Lecture 1: Emergence of the laws of thermodynamics from quantum mechanics

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Advanced School on Ubiquitous Quantum Physics:
The New Quantum Revolution

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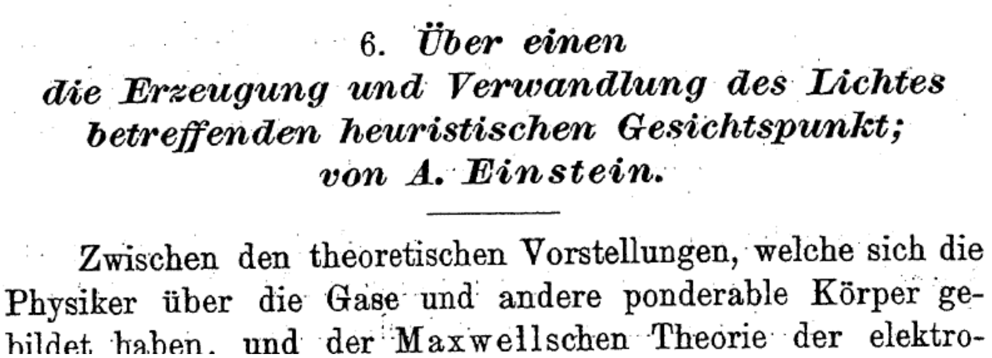
FOR MOLECULAR DYNAMICS

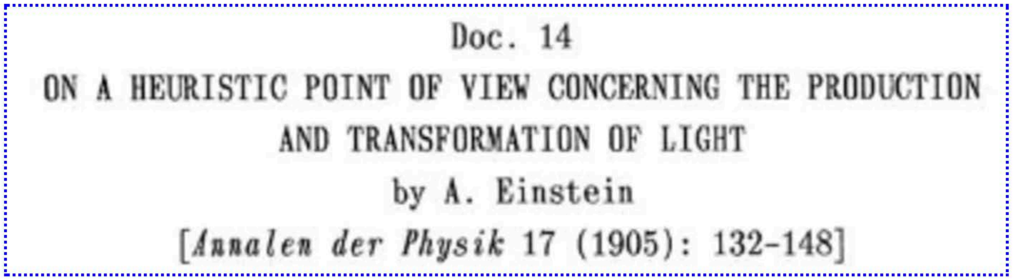
Quantum Thermodynamics

Any theory should be consistent with Thermodynamics



6. *Über einen*
die Erzeugung und Verwandlung des Lichtes
betreffenden heuristischen Gesichtspunkt;
von A. Einstein.

Zwischen den theoretischen Vorstellungen, welche sich die Physiker über die Gase und andere ponderable Körper gebildet haben, und der Maxwellschen Theorie der elektro-

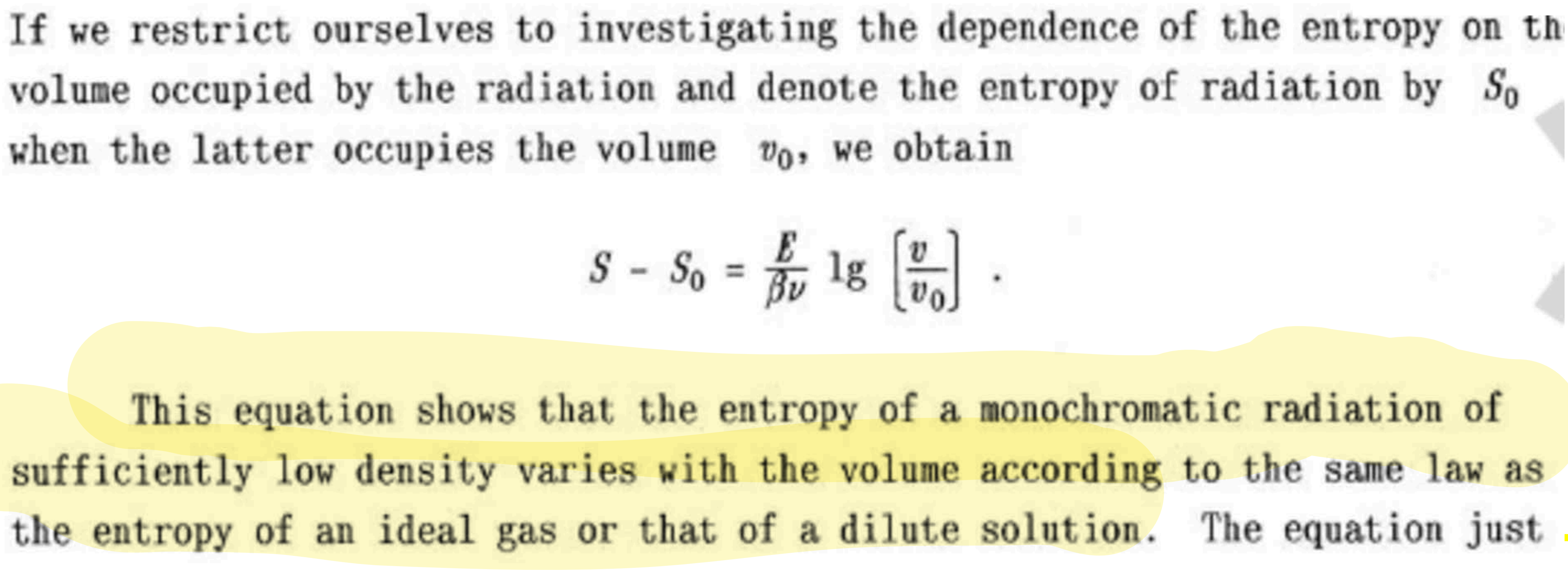


Doc. 14

ON A HEURISTIC POINT OF VIEW CONCERNING THE PRODUCTION
AND TRANSFORMATION OF LIGHT
by A. Einstein
[*Annalen der Physik* 17 (1905): 132-148]

Einstein 1905

$$\boxed{E = h\nu}$$



If we restrict ourselves to investigating the dependence of the entropy on th volume occupied by the radiation and denote the entropy of radiation by S_0 when the latter occupies the volume v_0, we obtain

$$S - S_0 = \frac{E}{\beta\nu} \lg\left[\frac{v}{v_0}\right] .$$

This equation shows that the entropy of a monochromatic radiation of sufficiently low density varies with the volume according to the same law as the entropy of an ideal gas or that of a dilute solution. The equation just

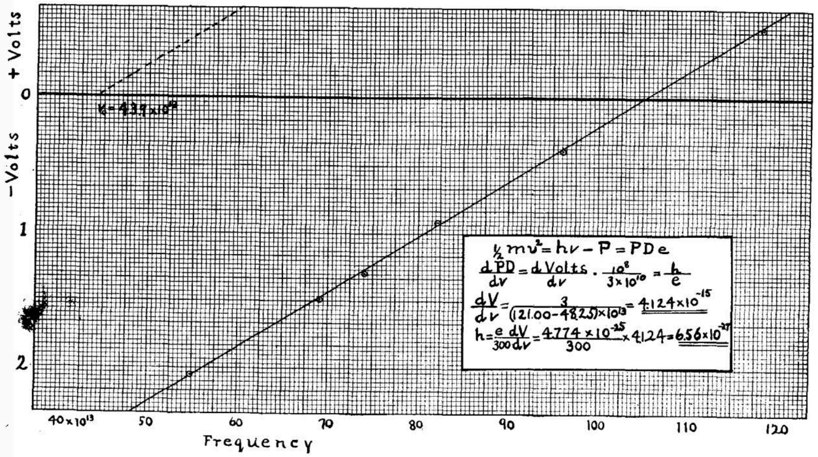
If monochromatic radiation of frequency ν and energy E is enclosed (by reflecting walls) in the volume v_0, the probability that at a randomly chosen instant the entire radiation energy will be contained in the portion v of the volume v_0 is

$$W = \left(\frac{v}{v_0}\right)^{\frac{N}{R}\frac{E}{\beta\nu}}$$

From this we further conclude:

Monochromatic radiation of low density (within the range of validity of Wien's radiation formula) behaves thermodynamically as if it consisted of mutually independent energy quanta of magnitude $R\beta\nu/N$.

