Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Non-Equilibrium Statistical Mechanics

Lecture given at ETH Zurich during HS 2011

Prof. Dr. Gian Michele Graf

Lecture notes by
Thomas T. Michaels

December 30, 2011

Part I

Lecture 1

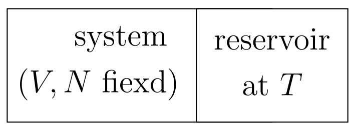
1.1 **Situation** Thermodynamic system, extensive variables $X_1, X_2, ..., X_n$. Define entropy function $S = S(X_1, X_2, ..., X_n)$. Intensive variables $F_1, F_2, ..., F_n$ obtained by taking partial derivatives of the entropy function $F_i = F_i(X_1, X_2, ..., X_n) = \frac{\partial S}{\partial X_i}$.

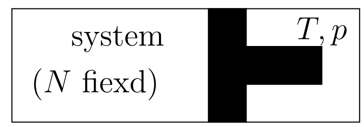
Example: Let $X_1 = U$ (energy), $X_2 = V$ (volume), $X_3 = N$ (particle number). Use $dS = \frac{1}{T}dU - \frac{p}{T}dV - \frac{\mu}{T}dN$ to get $F_1 = \frac{1}{T}$, $F_2 = -\frac{p}{T}$ and $F_3 = -\frac{\mu}{T}$.

Remark: We are more used to obtain intensive parameters from the internal energy U rather than from the entropy S.

1.2 Consider a system with some of the intensive parameters F_i $i = 1, ..., r$ fixed (the complementary, fixed X_j, omitted from the notation).

Examples: 1) $r = 1$ $X_1 = U$
2) $r = 2$ $X_1 = U$, $X_2 = V$

1) 

2) 

1.3 **Postulate** The probability distribution for X_i $i = 1, ..., r$ is

$$W(X_1, ..., X_r)dX_1 \cdots dX_r = \exp\left\{\frac{1}{k}\left[S(X_1, ..., X_r) - \sum_{i=1}^{r} F_i X_i - \hat{S}(F_1, ..., F_r)\right]\right\}$$

(the function $\hat{S}$ is introduced in order to normalize W to unity).

1.4 **Example**: Consider the situation of example 1. To describe the system in terms of statistical physics one would use the canonical ensemble $W(x)dx = \frac{1}{Z}e^{-\beta\mathcal{H}(x)}dx$. In terms of energy

$$\begin{aligned} W(U) &= \int \delta(\mathcal{H}(x) - U)W(x)dx = \int \frac{1}{Z}\delta(\mathcal{H}(x) - U)e^{-\beta\mathcal{H}(x)}dx = \\ &= \frac{e^{-\beta U}}{Z}\int dx\delta(\mathcal{H}(x) - U) = \frac{1}{Z}e^{\frac{1}{k}\left(S(U) - \frac{1}{T}U\right)} \end{aligned}$$

We recognize the structure of the result to be the one of 1.3. The normalisation factor is $\frac{1}{Z} = e^{-\beta F(T)}$, such that $\hat{S} = \frac{F}{T}$.

1.5 The parameters X_i fluctuate around

- average values:

$$\langle X_i \rangle = \int X_i W dX_1 \cdots dX_r$$

- most probable values: W = maximal $\Leftrightarrow$ exponent maximal $\Leftrightarrow$ $S - \sum_i F_i X_i$ = maximal $\Leftrightarrow$ $F_i = \frac{\partial S}{\partial X_i}$. Interpretation: $F_i(X_1, ..., X_r)$ = the prescribed value for F_i.

Note that average values and most probable values are not the same: they are close together for large systems (except at a phase transition).

Examples: 1) In the first example we would maximize $S - X_1 F_1 = S - \frac{1}{T}U = -\frac{F}{T}$. Note that $F = F(1/T)$ (free energy).

2) In the second example we would maximize $S - X_1F_1 - X_2F_2 = S - \frac{1}{T}U + \frac{p}{T}V = -\frac{1}{T}(U - TS + pV) = -\frac{1}{T}G$ (Gibbs free energy).

1.6 **Average values** To obtain a closed formula for the average $\langle X_i \rangle$ differentiate normalization condition $\int W dX_1 \cdots dX_r = 1$ with respect to F_i:

$$0 = \int \frac{1}{k}\left(-X_i - \frac{\partial \hat{S}}{\partial F_i}\right) W dX_1 \cdots dX_r \quad \Rightarrow \quad \langle X_i \rangle = -\frac{\partial \hat{S}}{\partial F_i}$$

1.7 **Fluctuations** Let $\delta X_i = X_i - \langle X_i \rangle$ (note $\langle \delta X_i \rangle = 0$ per construction). We calculate the second moments

$$\langle \delta X_i \delta X_j \rangle = \int \delta X_i \delta X_j W dX_1 \cdots dX_r = -k \int \delta X_i \frac{\partial W}{\partial F_j} dX_1 \cdots dX_r =$$

$$= -k \int \left(\frac{\partial}{\partial F_j}(\delta X_i W) - \frac{\partial \delta X_i}{\partial F_j} W\right) dX_1 \cdots dX_r = -k \left(\frac{\partial \langle X_i \rangle}{\partial F_j}\right) \int W dX_1 \cdots dX_r$$

$$\Rightarrow \langle \delta X_i \delta X_j \rangle = -k \left(\frac{\partial \langle X_i \rangle}{\partial F_j}\right)_{F_k, k \neq j} = -k \left(\frac{\partial \langle X_j \rangle}{\partial F_i}\right)_{F_k, k \neq i} = k \left(\frac{\partial^2 \hat{S}}{\partial F_i \partial F_j}\right)$$

1.8 **Examples**: 1) Consider the situation of example 1) in 1.2; $U \equiv \langle U \rangle$

$$\langle (\delta U)^2 \rangle = -k \left(\frac{\partial U}{\partial \left(\frac{1}{T}\right)}\right)_{V,N} = kT^2 \frac{\partial U}{\partial T} = kT^2 C_V$$

with $C_V = Nc_V$, c_V: specific heat per mole. Why to stress this? Because for a system of size N we have $U \sim \mathcal{O}(N)$ (extensive) $\Rightarrow$ fluctuations $\langle (\delta U)^2 \rangle^{1/2} = \mathcal{O}(\sqrt{N})$. (not true when $c_V \to \infty$ (at phase transition))

2) Situation of example 2 in 1.2.

$$\langle (\delta U)^2 \rangle = -k \left(\frac{\partial U}{\partial \left(\frac{1}{T}\right)}\right)_{-\frac{p}{T},N} = kT^2 \left(\frac{\partial U}{\partial T}\right)_{\frac{p}{T},N} = kT^2 \left(Nc_p - 2pV\alpha + \frac{p^2}{T} V \kappa_T\right)$$

$$\langle \delta U \cdot \delta V \rangle = -k \left(\frac{\partial V}{\partial \left(\frac{1}{T}\right)}\right)_{\frac{p}{T},N} = kT^2 \left(\frac{\partial V}{\partial T}\right)_{\frac{p}{T}} = VkT^2 \left(\alpha - \frac{p}{T}\kappa_T\right)$$

$$\langle (\delta V)^2 \rangle = -k \left(\frac{\partial V}{\partial \left(\frac{p}{T}\right)}\right)_{\frac{1}{T},N} = -kT \left(\frac{\partial V}{\partial p}\right)_{T,N} = VkT\kappa_T$$

with $c_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N}$ = specific heat at fixed pressure
$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N}$ = coeff. of thermal expansion
$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ = isothermal compressibility

(To prove the results use the relation $\left(\frac{\partial f}{\partial T}\right)_{\frac{p}{T}} = \left(\frac{\partial f}{\partial T}\right)_p + \frac{p}{T}\left(\frac{\partial f}{\partial p}\right)_T$ on $U = G + TS - pV$, $dG = -SdT + Vdp \Rightarrow \left(\frac{\partial U}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial T}\right)_p$ and $\left(\frac{\partial U}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T$)

1.9 **Higher moments** To calculate average values of products introduce the generating function

$$\left\langle \prod_{i=1}^{n} X_{j_i} \right\rangle = k^n \int dX_1 \cdots dX_r \left(\prod_{i=1}^{r} \frac{\partial}{\partial \lambda_{j_i}} \right) \exp \left\{ \frac{1}{k} \left[S(X_1, ..., X_r) - \sum_{i=1}^{r} (F_i - \lambda_i) X_i - \hat{S}(F_1, ..., F_r) \right] \right\}_{\lambda_i = 0} =$$

$$= k^n \left(\prod_{i=1}^{r} \frac{\partial}{\partial \lambda_{j_i}} \right) \int dX_1 \cdots dX_r \exp \left\{ \frac{1}{k} \left[S(X_1, ..., X_r) - \sum_{i=1}^{r} (F_i - \lambda_i) X_i - \hat{S}(F_1, ..., F_r) \right] \right\}_{\lambda_i = 0} =$$

$$= k^n \left(\prod_{i=1}^{r} \frac{\partial}{\partial \lambda_{j_i}} \right) \int dX_1 \cdots dX_r \exp \left\{ \frac{1}{k} \left[\hat{S}(F_1 - \lambda_1, ..., F_r - \lambda_r) - \hat{S}(F_1, ..., F_r) \right] \right\} \times$$

$$\times \exp \left\{ \frac{1}{k} \left[S(X_1, ..., X_r) - \sum_{i=1}^{r} (F_i - \lambda_i) X_i - \hat{S}(F_1 - \lambda_1, ..., F_r - \lambda_r) \right] \right\}_{\lambda_i = 0} =$$

$$= k^n \left(\prod_{i=1}^{r} \frac{\partial}{\partial \lambda_{j_i}} \right) \exp \left\{ \frac{1}{k} \left[\hat{S}(F_1 - \lambda_1, ..., F_r - \lambda_r) - \hat{S}(F_1, ..., F_r) \right] \right\}_{\lambda_i = 0} =$$

$$= \frac{k^n}{Z(0, ..., 0)} \left(\prod_{i=1}^{r} \frac{\partial}{\partial \lambda_{j_i}} \right) Z(\lambda_1, ..., \lambda_r)|_{\lambda_i = 0}$$

$Z(\lambda_1, ..., \lambda_r) = \exp \left\{ \frac{1}{k} \left[\hat{S}(F_1 - \lambda_1, ..., F_r - \lambda_r) - \hat{S}(F_1, ..., F_r) \right] \right\}$ is called the generating function of moments.

Example: $j_1 = 1,\ j_2 = 1,\ j_3 = 2 \Rightarrow \langle UUV \rangle = \frac{k^3}{Z(0)} \frac{\partial^3}{\partial \lambda_1^2 \lambda_2} Z(\lambda_1, \lambda_2, \lambda_3)|_{\lambda_i = 0}$.

1.10 **Cumulants** $\langle\langle \prod_{i=1}^{n} X_{j_i} \rangle\rangle$ are defined recursively by the formula

$$\left\langle \prod_{i=1}^{n} X_{j_i} \right\rangle =: \sum_{\mathcal{P}} \prod_{C \in \mathcal{P}} \left\langle \left\langle \prod_{i \in C} X_{j_i} \right\rangle \right\rangle$$

where $\mathcal{P} = (C, C', ...)$ runs over all partitions of $\{1, ..., n\}$ (Partitions: $\mathcal{P}_i^n := \{I \subseteq \{1, \ldots, n\}; |I| = i\}$, $\mathcal{P} = \mathcal{P}_n^n$).

Examples 1) Clearly we have $\langle X_i \rangle = \langle\langle X_i \rangle\rangle$ for one X_i.
2) For two X_i's we have $\langle X_i X_j \rangle = \langle\langle X_i \rangle\rangle \langle\langle X_j \rangle\rangle + \langle\langle X_i X_j \rangle\rangle$ such that $\langle\langle X_i X_j \rangle\rangle = \langle X_i X_j \rangle - \langle\langle X_i \rangle\rangle \langle\langle X_j \rangle\rangle = \langle X_i X_j \rangle - \langle X_i \rangle \langle X_j \rangle = \langle (X_i - \langle X_i \rangle)(X_j - \langle X_j \rangle) \rangle = \langle \delta X_i \delta X_j \rangle$
3) Higher cumulants are obtained recursively.

1.11 **Generating function for cumulants** Without proof we have

$$\left\langle \left\langle \prod_{i=1}^{n} X_{j_i} \right\rangle \right\rangle = k^{n-1} \left(\prod_{i=1}^{r} \frac{\partial}{\partial \lambda_{j_i}} \right) \left(\hat{S}(F_1 - \lambda_1, ..., F_r - \lambda_r) - \hat{S}(F_1, ..., F_r) \right)_{\lambda_i = 0}$$

In other words the generating function of cumulants is almost the logarithm of the generating function of moments.

Lecture 2

2.1 **Recap lecture 1** - Thermodynamic system characterized by extensive variables $X_1, X_2, ...$. Entropy $S = S(X_1, X_2, ...)$ concave. Intensive variables $F_i = \frac{\partial S}{\partial X_i} = F_i(X_1, X_2, ...)$.

- Legendre transformation: $F(T) = \inf_S(U(S) - TS)$
- Statistical mechanics: canonical partition function

$$Z(\beta) = \int dx e^{-\beta H(x)} = \int dU e^{-\beta U} \underbrace{\int dx \delta(H(x) - U)}_{\Sigma(U):\text{ microcan. part. fct.}}$$

- Equivalence of ensembles: diagram commutative for large systems
- System with fixed values of intensive parameters.
- Postulate: probability for $X_i \in dX_i$ is

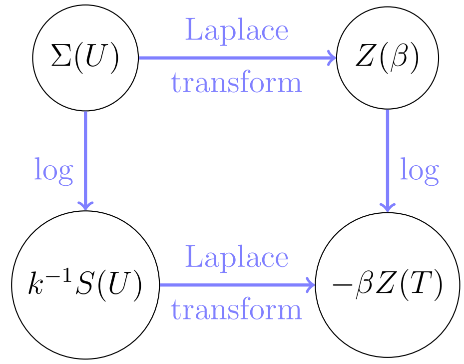


Figure: equivalence of ensembles.

$$W(X_1, ..., X_r)dX_1 \cdots dX_r = \exp\left\{\frac{1}{k}\left[S(X_1, ..., X_r) - \sum_{i=1}^{r} F_i X_i - \hat{S}(F_1, ..., F_r)\right]\right\}$$

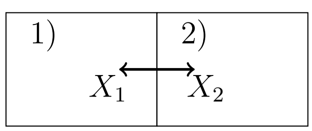
For large systems $\hat{S}$ is the LT of the entropy function, convex.

- Main results on fluctuations:

$$\langle \delta X_i \delta X_j \rangle = -k\left(\frac{\partial \langle X_i \rangle}{\partial F_j}\right)_{F_k, k\neq j} = -k\left(\frac{\partial \langle X_j \rangle}{\partial F_i}\right)_{F_k, k\neq i} = k\left(\frac{\partial^2 \hat{S}}{\partial F_i \partial F_j}\right)$$

Matrix $\frac{\partial^2 \hat{S}}{\partial F_i \partial F_j}$ is pos. semi-definite.

2.2 **Affinities and fluxes (1)**: discontinuous systems.



