NONEQUILIBRIUM STAT. MECH. & THE FUNDAMENTAL LAWS OF THERMODYNAMICS —

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CONTENTS

1. Goals and problems

- Derive fundamental laws (0^{th} – 3^{rd} law) of thermodynamics from nonequilibrium stat. mech.
- Clarify basic notions, such as TD system, heat bath (reservoir), TD processes: rev., irrev., cyclic,

adiabatic, isothermal,
"quasi-static" ...

- Return to equilibrium,
... $\longrightarrow$ 0^{th} law
- Internal energy, heat energy, work $\longrightarrow$ 1^{st} law
- entropy, degree of efficiency $\longrightarrow$ 2^{nd} law
- Onsager reciprocity, Fourier, Ohm, Kubo, Transport Theory (QBM...)

- Magnetism … FM SG
- Thermodynamics, irrev. behaviour from (quantum) stat. mech. QBM
- Meaning of quantum mechanics, quantum theory of experiments
- emergence of space-time … from fund. quantum theory, cosmol. puzzles, … $\Lambda, \vec{B}$

Relatively hard analytical problems are:

✓ 1) R to E

(✓) 2) Construction and char. of NESS

(✓) 3) Construction and char. of t-periodic states

✓ 4) Generalized "adiabatic theorems";

? adiabatic processes

? 5) Metastability, hysteresis

In this lecture, focus on

heat energy, entropy, (reversible) isothermal processes, $\eta \leq \eta^{Carnot}$.

generalizations of adiabatic theorems!

Adiabatic Processes?

These are steps towards understanding $k_B \to 0$, irreversibility.

2. TD systems, heat baths, processes.

- TD system Σ : qm syst. confined to compact region, $\mathcal{O}_\Sigma$, of phys. space E^3; kinematical *alg., $\mathcal{F}^\Sigma$, of ops. (~quant. phase space) – here usually $\dim \mathcal{F}^\Sigma < \infty$ –, "with Σ, $\Sigma^{(\theta)}$ is TD syst., too, $\mathcal{O}_{\Sigma^{(\theta)}} = \theta\, \mathcal{O}_\Sigma$, $0 < \theta < \infty$"; thermodyn. stability.

$\mathcal{S}$: all such systs.; (action of group of resc., θ, on $\mathcal{S}$; ...).

- <u>Heat bath</u> W : TD limit of incr. family of TD systems $W \sim \lim_{\theta\to\infty} \Sigma^{(\theta)}$,

$W^{(\theta)} = W$,

$$\mathcal{F}^W = \overline{\bigvee_{\mathcal{O}\nearrow E^3} \mathcal{F}^{\mathcal{O}}}^{\|(\cdot)\|}$$

(a C^*-algebra)

When W is isolated, state of W is KMS state on $\mathcal{F}^W$

corresp. to some $\beta = (k_B T)^{-1}$,

(chem. potentials): For

$$a \in \bigvee_{\mathcal{O} \nearrow \mathbb{E}^3} \mathcal{F}^{\mathcal{O}},$$

$$\omega^W(a) = \lim_{\mathcal{O} \nearrow \mathbb{E}^3} tr(P_{\mathcal{O}}^W a),$$

$$P_{\mathcal{O}}^W = \frac{1}{\Xi_{\mathcal{O}}^W(\beta, \underline{\mu})} e^{-\beta[H_{\mathcal{O}}^W - \sum \mu_j N_{\mathcal{O}}^j]}.$$

$\mathcal{W}$: set of "all" heat baths.

Diathermal contact or "wall": spatially loc. interaction betw. W & $\Sigma \in \mathcal{S}$ (or $W' \in \mathcal{W}$), s.t. <u>all</u> extensive quant.,

<u>except</u> int. energy of Σ, ($W' \in \mathcal{W}$), remain constant.

(Part of) <u>0^{th} law</u>: After all contacts betw. W & $\Sigma \in \mathcal{S}$ ($W' \in \mathcal{W}$) are broken state of W always returns to <u>same</u> ω^W ($t \to \infty$), char. by β_W.

If $(W, \Sigma) \xrightarrow[I]{} W \vee \Sigma$ state of $W \vee \Sigma$ appr. equ. state indep. of initial state of Σ, with $\beta = \beta_W$. If $I \to 0$, adiabatically, state of $\Sigma \to$ equ. state only dep. on β_W.