The paper is wrongly interpreted as the photoelectric effect



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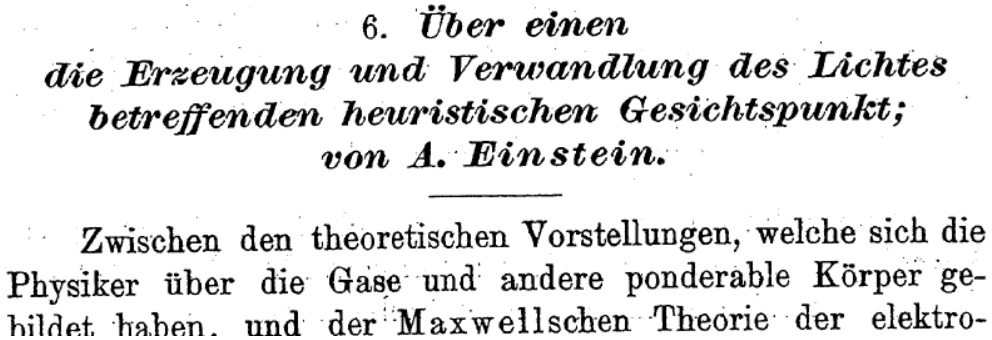

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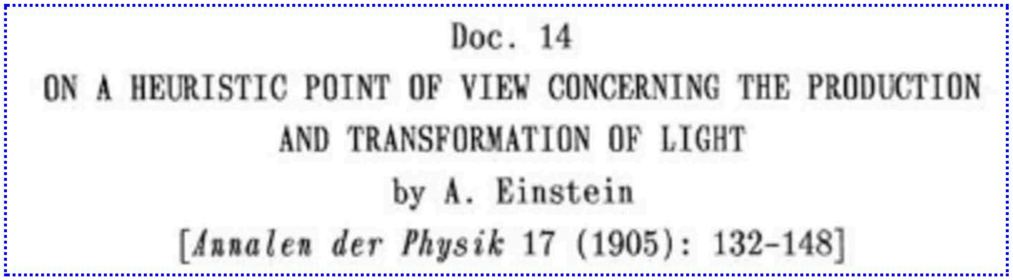

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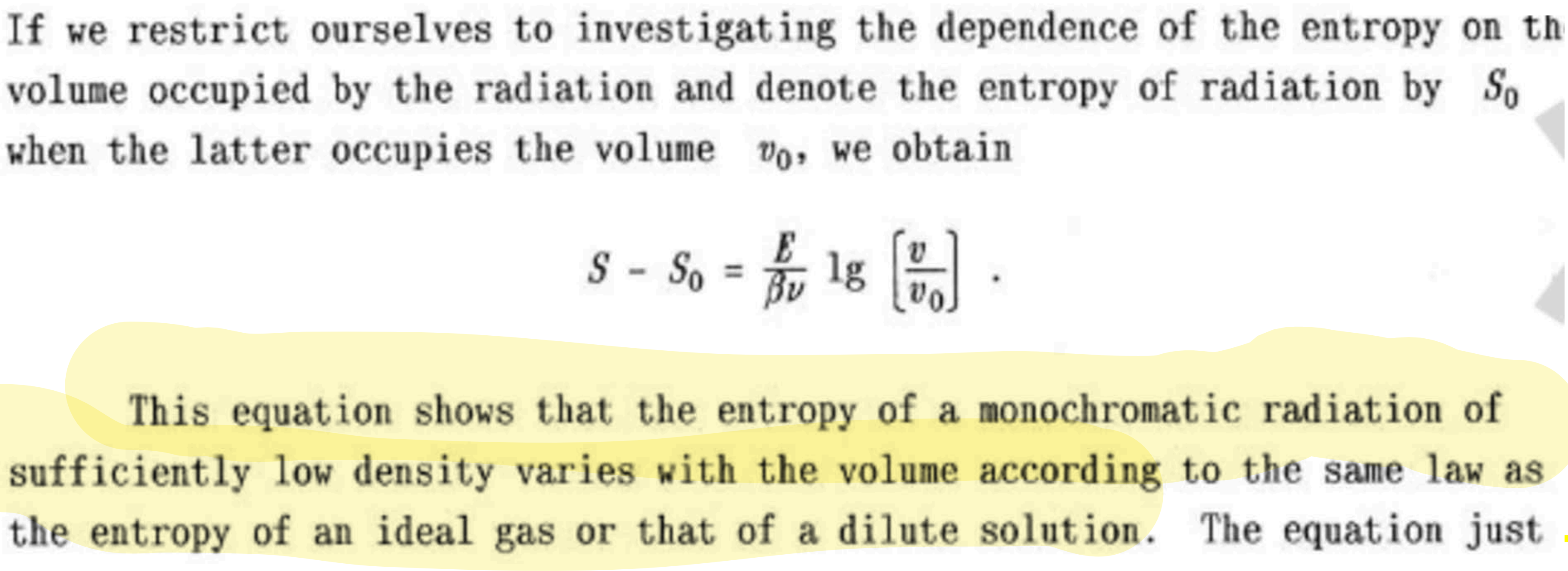

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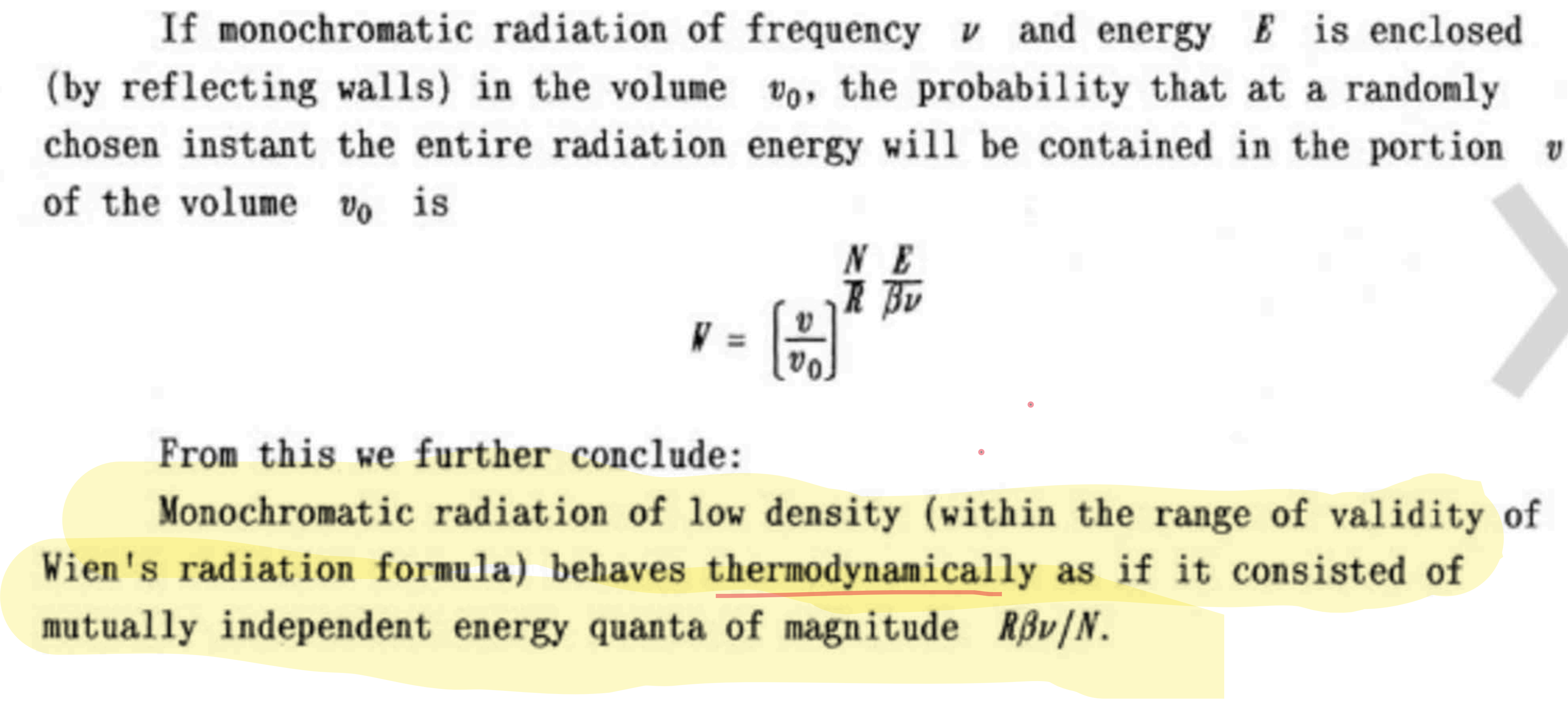

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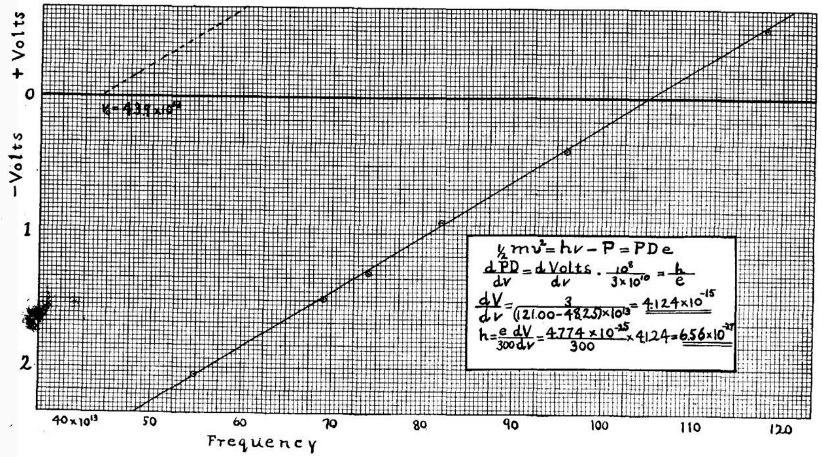