Assume 1) & 2) at TD equilibrium, but not mutually (at first). Can exchange ext. quantities X_k $(k = 1, ..., r)$. Set $r = 1$ and drop indices. But use index to denote system:

$$\text{index } 1, 2 \quad \Leftrightarrow \quad \text{system, subsystem :} \qquad X_1 + X_2 = X_0 \text{ fixed}$$

- Flux: $J = \frac{dX_2}{dt}$
- Entropy, dep. on split:

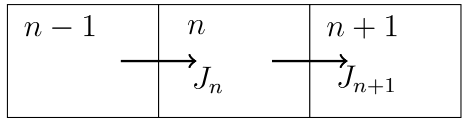
$$\frac{\partial}{\partial X_2}(S_1(X_1) + S_2(X_2)) = \frac{\partial}{\partial X_2}(S_1(X_0 - X_2) + S_2(X_2)) = -F_1 + F_2 : \text{ affinity}$$

- Equilibrium $\Leftrightarrow$ maximal entropy $\Leftrightarrow$ no affinity $(\delta S = 0)$ $\Leftrightarrow$ no fluxes (no change in time)
- Entropy production

$$\dot{S} = \frac{d}{dt}(S_1(X_1) + S_2(X_2)) = (F_2 - F_1)J$$

Example: 1) $X = U$, $F = 1/T$, $J =$ energy flux, $\dot{S} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right) J$.

2.3 **Affinities and fluxes (2)**: cells of equal volume.



- rate of change of X in cell n:

$$\frac{dX_n}{dt} = J_n - J_{n+1}$$

- rate of production of X at boundary n: 0 (X is not produced, X is exchanged)
- rate of change in entropy in cell n:

$$\frac{dS_n}{dt} = \frac{\partial S}{\partial X_n}(J_n - J_{n+1}) = F_n(J_n - J_{n+1})$$

- rate of production of entropy at boundary

$$\dot{S}_n = \left(\frac{\partial S}{\partial X_n} - \frac{\partial S}{\partial X_{n-1}}\right) J_n = (F_n - F_{n-1})J_n \qquad \left(\neq \frac{dS}{dt}\right)$$

- entropy flux through cell n

$$J_{S,n} = F_n J_n$$

$$\Rightarrow \quad \frac{dS_n}{dt} = \underbrace{(F_{n+1} - F_n)J_{n+1}}_{\dot{S}_{n+1}} - F_{n+1}J_{n+1} + F_n J_n = \dot{S}_{n+1} - (J_{S,n+1} - J_{S,n})$$

$\Rightarrow$ rate of change: production + transport: $\displaystyle\sum_n \frac{dS_n}{dt} = \sum_n \dot{S}_n$

2.4 **Affinities and fluxes (3)**: continuum limit: replace $n \mapsto x$ and $(n+1) - n \mapsto dx$, $X_n \mapsto X(x)dx$, $\frac{dX_n}{dt} \mapsto \frac{\partial X}{\partial t}dx$, $J_{n+1} - J_n \mapsto \nabla J(x)dx$, $S_n \mapsto S(x)dx$, $F_n \mapsto F(x)$, $F_n - F_{n-1} \mapsto \nabla F(x)dx$, where $X(x)$ = density, $J(x)$ = flux density and $S(x)$ = entropy density. Then

$$0 = \frac{\partial X}{\partial t} + \nabla J \quad \text{(cont. eq.)} \qquad \dot{S} = \frac{\partial S}{\partial t} + \nabla J_S$$

with
$\dot{S} = \nabla F \cdot J$ = entropy production
$\frac{\partial S}{\partial t} = -F\nabla J$ = rate of change of entropy
$J_S = F \cdot J$ = entropy flux

After reinserting indices:
$\dot{S} = \sum_{k=1}^r \nabla F_k \cdot J_k$
$\frac{\partial S}{\partial t} = -\sum_{k=1}^r F_k \nabla J_k$
$J_S = \sum_{k=1}^r F_k J_k$

2.5 **Remarks**: 1) In the steady state ($\frac{\partial X_i}{\partial t} = 0$): $\frac{\partial S}{\partial t} = 0$ but $\dot{S} \neq 0$ in general
2) Heat flux J_Q ($dS = \frac{\delta Q}{T}$) $\Rightarrow J_S = \frac{J_Q}{T}$. In the steady state $\dot{S} = \nabla J_S = \nabla\left(\frac{1}{T}\right) J_Q + \frac{1}{T}\nabla J_Q$ (1st term: "heat transfer from hot to cold"; 2nd term: "heat source at temperature T)

2.6 **Markov processes** Fluxes J_k depend instantaneously and locally on affinities $\mathcal{F}_i = \nabla F_i$:

$$J_k = J_k(\mathcal{F}_1, ..., \mathcal{F}_r, F_1, ..., F_r)$$

Process is linear if moreover $J_k = \sum_j L_{kj}\mathcal{F}_j$ with $L_{kj} = L_{kj}(F_1, ..., F_r)$.

Example: $X = U$, $F = \frac{1}{T}$. Fourier's law: $J_U = -\kappa \nabla T$. This may be written as $J_S = \kappa T^2 \nabla \left(\frac{1}{T}\right)$ $\Rightarrow L_{UU} = \kappa T^2$.

2.7 **Onsager relations** For time-reversal invariant systems (in the microscopic sense)

$$L_{kj}(F_1, F_2, ...) = L_{jk}(F_1, F_2, ...)$$

(Onsager, 1931). More generally: under time-reversal $\tilde{\cdot}$ two types of behaviour:

$$X_i \mapsto \tilde{X}_i = \begin{cases} X_i & \text{(e.g. } U, V, N, ...) \\ -X_i & \text{(e.g. M=magnetisation,...)} \end{cases}$$

Accordingly

$$F_i \mapsto \tilde{F}_i = \begin{cases} F_i & \text{(e.g. } \frac{1}{T}, \frac{p}{T}, -\frac{\mu}{T} ...) \\ -F_i & \text{(e.g. } -\frac{H}{T}, ...) \end{cases}$$

(in fact: $S \mapsto \tilde{S} = S$, $dS \mapsto d\tilde{S} = dS$ for irreversible processes, $dS = \sum_i F_i dX_i$. Thus if X_i changes also F_i has to change, since dS does not change)

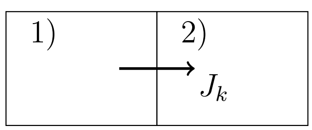
Then

$$L_{kj}(F_1, F_2, ...) = \pm L_{jk}(\tilde{F}_1, \tilde{F}_2, ...)$$

with $\pm$ for kj of same/opposite type.

Example: $L_{UV}(H) = L_{VU}(-H)$ since $\tilde{V} = V$ and $\tilde{U} = U$ (same type).

2.8 **Origin of the Onsager relations** Situation (1).



A linear process has J_k = linear answer to affinity $= L_{kj}(F_j^{(2)} - F_j^{(1)})$. At equilibrium: $\langle J_k \rangle = 0$.

Hypothesis: if there is a fluctuation $\delta X_k \neq 0$, and hence $F_j(X_1, ..., X_r) = F_j$, then $J_k = \sum_j L_{kj}(F_j(X_1, ..., X_r) - F_j)$ ("fluxes due to spontaneous fluctuations obey same law as if due to an imposed affinity")

Side computation: from $\frac{\partial W}{\partial X_j} = \frac{1}{k}(F_j(X_1, ..., X_r) - F_j)W = \delta F_j W$

$$\begin{aligned} \langle \delta X_i \delta F_j \rangle &= \int \delta X_i \delta F_j W dX_1 \cdots dX_r = k \int \delta X_i \frac{\partial W}{\partial X_j} dX_1 \cdots dX_r \\ &= -k \int \frac{\partial \delta X_i}{\partial X_j} W dX_1 \cdots dX_r = -k \delta_{ij} \end{aligned}$$

System time-reversal invariant with + type obs's: $X_i \mapsto \tilde{X}_i = X_i$. It follows

$$\langle \delta X_i \delta X_j(t) \rangle = \langle \delta X_i \delta X_j(-t) \rangle = \langle \delta X_i(t) \delta X_j \rangle \qquad \text{(time-reversal + stationarity).}$$

Divide by t and let $t \to 0$:

$$\left\langle \delta \dot{X}_i \delta X_j \right\rangle = \left\langle \delta X_i \delta \dot{X}_j \right\rangle \quad \Rightarrow \quad \sum_k L_{jk} \langle \delta X_i \delta F_k \rangle = \sum_k L_{ik} \langle \delta F_i \delta X_j \rangle \quad \Rightarrow \quad L_{ji} = L_{ij}.$$

Lecture 3

3.1 **Recap lecture 2** - Extensive quantities X_i, $i = 1, ..., r$. Densities:

- $X_i(x,t)$ ($i = 1, ..., r$ density of extensive quantities)
- $J_i(x,t)$ (density flux)
- $S(x,t)$ (entropy density)
- $F_i(x,t)$ (associated conj. intensive quantities)
- $\frac{\partial S}{\partial t} = \sum_i F_i \frac{\partial X_i}{\partial t}$ (change of entropy)
- $J_S = \sum_i F_i J_i$ (entropy flux)
- $\dot{S} = \sum (\nabla F_i) J_i$ (entropy production)

- Relations between quantities: $\quad 0 = \frac{\partial X_i}{\partial t} + \nabla J_i; \qquad \dot{S} = \frac{\partial S}{\partial t} + \nabla J_S$

- Linear Markov processes: $\quad J_k = \sum_j L_{kj} \nabla F_j \qquad (\nabla F_j = \mathcal{F}_j$: affinity), $\quad L_{kj} = L_{kj}(F_1, ..., F_r)$

- Onsager reciprocity relations: for time-reversal invariant systems (and observables X_i)

$$L_{kj} = L_{jk}$$

3.2 **Application:** Entropy production:

$$\dot{S} = \sum_{kj} \nabla F_k \underbrace{L_{kj} \nabla F_j}_{=J_k} \geq 0$$

(from 2nd law) $\Rightarrow L_{kj}$ is positive semi-definite

3.3 **Variational principle (minimum entropy production, Prigogine, 1947)**: consider time-reversal invariant system occupying Ω and fields $F_i(x)$ ($x \in \Omega$), with

(i) $L_{kj}(F_1, ..., F_r) \equiv L_{kj}$ constant, independent of F_i $i = 1, ..., r$ (doubtful: $r = 1$, $X = U \Rightarrow L_{UU} = \kappa(T)T^2$)

(ii) $F_j(x)$ prescribed on $\partial\Omega$ or no flux: $J_k \cdot d\sigma = 0$

Then the entropy production

$$P := \int_\Omega \dot{S} d^n x = \sum_k \int_\Omega \nabla F_k \cdot J_k d^n x$$

is minimal among all fields F_i with (ii) iff $F_i(x)$ is the stationary distribution ($\frac{\partial X_i}{\partial t} = 0$); moreover, in general, $\frac{\partial P}{\partial t} \leq 0$, i.e. $P(t) \geq P_{stat} \overset{(\dot{S} \geq 0 \text{ seen before})}{\geq} 0$.

3.4 **Proof**: Variation of P:

$$\delta P = \sum_k \int_\Omega \left(\nabla \delta F_k \cdot J_k + \nabla F_k \cdot \delta J_k \right) d^n x \overset{\text{Onsager}}{=} 2 \sum_k \int_\Omega \nabla \delta F_k \cdot J_k d^n x$$

$$= \sum_k \left(\int_{\partial\Omega} \underbrace{\delta F_k}_{=0 \text{ or}} \underbrace{J_k}_{=0} d\sigma - \int_\Omega \delta F_k \nabla J_k d^n x \right) \overset{\text{(ii)}}{=} - \sum_k \int_\Omega \delta F_k \underbrace{\nabla J_k}_{= -\frac{\partial X_k}{\partial t}} d^n x$$

Thus $\qquad \delta P = 0 \quad \text{for all} \quad \delta F_i \quad \Longleftrightarrow \quad \frac{\partial X_k}{\partial t} = 0 \quad \forall k$

Moreover, for $\quad \delta F_i = \frac{\partial F_i}{\partial t}\delta t, \quad \delta P = \frac{\partial P}{\partial t}\delta t, \quad X_k = X_k(F_1, ..., F_r)$

$$\frac{\partial P}{\partial t} = 2\sum_k \int_\Omega \frac{\partial F_k}{\partial t}\frac{\partial X_i}{\partial t} = 2\sum_{kl}\int_\Omega \frac{\partial F_k}{\partial t}\left(\frac{\partial X_k}{\partial F_l}\right)_{F_i,(i\neq l)}\frac{\partial F_l}{\partial t} = 2\sum_{kl}\int_\Omega \frac{\partial F_k}{\partial t}\left(-\underbrace{\frac{\partial^2 \hat{S}}{\partial F_l \partial F_k}}_{\geq 0}\right)\frac{\partial F_l}{\partial t} \leq 0$$

Note: $\qquad \delta^2 P = 2\sum_{kj} \nabla \delta F_k \underbrace{L_{kj}}_{\geq 0} \nabla \delta F_j \geq 0 \quad \Rightarrow \quad \text{minimum} \qquad \square$

3.5 **Transformation properties of fluxes and affinities** Recall: $J_j = \sum_k L_{jk}\mathcal{F}_k$ ($\mathcal{F}_j = \nabla F_j$). Linear transformation of differentials:

$$\delta X_i' = \sum_j a_{ij}(F_1, ..., F_r)dX_j \qquad F_i' = \sum_j b_{ij}(F_1, ..., F_r)F_j$$

Then $dS = \sum_j F_j dX_j = \sum_j F_j' dX_j'$ if the two transformations are contragradient i.e. $B = \left(A^T\right)^{-1}$.
Correspondingly:

- $J_i' := \sum_j a_{ij}J_j$ ($\Rightarrow \nabla J_i' \neq \sum_j a_{ij}\nabla J_j$, no continuity equation for $'$ quantities)
- $\mathcal{F}_i' = \sum_j b_{ij}\mathcal{F}_j$ ($\neq \nabla F_i' := \nabla\left(\sum_j b_{ij}F_j\right)$)

Then $J_k' = \sum_j L_{ij}'\mathcal{F}_j'$ with $L' = ALB^{-1} = ALA^T \Rightarrow L'^T = L'$ is inherited.

3.6 **Example**: extensive variables U, N. Fluxes J_N, J_U: $dS = -\frac{\mu}{T}dN + \frac{1}{T}dU$. Instead want to have $J_N, J_Q = TJ_S = -\mu J_N + J_U$. In matrix form

$$\begin{pmatrix} J_N \\ J_Q \end{pmatrix} = A\begin{pmatrix} J_N \\ J_U \end{pmatrix} \qquad \text{with} \qquad A = \begin{pmatrix} 1 & 0 \\ -\mu & 1 \end{pmatrix}, \qquad (A^T)^{-1} = \begin{pmatrix} 1 & \mu \\ 0 & 1 \end{pmatrix}$$

Affinities: $\qquad (A^T)^{-1}\begin{pmatrix} -\nabla\left(\frac{\mu}{T}\right) \\ \nabla\left(\frac{1}{T}\right) \end{pmatrix} = \begin{pmatrix} -\nabla(\frac{\mu}{T}) + \mu\nabla(\frac{1}{T}) \\ \nabla(\frac{1}{T}) \end{pmatrix} = \begin{pmatrix} -\frac{\nabla\mu}{T} \\ \nabla(\frac{1}{T}) \end{pmatrix}$

$\Rightarrow \quad J_N = L_{NN}\left(-\frac{\nabla\mu}{T}\right) + L_{NQ}\nabla\left(\frac{1}{T}\right)$ and $J_Q = L_{QN}\left(-\frac{\nabla\mu}{T}\right) + L_{QQ}\nabla\left(\frac{1}{T}\right)$ Here: $L_{NQ} = L_{QN}$.