R to E ; ↗ M.M., sect. 4.

- <u>Dynamics</u>: (finite vol.!)

$$H(t) \equiv H^{W \vee \Sigma}(t) := H^{W} + H^{\Sigma}(t)$$

$$\begin{array}{ccc} H(t) & H^W & H^\Sigma(t) \\ \downarrow & \downarrow & \downarrow \\ \mathcal{L}(t) & \mathcal{L}^W & \mathcal{L}^\Sigma(t) \end{array}$$

dep. on β_W

$$H^{\Sigma}(t) = H_0^{\Sigma}(\underline{\lambda}_t) + g(t)\, I^{W \vee \Sigma}$$

$\underline{\lambda}_t$: t-dep. param. $\qquad I^{W\vee\Sigma} \in \mathcal{F}^W \otimes \mathcal{F}^\Sigma$

$\mathcal{L}(t) \rightarrow$ prop. $U(t,s)$ (↗ R&S)

- P_t : "true" state of $W \vee \Sigma$ at time t

$$P_t = U(t,s) P_s U(t,s)^*,$$

$$\dot{P}_t = -\frac{i}{\hbar}[H(t), P_t].$$

(Liouville eq.)

"Reference state" at time t:

$$P_t^\beta := \Xi_t(\beta,\underline{\mu})^{-1}\, e^{-\beta[H(t)-\underline{\mu}\cdot N^{W\vee\Sigma}]}$$

Principle conc. TD limit! <

(GNS, HHW, $(AW)^2$, R, BR)

$$\rho_t(a) = \mathrm{TD}\lim \operatorname{tr}(P_t\, a)$$

$$\omega_t^\beta(a) = \mathrm{TD}\lim \operatorname{tr}(P_t^\beta\, a)$$

$$\rho_t^\Sigma := \rho_t\big|_{\mathbb{1}\otimes\mathcal{F}^\Sigma}$$

. . . .

- Processes: Choice of $\{H^\Sigma(t)\}$

$\longrightarrow$ traj. of states $\{\rho_t^\Sigma\}$ of Σ, alternatingly in contact with 0, 1, 2, ... heat baths from $\mathcal{W}$.

- Isothermal process: diath. contact of Σ to 1 heat bath.
- Cyclic process:

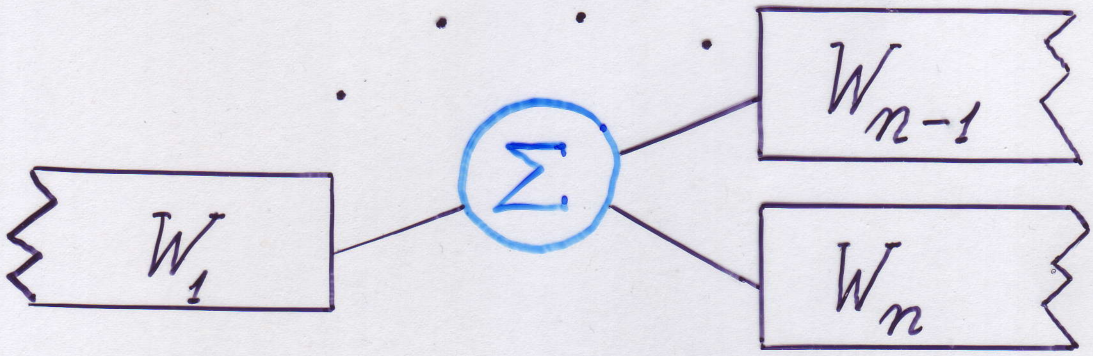
$$H(t+t_*) = H(t), \text{ some } t_* < \infty.$$

. . . .