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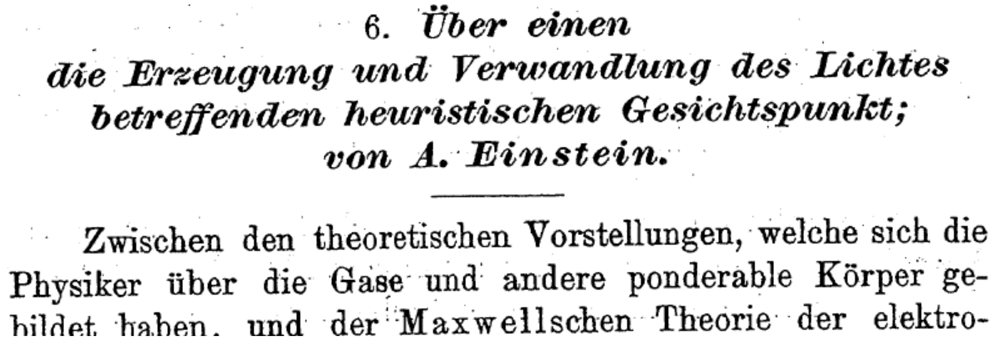

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Finding quantum analogies to:

0) System bath partition:
Approach to equilibrium.
1) The first law:
Energy change.
2) The second law:
Entropy change.
3) The third law:
Approaching the absolute zero.

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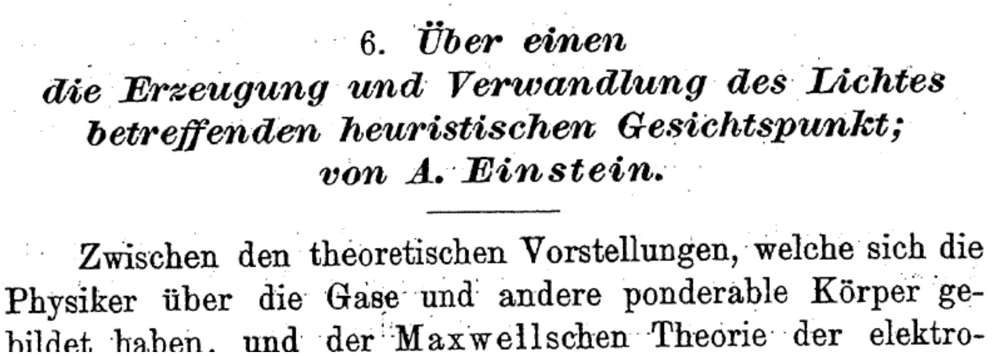

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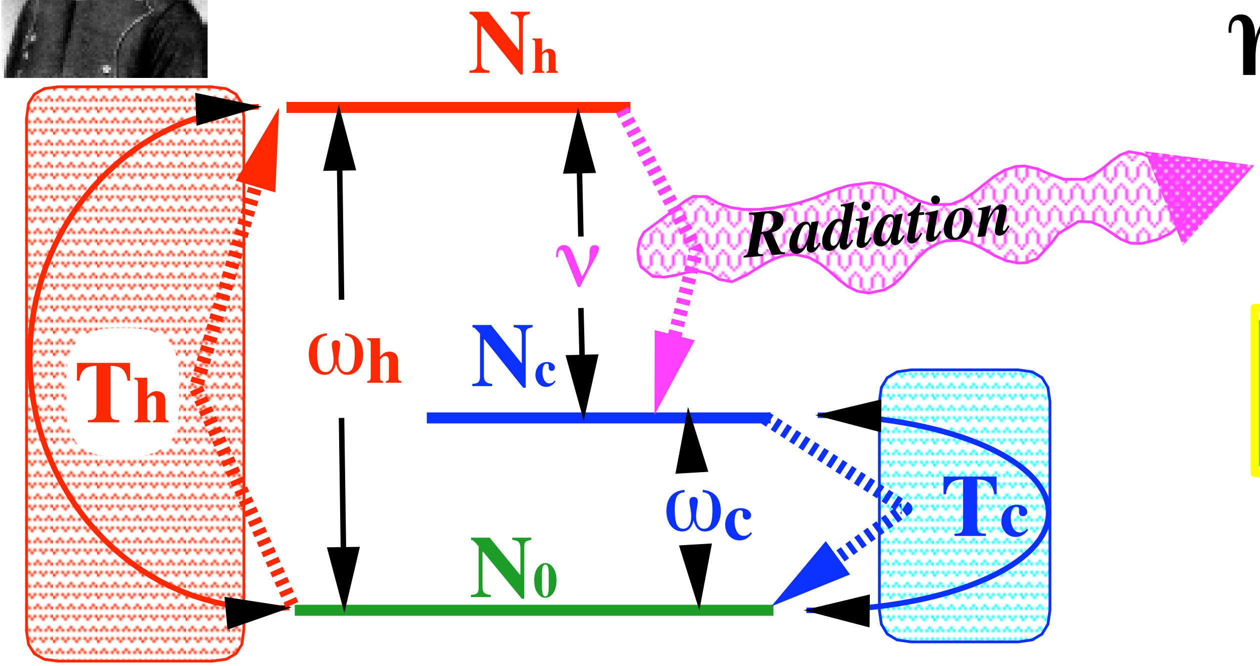
Carnot efficiency of a 3–level amplifier



$$\eta = \frac{\nu}{\omega_h} = \frac{\omega_h - \omega_c}{\omega_h}$$

$$N_c = N_0 \, e^{-\frac{\hbar \omega_c}{k T_c}}$$

$$N_h = N_0 \, e^{-\frac{\hbar \omega_h}{k T_h}}$$

$$\boxed{G = N_h - N_c \geq 0}$$

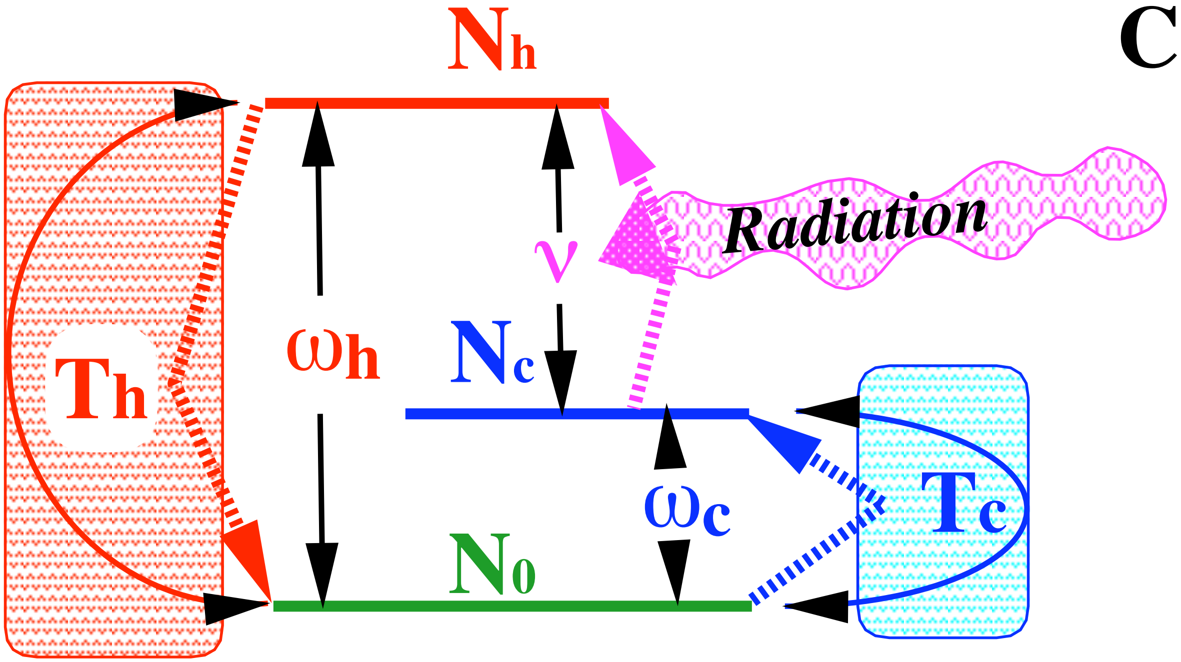
$$\frac{\hbar \omega_h}{k T_h} - \frac{\hbar \omega_c}{k T_c} \leq 0$$

$$\frac{\omega_c}{\omega_h} \leq \frac{T_c}{T_h}$$

$$\boxed{\eta = 1 - \frac{\omega_c}{\omega_h} \leq 1 - \frac{T_c}{T_h}}$$

Scuvil & Sultz de Bois PRL 2 262 (1959)

