$\sim (\omega-\omega')^{-1}$, $e^{-i(\omega-\omega)t}$ is fast oscillating for considerable elapse of time $t \gg \tau_R$. Therefore, one neglect the terms with $\omega \neq \omega'$ in the summation. This is called the rotating wave approximation (RWA). We expect that the RWA also holds for the time-dependent cases if the modulation of energy level $\epsilon(t)$ or effective field $h(t)$ is much slow over τ_R. Using the RWA, we get

$$d_t\tilde{\rho}_S(t) = \sum_\omega\sum_{\alpha,\beta}\Gamma_{\alpha\beta}(\omega)\left[\tilde{S}_\alpha(t,\omega)\tilde{\rho}_S(t)\tilde{S}_\beta^\dagger(t,\omega) - \tilde{S}_\beta^\dagger(t,\omega)\tilde{S}_\alpha(t,\omega)\tilde{\rho}_S(t)\right] + \text{h.c.} \tag{56}$$

Note that the form of the master equation for time-dependent case in the interaction picture remains the same as for time-independent case. It is interesting that the time-dependence of external field is not explicit while the time-dependence of level spacing $\omega = \omega(t)$ between transitions is explicitly shown.

It is convenient to write

$$\Gamma(\omega) = \frac{1}{2}\gamma(\omega) + i\Delta(\omega) \tag{57}$$

Using $\Gamma = (\Gamma+\Gamma^*)/2 + (\Gamma-\Gamma^*)/2$ Then, the master equation leads to

$$\begin{aligned} d_t\tilde{\rho}_S(t) &= \sum_\omega\sum_{\alpha,\beta}\gamma_{\alpha\beta}(\omega)\left[\tilde{S}_\alpha(t,\omega)\tilde{\rho}_S(t)\tilde{S}_\beta^\dagger(t,\omega) - \frac{1}{2}\{\tilde{S}_\beta^\dagger(t,\omega)\tilde{S}_\alpha(t,\omega), \tilde{\rho}_S(t)\}\right] \\ &\quad -i\sum_\omega\sum_{\alpha,\beta}\Delta_{\alpha\beta}(\omega)[\tilde{S}_\beta^\dagger(t,\omega)\tilde{S}_\alpha(t,\omega), \tilde{\rho}_S(t)] \end{aligned} \tag{58}$$

The first line is the desired form of the Lindblad equation and the second line describes the unitary evolution due to the renormalized Hamiltonian, called the Lamb shift Hamiltonian, given as

$$H_{LS} = \sum_\omega\sum_{\alpha,\beta}\Delta_{\alpha\beta}(\omega)\tilde{S}_\beta^\dagger(t,\omega)\tilde{S}_\alpha(t,\omega) \tag{59}$$

2.4 Schroedinger picture

Writing $U_0(t,0) = U_0^S(t,0)U_0^E(t,0)$

$$\begin{aligned} \tilde{\rho}_S &= \text{Tr}_E U_0^{E\dagger}(t,0)U_0^{S\dagger}(t,0) \underbrace{\rho(t)}_{\text{Sch picture}} U_0^S(t,0)U_0^E(t,0) \\ &= U_0^{S\dagger}(t,0)\underbrace{[\text{Tr}_E\rho(t)]}_{\rho_S(t,u)}U_0^S(t,0) \end{aligned} \tag{60}$$

$$
\begin{aligned}
d_t\tilde{\rho}_S &= U_0^{S\dagger}(t,0)iH_S(t)\rho_S(t)U_0^S(t,0) - U_0^{S\dagger}(t,0)\rho_S(t)iH_S(t)U_0^S(t,0) \\
&\quad + U_0^{S\dagger}(t,0)\dot{\rho}_S(t)U_0^S(t,0) \\
&= U_0^{S\dagger}(t,0)\left[i[H_S(t),\rho_S(t)] + d_t\rho_S(t)\right]U_0^S(t,0) \qquad (61)
\end{aligned}
$$