- Adiabatic process: Σ isolated.
- Reversible process:

$$\rho_t \simeq \omega_t^{\beta(t)}.$$

3. Heat energy & entropy of TD systems



Int. energy:

$$U^{\Sigma}(t) := \rho_t\left(H^{\Sigma}(t)\right)$$

Heat energy:

$$\frac{dQ}{dt}(t) := -\sum_j \frac{d}{dt}\,\rho_t\left(H^{W_j}\right)$$

$$\parallel$$

$$\mathcal{P}(t)$$

$$= -\frac{i}{\hbar}\sum_j \rho_t\left([H(t), H^{W_j}]\right)$$

$$= \frac{i}{\hbar}\sum_j \rho_t\left([H^{W_j}, I^{\vee W_j \vee \Sigma}(t)]\right)$$

$$=: \sum_j \frac{dQ^{W_j}}{dt}(t)$$

$$\Rightarrow \dot{U}^{\Sigma}(t) - \frac{đQ}{dt}(t) = \rho_t\left(\dot{H}^{\Sigma}(t)\right) =: \frac{đA}{dt}(t)$$

1st law

<u>Entropy:</u>

$$S^{\Sigma}(t) := -k_B \, TD\lim \, tr\left(P_t\left[\ln P_t - \sum_j \ln P^{W_j}\right]\right)$$

$$= -k_B \, TD\lim \, tr\left(P_t\left[\ln P_t + \sum_j \left\{\beta_j\left(H^{W_j} - \underline{\mu}_j \cdot \underline{N}^{W_j}\right) + \ln \Xi^{W_j}\right\}\right]\right)$$

≤ 0 !

$$\left.\begin{array}{l} (i)\ tr\, P_t \ln P_t \\ (ii)\ tr\left(P_t\, \underline{\mu}_j \cdot \underline{N}^{W_j}\right) - \\ (iii)\ tr\left(P_t \ln \Xi^{W_j}\right) \end{array}\right\} \text{indep. of } t\,!$$

$$\Rightarrow \dot{S}^{\Sigma}(t) = -\sum_j \frac{1}{T_j} \frac{d}{dt} \rho_t(H^{W_j})$$

$$= \sum_j \frac{1}{T_j} \frac{đQ^{W_j}}{dt}(t),$$

for diathermal contacts.

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4. Isothermal processes, & "isothermal theorem"

For only 1 reservoir, $W \in \mathcal{W}$, have isothermal process,

$$\dot{U}^{\Sigma}(t) = \frac{đQ}{dt}(t) + \frac{đA}{dt}(t),$$

$$\dot{S}^{\Sigma}(t) = \frac{1}{T^W} \frac{đQ}{dt}(t), \text{ or}$$

$$\Delta S^{\Sigma} = \frac{1}{T^W} \Delta Q$$

<u>Question:</u> What happens (<u>after</u> R to E) in isoth. pr. of $W \vee \Sigma$, e.g. when diath. contact betw. Σ & W is slowly interrupted, ...? What char. reversible isoth. processes?

Isothermal Theorem.

$$H_t^{(\tau)} := H\left(\frac{t}{\tau}\right), \quad s := \frac{t}{\tau}.$$

$$\frac{\partial}{\partial s} U(\tau s, \tau u) = -i\hbar\tau \mathcal{L}(s) U(\tau s, \tau u)$$

Consider isoth. process of $W \vee \Sigma$ from $t_0 = \tau s_0$ till $t_1 = \tau s_1$, s_0, s_1 fixed, initial state ω^β,

($H(s)$ indep. of s, for $s < s_0$)

$\tau \to \infty$

Let ω^{β}_{t} be reference (equ.-, i.e., KMS-) state for $H(\frac{t}{\tau})$

Hypotheses: $\{\mathcal{L}(t)\}$ have common dense domain of def.; $(\mathcal{L}(t)+i)^{-1}$ diff. in t, $\mathcal{L}(t)\frac{d}{dt}(\mathcal{L}(t)+i)^{-1}$ unif. bd. in norm; $\sigma_{pp}(\mathcal{L}(t)) = \{0\}$, $\sigma(\mathcal{L}(t)) \setminus \{0\} = \sigma_c(\mathcal{L}(t))$, $\forall t$.

Theorem. Under these hyp.,

$$\rho_{\tau s}(a) = \omega^{\beta}_{\tau s}(a) + o(1),$$

as $\tau \to \infty$, $\forall a \in \mathcal{F}^W \otimes \mathcal{F}^\Sigma$,

$\forall s \in I$, $I \subset \mathbb{R}$ arb. comp. int.

Pf. Follow, e.g., AE, T, &

get rid of superfluous hyp.;

(Abou-Salem-F).

Cor1. Reversible isoth. proc.

= quasi-static —"— —"—;

$\tau \gg$ relaxation times.