3.7 Electric, thermal and thermoelectric effects. Consider a wire with

- electric current
- heat current

Need 4 effects (experiments) to identify the coefficients L_{ij}. Onsager relation $L_{UN} = L_{NU}$ makes a prediction. N = number of electrons; $\mu = \mu_0 + e\phi$ electrochemical potential (μ_0: chemical potential, ϕ: electric potential); $\rho = \rho(\mu_0, T)$: density, fixed by neutrality $\Rightarrow$ (i) $\frac{\partial N}{\partial t} + \nabla \cdot J_N = \nabla \cdot J_N = 0$; (ii) $\mu_0 = \mu_0(T)$; (iii) $L_{ij} = L_{ij}(\mu_0, T) = L_{ij}(T)$

Remark: J_Q is heat flux between parts of wire; does not include flux to any thermostat needed to keep T constant in time. Energy production (accumulation) $\frac{\partial U}{\partial t} = -\nabla J_U$, $J_U = J_Q + \mu J_N$ $J_Q = \frac{L_{QN}}{LNN}J_N$ and hence $\nabla J_U = \left(\frac{L_{QN}}{L_{NN}} + \mu\right)\nabla J_N + \nabla\mu J_N \Rightarrow \frac{\partial U}{\partial t} = -\nabla\mu \cdot J_N = \frac{T}{L_{NN}}J_N^2 = \frac{e^2}{\sigma}J_N^2$ (Joule heat)

Lecture 4

4.1 **Recap lecture 3**: - System with extensive variables N, U (fluxes J_N, J_U; affinities $-\nabla\frac{\mu}{T}$, $-\nabla\frac{1}{T}$). Instead J_N and $J_Q = J_U - \mu J_N$
- Fluxes proportional to affinities

$$J_N = L_{NN}\left(-\frac{\nabla\mu}{T}\right) + L_{NQ}\nabla\frac{1}{T}$$
$$J_Q = L_{QN}\left(-\frac{\nabla\mu}{T}\right) + L_{QQ}\nabla\frac{1}{T}$$

- Onsager relations:

$$L_{NU} = L_{UN}$$

- Thermoelectricity: N = number of electrons $\quad \mu = \mu_0 + e\varphi$
- Neutrality: i) $\nabla J_N = 0$, ii) $\mu_0 = \mu_0(T)$, iii) $L_{ij} = L_{ij}(T)$.

4.2 **Isothermal electric conductivity** σ: T = const, $\nabla\mu = e\nabla\phi$, since $\nabla\mu_0 = 0$, T = const.

Phenomenologically: $\quad eJ_N = \sigma(-\nabla\phi), \quad \sigma$: conductivity

Comparison: $\quad J_N = -\frac{LNN}{T}\nabla\mu \quad \Rightarrow \quad \sigma = e^2\frac{LNN}{T}$

Energy accumulation in the wire: $\quad \frac{\partial U}{\partial t} = \nabla\cdot J_U = \frac{e^2}{\sigma}J_N^2 = \frac{T}{L_{NN}}J_N^2 \quad$ (Joule heat).

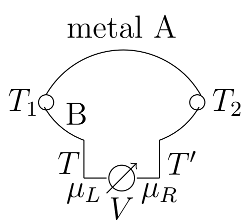
4.3 **Heat conductivity** κ: Temperature gradient $T = T(x)$, no current $J_N = 0$.

Phenomenologically: $\quad J_Q = -\kappa\nabla T, \quad$ (Fourier's law)

$$J_N = 0 \quad \Rightarrow \quad \frac{\nabla\mu}{T} = \frac{L_{NQ}}{L_{NN}}\nabla\frac{1}{T} \quad J_Q = \left(-\frac{L_{QN}L_{NQ}}{L_{NN}} + L_{QQ}\right)\nabla\frac{1}{T} \quad \Rightarrow \quad \kappa = \frac{\det L}{L_{NN}T^2}$$

Energy accumulation: $\quad \frac{\partial U}{\partial t} = \nabla\cdot J_U = \nabla(\kappa\nabla T), \qquad$ where we used $J_U = J_Q + \mu J_N = J_U$

4.4 **Seebeck effect**: voltage, but no current J_N.



Phenomenon: difference in temperature $T_2 - T_1$ induces potential difference $eV = \mu_R - \mu_L$. $\varepsilon_{AB} = \frac{\partial V}{\partial T_2}$ (Seebeck coefficient or relative "termopower").

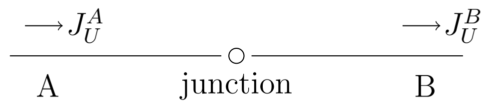
$J_N = 0$:

$$\nabla\mu = -\frac{L_{NQ}}{L_{NN}}\frac{\nabla T}{T} \quad \Rightarrow \quad V = \frac{1}{e}\int_{\text{path}}\nabla\mu\cdot ds = -\frac{1}{e}\int_{T_1}^{T_2}\frac{L_{NQ}}{L_{NN}}\bigg|_B^A\frac{dT}{T}$$

$\Rightarrow \varepsilon_{AB} = \varepsilon_B - \varepsilon_A$ with $\varepsilon_A = \frac{L_{NQ}^{(A)}}{eTL_{NN}^{(A)}}$ (absolute "termopower")

4.5 **Peltier effect**:

Phenomenon: isothermal junction, current $eJ_N \Rightarrow$ energy is accumulated at junction: Peltier coefficient: $\Pi_{AB} = -\frac{J_U|_B^A}{J_N}$.



μ, J_N continuous at junction (because of neutrality), $T = \text{const.}$

$$J_U|_B^A = J_Q|_B^A = \frac{L_{QN}}{L_{NN}}\Big|_B^A J_N$$

(Interpretation: $\frac{L_{QN}}{L_{NN}}$ = heat transported per carried electron). Given that $L_{QN} = L_{NQ}$, then $\Pi_{AB} = T(\varepsilon_B - \varepsilon_A)$ (2nd Kelvin relation, 1854, empirical). Interpretation: $e\varepsilon_A$ = entropy per carried electron.

4.6 **Thomson effect**:

Phenomenon: (a) temperature $T(x)$

(b) current $eJ_N \Rightarrow$ energy accumulation is more (or less) than the sum of each case alone.

$$\frac{\partial U}{\partial t} = \underbrace{\frac{e^2}{\sigma}J^2}_{\text{(b)}} + \underbrace{\nabla(\kappa\nabla T)}_{\text{(a)}} - \underbrace{H}_{\text{Thomson Heat}}$$

with Thomson heat (absorbed heat by the metal, thus minus sign):

$$H = \tau\nabla T \cdot eJ_N \qquad \tau: \text{ Thomson coefficient}$$

($\tau > 0$: Cu, Sn, Ag, Cd, Zn, ... $\tau < 0$: Fe, Co, Bi, Pt, Hg, ...)

$$\nabla\mu = \frac{L_{NQ}}{L_{NN}}\frac{\nabla T}{T} - \frac{T}{L_{NN}}J_N \qquad J_Q = \frac{\det L}{L_{NN}T^2}\nabla T + \frac{L_{NQ}}{L_{NN}}J_N$$

$$\begin{aligned}\Rightarrow \quad \frac{\partial U}{\partial t} &= -\nabla\cdot J_U = -(\nabla\cdot J_Q + (\nabla\mu)\cdot J_N)\\ &= -\left[\nabla\left(\frac{\det L}{L_{NN}T^2}\nabla T\right) + \nabla\left(\frac{L_{QN}}{L_{NN}}J_N\right) - \frac{L_{NQ}}{L_{NN}}\frac{\nabla T}{T}J_N - \frac{T}{L_{NN}}J_N^2\right]\end{aligned}$$

After identifying terms:

$$H = \left(\nabla\left(\frac{L_{QN}}{L_{NN}}\right) - \frac{L_{NQ}}{L_{NN}}\frac{\nabla T}{T}\right)J_N = T\nabla\left(\frac{L_{NQ}}{eL_{NN}}\frac{1}{T}\right) = T\frac{d\varepsilon}{dT}\nabla T\cdot eJ_N \quad \Rightarrow \quad \tau = T\frac{d\varepsilon}{dT}$$

4.7 **Remark**: $\frac{d\Pi_{AB}}{dT} = \varepsilon_B - \varepsilon_A + \tau_B - \tau_A$ (1st Kelvin relation: involves three effects, no need of Onsager relations).

Part II

Statistical mechanics of linear response

Lecture 5

5.1 Consider a quantum system with Hamiltonian H_0, mechanically perturbed

$$H(t) = H_0 + H_I(t) \qquad \text{with} \qquad H_I(t) = -X(t)A$$

$X(t)$: prescribed "force", $X(t) \to 0$ $(t \to -\infty)$ $(X \in \mathbb{R})$
A: "displacement" (A is an operator)

Examples: 1) Particle perturbed by a force $H_I(t) = -\vec{F}(t) \cdot \vec{x}$ (A is the position operator)
2) Atom in magnetic field $H_I(t) = -\frac{e\hbar}{2mc}\vec{B}(t) \cdot (\vec{L} + 2\vec{S})$ (A is angular momentum operator)
3) System open to a particle reservoir with chemical potential $\mu(t)$: $H_I(t) = -\mu(t)N$ (A is the particle number operator)

5.2 State initially $(t \to -\infty)$ in equilibrium state ρ_0: $[H_0, \rho_0] = 0$. This means $\rho_0 = e^{iH_0t/\hbar}\rho_0 e^{-iH_0t/\hbar}$ e.g. thermal state.

Time evolution of $\rho(t)$ under $H(t)$: $\qquad i\hbar\dot{\rho} = [H(t), \rho(t)]$

Let $B = B^*$ be any observable. With $\langle B \rangle_\rho = tr(\rho B)$ we denote $\Delta B(t) = \langle B \rangle_{\rho(t)} - \langle B \rangle_{\rho_0}$.To first order in $X(T)$: dynamic response:

$$\Delta B(t) = \int_{-\infty}^{t} \chi(t-s)X(s)ds \qquad \chi(t): \text{ isolated susceptibility.}$$

Properties: 1) causality
2) dissipativity

5.3 **Remark**: 2nd term my be omitted. Just consider $B - \langle B \rangle_{\rho_0}$ instead of B
Scheme does not allow for thermal perturbations (e.g. reservoirs at different temperatures or temperature gradients)

5.4 **Causality**:

$$\Delta B(t) = \int_{-\infty}^{\infty} \chi(t-s)X(s)ds, \qquad \text{with } \chi(t) = 0 \text{ for } t < 0 \text{ (causality)}$$

Fourier transform

$$\hat{\chi}(\omega) = \int \chi(t)e^{i\omega t} \qquad \omega \in \mathbb{R}$$

Note: $\chi(t)$ is real (as expectation value of a self-adjoint operator) but $\bar{\hat{\chi}} = \hat{\chi}(-\omega)$ i.e. $\text{Re}\hat{\chi}(\omega) = \text{Re}\hat{\chi}(-\omega)$ (even) and $\text{Im}\hat{\chi}(\omega) = -\text{Im}\hat{\chi}(-\omega)$ (odd).

Example: 1) For $X(t) = \delta(t)$ we have $\Delta B = \chi(t)$: response to a pulse.
2) For $X(t) = e^{-i\omega t}$ we have $\Delta B(t) = \int_{-\infty}^{t} \chi(t-s)X(s)ds = \hat{\chi}(\omega)e^{-i\omega t}$: $\hat{\chi}(\omega)$ is response to harmonic driving; $\hat{\chi}(0)$: static susceptibility (const. driving).

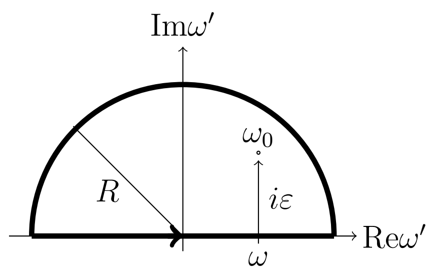
5.5 **Properties**: 1) $\hat{\chi}$ has an analytic extension in $\text{Im}\omega > 0$, continuous up to $\text{Im}\omega = 0$
2) $\hat{\chi}(\omega) \to 0$ as $\omega \to \infty$ in $\text{Im}\omega \geq 0$.

Proof: 1) $\hat{\chi}(\omega) = \int_0^\infty ..;$ $e^{i\omega t} = e^{i\text{Re}\omega t}e^{-\text{Im}\omega t}$, i.e $|e^{i\omega t}| \leq 1$ for $\text{Im}\omega \geq 0 \Rightarrow \hat{\chi}(\omega)$ is absolutely convergent. 2) By Riemann-Lebesgue lemma. $\square$

5.6 **Dispersion relations (Kramers-Kronig)**: For $\omega > 0$

$$\mathrm{Im}\hat{\chi}(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\mathrm{Re}\hat{\chi}(\omega')}{\omega'^2 - \omega^2} d\omega'$$
$$\mathrm{Re}\hat{\chi}(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \mathrm{Im}\hat{\chi}(\omega')}{\omega'^2 - \omega^2} d\omega'$$

5.7 **Proof Kramers-Kronig relations**: Use Cauchy formula



Let $\omega_0 = \omega + i\varepsilon$

- semicircle does not contribute as $R \to \infty$
- $x = \omega' - \omega$: use $\lim_{\varepsilon \downarrow 0} \frac{1}{x - i\varepsilon} = \mathcal{P}\frac{1}{x} + i\pi\delta(x)$.

$$\hat{\chi}(\omega) = \lim_{\varepsilon \downarrow 0} \frac{1}{2\pi i} \int \frac{\hat{\chi}(\omega')}{\omega' - \omega - i\varepsilon} d\omega' = \frac{1}{2\pi i} \left(\mathcal{P} \int_{-\infty}^\infty \frac{\hat{\chi}(\omega')}{\omega' - \omega} d\omega' + i\pi \hat{\chi}(\omega) \right)$$

$\Rightarrow \quad \frac{1}{2}\hat{\chi}(\omega) = \frac{1}{2\pi i} \mathcal{P} \int_{-\infty}^\infty \frac{\hat{\chi}(\omega')}{\omega' - \omega} d\omega'$ & separate integral using symmetries of Re(..) and Im(..) $\square$

5.8 **Dissipativity**: a property of $\hat{\chi}(\omega)$ in the particular case where $A = B$ (ρ_0: thermal state).
Energy increase

$$\langle H(t) \rangle_{\rho(t)} = \frac{d}{dt} \mathrm{tr}(H(t)\rho(t)) = \mathrm{tr}(\dot{H}(t)\rho(t)) + \mathrm{tr}(H(t)\dot{\rho}(t))$$

(1st term: work done, 2nd term: heat). Here 2nd term is 0, because $i\hbar \mathrm{tr}(H\dot{\rho}) = \mathrm{tr}(H[H, \rho]) = 0$
Work done: ($\dot{H} = -\dot{X}A$) let $X(t) \to 0$ as $t \to \pm\infty$

$$W = \int_{-\infty}^\infty dt \left\langle \dot{H} \right\rangle_{\rho(t)} = -\int_{-\infty}^\infty \dot{X}(t) (\langle A \rangle_{\rho(t)} - \langle A \rangle_{\rho_0}) dt = -\int_{-\infty}^\infty \int_{-\infty}^\infty \dot{X}(t) \chi(t-s) \chi(t) ds dt$$

Dissipativity: $W \geq 0$ (2nd law)

5.9 **Consequences**: 1) static susceptibility $\hat{\chi}(0) \geq 0$
2) $\mathrm{Im}\hat{\chi}(\omega) \geq 0$ ($\omega > 0$).