Laser Cooling reversing the 3–level amplifier



$$\mathrm{COP} = \frac{\omega_c}{\nu} = \frac{\omega_c}{\omega_h - \omega_c}$$

$$\boxed{G = N_h - N_c \leq 0}$$

$$\frac{\hbar\omega_h}{k\,T_h} - \frac{\hbar\omega_c}{k\,T_c} \leq 0$$

$$\frac{\omega_c}{\omega_h} \geq \frac{T_c}{T_h}$$

$$N_c = N_0\, e^{-\frac{\hbar\omega_c}{k\,T_c}}$$

$$\boxed{T_c > \frac{\omega_c}{\omega_h}\, T_h}$$

$$N_h = N_0\, e^{-\frac{\hbar\omega_h}{k\,T_h}}$$

D. J. Wineland and H. Dehmelt, Bull. Am. Phys. Soc. 20, 637 (1975); T. W. Hänsch and A. L. Schawlow, "Cooling of Gases by Laser Radiation," Opt. Commun. 13, 68 (1975).

$$\boxed{\mathrm{COP} \approx \frac{T_c}{T_h}}$$

The von Neumann mathematical formalism of Open systems

i) quantum observables are represented by self-adjoint (hermitian) operators (denoted by $\hat{\mathbf{A}}, \hat{\mathbf{B}}, ..$) acting on the Hilbert space $\mathcal{H}$,
ii) quantum events are the particular *yes-no* observables described by projectors ($\hat{\mathbf{P}} = \hat{\mathbf{P}}^2$),
iii) the state of the system is represented by density matrices, i.e. positive operators with trace one (denoted by $\hat{\boldsymbol{\rho}}, \hat{\sigma}, ..$),
iv) probability of the event $\hat{\mathbf{P}}$ for the state $\hat{\boldsymbol{\rho}}$ is given by

$$\mathcal{P} = \mathrm{Tr}(\hat{\boldsymbol{\rho}}\hat{\mathbf{P}}), \tag{1}$$

v) an averaged value of the observable $\hat{\mathbf{A}}$ at the state $\hat{\boldsymbol{\rho}}$ is equal to

$$\langle \hat{\mathbf{A}} \rangle_{\rho} = \mathrm{Tr}(\hat{\boldsymbol{\rho}}\hat{\mathbf{A}}). \tag{2}$$

The dynamics of a closed quantum system is described by a unitary map $\mathcal{U}_t$:

$$\hat{\boldsymbol{\rho}}(t) = \mathcal{U}_t \hat{\boldsymbol{\rho}}(0) \equiv \hat{\mathbf{U}}(t)\hat{\boldsymbol{\rho}}(0)\hat{\mathbf{U}}^{\dagger}(t) \tag{3}$$

where $\hat{\mathbf{U}}$ is a unitary operator generated by the Hamiltonian operator $\hat{\mathbf{H}}(t)$.

$$\frac{d}{dt}\hat{\mathbf{U}}(t) = -\frac{i}{\hbar}\hat{\mathbf{H}}(t)\hat{\mathbf{U}}(t) \tag{4}$$

with $\hat{\mathbf{U}}(0) = \hat{\mathbf{I}}$. For time independent Hamiltonians $\hat{\mathbf{U}}(t) = \exp\{-\frac{i}{\hbar}\hat{\mathbf{H}}t\}$. An equivalent differential form of the dynamics is described by the von Neumann evolution equation with the time-dependent Hamiltonian $\hat{\mathbf{H}}(t)$

$$\frac{d}{dt}\hat{\boldsymbol{\rho}}(t) = -\frac{i}{\hbar}[\hat{\mathbf{H}}(t), \hat{\boldsymbol{\rho}}(t)], \tag{5}$$

Quantum entropy

Quantum entropy was also introduced by von Neumann called now von Neumann entropy and defined by

$$\mathcal{S}_{vn}(\hat{\boldsymbol{\rho}}) = -k_B \mathrm{Tr}(\hat{\boldsymbol{\rho}} \ln \hat{\boldsymbol{\rho}}) = -k_B \sum_j \lambda_j \ln \lambda_j \geq 0 \tag{6}$$

where $\hat{\boldsymbol{\rho}} = \sum_j \lambda_j |j\rangle\langle j|$ is a spectral decomposition of the density operator. The von Neumann entropy is an invariant of the state $\hat{\boldsymbol{\rho}}$ and is the lower bound for all possible diagonal entropies $S_A(\hat{\boldsymbol{\rho}}) \geq \mathcal{S}_{vn}(\hat{\boldsymbol{\rho}})$ where $\mathcal{S}_A = -k_B \sum_j p_j \ln p_j$ is the Shannon entropy defined by the probability distribution obtained by a complete measurement of the operator $\hat{\mathbf{A}}$.

The quantum counterpart of the canonical (Gibbs) ensemble, corresponding to the thermodynamic equilibrium state at the temperature T, for the system with the Hamiltonian $\hat{\mathbf{H}}$, is described by the density matrix of the form

$$\hat{\boldsymbol{\rho}}_\beta = \frac{1}{Z} e^{-\beta \hat{\mathbf{H}}}, \quad \beta = \frac{1}{k_B T}, \quad Z = \mathrm{Tr} e^{-\beta \hat{\mathbf{H}}}. \tag{7}$$

The Gibbs state maximizes entropy under the condition of a fixed mean energy (internal energy in thermodynamic language) $E = \mathrm{Tr}(\hat{\boldsymbol{\rho}} \hat{\mathbf{H}})$ or minimizes E for a fixed entropy $\mathcal{S}_{vn}$. In this case $\mathcal{S}_{vn} = \mathcal{S}_H$.

The Markovian Master Equation and isothermal partition

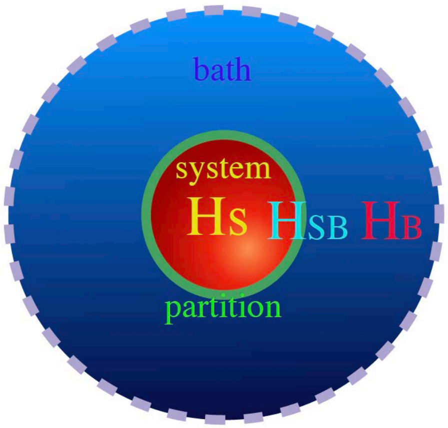
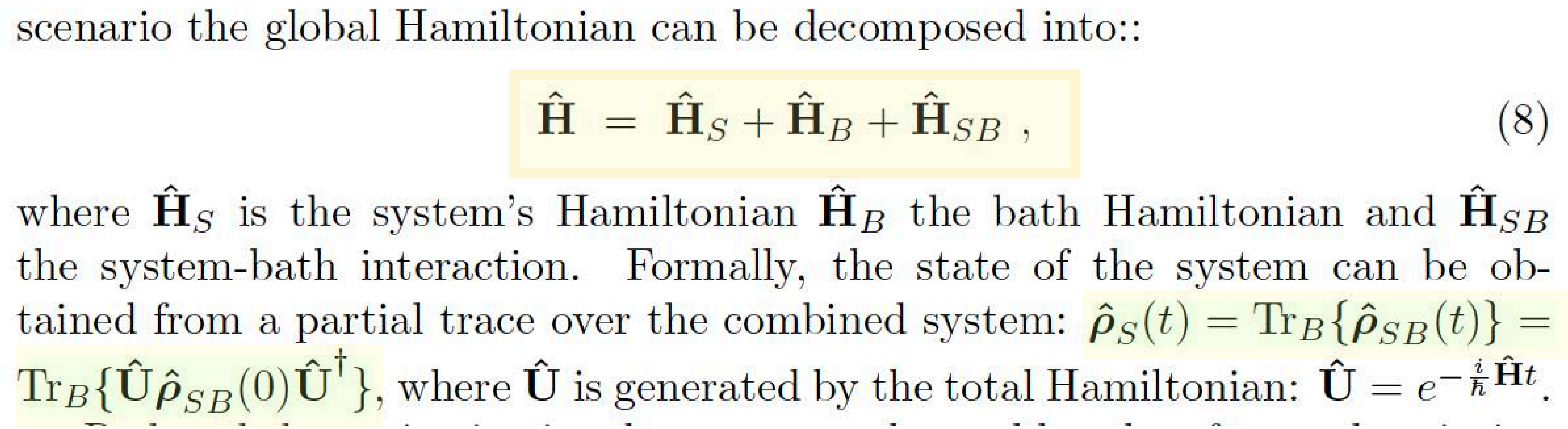


Figure 1: System embedded in a bath.



scenario the global Hamiltonian can be decomposed into::

$$\hat{\mathbf{H}} \;=\; \hat{\mathbf{H}}_S + \hat{\mathbf{H}}_B + \hat{\mathbf{H}}_{SB} \ , \tag{8}$$

where $\hat{\mathbf{H}}_S$ is the system's Hamiltonian $\hat{\mathbf{H}}_B$ the bath Hamiltonian and $\hat{\mathbf{H}}_{SB}$ the system-bath interaction. Formally, the state of the system can be obtained from a partial trace over the combined system: $\hat{\boldsymbol{\rho}}_S(t) = \mathrm{Tr}_B\{\hat{\boldsymbol{\rho}}_{SB}(t)\} = \mathrm{Tr}_B\{\hat{\mathbf{U}}\hat{\boldsymbol{\rho}}_{SB}(0)\hat{\mathbf{U}}^\dagger\}$, where $\hat{\mathbf{U}}$ is generated by the total Hamiltonian: $\hat{\mathbf{U}} = e^{-\frac{i}{\hbar}\hat{\mathbf{H}}t}$.