The system DM in Schroedinger picture:

$$
\begin{aligned}
d_t\rho_S(t) &= -i[H_S(t),\rho_S(t)] + U_0^S(t,0)\dot{\tilde{\rho}}(t,u)U_0^{S\dagger}(t,0) \\
&= -i[H_S(t),\rho_S(t)] \qquad (62) \\
&\quad -\int_{-\infty}^{t} d\tau \mathrm{Tr}_E U_0^S(t,0)[\tilde{H}_{SE}(t),[\tilde{H}_{SE}(\tau),\tilde{\rho}_S(t)\otimes\rho_E^{eq}]]U_0^{S\dagger}(t,0)
\end{aligned}
$$

Therefore, we have

$$
d_t\rho_S(t) = \mathcal{L}(\rho_S) = -i[H_S + H_{LS},\rho_S(t)] + \mathcal{D}(\rho_S) \qquad (63)
$$

where

$$
\begin{aligned}
\mathcal{D}(\rho_S) &= \sum_{\omega>0}\sum_{\alpha,\beta}\Big[\gamma_{\alpha\beta}(\omega)\left(S_\alpha(\omega)\rho_S(t)S_\beta^\dagger(\omega) - \frac{1}{2}\{S_\beta^\dagger(\omega)S_\alpha(\omega),\rho_S(t)\}\right) \\
&\quad + \gamma_{\alpha\beta}(-\omega)\left(S_\alpha^\dagger(\omega)\rho_S(t)S_\beta(\omega) - \frac{1}{2}\{S_\beta(\omega)S_\alpha^\dagger(\omega),\rho_S(t)\}\right)\Big] \qquad (64)
\end{aligned}
$$

$\mathcal{L}$ is the total Linblad superoperator and $\mathcal{D}$ is called the dissipator.

2.5 Equilibrium

For time-independent cases, we expect that the system reaches equilibrium with DM

$$
\rho_S \propto e^{-\beta H_S} \qquad (65)
$$

First note that $[H_S, S_\alpha^\dagger(\omega)S_\beta(\omega)] = 0$ by using (37) and $[H_S + H_{LS}, e^{-\beta H_S}] = 0$. From the relation (39), we get

$$
e^{\beta H_s}S_\alpha(\omega)e^{-\beta H_S} = e^{-\beta\omega}S_\alpha(\omega)\ , \quad e^{\beta H_s}S_\alpha^\dagger(\omega)e^{-\beta H_S} = e^{+\beta\omega}S_\alpha^\dagger(\omega). \qquad (66)
$$

Therefore, we can show

$$
\mathcal{D}(e^{-\beta H_S}) = 0 \qquad (67)
$$

if the following condition is met:

$$
\gamma(-\omega) = e^{-\beta\omega}\gamma(\omega). \qquad (68)
$$

In fact this condition is the property of equilibrium bath.

3 Perspective from the Lindblad equation

Let us drop the subscript S denoting open system for simplicity. We can simply write the Lindblad (LB) equation:

$$d_t \rho = \mathcal{L}(\rho) = -i[H, \rho] + \mathcal{D}(\rho) \tag{69}$$

The formal solution is given as

$$\rho(t) = \mathcal{V}(t, 0)\rho(0) = \overleftarrow{T} e^{\int_0^t d\tau \mathcal{L}} \rho(0) \tag{70}$$

1. First law
Energy E of the system can be found from $E = \mathrm{Tr}\rho H$. Then, we can get the first law of thermodynamics:

$$\begin{aligned} d_t E &= \mathrm{Tr}\rho \dot{H} + \mathrm{Tr} H d_t \rho \\ &= \underbrace{\mathrm{Tr}\rho \dot{H}}_{\dot{W}} + \underbrace{\mathrm{Tr} H \mathcal{L}(\rho)}_{-\dot{Q}} \end{aligned} \tag{71}$$

where $\dot{W}$ is work production rate and $\dot{Q}$ heat production rate dissipated into the reservoir.