Proof: After integration by parts

$$W = \int_{-\infty}^\infty X(t) \frac{d}{dt} \langle A \rangle_{\rho(t)}$$

1) With $\chi(t) = \theta(t)(\cdot e^{-\epsilon t}, \epsilon \to 0)$

$$\langle A \rangle_{\rho(t)} = \int_{-\infty}^\infty \theta(s) \chi(t-s) ds = \int_{-\infty}^t \chi(\tau) d\tau \quad \Rightarrow \quad \frac{d}{dt} \langle A \rangle_{\rho(t)} = \chi(t)$$

$$\Rightarrow \quad 0 \leq W = \int_0^\infty \chi(t) dt = \int_{-\infty}^\infty \chi(t) dt = \hat{\chi}(0)$$

2) $\langle A\rangle_{\rho(t)})dt = -\int_{-\infty}^{\infty}\chi(t-s)X(s)ds = \int d\omega ds\chi(t-s)\hat{X}(\omega)e^{-i\omega s}e^{i\omega t}e^{-i\omega t} = \int d\omega\hat{\chi}(\omega)\hat{X}(\omega)e^{-i\omega t}$.
Parseval:

$$W = \frac{1}{2\pi}\int_{-\infty}^{\infty}(-i\omega)\hat{\chi}(\omega)|\hat{X}(\omega)|^2 d\omega = \frac{1}{\pi}\int_0^{\infty}\omega\mathrm{Im}\hat{\chi}(\omega)|\hat{X}(\omega)|^2 d\omega$$

requires $Im\hat{\chi}(\omega)$ to be non negative. □

5.10 **Kubo formula**: Solve von Neumann equation

$$i\hbar\dot{\rho} = [H(t), \rho(t)]$$

with initial condition $\rho(t)\to\rho_0$ as $t\to-\infty$.
Interaction picture: $\tilde{\rho}(t) = e^{iH_0t/\hbar}\rho(t)e^{-iH_0t/\hbar}$ and $\tilde{H}_I = e^{iH_0t/\hbar}H_I(t)e^{-iH_0t/\hbar}$

$$\Rightarrow i\hbar\dot{\tilde{\rho}}(t) = e^{iH_0t/\hbar}([H_0,\rho(t)] + [H(t),\rho(t)])e^{-iH_0t/\hbar} = [\tilde{H}_I(t),\tilde{\rho}(t)]$$

with $\tilde{\rho}(t)\to\rho_0$ as $t\to-\infty$ (since ρ_0 is an equilibrium state).

$$\tilde{\rho}(t) = \rho_0 - \frac{i}{\hbar}\int_{-\infty}^{t}[\tilde{H}_I(s),\tilde{\rho}(s)]ds = \rho_0 - \frac{i}{\hbar}\int_{-\infty}^{t}e^{-iH_0(t-s)/\hbar}[H_I(s),\rho(s)]e^{iH_0(t-s)/\hbar}ds$$

where we used $\tilde{\rho} = \rho_0 + \mathcal{O}(X)$ (only linear response). Thus we get

$$\Delta\langle B\rangle_t = \int_{-\infty}^{t}\mathrm{tr}(B(t-s)\frac{i}{\hbar}[A,\rho_0]X(s))ds$$

Hence

$$\chi_{BA}(t) = \frac{i}{\hbar}\mathrm{tr}(B(t)[A,\rho_0])\theta(t) = \frac{i}{\hbar}\mathrm{tr}([B(t),A]\rho_0])\theta(t)$$

(Kubo formula: expresses linear response in terms of the unperturbed system) (use $[A,B\rho] = B[A,\rho] + [A,B]\rho$ to rewrite last term)

5.11 **Remarks**: 1) $\chi(t)$ is real. In fact, $\overline{\mathrm{tr}A} = \mathrm{tr}\ A^*$ (since $\overline{\langle\phi|A|\phi\rangle} = \langle\phi|A^*|\phi\rangle$). Thus

$$\overline{\mathrm{tr}([B(t),A(t)]\rho_0)} = \mathrm{tr}(\rho_0[A,B(t)]) = -\mathrm{tr}([B(t),A]\rho_0)$$

2) Symmetry: In $J_i = L_{ij}\nabla F_j$: J_i flux of X_i.
Consider B's which are fluxes $B = \frac{i}{\hbar}[H_0,\tilde{A}]$ (B is rate of change of $\tilde{A}$)

$$L_{\tilde{A}A}(t) = \chi_{BA}(t) = \frac{1}{\hbar^2}\mathrm{tr}([[\tilde{A}(t),H_0],A]\rho_0) = \frac{1}{\hbar^2}\mathrm{tr}([[A,H_0],\tilde{A}]\rho_0)$$

where we used the Jacobi identity and $\mathrm{tr}[[A,\tilde{A}],H_0]\rho_0 = \mathrm{tr}[[A,\tilde{A}]\rho_0,H_0] = 0$.

5.12 **Lemma (Klein)**: f convex, $A = A^*$, $B = B^*$ then

$$\mathrm{tr}f(B) \geq \mathrm{tr}f(A) + \mathrm{tr}f'(A)(B-A)$$

Application: for $f(x) = x\log x$, $f'(x) = 1 + \log x$:

$$\mathrm{tr}B\log(B) \geq \mathrm{tr}A\log(A) + \mathrm{tr}(B-A) + \mathrm{tr}(B-A)\log(A) = \mathrm{tr}(B\log(A) + B - A)$$

5.13 **Application**: $H(\alpha)$ with α = work-coordinate, $\alpha = \alpha(t)$ $(0 \leq t \leq T)$, $\alpha(0) = \alpha(T)$, $H = H(\alpha(0)) = H(\alpha(T))$.

Evolution from $t = 0$ to $t = T$: U unitary.

Initial state: ρ.

Work done (= energy accumulation in expectation):

$$\Delta E = \operatorname{tr}(HU\rho U^*) - \operatorname{tr}(H\rho)$$

2nd law: If ρ is a thermal state, i.e. $\rho = e^{-\beta H}/Z$ then

$$\Delta E \geq 0$$

5.14 **Proof**: Take logarithm: $-\beta H = \log\rho + \log Z$. Then

$$\beta\Delta E \overset{\operatorname{tr}\rho=1}{=} \operatorname{tr}(\rho\log\rho) - \operatorname{tr}(U\rho U^*\log\rho) \overset{U^*\log\rho U = \log(U^*\rho U)}{=} \operatorname{tr}(\rho\log\rho) - \operatorname{tr}(\rho\log(U^*\rho U)) \overset{\text{Klein}}{\geq} \operatorname{tr}(\rho - U^*\rho U) = 0$$

Lecture 6

6.1 **Recap Lecture 5**: Statistical mechanics of linear response:

- $H(t) = H_0 - X(t) \cdot A$ with $X \in \mathbb{R}$ and A operator.
- $\rho(t) \to \rho_0$ equilibrium state ($t \to -\infty$)
- Dynamic response

$$\Delta \langle B \rangle_t = \int_{-\infty}^{\infty} ds \chi_{BA}(t-s) X(s)$$

- Kubo formula

$$\chi_{BA}(t) = \frac{i}{\hbar} \text{tr}(B(t)[A, \rho_0])\theta(t) \overset{\text{tr}[A, B\rho_0]=0}{=} \frac{i}{\hbar} \text{tr}([B(t), A]\rho_0])\theta(t) \overset{\text{tr}[AB, \rho_0]=0}{=} -\frac{i}{\hbar} \text{tr}(A[B(t), \rho_0])\theta(t)$$

- Symmetry: Onsager relations. Systems (1) and (2), $X_i^{(1}$, $X_i^{(2)}$, $i = 1, ..., r$, $J_i = \frac{dX_i^{(2)}}{dt}$ is a flux (of X_i, conj of F_i) Linear Ansatz $J_i = \sum_j L_{ij}(F_j^{(2)} - F_j^{(1)})$ then $L_{ij} = L_{ji}$.
- Consider B's which are fluxes

$$B = \frac{i}{\hbar}[H, \tilde{A}] \quad \Rightarrow \quad L_{A\tilde{A}}(t) = \chi_{BA}(t) = \frac{1}{\hbar^2} \text{tr}([[A, H_0], \tilde{A}(t)]\rho_0)$$

- Time reversal T (is anti-unitary operator)
  - invariance of dynamics $T^* H_0 T = H_0 \Rightarrow T^* e^{-iH_0 t/\hbar} T = e^{iH_0 t/\hbar}$
  - invariance of a state $T^* \rho_0 T = \rho_0$
  - invariance of observables $T^* A T = A \Rightarrow T^* A(t) T = A(-t)$

6.2 **Remark**: $\langle T\phi | A | T\phi \rangle = \langle T\phi | AT\phi \rangle = \langle \phi | T^* A T | \phi \rangle = \text{tr}(T^* A T) = \overline{\text{tr}(A)}$
Thus $L_{A\tilde{A}}(t) = \overline{L_{A\tilde{A}}(t)} = \frac{1}{\hbar^2} \text{tr}([[A, H_0], \tilde{A}(-t)]\rho_0) \overset{\text{conj. with } e^{-iH_0 t/\hbar}}{=} \frac{1}{\hbar^2} \text{tr}([[A(t), H_0], \tilde{A}]\rho_0) = L_{A\tilde{A}}(t)$

6.3 **Thermal state**: $\rho_0 = e^{-\beta H}/Z$ where $Z = \text{tr} e^{-\beta H_0}$.

6.4 **Remark**: Recall $\text{tr}(AB) = \text{tr}(BA)$ and $\text{tr}(A^2) \geq 0$.
But expectation not symmetric: $\langle AB \rangle = \text{tr}(AB\rho_0) \neq \text{tr}(BA\rho_0) = \langle BA \rangle$
However: for

$$(B; A) = \beta^{-1} \int_0^{\beta} d\lambda \frac{\text{tr}(e^{(\lambda-\beta)H_0} B e^{-\lambda H_0} A}{\text{tr} e^{-\beta H_0}} \qquad \text{(Bogoliubov, Kubo, Mari)}$$

we have

1) $(B; A) = (A; B)$.
2) for $A^* = A$: $(A; A) \geq 0$

6.5 **Proof**: 1) change of variable $\lambda' := \beta - \lambda$
2) $B = A = A^*$; follows with

$$\text{tr}(e^{(\lambda-\beta)H_0} B e^{-\lambda H_0} A) = \text{tr}((e^{-\lambda H_0/2} A e^{(\lambda-\beta)H_0/2})^* (e^{-\lambda H_0/2} A e^{(\lambda-\beta)H_0/2})) \geq 0 \quad \square$$

By fundamental theorem of calculus (FTC)

$$[A, e^{-\beta H_0}] = e^{-\beta H_0}(e^{\beta H_0} A e^{-\beta H_0} - A) \overset{\text{FTC}}{=} \frac{i}{\hbar}[A, e^{-\beta H_0}] = e^{-\beta H_0} \int_0^\beta d\lambda e^{-\lambda H_0} \frac{i}{\hbar}[H_0, A] e^{-\lambda H_0}$$
$$= e^{-\beta H_0} \int_0^\beta d\lambda e^{-\lambda H_0} \dot{A} e^{-\lambda H_0}$$

Thus

$$\chi_{BA}(t) = \beta(B(t); \dot{A})\theta(t) = -\beta(\dot{B}(t); A)\theta(t)$$

(Kubo formula when ρ_0 is thermal state).
If B is in addition a flux (i.e. $B = \dot{\tilde{A}}$) then

$$L_{A\tilde{A}} = \chi_{BA}(t) = \beta(\dot{\tilde{A}}, \dot{A})\theta(t)$$

6.6 **Notation**: Write

$$\chi_{BA}(t) = \phi_{BA}(t)\theta(t) \quad \text{where} \quad \phi_{BA}(t) = \frac{i}{\hbar}\text{tr}(B(t)[A, \rho_0])$$

Then $\phi_{BA}(-t) = -\phi_{AB}(t)$ $\phi_{BA}(-t)$
Moreover:

$$\hat{\phi}_{AA}(\omega) = 2i \cdot \text{Im}\hat{\chi}_{AA}(\omega)$$

In fact:

$$2i \cdot \text{Im}\hat{\chi}_{AA}(\omega) = \hat{\chi}_{AA}(\omega) - \hat{\chi}_{AA}(-\omega) = \int_0^\infty \phi_{AA}(t)(e^{i\omega t} - e^{-i\omega t})dt$$
$$= \int_0^\infty \phi_{AA}(t)e^{i\omega t}dt - \int_{-\infty}^0 \underbrace{\phi_{AA}(-t)}_{-\phi_{AA}(t)} e^{i\omega t}dt = \int_{-\infty}^\infty \phi_{AA}(t)e^{i\omega t}dt$$
$$= \hat{\phi}_{AA}(\omega)$$

Set $G_{BA}(t) = \frac{1}{2}\text{tr}(\{B(t), A\}\rho_0) = \frac{1}{2}(\langle AB\rangle + \langle BA\rangle)$ (symmetrized correlation function) If $\langle A\rangle_{\rho_0} = 0$ and $\langle B\rangle_{\rho_0} = 0$ then it expresses fluctuations.

6.7 **Theorem (Callan-Welton)**: Let $\rho_0 = e^{-\beta H_0}$ (thermal state). Then

$$\hat{G}_{BA}(\omega) = -\frac{i\hbar}{2}\coth\frac{\beta\hbar\omega}{2}\hat{\phi}_{BA}(\omega)$$

In particular

$$\underbrace{\hat{G}_{AA}(\omega)}_{\text{Fluctuation}} = \hbar\coth\frac{\beta\hbar\omega}{2}\text{Im}\underbrace{\hat{\chi}_{AA}(\omega)}_{\text{Dissipation}}$$

6.8 **Remarks**: 1) $\coth\frac{x}{2} = \frac{\cosh(x/2)}{\sinh(x/2)} = \frac{1+e^{-x}}{+-e^{-x}}$
2) In the classical limit ($\hbar\omega << k_B T$): $\hbar\coth\frac{\beta\hbar\omega}{2} \simeq \hbar\frac{2}{\beta\hbar\omega} = \frac{2kT}{\omega}$

6.9 **Lemma (Kubo-Martin-Schwinger)**: ρ_0 as above. Then

$$\text{tr}(B(t)A\rho_0) = \text{tr}(AB(t + i\beta\hbar)\rho_0)$$

More precisely: $f(t) = \mathrm{tr}(B(t)A\rho_0)$ has an analytic extension from $t \in \mathbb{R}$ to the strip $-\beta\hbar < \mathrm{Im}(t) < 0$, continuous up to boundary with $f(t - i\beta\hbar) = \mathrm{tr}(AB(t)\rho_0)$

6.10 **Proof of Lemma**: use cyclicity

$$\mathrm{tr}(e^{itH_0/\hbar}Be^{-itH_0/\hbar}Ae^{-\beta H_0}) = \mathrm{tr}(A\underbrace{e^{i(t+i\beta\hbar)H_0/\hbar}Be^{-i(t+i\beta\hbar)H_0/\hbar}}_{=B(t+i\beta\hbar)}e^{-\beta H_0}) = \mathrm{tr}(AB(t+i\beta\hbar)e^{-\beta H_0}) \qquad \square$$

6.11 **Proof of Theorem**: We have

$$\hat{f}(\omega) = \int_{\mathbb{R}} \underbrace{\mathrm{tr}(B(t)A\rho_0)}_{f(t)} e^{i\omega t}dt \overset{\text{shift contour}}{=} \int_{\mathbb{R}} f(t - i\beta\hbar)e^{i\omega(t-i\beta\hbar)}dt = e^{\beta\hbar\omega}\int_{\mathbb{R}} \mathrm{tr}(AB(t)\rho_0)e^{i\omega t}dt$$