Reduceed dynamics

system and bath are uncorrelated:

$$\hat{\rho}_{SB}(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_B(0) \tag{9}$$

This assumption can be moved to $t \to -\infty$ and will be scrutinized later.

Assuming unitary dynamics generated by the total Hamiltonian (8), starting from an uncorrelated initial system-bath state Eq. (9), the reduced map $\Lambda_S(t)$ has the structure:

$$\hat{\rho}_S(t) = \Lambda_S(t)\hat{\rho}_S(0) = \sum_j \hat{\mathbf{K}}_j(t)\hat{\rho}_S(0)\hat{\mathbf{K}}_j^\dagger(t) \quad , \tag{10}$$

where $\hat{\mathbf{K}}$ are system operators and $\sum_j \hat{\mathbf{K}}_j \hat{\mathbf{K}}_j^\dagger = \hat{\mathbf{I}}$. This general result has been derived by Kraus [55] and is termed completely positive trace preserving map(CPTP).

The CPPT map is contracting meaning that the distance between two states diminishes. This distance between $\hat{\rho}_1$ and $\hat{\rho}_2$ can be defined by the conditional entropy: $\mathcal{S}(\hat{\rho}_1|\hat{\rho}_2) = \mathrm{Tr}\left\{\hat{\rho}_1 \ln \hat{\rho}_1 - \hat{\rho}_1 \ln \hat{\rho}_2\right\}$. Aplying the map Λ leads to a quantum version of the H-theorem [56]:

$$\mathcal{S}(\Lambda\hat{\rho}_A|\Lambda\hat{\rho}_B) \leq \mathcal{S}(\hat{\rho}_A|\hat{\rho}_B) \tag{11}$$

If the map has a unique fixed point $\Lambda\hat{\rho}_{st} = \hat{\rho}_{st}$ then using Eq. (11) it becomes clear that repeated applications of the map will lead monotonically to this fixed point, a mathematical property associated with thermal equilibrium [57].

Markovian quantum Master equation LGKLS

A differential form of the CPTP map can be obtained by imposing a Makovian property: $\Lambda_S(t+s) = \Lambda_S(t)\Lambda_S(s)$. The differential generator of the dynamics can be defined by $\Lambda_S(t) = e^{\mathcal{L}t}$ leading to the quantum Master equation:

$$\frac{d}{dt}\hat{\boldsymbol{\rho}}_S = \mathcal{L}\hat{\boldsymbol{\rho}}_S \tag{12}$$

An important milestone was the derivation of the most general form of the generator of Markovian dynamics by Gorini-Kossakowski-Lindblas-Sudarshan (GKLS) [4, 5]. The differential generator $\mathcal{L}$ of the map becomes:

$$\frac{d}{dt}\hat{\boldsymbol{\rho}}_S = \left(\mathcal{L}_H + \mathcal{L}_D\right)\hat{\boldsymbol{\rho}}_S = -\frac{i}{\hbar}[\hat{\mathbf{H}}_S, \hat{\boldsymbol{\rho}}_S] + \sum_j \left(\hat{\mathbf{L}}_j\hat{\boldsymbol{\rho}}_S\hat{\mathbf{L}}_j^\dagger - \frac{1}{2}\{\hat{\mathbf{L}}_j^\dagger\hat{\mathbf{L}}_j, \hat{\boldsymbol{\rho}}_S\}\right) \;, \tag{13}$$

where $\hat{\mathbf{L}}$ are system operators and $\hat{\mathbf{H}}_S$ is a renormalized system Hamiltonian.

The dynamics generated by the GKLS form (13) based on Kraus mapping Eq. (10), implies a tensor product form between system and bath at all times $\hat{\boldsymbol{\rho}}_{SB}(t) = \hat{\boldsymbol{\rho}}_S(t) \otimes \hat{\boldsymbol{\rho}}_B(t)$. This structure is equivalent to a partition between system and bath. All system observables are defined by the system state $\hat{\boldsymbol{\rho}}_S$: $\langle\hat{\mathbf{A}}\rangle = Tr\{\hat{\mathbf{A}}\hat{\boldsymbol{\rho}}_S\}$,

The GKLS equation describes irreversible dynamics with positive entropy production leading to a fixed point [58, 59]

$$\frac{d}{dt}\mathcal{S}(\hat{\boldsymbol{\rho}}(t)|\hat{\boldsymbol{\rho}}_{st}) = -\mathrm{Tr}\left[\mathcal{L}\hat{\boldsymbol{\rho}}(t)\left(\ln\hat{\boldsymbol{\rho}}(t) - \ln\hat{\boldsymbol{\rho}}_{st}\right)\right] \geq 0 \text{ , for } \quad \mathcal{L}\hat{\boldsymbol{\rho}_{\mathbf{st}}} = 0 \;, \tag{14}$$

where the fixed point for the dynamics is $\hat{\boldsymbol{\rho}}_{st}$.

The Born-Markov weak coupling approximation

A constructive approach to derive the GKLS Master equation from first principles is desirable allowing to address directly physical reality. The method known as Davis construction [60] is based on a second order expansion where the small parameter λ scales the system-bath interaction:

$$\hat{\mathbf{H}}_{int} = \lambda \sum_k \hat{\mathbf{S}}_k \otimes \hat{\mathbf{B}}_k \tag{15}$$

where $\hat{\mathbf{S}}$ are system operators and $\hat{\mathbf{B}}$ bath operators. The rigorous derivation of

A basic step in the derivation is to transform to the interaction representation generated by the free evolution $\hat{\mathbf{U}}(t) = e^{-\frac{i}{\hbar}\hat{\mathbf{H}}_S t} \otimes e^{-\frac{i}{\hbar}\hat{\mathbf{H}}_B t}$. At this point the system coupling operators $\hat{\mathbf{S}}_k$ in Eq. (15) are expanded by eigen-operators of the free system propagator:

$$\mathcal{U}_S(t)\hat{\mathbf{A}}_\omega = e^{\frac{i}{\hbar}\hat{\mathbf{H}}_S t}\hat{\mathbf{A}}_\omega e^{-\frac{i}{\hbar}\hat{\mathbf{H}}_S t} = e^{-i\omega t}\hat{\mathbf{A}}_\omega \tag{16}$$

($\{\omega\}$- denotes the set of Bohr frequencies of $\hat{\mathbf{H}}_S$). Then:

$$e^{\frac{i}{\hbar}\hat{\mathbf{H}}_{\mathbf{S}}t}\hat{\mathbf{S}}_k e^{-\frac{i}{\hbar}\hat{\mathbf{H}}_{\mathbf{S}}t} = \sum_{\{\omega\}} s_k(\omega)\hat{\mathbf{A}}_\omega e^{-i\omega t}, \tag{17}$$

Adding to the WCL method a renormalization procedure which allows to use the physical Hamiltonian $\hat{\mathbf{H}}_{\mathbf{S}}$ of the system, containing lowest order Lamb corrections, one obtains the following structure of Markovian Master equation which is in the GKLS form:

$$\frac{d}{dt}\hat{\boldsymbol{\rho}}_S = -i[\hat{\mathbf{H}}_{\mathbf{S}}, \hat{\boldsymbol{\rho}}_{\mathbf{S}}] + \mathcal{L}_D\hat{\boldsymbol{\rho}}_{\mathbf{S}}, \quad \mathcal{L}_D\hat{\boldsymbol{\rho}}_{\mathbf{S}} = \sum_{k,l}\sum_{\{\omega\}}\mathcal{L}^{\omega}_{lk}\hat{\boldsymbol{\rho}}_{\mathbf{S}} \tag{18}$$

where

$$\mathcal{L}^{\omega}_{lk}\hat{\boldsymbol{\rho}}_{\mathbf{S}} = \frac{1}{2\hbar^2}\tilde{R}_{kl}(\omega)s_l(\omega)s_k(\omega)\left\{[\hat{\mathbf{A}}_\omega\hat{\boldsymbol{\rho}}_{\mathbf{S}}, \hat{\mathbf{A}}^{\dagger}_{\omega}] + [\hat{\mathbf{A}}_\omega, \hat{\boldsymbol{\rho}}_{\mathbf{S}}\hat{\mathbf{A}}^{\dagger}_{\omega}]\right\}. \tag{19}$$