2. Fluctuation theorem for work
Classically, work W performed over period t is equal to $\int_0^t d\tau \dot{H}(\tau)$. The fluctuation theorem (FT) $\langle e^{-\beta W} \rangle = 1$ can be proven to hold if initial distribution is Boltzmann for Hamiltonian $H(0)$. Then FT leads to $\langle W \rangle \geq 0$, which can be shown by using the inequality $\langle e^{-x} \rangle \geq 1 - \langle x \rangle$. Quantum mechanically, the corresponding *exponentiated* work can be written as the multi-time correlation function:

$$\begin{aligned} \langle e^{-\beta W} \rangle &= \langle e^{-\beta \dot{H}(t) dt} \cdot e^{-\beta \dot{H}(t-dt) dt} \cdots e^{-\beta \dot{H}(dt) dt} \rangle \\ &= \mathrm{Tr} e^{-\beta \dot{H}(t) dt} \mathcal{V}(t, t-dt) e^{-\beta \dot{H}(t-dt) dt} \mathcal{V}(t-dt, t-2dt) \cdots \\ &\quad \cdots e^{-\beta \dot{H}(dt) dt} \mathcal{V}(dt, 0) \rho_{ss}(0) \end{aligned} \tag{72}$$

The initial DM $\rho_{ss}(0)$ is Boltzmann for $H(0)$ as needed for FT. For the first time slice,

$$\begin{aligned} e^{-\beta \dot{H}(dt) dt} \mathcal{V}(dt, 0) \rho_{ss}(0) &= e^{-\beta \dot{H}(dt) dt} \frac{e^{-\beta H(0)}}{Z_0} \\ &= \frac{e^{-\beta H(dt)}}{Z_0} = \frac{Z_1}{Z_0} \rho_{ss}(dt) \quad \text{only if } [H, \dot{H}] = 0 \end{aligned} \tag{73}$$

Note that the last line only true for $[H, \dot{H}] = 0$, which repeatedly produces $(Z_1/Z_0)(Z_2/Z_1) \cdots$ and finally leads to FT: $\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$. which is equal to 1 only if $[H, \dot{H}] = 0$. It is not generally true and the FT for work in quantum mechanics does not hold in strict sense.

We can define the instantaneous stationary DM as $\rho_{ss}(t) = Z^{-1}(t)e^{-\beta H(t)}$ with the property: $\mathcal{L}(\rho_{ss}) = 0$. Note that it is not a solution of LB equation. Consider time series $t_n = n\Delta t$ for $n = 0, 1, \ldots N$ and $\Delta t = t/N$ in $N \to \infty$ limit. Let $\mathcal{V}_n$ be $\mathcal{V}(t_{n+1}, t_n)$ and $\rho^n_{ss} = \rho_{ss}(t_n)$. Then, we have equality:

$$\begin{aligned} 1 &= \mathrm{Tr}\mathcal{V}_{N-1}\rho^{N-1}_{ss}\frac{1}{\rho^{N-2}_{ss}}\cdots\mathcal{V}_n\rho^n_{ss}\frac{1}{\rho^{n-1}_{ss}}\mathcal{V}_{n-1}\rho^{n-1}_{ss}\frac{1}{\rho^{n-2}_{ss}}\cdots \\ &\quad \cdots\mathcal{V}_2\rho^2_{ss}\frac{1}{\rho^1_{ss}}\mathcal{V}_1\rho^1_{ss}\frac{1}{\rho^0_{ss}}\mathcal{V}_0\rho^0_{ss} \end{aligned} \tag{74}$$

where $\mathcal{V}_n\rho^n_{ss} = \rho^n_{ss}$ is used. The inserted factors can be rewritten as

$$\begin{aligned} \rho^n_{ss}\frac{1}{\rho^{n-1}_{ss}} &= \rho^n_{ss}[\rho^n_{ss} - \Delta t(d_t\rho^n_{ss})]^{-1} \\ &= [1 - \Delta t(d_t\rho^n_{ss})(\rho^n_{ss})^{-1}]^{-1} \\ &= e^{\Delta t(d_t\rho^n_{ss})(\rho^n_{ss})^{-1}} \end{aligned} \tag{75}$$