It follows

$$\hat{\phi}_{BA}(\omega) = \frac{i}{\hbar}(1 - e^{-\beta\hbar\omega})\hat{f}(\omega)$$

Thus

$$\hat{G}_{BA}(\omega) = \frac{1}{2}(1 + e^{-\beta\hbar\omega})\hat{f}(\omega) = \frac{1}{2}\left(\frac{\hbar}{i}\right)\coth\frac{\beta\hbar\omega}{2}\hat{\phi}_{BA}(\omega) \qquad \square$$

Lecture 7

7.1 **Recap lecture 6**: - Response function : χ_{BA}
- symmetrized correlation fct. (between A at $t = 0$ and B at t):

$$G_{BA} = \frac{1}{2}\text{tr}(\{B(t), A\}\rho_0)$$

& fluctuation if $\langle A\rangle_{\rho_0} = \langle B\rangle_{\rho_0}$.
- Theorem: If ρ_0 is thermal state, then

$$\underbrace{\hat{G}_{AA}(\omega)}_{\text{Fluctuation}} = \underbrace{\hbar\coth\frac{\beta\hbar\omega}{2}}_{\to\frac{2kT}{\omega}\text{ class. lim.}} \text{Im}\,\underbrace{\hat{\chi}_{AA}(\omega)}_{\text{Dissipation}}$$

7.2 **Brownian motion (Einstein 1905)**:

Phenomenon: particles of size $\sim 10^{-6}$m suspended in a medium (liquid or gas) perform random motion

Einstein formula: $D = \mu kT$ D: diffusion constant ("fluctuation")
μ: mobility ("dissipation")

Diffusion: density $n(\vec{x}, t)$ of particles $\Leftrightarrow$ current density $\vec{j}_{\text{diff}}$

- continuity equation: $\frac{\partial n}{\partial t} + \nabla \cdot \vec{j} = 0$
- with $\vec{j} = -D\nabla n$ (D: const.; Fick's law) we get: $\frac{\partial n}{\partial t} = -\nabla \cdot \vec{j} = D\Delta n$

Probability interpretation: $n(\vec{x}, t)$ probability distribution of a single particle

$$\int n(\vec{x}, t)d^3x = 1$$

- note consistency

$$\frac{\partial}{\partial t}\int n(\vec{x}, t)d^3x = \int \underbrace{\frac{\partial n}{\partial t}}_{1\cdot Dn} d^3x \overset{\text{Green's id.}}{=} \int \underbrace{(\Delta 1)}_{=0} Dnd^3x = 0$$

- mean position

$$\langle\vec{x}(t)\rangle = \int \vec{x}n(\vec{x}, t)d^3x$$

$$\frac{d}{dt}\langle x_i\rangle = \int x_i\frac{\partial n}{\partial t}d^3x = D\int \Delta(x_i)nd^3x = 0$$

- variance

$$\langle(\Delta\vec{x})^2\rangle(t) = D\int d^3x(\vec{x} - \langle\vec{x}\rangle)^2n(\vec{x}, t) = \langle\vec{x}^2\rangle - \langle\vec{x}\rangle^2$$

$$\frac{d}{dt}\langle(\Delta\vec{x})^2\rangle(t) = D\int d^3x\,\underbrace{(\Delta\vec{x}^2)}_{=6}\,n = 6D$$

$$\langle(\Delta\vec{x})^2\rangle(t) = \langle(\Delta\vec{x})^2\rangle(0) + 6Dt$$

spread of distribution increases at rate D ($\Rightarrow D$: diffusion constant)

7.3 **Einstein's thought experiment**: Let us perturb the system & drive with a force $\vec{F}$ on a particle (1st accelerate, then feel friction $\Rightarrow$ attend limiting velocity). It attains limiting velocity (as a result of friction)

$$\vec{v} = \mu \vec{F} \qquad \text{"linear response"}$$

hence

$$\vec{j}_{\text{diff}} \neq \vec{j}_{\text{drift}} = n\vec{v} = n\mu\vec{F}$$

$\vec{j}_{\text{drift}}$: due to $\vec{F}$ and not ∇n.
For a conservative force $\vec{F} = -\nabla U$ we calculate the total current:

$$\vec{j}_{\text{diff}} + \vec{j}_{\text{drift}} = -D\nabla n + n\mu\vec{F}$$

Total current vanishes at equilibrium: $n(\vec{x}) \propto e^{-U(\vec{x})/kT}$. Thus $\nabla n = -n\frac{\nabla U}{kT} \Rightarrow \frac{D}{kT}\nabla U = \mu\nabla U$. Thus $D = \mu kT$.

7.4 **Derivation from general theory (1-dim)**: $H_I(t) = -X(t)A = -F(t)X$ ($\vec{v} = \mu\vec{F}$: v = response, F = driving), $A = x$, $B = \dot{x}$.

Response function: $\hat{\chi}_{BA}(\omega) = \mu(\omega)$ since $\langle \dot{x} \rangle(\omega) = \mu(\omega)F(\omega)$.

Formula: $\hat{\chi}_{BA}(t) = \beta(\dot{A}(t); \dot{A})\theta(t)$

In our case

$$\mu(\omega) = \hat{\chi}_{BA}(\omega) = \beta \int_0^\infty \underbrace{(\dot{x}(t); \dot{x})}_{=\langle \dot{x}(t)\dot{x}\rangle} e^{i\omega t} dt$$

On the other side

$$\begin{aligned} D &= \lim_{t\to\infty} \frac{1}{2t}\langle (x(t)-x)^2\rangle = \lim_{t\to\infty} \frac{1}{2t}\int_0^t dt_1 \int_0^t dt_2 \langle \dot{x}(t_1)\dot{x}(t_2)\rangle \overset{t_2 = t_1 + t'}{=} \\ &= \lim_{t\to\infty} \frac{1}{2t} 2\int_0^t dt_1 \int_0^{t-t_1} dt' \langle \dot{x}(t_1)\dot{x}(t_1+t')\rangle = \lim_{t\to\infty} \frac{1}{t}\int_0^t dt_1 \int_0^\infty dt' \langle \dot{x}(0)\dot{x}(t')\rangle = \\ &= \int_0^\infty \langle \dot{x}(0)\dot{x}(t)\rangle dt \end{aligned}$$

$\Rightarrow \mu = \beta D$.

7.5 **The Langevin equation (1908)**: Forces on Brownian particle

- friction: average, combined effect of collisions $\Rightarrow -\mu\dot{\vec{x}}$
- fluctuating force: deviation from average $\Rightarrow \vec{\xi}(t)$: random variable with $\langle \vec{\xi}(t)\rangle = 0$, uncorrelated at different times $\langle \vec{\xi}(t)\vec{\xi}(t')\rangle = \alpha\delta(t-t')$ (α to be determined).

Note difference: Einstein: velocities
Langevin: acceleration

Newton: $m\frac{d\vec{v}}{dt} = -\mu\vec{v} + \vec{\xi}(t), \quad (\vec{v} = \dot{\vec{x}})$

Initial condition: velocity distribution as given by equipartition: $\frac{1}{2}m\langle \vec{v}^2(0)\rangle = \frac{3}{2}kT \Rightarrow \langle \vec{v}^2(0)\rangle = \frac{3kT}{m}$.
α to be determined such that $\langle \vec{v}^2(t)\rangle = \langle \vec{v}^2(0)\rangle$

7.6 **Heuristic solution**:

$$0 = \frac{d}{dt}\frac{m}{2}\langle \vec{v}^2(t)\rangle = m\langle \vec{v}(t)\frac{d\vec{v}}{dt}\rangle = -\mu\langle \vec{v}^2(t)\rangle + \langle \vec{v}(t)\vec{\xi}(t)\rangle$$

Let $\epsilon > 0$:

- we have

$$\langle \vec{v}(t-\epsilon)\vec{\xi}(t)\rangle = \langle \vec{v}(t-\epsilon)\rangle\langle\vec{\xi}(t)\rangle = 0$$

  since $\vec{v}(t-\epsilon)$ depends only on $\{\vec{\xi}(s)|0 \le s \le t-\epsilon\}$ (i.e. independent of $\vec{\xi}(t)$).

- and

$$m\vec{v}(t+\epsilon) \approx m\vec{v}(t-\epsilon) - \mu \underbrace{\vec{v}(t)\cdot 2\epsilon}_{\int_{t-\epsilon}^{t+\epsilon}\frac{d\vec{v}}{dt}dt} + \int_{t-\epsilon}^{t+\epsilon}\vec{\xi}(s)ds$$

Hence $m\langle \vec{v}(t+0)\vec{\xi}(t)\rangle = \alpha$.

Pick: $\langle \vec{v}(t+0)\vec{\xi}(t)\rangle = \frac{\alpha}{2m} \Rightarrow \mu\langle\vec{v}^2\rangle = \frac{\alpha}{2m}$ or $\alpha = 2m\mu\langle\vec{v}^2\rangle$.

7.7 **Better solution**:

$$\frac{d}{dt}\left(\vec{v}(t)e^{\frac{\mu}{m}t}\right) = \left(\frac{d\vec{v}}{dt} + \frac{\mu}{m}\vec{v}\right)e^{\frac{\mu}{m}t} = \frac{\vec{\xi}}{m}e^{\frac{\mu}{m}t} \quad \Rightarrow \quad \vec{v}(t) = e^{-\frac{\mu}{m}t}\left(\vec{v}(0) + \frac{1}{m}\int_0^t \vec{\xi}(s)e^{\frac{\mu}{m}s}ds\right)$$

$$\begin{aligned}\langle\vec{v}^2(t)\rangle &= e^{-\frac{2\mu}{m}t}\left(\langle\vec{v}^2(0)\rangle + \frac{1}{m^2}\int_0^t ds_1\int_0^t ds_2\langle\vec{\xi}(s_1)\vec{\xi}(s_2)\rangle e^{\frac{\mu}{m}(s_1+s_2)}\right) = e^{-\frac{2\mu}{m}t}\left(\langle\vec{v}^2(0)\rangle + \frac{\alpha}{m^2}\int_0^t ds e^{\frac{2\mu}{m}s}\right)\\ &= \frac{\alpha}{2\mu m} + e^{-\frac{2\mu}{m}t}\left(\langle\vec{v}^2(0)\rangle - \frac{\alpha}{2\mu m}\right) \stackrel{!}{=} \langle\vec{v}^2(0)\rangle\end{aligned}$$

This means, in particular time, independence. Thus $(...) = 0 \Rightarrow \langle\vec{v}^2(0)\rangle = \frac{\alpha}{2\mu m}$.

Diffusion: $\langle\vec{x}^2(t)\rangle \sim t$ diffusion behaviour

$$\frac{d^2}{dt^2}\langle\vec{x}^2(t)\rangle = 2\langle\left(\frac{d\vec{v}}{dt}\right)^2\rangle + 2\langle\vec{x}(t)\frac{d^2\vec{x}}{dt^2}\rangle = 2\langle\vec{v}^2(t)\rangle - \frac{2\mu}{m}\langle\underbrace{\vec{x}(t)\overbrace{\vec{v}(t)}^{\frac{d\vec{x}}{dt}}}_{\frac{1}{2}\frac{d\vec{x}^2}{dt}}\rangle + \frac{2}{m}\langle\vec{x}(t)\vec{\xi}(t)\rangle$$

Note: $\langle\vec{x}(t)\vec{\xi}(t)\rangle = \langle\vec{x}(t)\rangle\langle\vec{\xi}(t)\rangle$ since $\vec{x}(t)$ depends on $\{\vec{\xi}(s)|0 \le s < t\}$, $\vec{x}(t)$ is continuous.

Hence:

$$\frac{d^2}{dt^2}\langle\vec{x}^2(t)\rangle + \frac{\mu}{m}\frac{d}{dt}\langle\vec{x}^2(t)\rangle = 2\langle\vec{v}^2\rangle \quad \Rightarrow \quad \dot{u}(t) + \frac{\mu}{m}u(t) = 2\langle\vec{v}^2\rangle$$

Initial condition: $u(0) = 2\langle\vec{v}(0)\vec{x}(0)\rangle = 0$ if $\vec{v}(0)$, $\vec{x}(0)$ are uncorrelated and $\langle\vec{v}(0)\rangle = 0 \Rightarrow \vec{v}(0)$ is even fct.

Solution of ODE is

$$\langle\vec{x}^2(t)\rangle - \langle\vec{x}^2(0)\rangle = \frac{2\mu}{m}\langle\vec{v}^2\rangle\left(t - \frac{m}{\mu}\left(1 - e^{-\mu t/m}\right)\right)$$

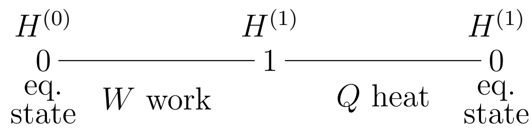
Discussion:

$$t >> \frac{m}{\mu}: \qquad \langle \vec{x}^2(t) \rangle - \langle \vec{x}^2(0) \rangle = 6Dt, \qquad \text{where} \quad D = \frac{m\langle \vec{v}^2 \rangle}{3\mu} = \frac{kT}{\mu}$$

$$t << \frac{m}{\mu}: \qquad \langle \vec{x}^2(t) \rangle - \langle \vec{x}^2(0) \rangle \approx \langle \vec{v}^2 \rangle t^2 \quad \text{(ballistic motion)},$$

Lecture 8

8.1 **Back to 2nd law** Consider process $0 \to 1 \to 0$.



2nd law: $W + W' \geq 0$ (I cannot have extracted work from the system). Free energy F, for quasi-static processes $dF = -SdT + \delta W$. $W' = -\Delta F = -(F_1 - F_0)$. Hence $W \geq \Delta F$ (*).

Remarks: 1) generalizes $W \geq 0$ (for $0 = 1$), seen earlier
2) $W + W' \geq 0 \Rightarrow Q + Q' \leq 0$, i.e. $\frac{Q}{T} + \frac{Q'}{T} \leq 0$ (Clausius inequality)

8.2 **Theorem (Jarzynski, 1997)**: For any classical mechanical system

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$$

with $\langle . \rangle$ = average at eq. state at temperature β^{-1}, $-\beta F_i = \log(Z)$ (Z: canonical partition function).

8.3 **Remarks**: 1) This is the equality behind the inequality (*). Convexity: $f(\langle y \rangle) \leq \langle f(y) \rangle$, e.g. $f(y) = e^{-\beta y}$. Thus $e^{-\beta \langle W \rangle} \geq \langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$. Hence $\langle W \rangle \geq \Delta F$.

2) Note average $\langle . \rangle$. In fact rare violations of 2nd law must occur.

Claim: if $\langle W \rangle > \Delta F$, then $\langle W(x) \rangle < \Delta F$ for some x of positive Gibbs measure (Gibbs measure: $\frac{e^{-\beta Z}}{Z} dx$).

Suppose otherwise: $\langle W(x) \rangle \geq \Delta F$ (for all x).
$\langle W \rangle > \Delta F$ (for some x of positive measure)
$\Rightarrow e^{-\beta W(x)} \leq e^{-\beta \Delta F}$ strict for some x. Then $\langle e^{-\beta W(x)} \rangle \leq e^{-\beta \Delta F}$ (violation of Jarzyski inequality).

8.4 **Proof of Jarzynski**: Let $H(x, \lambda)$, x: phase space coordinate ($x(t)$: trajectory with $x(0) = x$), λ: work coordinate ($\lambda = \lambda(t)$).