The rate matrix $R_{kl}(\omega)$ is the Fourier transform of the bath correlation function $\langle\hat{R}_k(t)\hat{R}_l\rangle_{bath}$ computed in the thermodynamic limit

$$\tilde{R}_{kl}(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t}\langle\hat{\mathbf{B}}_k(t)\hat{\mathbf{B}}_l\rangle_{bath}\,dt. \tag{20}$$

The derivation of (18),(19) imposes additional thermodynamical properties of the Master equation:

1) the Hamiltonian part $[\hat{\mathbf{H}}_{\mathbf{S}}, \bullet]$ commutes with the dissipative part $\mathcal{L}_D$,
2) the diagonal (in $\hat{\mathbf{H}}_{\mathbf{S}}$-basis) matrix elements of $\hat{\boldsymbol{\rho}}_S$ evolve (independently of the off-diagonal ones) according to the Pauli Master Equation with transition rates given by the Fermi Golden Rule [66, 67].
If additionally the bath is a heat bath [68, 69] then:
3) Gibbs state $\hat{\boldsymbol{\rho}}_\beta = Z^{-1} e^{-\beta \hat{\mathbf{H}}_{\mathbf{S}}}$ is a stationary solution of (18),
4) Any initial state relaxes asymptotically to the Gibbs state: *The 0-Law of Thermodynamics* [57].

The derivation of (18),(19) can be extended to describe driven systems with a time dependent system Hamiltonian $\hat{\mathbf{H}}_S(t)$. The jump operators $\hat{\mathbf{A}}_\omega$ become eigen-operators of the free time dependent propagator $\mathcal{U}_S(t)$. The adiabatic case of a slowly varying time-dependent Hamiltonian is the most simple case. The jump operators become the eigen-operators of the instantaneous propagator or $[\hat{\mathbf{H}}_S(t), \hat{\mathbf{A}}_\omega] = -i\omega(t)\hat{\mathbf{A}}_\omega$ [70].

A quantum dynamical version of the first law of thermodynamics is obtained by examining the energy conservation law in the adiabatic case [6, 61]:

$$E(t) = \mathrm{Tr}\Big(\hat{\boldsymbol{\rho}}_S(t)\hat{\mathbf{H}}_S(t)\Big) \tag{21}$$

Taking the time derivative of Eq. (21) results in the change in energy partitioned to power and heat currents:

$$\frac{d}{dt}E(t) = \mathcal{J}(t) - \mathcal{P}(t). \tag{22}$$

where the power provided by the system becomes:

$$\mathcal{P}(t) \equiv -\mathrm{Tr}\Big(\hat{\boldsymbol{\rho}}_S(t)\frac{d\hat{\mathbf{H}}_S(t)}{dt}\Big), \tag{23}$$

The heat current becomes:

$$\mathcal{J}(t) \equiv \mathrm{Tr}\Big(\hat{\mathbf{H}}_S(t)\frac{d}{dt}\hat{\boldsymbol{\rho}}_S(t)\Big) = \sum_k \mathcal{J}_k(t), \quad \mathcal{J}_k(t) = \mathrm{Tr}\Big(\hat{\mathbf{H}}_S(t)\mathcal{L}_k(t)\hat{\boldsymbol{\rho}}_S(t)\Big).$$

The repeated Collision model

and j gas particle are initially uncorrelated $\hat{\boldsymbol{\rho}}_i = \hat{\boldsymbol{\rho}}_{S_i} \otimes \hat{\boldsymbol{\rho}}_{B_j}$. The individual collision event is then described by a unitary scattering matrix $\hat{\mathbf{S}}$.

$$\hat{\boldsymbol{\rho}}_f = \hat{\mathbf{S}} \hat{\boldsymbol{\rho}}_i \hat{\mathbf{S}}^\dagger \quad . \tag{43}$$

Assuming independent random collisions with identical bath particles a reduced map is obtained:

$$\hat{\boldsymbol{\rho}}_{S_f} = \Lambda_\beta \hat{\boldsymbol{\rho}}_{S_i} = \mathrm{Tr}_B \left\{ \hat{\boldsymbol{\rho}}_f \right\} \tag{44}$$

To generalize to many repeated encounters at rate γ, the collision duration has to be much faster than the average waiting time between collisions $\sim 1/\gamma$. The differential description leads to a GKLS Master equation [80, 81]:

$$\frac{d}{dt} \hat{\boldsymbol{\rho}}_S = -\frac{i}{\hbar} [\hat{\mathbf{H}}_S, \hat{\boldsymbol{\rho}}_S] + \gamma \left(\mathrm{Tr}_B \left\{ \hat{\mathbf{S}} \hat{\boldsymbol{\rho}}_S \otimes \hat{\boldsymbol{\rho}}_B \hat{\mathbf{S}}^\dagger \right\} - \hat{\boldsymbol{\rho}}_S \right) \tag{45}$$

The repeated collision GKLS equation Eq. (45) depends on the bath state. A natural choice is a bath in thermal equilibrium $\hat{\boldsymbol{\rho}}_B = \frac{1}{Z} \exp\{-\beta \hat{\mathbf{H}}_B\}$.

As any CPTP map, the collision dynamics leads to a fixed point $\mathcal{L} \hat{\boldsymbol{\rho}}_{st} = 0$.

For modeling it would be desirable that this fixed point is a thermal equilibrium state of the system $\hat{\boldsymbol{\rho}}_S = \frac{1}{Z}\exp(-\beta\hat{\mathbf{H}}_S)$. To study this possibility, the unitary scattering matrix $\hat{\mathbf{S}}$ can be described by a generator $\hat{\mathbf{V}}$, then $\hat{\mathbf{S}} = e^{-\frac{i}{\hbar}\hat{\mathbf{V}}\phi}$ where ϕ is a phase shift.

The Master equation Eq. (45) can be expanded to second order in ϕ leading to [82]:

$$\frac{d}{dt}\hat{\boldsymbol{\rho}}_S = -\frac{i}{\hbar}[\hat{\mathbf{H}}_S', \hat{\boldsymbol{\rho}}_S] - \gamma' \mathrm{Tr}_B \left\{ [\hat{\mathbf{V}}, [\hat{\mathbf{V}}, \hat{\boldsymbol{\rho}}_S \otimes \hat{\boldsymbol{\rho}}_B]] \right\} \tag{46}$$

and $\gamma' = \gamma\frac{\phi^2}{2\hbar^2}$ and $\hat{\mathbf{H}}_S' = \hat{\mathbf{H}}_S + \gamma\frac{\phi}{\hbar}\mathrm{Tr}_B\left\{\hat{\mathbf{V}}\right\}$.

To obtain a thermalizing model we can choose $\hat{\mathbf{V}}$ as follows [83, 84, 85, 86]:

$$\hat{\mathbf{V}} = \sum_k g_k(\hat{\mathbf{A}}_k^\dagger \otimes \hat{\mathbf{B}}_k + \hat{\mathbf{A}}_k \otimes \hat{\mathbf{B}}_k^\dagger) \tag{47}$$

where $\hat{\mathbf{A}}_k$ and $\hat{\mathbf{B}}_k$ are eigen-operators of the commutators of the free Hamiltonians with the same eigenvalue:

$$\begin{aligned} [\hat{\mathbf{H}}_S, \hat{\mathbf{A}}_k] &= -\omega_k \hat{\mathbf{A}}_k \\ [\hat{\mathbf{H}}_B, \hat{\mathbf{B}}_k] &= -\omega_k \hat{\mathbf{B}}_k \end{aligned} \tag{48}$$