Therefore, we obtain

$$1 = \left\langle \exp\left(\int_0^t d\tau\frac{d\rho_{ss}}{d\tau}\cdot\rho^{-1}_{ss}\right)\right\rangle. \tag{76}$$

If $[H, \dot{H}] = 0$,

$$\frac{d\rho_{ss}}{dt}\rho^{-1}_{ss} = \beta(\dot{F} - \dot{H})e^{\beta(F-H)}\rho^{-1}_{ss} = \beta(\dot{F} - \dot{H}) \tag{77}$$

Equation (76) leads to

$$\langle e^{-\beta\int_0^t d\tau\dot{H}}\rangle = e^{-\beta\Delta F}, \tag{78}$$

which is the quantum Jarzynski equality. One may refer to equation (76) as the FT (Jarzynski equality) for modified irreversible work rate

$$\dot{W}^{irr}_{mod} = -\frac{d\rho_{ss}}{dt}\cdot\rho^{-1}_{ss} \tag{79}$$

3. Entropy production:
   Define the entropy production rate using Eq. (71) as

$$\begin{aligned} \dot{\Sigma} &= -d_t\mathrm{Tr}\rho\ln\rho + \beta\dot{Q} \\ &= -\mathrm{Tr}\mathcal{L}(\rho)\ln\rho - \beta\mathrm{Tr}H\mathcal{L}(\rho) \\ &= -\mathrm{Tr}\mathcal{L}(\rho)[\ln\rho - \ln\rho_{ss}] \end{aligned} \tag{80}$$

   where the positivity of $\dot{\Sigma}$ will be proven below. Let define the *instantaneous stationary* DM as $\rho_{ss} = Z^{-1}(t)e^{-\beta H(t)}$ satisfying

$$\mathcal{L}(\rho_{ss}) = 0 \tag{81}$$

   Let us define the relative entropy or Kullback-Leibler divergence as

$$D(\rho||\sigma) = \mathrm{Tr}\rho(\ln\rho - \ln\sigma)$$

For any CPTP (completely positive trace conserving) quantum map $\mathcal{V}(t,0)$: $\rho(t) = \mathcal{V}(t,0)\rho_0$

$$D(\rho(t)||\sigma(t)) \leq D(\rho(0)||\sigma(0)) \tag{82}$$

which says that the relative entropy always decrease in time-evolution. For the Lindblad equation, $\mathcal{V}(t,0) = \overleftarrow{T} e^{\int_0^t \mathcal{L} d\tau}$. Letting $\sigma = \rho_{ss}(t)$ and using $\mathcal{L}\rho_{ss}(t) = 0$,

$$\begin{aligned}
0 &< -\frac{1}{dt}\Big[D[\mathcal{V}(t+dt,t)\rho(t)||\rho_{ss}(t)] - D[\rho(t)||\rho_{ss}(t)\Big] \\
&= -\frac{1}{dt}\mathrm{Tr}\Big[\rho(t+dt)\ln\rho(t+dt) - \rho(t)\ln\rho(t) - \rho(t+dt)\rho_{ss}(t) + \rho(t)\ln\rho_{ss}(t)\Big] \\
&= -\mathrm{Tr}\mathcal{L}(\rho(t))(\ln\rho(t) - \ln\rho_{ss}(t)) = \dot{\Sigma}
\end{aligned} \tag{83}$$

where used are $d_t\rho = \mathcal{L}\rho$ and

$$d_t \mathrm{Tr}\rho\ln\rho = \mathrm{Tr}[(d_t\rho)\ln\rho + \rho\rho^{-1}d_t\rho] = \mathrm{Tr}\mathcal{L}(\rho)\ln\rho$$

There, $\dot{\Sigma}$ is always non-negative, which is not guaranteed for the total closed system where only $\Delta\Sigma \geq 0$ provided initial DM is of product state, $\rho \otimes \rho_E$.

Postface

This is the end of the lecture note, but not the end of the story. Further study will be pursued in future. I hope I would sometime be able to make a complete and helpful lecture note.