"Equ.-stat.-mech." def. of

entropy:

$$S^\Sigma_{rev.}(t) = -k_B \, tr\left(P^\beta_t \left[\ln P^\beta_t - \ln P^W\right]\right)$$

$$= k_B \, \omega_t^\beta \left(\beta H^\Sigma(t)\right) + k_B \ln \frac{\Xi_t(\beta)}{\Xi^W}$$

$$= \frac{1}{T^W} \left(U^\Sigma_{rev.}(t) - F^\Sigma(t) \right)$$

$$\Rightarrow T^W \Delta S^\Sigma_{rev.} = \omega^\beta_{\tau s_1}\left(H^\Sigma(s_1)\right) - \omega^\beta_{\tau s_0}\left(H^\Sigma(s_0)\right)$$

$$- \int_{s_0}^{s_1} ds \, \omega^\beta_{\tau s}\left(\dot H^\Sigma(s)\right)$$

$\rho_{\tau s}$

$$\overset{\tau \to \infty}{=} \Delta U^\Sigma - \Delta A = \Delta Q$$

Isoth. Thm. 1st law

Cor. 2. $\Delta S^\Sigma_{rev.} \underset{\tau \to \infty}{=} \Delta S^\Sigma$

Cor. 3. If $H^\Sigma(t) \to H^\Sigma_\infty \in \mathcal{F}^\Sigma$, $(g(t) \to 0)$, as $t \to \infty$,

$\rho^\Sigma_{\tau s} \to$ Gibbs state for H^Σ_∞, as $\tau \to \infty$, $s \to \infty$.

$$= k_B\, \omega_t^\beta(\beta H^\Sigma(t)) + k_B \ln \frac{\Xi_t(\beta)}{\Xi^W}$$

$$= \frac{1}{T^W}\left(U^\Sigma_{rev.}(t) - F^\Sigma(t)\right)$$

$$\Delta A = \int_{s_0}^{s_1} ds\; \rho_{\tau s}(\dot{H}^\Sigma(s))$$

$$\underset{\tau\to\infty}{\simeq} \int_{s_0}^{s_1} ds\; \omega^\beta_{\tau s}(\dot{H}^\Sigma(s)) = \Delta F$$

$$\Delta S^\Sigma_{rev.} \underset{\tau\to\infty}{=} \Delta S^\Sigma$$

Cor. 2 If $H^\Sigma(t) \longrightarrow H_\infty \in \mathcal{F}^\Sigma$, $(g(t) \to 0)$, as $t \to \infty$, then

$\rho^\Sigma_{\tau s} \longrightarrow$ Gibbs state for H^Σ_∞,

as $\tau \to \infty$, $s \to \infty$.

This is easy part of 0^{th} Law of TD.

<u>Theorem.</u> If $H^{\Sigma}(t) \xrightarrow[t\to\infty]{} H^{\Sigma}_{\infty}$ suff. rapidly, W_j's free & dispersive, ... then

$$\rho_t \longrightarrow \rho_\infty \quad (NESS)$$

ρ_∞ <u>time-transl. inv.</u> (JP, FMUe, ... DeRK)

<u>Cor. 1.</u>

$$\frac{đQ}{dt}(t) = \sum_{j=1}^{n} \frac{đQ^{W_j}}{dt}(t)$$

$$= \frac{i}{\hbar}\rho_t\left(\left[H(t), \sum H^{W_j}\right]\right)$$

$$= \frac{i}{\hbar}\rho_t\left(\left[H(t), \cancel{H(t)} - H^{\Sigma}(t)\right]\right)$$

$$= \frac{i}{\hbar}\left(\frac{d}{dt}\rho_t\right)\big(\underbrace{H^{\Sigma}(t)}_{\to H^{\Sigma}_{\infty}}\big)$$