As a result the operator $\hat{\mathbf{V}}$ commutes with $[\hat{\mathbf{H}}_S + \hat{\mathbf{H}}_B, \hat{\mathbf{V}}] = 0$. Using these properties Eq. (46) reduces to a thermalizing GKLS:

$$\frac{d}{dt}\hat{\boldsymbol{\rho}}_S = -\frac{i}{\hbar}[\hat{\mathbf{H}}_S, \hat{\boldsymbol{\rho}}_S] - \sum_k \left(\gamma_k^- \mathcal{L}_k^-(\hat{\boldsymbol{\rho}}_s) + \gamma_k^+ \mathcal{L}_k^+(\hat{\boldsymbol{\rho}}_s)\right) \tag{49}$$

where: $\mathcal{L}_k^-(\hat{\boldsymbol{\rho}}_s) = [\hat{\mathbf{A}}_k\hat{\boldsymbol{\rho}}_{\mathbf{S}}, \hat{\mathbf{A}}_k^\dagger] + [\hat{\mathbf{A}}_k, \hat{\boldsymbol{\rho}}_{\mathbf{S}}\hat{\mathbf{A}}_k^\dagger]$ and $\mathcal{L}_k^+(\hat{\boldsymbol{\rho}}_s) = [\hat{\mathbf{A}}_k^\dagger\hat{\boldsymbol{\rho}}_{\mathbf{S}}, \hat{\mathbf{A}}_k] + [\hat{\mathbf{A}}_k^\dagger, \hat{\boldsymbol{\rho}}_{\mathbf{S}}\hat{\mathbf{A}}_k]$. The rate coefficients obay:

$$\begin{aligned} \gamma_k^- &= \gamma' g_k^2 \langle \hat{\mathbf{B}}_k \hat{\mathbf{B}}_k^\dagger \rangle \\ \gamma_k^+ &= \gamma' g_k^2 \langle \hat{\mathbf{B}}_k^\dagger \hat{\mathbf{B}}_k \rangle \end{aligned} \tag{50}$$

When the bath is in thermal equilibrium the ratio of rate coefficients obeys detailed balance:

$$\frac{\gamma_k^+}{\gamma_k^-} = e^{-\beta\omega_k} \tag{51}$$

This concludes the derivation of a thermalizing GLKS collision model.

The Gaussian semi-group: the singular bath limit

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_S + \hat{\mathbf{V}} f(t) \tag{52}$$

where the random force typically $\langle f(t) \rangle = 0$ and $\langle f(t) f(t') \rangle = \gamma \delta(t - t')$. Such a process leads to a GLKS equation when averaging over the random noise [90]:

$$\frac{d}{dt} \hat{\boldsymbol{\rho}}_S = -\frac{i}{\hbar} [\hat{\mathbf{H}}_S, \hat{\boldsymbol{\rho}}_S] - \frac{\gamma^2}{2} [\hat{\mathbf{V}}, [\hat{\mathbf{V}}, \hat{\boldsymbol{\rho}}_S]] \tag{53}$$

The phenomena most associated with Gaussian noise is dephasing. If we choose $\hat{\mathbf{V}} = g(\hat{\mathbf{H}}_S)$ where $g(x)$ is any analytic function then Eq. (53) conserves energy and the dissipation causes dephasing. In the language of magnetic resonance a pure T_2 process [93].

Pure dephasing will also occur if the $\hat{\mathbf{S}}$ matrix in the scattering event Eq. (45) commutes with $\hat{\mathbf{H}}_S$: $[\hat{\mathbf{H}}_S, \hat{\mathbf{S}}] = 0$. The Poisson dephasing due to repeated

The laws of quantum thermodynamics

6.1 The zero law

The zero law of thermodynamics is typically stated as: *If A and C are each in thermal equilibrium with B, A is also in equilibrium with C.* A thermodynamical description is based on idealised partitions between subsystems. An isothermal partition, for example, allows heat to flow from system to bath maintaining the integrity of the subsystems. Consistency with quantum mechanics due to the global structure of the theory is therefore a non-trivial statement.

6.2 System bath partition

Quantum thermodynamics idealises that the system can be fully described by local operators, which is equivalent to the condition:

$$\hat{\rho} \approx \hat{\rho}_S \otimes \hat{\rho}_B \quad , \tag{54}$$

In Eq. (54) there is no system-bath entanglement, which is also true for Markovian dynamics. Thermodynamically the local description of the system is equivalent to the extensivity of its observables. We conclude that the dynamics represented by the LGKS generator Eq. (13) is closely linked to a thermodynamical framework.

6.3 Thermal equilibrium

An equilibrium state in general is defined as stationary and stable. This assumption is used to derive the Kubo-Martin-Schwinger stability criterion for thermal equilibrium [68, 69]. This criterion will imply that in equilibrium there

6.4 The I-law

The I-law addresses the issue of conserved quantities. The primary quantity is the total energy. An additional variable important in transport is the number of particles.

To obtain the conservation laws in a differential form we can write the equations of motion in Heisenberg form:

$$\frac{d}{dt}\hat{\mathbf{X}} = -\frac{i}{\hbar}[\hat{\mathbf{H}}_S, \hat{\mathbf{X}}] + \mathcal{L}_S(\hat{\mathbf{X}}) + \frac{\partial}{\partial t}\hat{\mathbf{X}} \tag{56}$$

where $\hat{\mathbf{X}}$ is a system operator which can be explicitly time dependent. Choosing for $\hat{\mathbf{X}}$ the Hamiltonian $\hat{\mathbf{H}}_S$ using the fact the $\hat{\mathbf{H}}$ commutes with itself, and taking expectation values we obtain :

$$\frac{d}{dt}E = \langle \mathcal{L}_D^*(\hat{\mathbf{H}}_S)\rangle + \langle \frac{\partial}{\partial t}\hat{\mathbf{H}}_S\rangle \tag{57}$$

which leads to the interpretation $\mathcal{J} = \dot{\mathcal{Q}} = \langle \mathcal{L}_D^*(\hat{\mathbf{H}}_S)\rangle$ as heat current and $\mathcal{P} = \langle \frac{\partial}{\partial t}\hat{\mathbf{H}}_S\rangle$ as power. This version derived using the Heisenberg equation of This dynamical version of the I-law Eq. (57) is equivalent to Eq. (25) obtained in the Schrödinger frame and is limited to the adiabatic regime [61].

6.6 The II-law

The Clausius statement for the II-law is that heat should flow through the system from a hot to a cold bath [96]. An alternative version due to Kelvin can be stated as the universal tendency in nature to dissipate mechanical energy [97]. Both these criteria can be employed directly to asses open system models.

The Clausius version of he II-law can be put in a test for the quantum heat transport problem of two connected quantum systems coupled to a hot and cold bath. The dynamics can be described by

$$\frac{d}{dt}\hat{\boldsymbol{\rho}} = -\frac{i}{\hbar}[\hat{\mathbf{H}}_0 + \hat{\mathbf{H}}_{hc}, \hat{\boldsymbol{\rho}}] + \mathcal{L}_h(\hat{\boldsymbol{\rho}}) + \mathcal{L}_c(\hat{\boldsymbol{\rho}}) \tag{62}$$

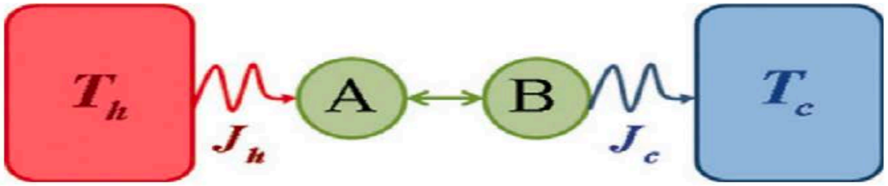
where the wire Hamiltonian is $\hat{\mathbf{H}}_0 = \hat{\mathbf{H}}_h + \hat{\mathbf{H}}_c$, $\hat{\mathbf{H}}_{hc}$ is the link Hamiltonian and $\mathcal{L}_{h/c}$ are the dissipative connections to the hot and cold baths. In constructing such model it is tempting to assign a local thermalizing GKLS generator to each subsystem and then to introduce a weak coupling term connecting the two subsystems. In this case the jump operators in $\mathcal{L}_h$ are the eigenoperators of $\hat{\mathbf{H}}_h$ and for $\mathcal{L}_c$ are the eigenoperators of $\hat{\mathbf{H}}_c$.

The global alternative is to use the full power of the Davis construction and fine the eigenoperators of $\hat{\mathbf{H}}_0$ to construct both generators $\mathcal{L}_h$ and $\mathcal{L}_c$ [98].

At steady state the heat flow from the hot (cold) bath is given by,

$$\mathcal{J}_{h(c)} = Tr[(\mathcal{L}_{h(c)}\hat{\boldsymbol{\rho}}_s)(\hat{\mathbf{H}}_0 + \hat{\mathbf{H}}_{AB})], \tag{63}$$

where $\hat{\boldsymbol{\rho}}_{st}$ is the steady state density operator.



6.7 The III-law

Two independent formulations of the III-law of thermodynamics exist, both originally stated by Nernst [102, 103, 104]. The first is a purely static (equilibrium) one, also known as the "Nernst heat theorem": phrased:

- The entropy of any pure substance in thermodynamic equilibrium approaches zero as the temperature approaches zero.