Partial time derivative: $$\frac{\partial H}{\partial t} = \frac{\partial H}{\partial \lambda} \dot{\lambda}$$

Total time derivative: $$\frac{dH}{dt} = \frac{d}{dt} H(x(t), \lambda(t)) = \{H, H\} + \frac{\partial H}{\partial t} = \frac{\partial H}{\partial t}$$

$$W(x) = \int_0^\tau \frac{\partial}{\partial t} H(x(t), \lambda(t)) = \int_0^\tau \frac{d}{dt} H(x(t), \lambda(t)) = H(x(\tau), \lambda_1) - H(x, \lambda_0)$$

$$\begin{aligned} \langle e^{-\beta W} \rangle &= \frac{1}{Z_0} \int dx e^{-\beta H(x_0, \lambda_0)} e^{-\beta W(x)} \\ &= \frac{1}{Z_0} \int dx e^{-\beta H(x(\tau), \lambda_1)} = \frac{1}{Z_0} \int dx_1 e^{-\beta H(x(\tau), \lambda_1)} = \frac{Z_1}{Z_0} = e^{-\beta \Delta F} \end{aligned}$$

(change of variables $x \to x_1 = x(\tau)$: symplectic transformation: $|\text{Jacobian}| = 1$) $\square$

8.5 **More consequences**: 1) Probability of violation of the 2nd law. For $\zeta > 0$

$$P(W(x) \leq \Delta F - \zeta) = \langle \chi(W(x) \leq \Delta F - \zeta) \rangle \leq \langle e^{-\beta W(x) + \beta \Delta F - \beta \zeta} \rangle = e^{\beta(\Delta F - \zeta)} \langle e^{-\beta W(x)} \rangle = e^{-\beta \zeta}$$

(we used $\chi(y \leq 0) \leq e^{-\beta y}$, result non trivial only for $\zeta > 0$).

2) Distribution of trajectories. $*$: time-reversal of configurations $x \to x^*$ (e.g. $(p, q)^* = (-p, q)$) of trajectories $\gamma \to \gamma^*(t) = \gamma(\tau - t)^*$. For time-reversal invariant Hamiltonian: $H(x^*, \lambda) = H(x, \lambda)$ we have: if γ is trajectory for $\lambda(t)$, the γ^* is trajectory for $\lambda(\tau - t)$. How big is the ratio $\frac{P[\gamma]}{P[\gamma^*]}$?

8.6 **Theorem (Crooks 1998)** Situation of 2). Then

$$\frac{P[\gamma]}{P[\gamma^*]} = e^{-\beta(W(\gamma) - \Delta F)}$$

$P[\gamma]$: probability density of γ i.e. (by determinism) of its initial condition $x_0 = \frac{1}{Z_0} e^{-\beta H(x_0, \lambda_0)}$
$W(\gamma)$

8.7 **Proof**:

$$\frac{P[\gamma]}{P[\gamma^*]} = \frac{Z_1}{Z_0} e^{-\beta H(x_0, \lambda_0) + \beta H(x_1^*, \lambda_1)} = \frac{Z_1}{Z_0} e^{-\beta H(x_0, \lambda_0) + \beta H(x_1, \lambda_1)} = e^{-\beta(W(\gamma) - \Delta F)}$$

Remark: $\frac{P[\gamma]}{P[\gamma^*]} >> 1$ if γ goes in the direction of the 2nd law.

8.8 **Quantum Jarzynski identity**: We saw $\langle W \rangle \geq \Delta F$ (actually, only for $1 = 0$ ($\to \Delta F = 0$), but the proof works in general when $\log(Z_1) \neq \log(Z_2)$). Interpretation of W

$$\langle W \rangle = \text{tr}(U \rho U^* H^{(1)}) - \text{tr}(\rho H^{(0)})$$

Statistics underlying $\langle W \rangle$: not measurement of $U^* H`(1) U - H^{(0)}$ (stupid choice, since objects live at different times), but two measurements of $H^{(0)}$ and of $H^{(1)}$ later, W are diff. of the two outcomes.

Lecture 9

9.1 **Recap Jarzynski** $W \geq \Delta F = F_1 - F_0$. Jarzynksi:

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$$

9.2 **Quantum Jarzynski identity**: We saw: ρ_0 equilibrium state at β^{-1}

$$\langle W \rangle = \operatorname{tr}(\underbrace{U\rho_0 U^*}_{\text{final state}} \underbrace{H^{(1)}}_{\text{final } H}) - \operatorname{tr}(\rho_0 H^{(0)}) \qquad \langle W \rangle \geq \Delta F \quad \text{(true also in QM)}$$

9.3 **Proof**: $-\beta H^{(1)} = \log \rho_i + \log Z_i$

$$\beta \langle W \rangle = \underbrace{\operatorname{tr}(\rho_0 \log \rho_0) - \operatorname{tr}(U\rho_0 U^* \log \rho_1)}_{(*)} + \underbrace{\log Z_0 - \log Z_1}_{\beta(F_1 - F_0)}$$

$$(*) = \operatorname{tr}(\rho_0 \log \rho_0) - \operatorname{tr}(\rho_0 \log U^* \rho_1 U) \geq \operatorname{tr}(\rho_0 - U^*\rho_1 U) = \operatorname{tr}(\rho_0) - \operatorname{tr}(U^*\rho_1 U) = 1 - 1 = 0$$

we used $\operatorname{tr}(B \log(B)) \geq \operatorname{tr}(B \log A) + \operatorname{tr}(B - A)$ (Klein). $\square$

9.4 Statistics underlying $\langle W \rangle$: not measurement of $U^* H(1) U - H^{(0)}$ (stupid choice, since objects live at different times), but two measurements of $H^{(0)}$ and of $H^{(1)}$ later, W are diff. of the two outcomes.

Let $H^{(0)} = \sum_i E_i^{(0)} P_i^{(0)}$, $\sum_i P_i^{(0)} = 1$.

State: - after 1st measurement:

$$\sum_i P_i^{(0)} \rho P_i^{(0)}$$

Energy is $E_i^{(0)}$ with probability $\operatorname{tr}(P_i^{(0)} \rho P_i^{(0)}) = \operatorname{tr}(\rho P_i^{(0)})$.

- after evolution:

$$U \sum_i P_i^{(0)} \rho P_i^{(0)} U^*$$

- after the 2nd measurement:

$$\sum_i \sum_j P_j^{(1)} U P_i^{(0)} \rho P_i^{(0)} U^* P_j^{(1)}$$

Work is $W = E_j^{(1)} - E_i^{(0)}$ with probability tr(...)

Expected work:

$$\begin{aligned}
\langle W \rangle &= \sum_i \sum_j (E_j^{(1)} - E_i^{(0)}) \operatorname{tr}(P_j^{(1)} U P_i^{(0)} \rho P_i^{(0)} U^* P_j^{(1)}) = \sum_i \sum_j (E_j^{(1)} - E_i^{(0)}) \operatorname{tr}(P_j^{(1)} U P_i^{(0)} \rho U^*) \\
&= \sum_i \left(\operatorname{tr}(H^{(1)} U P_i^{(0)} \rho U^*) \right) - \operatorname{tr}(U H^{(0)} \rho U^*) = \operatorname{tr}(H^{(1)} U \rho U^*) - \operatorname{tr}(H^{(0)} \rho)
\end{aligned}$$

9.5 **Tasaki Identity (2000)**:

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$$

9.6 **Proof**:

$$\langle e^{-\beta W}\rangle = \sum_i \sum_j e^{-\beta(E_j^{(1)}-E_i^{(0)})}\mathrm{tr}(P_j^{(1)}UP_i^{(0)}\rho P_i^{(0)}U^*) = \sum_i \sum_j e^{-\beta(E_j^{(1)}-E_i^{(0)})}\mathrm{tr}(P_j^{(1)}U\frac{e^{-\beta E_i^{(0)}}}{Z_0}P_i^{(0)}U^*)$$
$$= \frac{1}{Z_0}\sum_i \mathrm{tr}(e^{-\beta H^{(1)}}UP_i^{(0)}U^*) = \frac{Z_1}{Z_0} = e^{-\beta\Delta F} \qquad \square$$

9.7 **Criticism**: 1) Superficially: the breaking of time-reversal symmetry occurs by hand: the state before W was done was equilibrium state (as opposed to after). Deeper: why is the state at some time an equilibrium state?
2) In which sense does entropy

$$S(\omega) = -\int dx\omega(x)\log\omega(x)$$

increase?

9.8 **Answer**: 2) $x' = \phi_t(x)$ evolution on phase space $\mathbb{R}^{2n}$. Induced evolution of densities: $\omega \to \omega_t$: $\omega_t(x')dx' = \omega(x)dx$. We have $dx' = |\det D\phi_t(x)|dx$. Special for Hamiltonian dynamics: $|\det D\phi_t(x)| = 1$ (Liouville). Thus there is no entropy increase

$$S(\omega_t) = -\int dx'\omega_t(x')\log\omega_t(x') = -\int dx\omega(x)\log\omega(x) = S(\omega)$$

1) $H(x) = H(\phi_t(x))$ (H time independent $\Rightarrow$ energy in conserved). Given energy E: $M = \{x \in \mathbb{R}^{2n} | H(x) = E\}$ is invariant under ϕ_t.
Ergodic hypothesis: almost all $x \in M$ have trajectories which fill M densely and uniformly. More precisely: for any function f, continuous on M, the limit

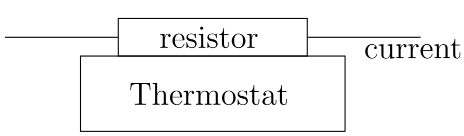
$$\underbrace{\lim_{T\to\infty}\frac{1}{T}\int_0^T f(\phi_t(x_0))dt}_{\text{time-average}} = \underbrace{\int_M d\mu_E(x)f(x)}_{\text{ensemble-average}}$$

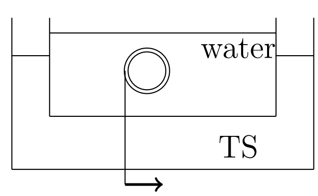
exists for almost all $x_0 \in M$, with $d\mu_E(x) = \frac{1}{\Sigma(E)}\delta(H(x)-E)d^{2n}x = \frac{1}{\Sigma(E)}\frac{dx^1\cdots dx^{2n}}{|\nabla H(x)|}$

9.9 **Remakrs**: 1) Ergodic hypothesis proven only for few systems.
2) For arbitrary f's: T has to be at least of the order of Poicare recurrence time; for macroscopic f's: T much shorter (not really proven)

9.10 **Fluctuation theorems** (far from equilibrium): Many systems are found in stationary states, though not in equilibrium states.

Examples:

1) 

2) 

Question: Is a purely mechanical understanding possible? e.g. increase of entropy?

- include TS $\Rightarrow$ mechanics of ∞-many degrees of freedom (Fröhlich et al.)
- exclude TS, but simulate mechanically its effects in system proper (Gallavotti, Cohen)

9.11 **Example**: Langevin equation: $\dot{F} = -\mu\dot{x} + \xi$ not time-reversal invariant. This system may well explain increase of entropy, but is not a good system. Better isokinetic thermostat

9.12 **Example**: Isokinetic thermostat

$$H(x,t) = \frac{p^2}{2m} + V(q,t)$$

($x = (p,q) \in \mathbb{R}^{2n}$). Equations of motions

$$\dot{p} = F = -\nabla V \qquad \dot{q} = \frac{p}{m}$$

Set $M = \{p^2 = \text{const}\}$= fixed kinetic energy. Replace F by its component tangential to M. Equations of motion modify to

$$\dot{p} = F - \frac{(F\cdot p)p}{p^2} := v_p(x) \qquad \dot{q} = \frac{p}{m} := v_q(x)$$

or

$$\dot{x} = v(x) = (v_p(x), v_q(x)) = \text{ vectorfield}$$

Solution: $x(t) = \phi_t(x_0)$
The system is not Hamiltonian, but dissipative

$$-\nabla\cdot v = -\partial_p v_p - \partial_q v_q = \partial_p \frac{(F\cdot p)p}{p^2} \neq 0$$

Yet reversible: time reversal $x \to Ix$, $I(p,q) = (-p,q)$, $Iv(x) = -v(Ix)$. Hence:

$$I\phi_t = \phi_{-t}I$$

(Indeed: $\frac{d}{dt}I\phi_t = IV(\phi_t(x)) = -V(I\phi_t(x))$. The claim follows by uniqueness of the solution.)
Moreover, $\text{div}(v)|_{Ix} = -\text{div}(v)|_x$ and $d(Ix) = dx$. Hence

$$\int_M (\text{div})(x) = 0 \quad \Rightarrow \quad \text{as much contraction as expansion}$$

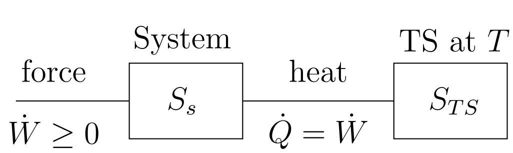
9.13 Typically: probability distribution $\omega_t(x)$ initially uniform concentrates on an "attractor": as a result entropy decreases!

Example: $\omega = \frac{1}{|\Delta|}\chi_\Delta(x)$ ($\Delta \subset M$): $S(\omega) = -\int_M dx\omega(x)\log(\omega(x)) = \log|\Delta| \Rightarrow$ the smaller $|\Delta|$ the smaller the entropy

Clarification: in a pure Hamiltonian description entropy does not change $\dot{S} = 0$. Here:

$$\dot{S}_S + \dot{S}_{TS} = 0$$

Clausius: $\dot{S}_{TS} = \frac{\dot{Q}}{T} > 0$ thus $\dot{S}_S < 0$.



9.14 **Question**: Irreversibility within a time-invariant dynamics?

9.15 **A framework**: - class of dynamical systems

$$\frac{dx}{dt} = V(x) \text{ vectorfield} \qquad \Rightarrow \qquad x \mapsto \phi_t(x) \text{ flow}$$

($x \in M$: differential manifold of $\dim M = n$) - Equip M with metric: $g_{ij}(x) \Rightarrow$ Measure: $d\mu_0(x) = \sqrt{g}dx_1 \cdots dx_n$ (Lebesgue measure). Here set: $g = 1$.
- Time-reversal $I : M \to M, x \mapsto Ix$ map with
  (i) $I \circ \phi_t = \phi_{-t} \circ I$
  (ii) $\det DI = 1$ (equivalent to: $\mu_0(IA) = \mu_0(A)\ \forall A \subset M$)
- Entropy:

$$S(\omega_t) = -\int dx' \omega_t(x') \log \omega_t(x')$$

- Entropy production:

$$\dot{S}(t) = \int_M dx \omega_t(x) \frac{\partial}{\partial t} \log |\det D\phi_t(x)| = \int_M dx \omega_t(x)(\mathrm{div} V(\phi_t(x)))$$

Thus: entropy production rate = phase space contraction rate $\dot{\sigma}(x) \equiv -\mathrm{div} V(x)$

9.16 **Proof of "entropy production formula"**: For any $A \subset M$

$$\int_{\phi_t(A)} dx' = \int_A dx |\det D\phi_t(x)| = \int_M dx \chi(x,t) = \int_M \chi(x,t) dx$$

where

$$\chi(x,t) = \begin{cases} 1 & x \in \phi_t(A) \\ 0 & \text{otherwise} \end{cases}$$

Chain rule: $V \cdot \nabla \chi + \frac{\partial}{\partial t}\chi = 0$. Hence:

$$\begin{aligned} \frac{d}{dt}\int_{\phi_t(A)} dx' &= \int_A dx \frac{\partial}{\partial t} |\det D\phi_t(x)| = \int_M dx \frac{\partial}{\partial t}\chi \\ &= -\int_M dx V \cdot \nabla \chi = \int_M dx (\mathrm{div} V)\chi = \int_{\phi_t(A)} (\mathrm{div} V(x')) dx' \\ &= \int_A (\mathrm{div} V(x)) |\det D\phi_t(x)| dx \end{aligned}$$

Now compare the integrands:

$$(\mathrm{div} V(x)) |\det D\phi_t(x)| = \frac{\partial}{\partial t} |\det D\phi_t(x)|$$

which is the claim.