$\longrightarrow 0$, as $t \to \infty$, i.e.,

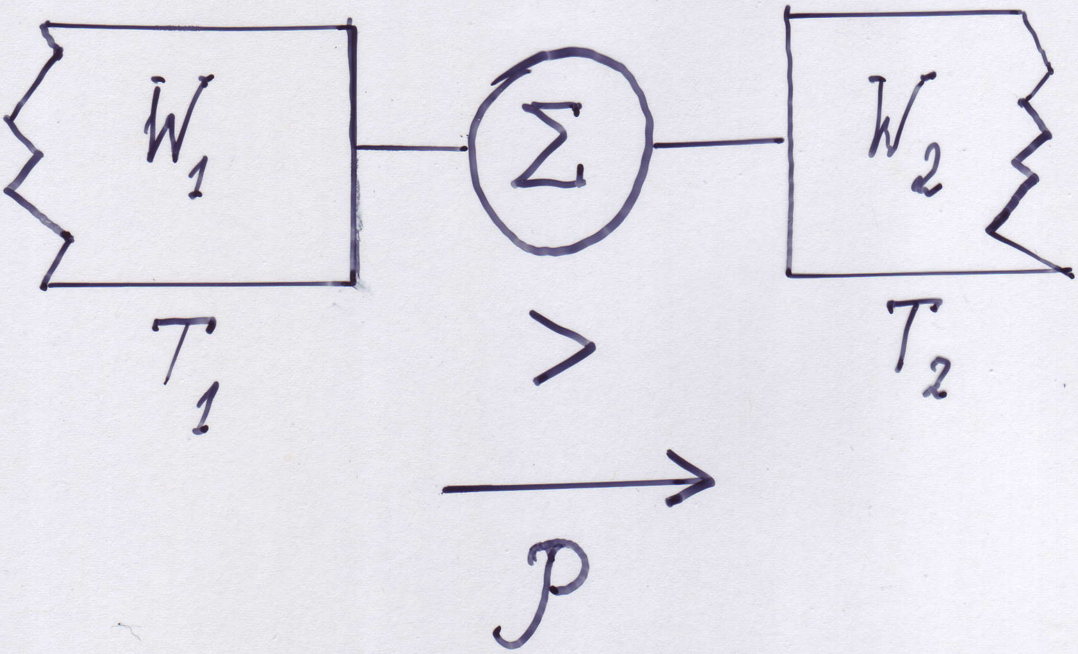
$$\sum_{j=1}^{n} \mathcal{P}^{W_j}(t) \underset{t\to\infty}{\longrightarrow} 0. \qquad (1)$$

Furthermore:

$$0 \geq -\mathcal{E} := \lim_{t\to\infty} \dot{S}^{\Sigma}(t)$$

$$= \lim_{t\to\infty} \sum_j \frac{1}{T_j} \mathcal{P}^{W_j}(t) \quad (2)$$

This implies Clausius' formulation of 2^{nd} Law of TD. --- Onsager rels.



Generalizations:

Particle currents, ...

Consider cyclic TD process: $H^{\Sigma}(t+t_*) = H^{\Sigma}(t)$, some $t_* < \infty$ (period).

For suitably chosen Σ, $W_1, \dots, W_n$, and $H^{\Sigma}(\cdot)$,

$$\rho_t \xrightarrow[t\to\infty]{} \omega_t ,$$

where $\omega_{t+t_*} = \omega_t$, i.e., ω_t periodic in t with same period t_*; (FMSUe).

For simplicity, $n=2$. Then

setting $\Delta A(t) := A(t+t_*) - A(t)$, we have that

(1) $\Delta U^{\Sigma}(t) \longrightarrow 0, \ (t \to \infty)$

(2) $\lim_{t\to\infty} \left(\frac{\Delta Q^{W_1}(t)}{T_1} + \frac{\Delta Q^{W_2}(t)}{T_2} \right) \leq 0$

If Σ performs work (i.e., Σ is a "<u>heat engine</u>") then

(3) $\Delta A(t) \xrightarrow[t\to\infty]{} \Delta Q^{W_1}(t) + \Delta Q^{W_2}(t) \geq 0$,

by 1^{st} law & (1)!

If $T_1 \geq T_2 \Rightarrow \Delta Q^{W_1} \geq 0$;

Clausius

(for >, see e.g. FMUe!)

Cor. 2 $T_1 \geqslant T_2$. Then

$$0 \leqslant \eta^{\Sigma} := \left(\frac{\Delta A^{\Sigma}}{\Delta Q^{W_1}}\right)_{t\to\infty}$$

$$\overset{(3)}{=} 1 + \left(\frac{\Delta Q^{W_2}}{\Delta Q^{W_1}}\right)_{t\to\infty}$$

$$\overset{(2)}{\leqslant} 1 - \frac{T_2}{T_1} =: \eta^{Carnot}$$

Difference, $\eta^{Carnot} - \eta^{\Sigma}$, computable in terms of entropy production (as, e.g., in FMUe).