The second formulation is dynamical, known as the unattainability principle:

- It is impossible by any procedure, no matter how idealised, to reduce any assembly to absolute zero temperature in a finite number of operations

The entropy production at the cold bath when $T_c \to 0$ scales as

$$\dot{S}_c \sim -T_c^{\alpha} \quad , \qquad \alpha \geq 0 \ . \tag{67}$$

the characteristic exponent ζ:

$$\frac{dT_c(t)}{dt} \sim -T_c^{\zeta}, \quad T_c \to 0 \ . \tag{68}$$

Solving Eq. (68), leads to;

$$T_c(t)^{1-\zeta} = T_c(0)^{1-\zeta} \ - ct \qquad , \ for \ \zeta < 1 \ , \tag{69}$$

where c is a positive constant. From Eq. (69) the cold bath is cooled to zero temperature at finite time for $\zeta < 1$. The III-law requires therefore $\zeta \geq 1$. In order to evaluate Eq.(68) the heat current can be related to the temperature change:

$$\mathcal{J}_c(T_c(t)) = -c_V(T_c(t))\frac{dT_c(t)}{dt} \quad . \tag{70}$$

Inserting Dynamics into Thermodynamics

Open quantum system

$$\boxed{\dot{\rho} = -i[H,\rho] + L_D(\rho)}$$

$$\boxed{\dot{X} = +i[H,X] + L_D^{*}(X) + \frac{\partial X}{\partial t}}$$

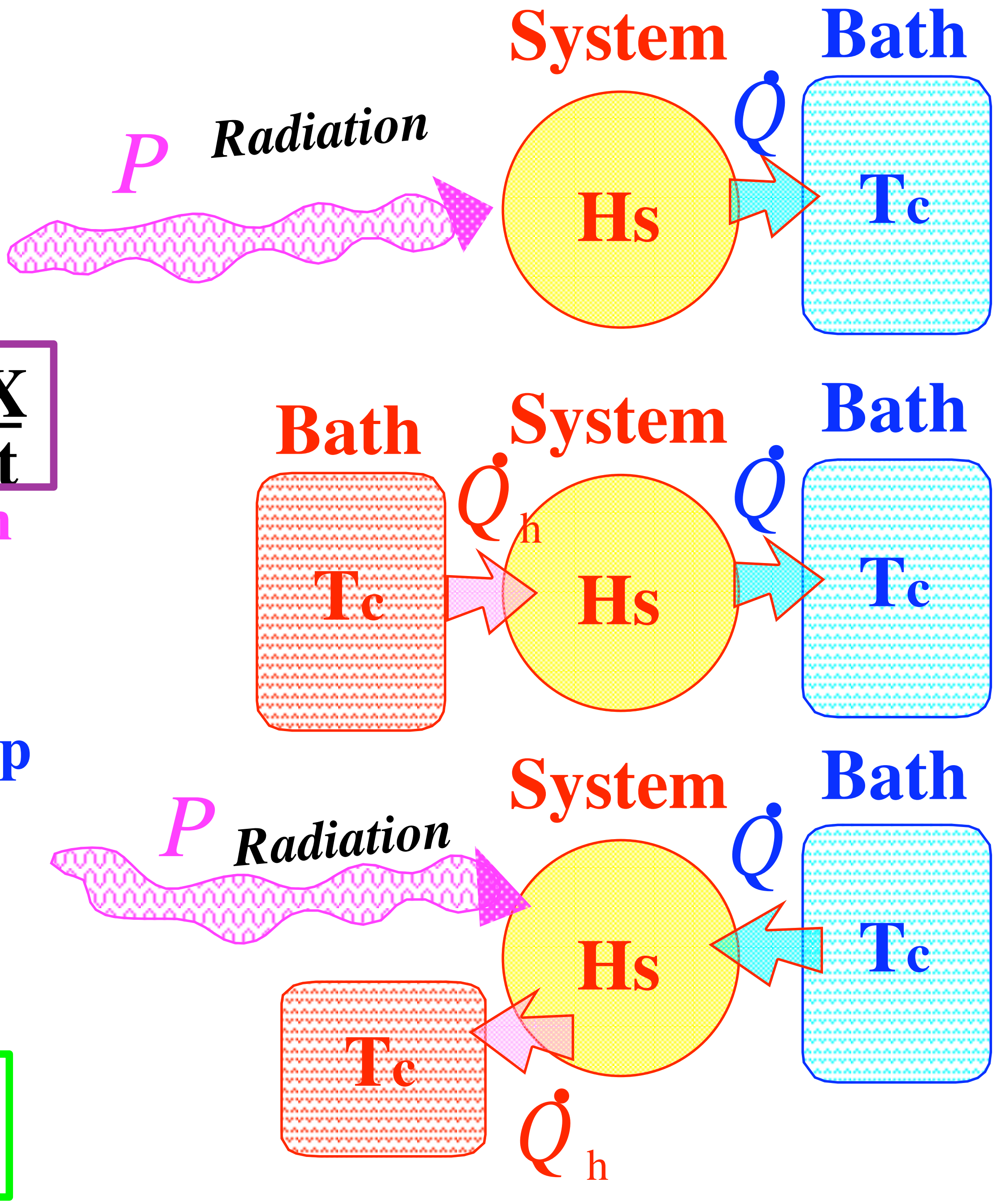
Heisenberg equation of motion

L_D is the generator of the quantum dynamical semigroup

(Quantum Master Equation)

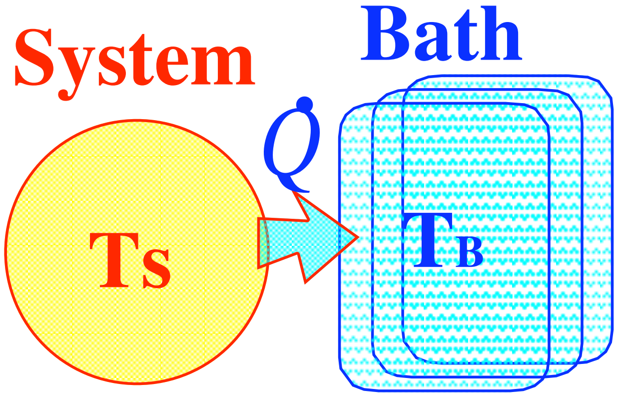
L_D Lindblad’s form

$$\boxed{L_D(X) = \sum_j V_j X V_j^{\dagger} - 1/2\{V_j V_j^{\dagger}, X\}}$$



Inserting Dynamics into Thermodynamics

0) The zeroth law of thermodynamics: $T_S \to T_B$



Q: Isothermal partition ≡ weak coupling limit

$$\boxed{\rho_{S\otimes B} = \rho_S \otimes \rho_B}$$

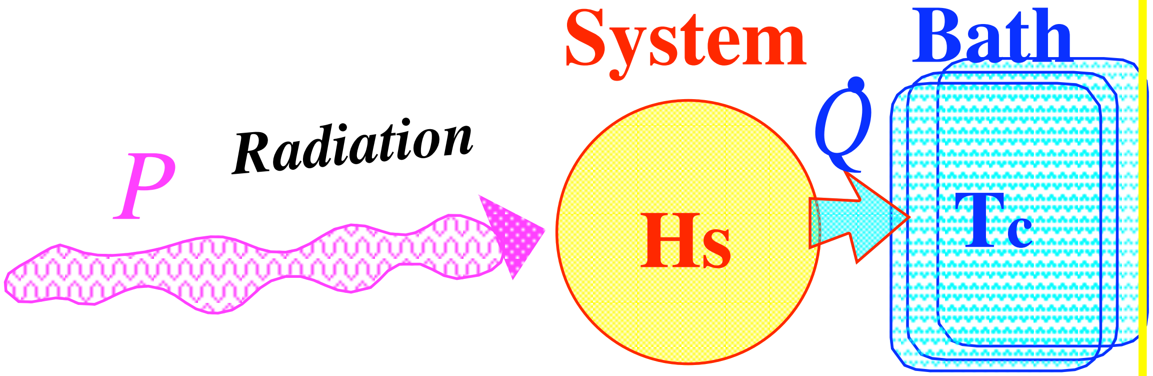
At all times.

1) Time derivative of first law of thermodynamics: energy balance

Q: Quantum definition of work and heat current

$$\dot{E} = \langle L_D(H)\rangle + \langle \frac{\partial H}{\partial t} \rangle$$

$$\dot{E} = \dot{Q} + P$$



2) Second law of thermodynamics: irreversibility: work → heat

$$\boxed{\frac{d}{dt} S_S + \frac{d}{dt} S_B \geq 0}$$

$$S = -\mathrm{tr}\{\rho \ln \rho\}$$

The quest to cool to the absolute zero temperature

Walter Nernst stated the third law of thermodynamics:

"it is impossible by any procedure, no matter how idealized, to reduce any system to the absolute zero of temperature in a finite number of operations"

1) Unattainability principle

Entropic view of the third law of thermodynamics:

"The entropy change of any process becomes zero when the absolute zero temperature is approached",

2) Nerst heat theorem isoentropic