Lecture 10

10.1 **Recap Lecture 8**: - Question: Irreversibility within a time-invariant dynamics?
- Example: isokinetic thermostat (time-reversal invariant, yet dissipative)
- Framework: class of dynamical systems ($x \in M$: diff. manifold, $V(x)$: vectorfield)

$$\frac{dx}{dt} = V(x) \qquad \Rightarrow \qquad x \mapsto \phi_t(x) \text{ flow}$$

Metric: $g_{ij}(x)$. Measure: $d\mu_0(x) = \sqrt{g}dx_1 \cdots dx_n$ (Lebesgue measure). Here: $g = 1$.

- Time-reversal $I : M \to M, x \mapsto Ix$ map with (i) $I \circ \phi_t = \phi_{-t} \circ I$ (ii) $\det DI = 1$ (equivalent to: $\mu_0(IA) = \mu_0(A) \forall A \subset M$)

- Entropy:

$$S(\omega_t) = -\int dx' \omega_t(x') \log \omega_t(x')$$

- Entropy production:

$$\dot{S}(t) = \int_M dx \omega_t(x) \frac{\partial}{\partial t} \log |\det D\phi_t(x)| = \int_M dx \omega_t(x) (\text{div} V(\phi_t(x))) = -\int_M d\mu_t \dot{\sigma}$$

Thus: entropy production rate = phase space contraction rate $\dot{\sigma}(x) \equiv -\text{div}V(x)$

10.2 **Definition**: Average entropy production, $p(x)$, along trajectory $\phi_t(x)$, ($t \in [0, T]$)

$$p(x) = \frac{1}{T} \int_0^T \dot{\sigma}(\phi_t(x))dt = -\frac{1}{T} \int_0^T \text{div}V(\phi_t(x))dt = -\frac{1}{T} \log |\det D\phi_T(x)|$$

10.3 Consider the probability of "observing" the event $p(x) \in [p, p + \Delta p] \equiv J$ for x random w.r.t. μ_0 (not invariant probability measure under the flow ϕ_t: μ_0 is transient)

$$E_J = \{x \in M | p(x) \in J\}$$

We are looking for

$$\mu_0(E_J) = \pi_T(p)\Delta p + \mathcal{O}(\Delta p) \qquad \Delta p \to 0$$

10.4 **Evans-Searle fluctuation identity (1994)** ϕ_t is time-reversal invariant, μ_0 too. Then

$$\frac{\pi_T(p)}{\pi_T(-p)} = e^{pT}$$

E.g. for $p > 0$: entropy production much more likely than entropy destruction!

10.5 **Proof**: Let $x \in E_J$. then $I\phi_T(x)$ is the initial datum of a "backward" trajectory: contracts at opposite rate, i.e. $I\phi_T(x) \in E_{-J}$ and viceversa. In fact:

$$p(I\phi_T(x)) = \frac{1}{T} \log |\det D\phi_T(I\phi_T(x))| = \frac{1}{T} \log |\det D\phi_T(x)| = -p(x)$$

We used $\phi_T \circ I\phi_T = I \circ \phi_{_T} \circ \phi_T = I \Rightarrow D\phi_T \cdot DI \cdot D\phi_T(x) = DI(x)$.

$$\mu_0(E_{-J}) = \mu_0(I\phi_T(E_J)) \overset{\mu_0 \text{ inv.}}{=} \mu_0(\phi_T(E_J)) = \int_{E_J} |\det D\phi_T(x)| dx$$

$$= \int_{E_J} e^{-Tp(x)} dx \in [e^{-T(p+\Delta p)}, e^{-Tp}] \cdot \mu_0(E_J)$$

Thus $\frac{\mu_0(E_J)}{\mu_0(E_{-J})} \in [e^{Tp}, e^{T(p+\Delta p)}]$. Finally, take $\Delta p \to 0$ to get the claim

$$\frac{\pi_T(p)}{\pi_T(-p)} = e^{pT} \qquad \square$$

10.6 **Criticism**: prob. is w.r.t to the (transient) Lebesgue measure and not w.r.t stationary distribution.

Lecture 11

11.1 **The stationary measure μ^+**: for any continuous function f on M the limit

$$\lim_{T\to\infty}\frac{1}{T}\int_0^T dt f(\phi_t(x_0)) = \int_M d\mu^+(x)f(x)$$

exists for μ_0-a-a x_0, and is independent of x_0 (initial data). μ^+ is stationary

$$\int d\mu^+(x)f(x) = \int d\mu^+(x)f(\phi_t(x)) \equiv \int d\mu_t^+(x)f(x)$$

11.2 **Remark**: 1) Analogy with ergodic hypothesis for Hamiltonian dynamics. Here: chaotic hypothesis.
2) $d\mu^+$: concentrated on some attractor; typically $d\mu^+$ is singular w.r.t $d\mu_0$ (general definition: μ_1 is singular w.r.t. μ_2 if $\mu_1(\mathbb{R}\setminus S) = 0$ (i.e. μ_1 lives on S) and $\mu_2(S) = 0$: e.g. on $\mathbb{R}$: $d\mu_2 = dx$, $d\mu_1$: Dirac measure)
3) Can also introduce $d\mu^-$ for $T \to -\infty$: in general $d\mu^- \neq d\mu^+$. But $\mu^-(A) = \mu^+(IA)$ if dynamics is time-reversal invariant.

11.3 **Theorem**: $d\mu^+$ exists and is a Sinai-Ruelle-Bowen (SRB) measure if V (resp. ϕ_t) is mixing Anosov system.

11.4 **Aside on stable/unstable manifolds**: Definition: given a point $x \in M$, the global stable/unstable manifold is

$$W_x^s = \{y \in M |\limsup_{t\to\infty}\frac{1}{t}\log\mathrm{dist}(\phi_t(x),\phi_t(y)) < 0\}$$

$$W_x^u = \{y \in M |\limsup_{t\to\infty}\frac{1}{t}\log\mathrm{dist}(\phi_{-t}(x),\phi_{-t}(y)) < 0\}$$

Note: 1) $y \in W_x^s \Leftrightarrow x \in W_y^s$ & transitive. M is partitioned into equivalence classes $\alpha \in I=$ index set. 2) $W_x^{s/u}$ consists of points y whose future/past trajectory approaches that of x exponentially fast. 3) $W_x^{s/u}$ is not a manifold in general.

Local stable/unstable manifold

$$W_x^s(\varepsilon) = \{y \in M|\mathrm{dist}(\phi_t(x),\phi_t(y)) \le \varepsilon e^{-\lambda t}, t \ge 0, \text{ for some } \lambda > 0\} \qquad W_x^s = \bigcup_{\varepsilon>0} W_x^s(\varepsilon)$$

Fact: for $\varepsilon > 0$ small enough, $W_x^s(\varepsilon)$ is a (smooth) manifold.

11.5 **Anosov system**: At each $x \in M$: $W_x^s(\varepsilon), W_x^u(\varepsilon), \{\phi_t(x)||t| < \varepsilon\}$ have transversal and complementary tangent spaces.

11.6 **Mixing system**: A dynamical system is mixing, if for any open, non empty sets $U, V \subset M$, there is $T > 0$ s.t. $\phi_t(U) \cap V \neq \emptyset$ $(t \ge T)$.

11.7 **Ergodic measure**: A measure μ on M is ergodic if it is (i) invariant i.e. $\mu(\phi_t(A)) = \mu(A)$ (ii) indecomposable i.e. $\mu = \mu_1 + \mu_2$ with μ_i both invariant $\Rightarrow \mu_1 = 0$ or $\mu_2 = 0$.

11.8 **Discussion**: future stationary measure μ_+ is (i) regular w.r.t Lebesgue in direction of W_x^u (ii) singular in transverse directions

11.9 **SRB: introduction**: μ ergodic. How does μ^+ look like?

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T dt \int_M d\mu(x_0) f(\phi_t(x_0)) = \int d\mu^+(x) f(x)$$

with coordinate transformation $x_0 = \phi_{-t}(x)$ we get

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T dt \int_M \underbrace{d\mu(x)|\det D\phi_{-t}(x)|}_{=d\mu_t} f(x) = \int d\mu^+(x) f(x)$$

Dropping the function f

$$\frac{1}{T}\int_0^T d\mu_t \to d\mu^+(x) \qquad \text{(weakly)}$$

$$d\mu_t(x) = \frac{1}{|\det D\phi_t(\phi_{-t}(x))|} d\mu_0(x) \equiv h(x) d\mu_0(x)$$

For $t \to \infty$: $d\mu_t$ is regular with respect to Lebesgue only in direction of W_x^u. Singular in transverse directions.

11.10 **Preliminary guess for μ being SRB**: μ is ergodic. Foliation of μ: decompose μ in global unstable manifolds (labelled by equivalence classes $\alpha \in I$)

$$\mu = \int_I \mu_\alpha dm(\alpha)$$

with μ_α is a measure on W_α^u and $dm(\alpha)$ is measure on I.
Wrong: contradicts indecomposability.

11.11 **Definition of μ being SRB**: μ is ergodic. Let $S \subset M$ be small enough. Then $S = \bigcup_{\alpha\in I} S_\alpha$ with $S_\alpha \subset W_\alpha^u(\varepsilon)$ (α labels local unstable manifolds)

$$\mu|_S = \int_I \mu_\alpha dm(\alpha)$$

and $\mu_\alpha(d\xi)$ is absolutely continuous w.r.t. $d\xi$ on S_α.

11.12 **Entropy production**: entropy production $p(x)$ averaged along trajectory $\phi_t(x)$ during time T

$$p_T(x) = \frac{1}{T}\int_{-T/2}^{T/2} \dot\sigma(\phi_t(x)) dt$$

Note: time average over $[-T/2, T/2]$ (in contrast to 9.2).

Mean entropy production in the stationary state

$$\mu_+(p_T) = \mu_+(\dot\sigma) \equiv: \sigma_+$$

11.13 **Lemma (Ruelle)**: $\sigma_+ \geq 0$ (as opposed to $\mu_0(\dot\sigma) = 0$).

11.14 **Proof (sketch)**: Recall

$$\mu_+ = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt\mu_t$$

in the weak sense (i.e. to be applied to test function). Apply this to function $\dot\sigma$

$$\mu_+(\dot\sigma) = \lim_{T\to\infty} \frac{1}{T}\int_0^T dt\, \underbrace{\mu_t(\dot\sigma)}_{=-\dot S(t)} = -\lim_{T\to\infty}\frac{1}{T}(S(T)-S(0)) = -\lim_{T\to\infty}\frac{1}{T}S(\mu_T)$$

Now, for any $d\mu(x) = w(x)dx$

$$S(w) = -\int dxw(x)\log w(x) = \int dxw(x)\log\frac{1}{w(x)} \le \log\left(\int_M dxw(x)\frac{1}{w(x)}\right) = \log|M|$$

Here we used: if f is concave, then $\langle f(\cdot)\rangle \le f(\langle\cdot\rangle)$. Finally

$$\mu_+(\dot\sigma) \ge -\lim_{T\to\infty}\frac{\log|M|}{T} = 0$$

11.15: $p_T(x) > \sigma_+$ more than mean; $p_T(x) < \sigma_+$ less than mean.
Probability of observing an entropy production rate $p_T(x) \in [p, p+dp]$

$$\pi_T(p)dp = \mu_+\{x \in M | p_T(x) \in [p, p+dp]\}$$

Note: not time-symmetric measure μ_0.

11.16 **Theorem (Gallavotti, Cohen)**: Anosov system, mixing, reversible. Then

$$\frac{\pi_T(p)}{\pi_T(-p)} \approx e^{pT}$$

Note: this is not an exact result, but a limiting statement. More precisely:

$$\lim_{T\to\infty}\frac{1}{T}\log\frac{\pi_T(p)}{\pi_T(-p)} = p$$

11.17 **Remarks**: 1) Note universal character of law: no parameters to be adjusted (cfr. $TdS = dU + pdV$ in eq. stat. mechanics)
2) Proof makes use of Markov partitions
3) Connection with Onsager relations
4) Numerical and physical experiments confirm this fluctuation relation.

Part III

Open Quantum Systems

Lecture 12

12.1: $\mathcal{H}_1 \equiv \mathcal{H}, \mathcal{H}_2$ Hilbert spaces ($\mathcal{H}$ will describe the system, $\mathcal{H}_2$ will describe auxiliary system (reservoir,...)). ρ arbitrarily linear map $\mathcal{H} \mapsto \mathcal{H}$ ($\rho \in \mathcal{L}(\mathcal{H})$), but think of ρ as a density matrix ($\rho = \rho^* \geq 0$, $\mathrm{tr}\rho = 1$)

12.2 **Quantum operations** Quantum operation: $\phi : \mathcal{L}(\mathcal{H}) \mapsto \mathcal{L}(\mathcal{H})$

12.3 **Examples of quantum operations**:

i) Evolution: U unitary; $\phi : \rho \mapsto U\rho U^*$

ii) Projective measurement (von Neumann): $\{P_i\}_i$ resolution of identity ($P_i^* = P_i, P_iP_j = P_i\delta_{ij}, \sum_i P_i = 1$); $\phi : \rho \mapsto \sum_i P_i\rho P_i$= post-measurement state (non selective measurement) Alternatively (selective measurement): $\phi : \rho \mapsto P_i\rho P_i$ if outcome i occurs (with probability $\mathrm{tr}(\rho P_i)$).

iii) (generalizes i) & ii)) POVM = positive operator valued measure $\{F_i\}_i$ $F_i \geq 0$ $\sum_i F_i = 1$ Then outcome: Post measurement state: provided additional structure is given, namely $F_i = M_i^* M_i$, then $\phi : \rho \mapsto \sum_i M_i\rho M_i^*$ (non selective) or $\phi : \rho \mapsto M_i\rho M_i^*$ (selective, if outcome is i with probability $\mathrm{tr}(M_i\rho M_i^*) = \mathrm{tr}(\rho F_i)$)

iv) Adjoining an uncorrelated system. State ρ_0 on $\mathcal{H}_2$ (distinguished, $\rho_0 \geq 0$, $\mathrm{tr}\rho_0 = 1$) $\phi : \mathcal{H} \mapsto \mathcal{H} \otimes \mathcal{H}_2, \rho \mapsto \rho \otimes \rho_0$

v) Forgetting part of a system $\phi : \mathcal{H} \otimes \mathcal{H}_2 \mapsto \mathcal{H}, \rho \mapsto \mathrm{tr}_2\rho$ (partial trace $\mathrm{tr}_2\rho \in \mathcal{H}$ is defined by $\mathrm{tr}((\mathrm{tr}_2\rho)A_1) = \mathrm{tr}(\rho \cdot (A_1 \otimes \mathbb{I})))$

12.4 **General features**: All maps ϕ are i) linear ii) positive i.e. $\rho \geq 0 \Rightarrow \phi(\rho) \geq 0$ iii) trace preserving i.e. $\mathrm{tr}(\phi(\rho) = \mathrm{tr}(\rho)$, except for selective measurements.

as by the way follows from the structure (to be shown): $\phi(\rho) = \sum_i A_i\rho A_i^*, \sum_i A_i^* A_i = 1$ with $A_i : \mathcal{H} \mapsto \mathcal{H} \otimes \mathcal{H}_2$ (possibily with $\mathcal{H}_2 = \mathbb{C}$: $\mathcal{H} \otimes \mathcal{H}_2 = \mathcal{H}$)

12.5 **Summary POVM**: POVM's result from indirect measurement (i.e. measurement on ancilla)

12.6: POVM: $\phi : \mathcal{L}(\mathcal{H}) \mapsto \mathcal{L}(\mathcal{H})$, $\phi :\mapsto \phi(\rho) = \sum_i M_i\rho M_i^*$ (Krans representation). What properties characterise the existence of such a representation? Seen: linear, trace-preserving and positive are necessary. Not sufficient for a Krans representation!

12.7 **Definitions**: $\phi : \mathcal{L}(\mathcal{H}) \mapsto \mathcal{L}(\mathcal{H})$ is m-positive ($m = 1, 2, 3, ...$) if $\hat{\phi} : \mathcal{L}(\mathcal{H} \otimes \mathbb{C}^m) \mapsto \mathcal{L}(\mathcal{H} \otimes \mathbb{C}^m)$ defined by $\hat{\phi}(\rho \otimes \sigma) = \phi(\rho) \otimes \sigma$ is positive; ϕ is completely positive if it is m-positive for all m.

12.8 **Remarks**: 1) If ϕ has POVM $\equiv$ Krans representation, then ϕ is completely positive. Indeed: $\hat{\phi}(\hat{\rho}) = \sum_i (M_i \otimes \mathbb{I})\hat{\rho}(M_i^* \otimes \mathbb{I})$

2) $\hat{\rho} \in \mathcal{L}(\mathcal{H} \otimes \mathbb{C}^m) = \mathcal{L}(\mathcal{H}) \otimes \mathcal{L}(\mathbb{C}^m)$ may be written as $\hat{\rho} = \sum_{ij=1}^m \rho_{ij} \otimes |i\rangle\langle j|$ with ($\rho_{ij} \in \mathcal{L}(\mathcal{H})$). Then

$$\hat{\phi} : (\rho_{ij})_{i,j=1}^m \mapsto (\phi(\rho_{ij}))_{i,j=1}^m$$

Fact: there are linear trace-preserving positive maps ϕ, such that ϕ is not 2-positive.

Example: $\phi(\rho) = \rho^T$ with $\mathcal{H} = \mathbb{C}^2$ is not 2-positive.

- Linearity, trace-preserving are trivial.
- Positive? $(\varphi, \rho^T \psi) = \overline{(\rho^T \psi, \bar{\varphi})} = (\rho^* \bar{\psi}, \bar{\varphi}) = (\bar{\psi}, \rho\bar{\varphi})$
- 2-positive? Not. Take for example

$$\underbrace{\hat{\rho} = \frac{1}{2}\left(\begin{array}{cc|cc} 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 \end{array}\right)}_{\text{Eigenvalues: 0,0,0,1}\Rightarrow\text{positive}} \mapsto \underbrace{\hat{\phi}(\hat{\rho}) = \frac{1}{2}\left(\begin{array}{cc|cc} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ \hline 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{array}\right)}_{\text{Eigenvalues: } \frac{1}{2},\frac{1}{2},\frac{1}{2},-\frac{1}{2}\Rightarrow\text{not positive}}$$

12.9 **Theorem (Krans, 1970)**: Let $\phi : \mathcal{L}(\mathcal{H}) \mapsto \mathcal{L}(\mathcal{H})$ be linear and completely positive. Then ϕ has a Krans representation

$$\phi(\rho) = \sum_i M_i \rho M_i^*$$

for some $M_i : \mathcal{H} \mapsto \mathcal{H}$. If ϕ is moreover trace-preserving, then $\sum_i M_i^* M_i = 1$ (other direction: already seen).

12.10 **Semigroups**: Recall: If U_t is a group (in t) of unitaries, then

$$\left.\frac{dU_t}{dt}\right|_{t=0} =: -iH$$

with $H^* = H$ (and viceversa: H are generators of group). U_t are invertible: $U_t^* = U_{-t}$. Note: ϕ need not to be invertible. Thus consider semigroups $\phi_t : \mathcal{L}(\mathcal{H}) \mapsto \mathcal{L}(\mathcal{H})$ with $\phi_{t+s} = \phi_t \circ \phi_s$ $(t, s \geq 0)$ and $\phi_0 = \text{id}$. Generator (Lindltadian):

$$L := \left.\frac{d\phi_t}{dt}\right|_{t=0} : \mathcal{L}(\mathcal{H}) \mapsto \mathcal{L}(\mathcal{H})$$

12.11 **Theorem (Gorimi, Kossakowski, Sudavskan; Lindltad)**: The generator of a trace-preserving, completely positive semigroup is of the form

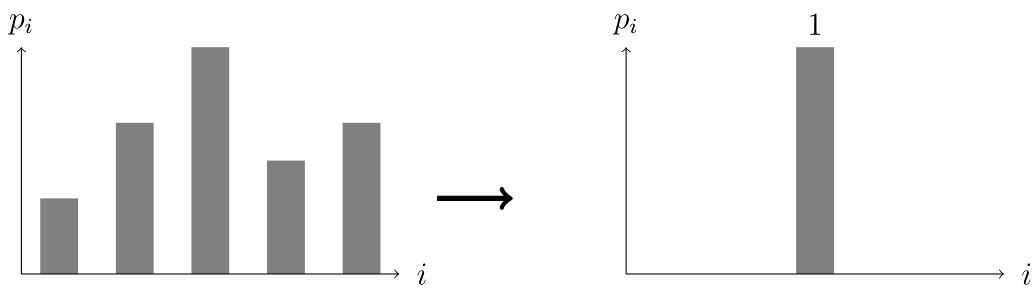
$$L(\rho) = -i[H, \rho] + \sum_\alpha (\Gamma_\alpha \rho \Gamma_\alpha^* - \frac{1}{2}\{\rho, \Gamma_\alpha^* \Gamma_\alpha\})$$

with $H^* = H$ and some Γ_α. The converse is also true.

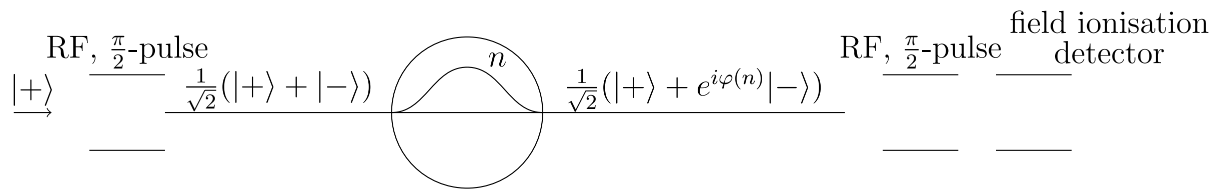
Lecture 13

13.1 **POVM and the gradual collapse of wavefunctions**: Recall: projective measurements ($\{P_i\}$ resolution of the identity) $\rho \mapsto \rho' = P_i \rho P_i / \mathrm{tr}(P_i \rho)$ if outcome is i (collapse).

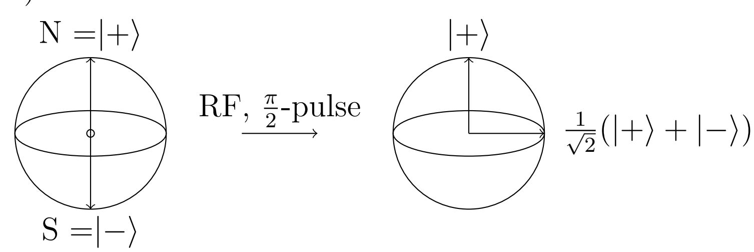
Comments: - repetition of measurement does not change state further
- If $P_i = |\Psi_i\rangle\langle\Psi_i|$ (1- dimensional projection), then $\rho' = |\Psi_i\rangle\langle\Psi_i|$ (pure)



13.2 **Examples**: 1) Spin 1/2: resolution of identity is $P_\uparrow + P_\downarrow = 1$; apparatus is Stern-Gerlach
2) E.m. field in a cavity (enough small such that modes do not form a continuum; focus on a single mode). N=number operator (number of photons in that mode) $= \sum_{n=0}^{\infty} n P_n$; resolution of identity: $\sum_{n=0}^{\infty} P_n = 1$. What is the apparatus which does the job?



13.3 **Rydberg atoms**: Rydberg atoms (circular levels $l = m = n - 1$ (l is maximal)) with $n = 51$ ($|+\rangle$) and $n = 50$ ($|-\rangle$) (2-level system)
- long lifetime
- transition frequency $\omega_0 = \omega + \delta$ (ω frequency of the mode)
- Bloch sphere (visualisation)



13.4 **Atom in cavity: Jaynes-Cummings model**:

$$H = \frac{\hbar\omega_0}{2}\sigma_z + \hbar\omega a^* a + \frac{\hbar g}{2}(a\sigma_+ + a^*\sigma_-)$$

on $\mathcal{H} \otimes \mathbb{C}^2$ (Basis: $\{|n\rangle \otimes |\pm\rangle\}$). H leaves $|n, +\rangle, |n+1, -\rangle$ invariant.
- Eigenvalues:

$$E_n^{\pm} = \hbar\omega(n + 1/2) \pm \frac{\hbar}{2}\sqrt{\delta^2 + (n+1)g^2}$$

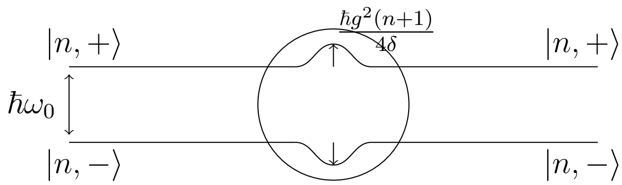
- For $g = 0$:

$$E_n^{\pm}(g=0) = \begin{cases} \hbar\omega(n+1/2) + \frac{\hbar}{2}\delta = \hbar\omega n + \frac{\hbar\omega_0}{2}, & |n, +\rangle \\ \hbar\omega(n+1/2) - \frac{\hbar}{2}\delta = \hbar\omega(n+1) - \frac{\hbar\omega_0}{2}, & |n+1, -\rangle \end{cases}$$

-For $g << \delta$:

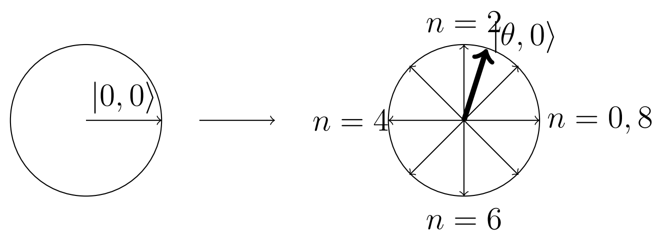
$$E_n^{\pm} = E_n^{\pm}(g=0) \pm \frac{\hbar g^2(n+1)}{4\delta}$$

In the cavity $g = g(t)$. Eigenvector follows adiabatically



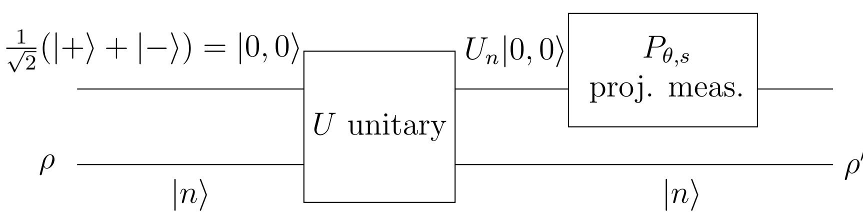
Quantum Non-demolition: $|n\rangle$ preserved.
Set $\varphi_0 = \frac{\int g^2(t)dt}{2\delta}$. Phase shift between $|n,\pm\rangle$: $\varphi(n) = (n+1/2)\varphi_0$ Thus φ_0: phase shift per photon.

<u>13.5</u> Pick parameter such that $2\varphi_0 = \frac{2\pi}{2q}$, e.g. $q = 4$ ($\rightarrow$ can only detect photons modulo 8). Pick θ. Equatorial plane of Bloch sphere



Measure (projectively) whether state is $|\theta,0\rangle$ or $|\theta,1\rangle$ (actually: after suitable $\pi/2$-pulse whether is $|+\rangle$ or $|-\rangle$).

Schematically



$$U(|n\rangle \otimes |0,0\rangle) = |n\rangle \otimes (U_n|0,0\rangle)$$

$$\rho \mapsto \rho' = \sum_{s=0,1} \mathrm{tr}_{\mathbb{C}^2}(P_{\theta,s}U(\rho \otimes |0,0\rangle\langle 0,0|)U^* P_{\theta,s}) = \sum_{s=0,1} \langle\theta,s|U(\rho \otimes |0,0\rangle\langle 0,0|)U^*|\theta,s\rangle$$

(non-selective) $P_{\theta,s} = |\theta,s\rangle\langle\theta,s|$.

$$\langle n|\rho'|m\rangle = \sum_{s=0,1} \langle\theta,s|U_n|0,0\rangle\langle n|\rho|m\rangle\langle 0,0|U_m^*|\theta,s\rangle.$$

For short

$$\rho' = \sum_{s=0,1} M_s \rho M_s^* \quad \leftarrow \quad \text{is POVM}$$

with M_s diagonal in n

$$M_s = \mathrm{diag}(\langle\theta,s|U_n|0,0\rangle$$

E.g. $s=0$: $\cos\left(\frac{n\cdot 2\varphi_0 - \theta}{2}\right)$. So: $M_0 = \cos\left(N\varphi_0 - \frac{\theta}{2}\right)$, $M_1 = \sin\left(N\varphi_0 - \frac{\theta}{2}\right)$, etc.

13.6 **Note**: If ρ is diagonal in N (as resulting from hypothetical proj. measurement) then $[\rho, M_s] = 0$, whence $\rho' = \rho$.

13.7 **Example**: 1) If $\theta = \frac{3}{2} 2\varphi_0$ & $s = 0$ comes out, then
$n = 0, 1, 2, 3$ are favoured
$n = 4, 5, 6, 7$ are unfavoured
But no n is sure (unlike proj. measurement)
2) If $\theta = 0$, then $n = 2$ and $n = 6$ cannot be discriminated (coherent superposition there of are preserved).

13.8 **Another reading of POVM**: selective

$$\rho' = \frac{M_s \rho M_s^*}{\mathrm{tr}(M_s \rho M_s^*)}$$

We have

$$\underbrace{\langle n|\rho'|n\rangle}_{=p(n|\theta,s)} = \frac{\overbrace{\langle n|\rho|n\rangle}^{=p(n)} \overbrace{|\langle \theta, s|U_n|0,0\rangle|^2}^{=p(\theta,s|n)}}{\underbrace{\mathrm{tr}(...)}_{=\sum_n p(n)p(\theta,s)=p(\theta,s)}} \qquad \Rightarrow \qquad p(n|\theta, s) = \frac{p(n)p(\theta, s|n)}{p(\theta, s)} \quad \text{(Beyes)}$$

The outcome s (for picked θ) changes prob. distr. $p(n) \mapsto p(n|\theta, s)$. By repeated (random) $\theta' s$ distribution p gradually collapses.

13.9 **References**:

1) J.M. Raimond, M. Brune, and S. Haroche, Colloquium: Manipulating quantum entanglement with atoms and photons in a cavity, Rev. Mod. Phys., 73, 565, 2001.

2) C. Guerlin et al., Progressive field-state collapse and quantum non-demolition photon counting, Nature 448, 889, 2007.