

From Quantum Mechanics to Thermodynamics?

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Motivation and Perspective

The main scope of our work is to:

- clarify or explain the origin of thermodynamical behavior entirely on the basis of Hamilton models and Schrödinger-type quantum dynamics.
- define the thermodynamical limit more precisely, especially with regard to small systems or small subunits of systems.
- improve the understanding of transport phenomena, especially in the regime of transport through small quantum systems.
- pave the road towards quantum thermodynamical machines?

Fundamental Law or Emergent Description?

Quantum Mechanics

$$i\hbar\frac{\partial}{\partial t}\Psi = \left(-\frac{\hbar^2}{2m}\Delta + V\right)\Psi$$

Classical Mechanics:

$$m\frac{d^2}{dt^2}\vec{x} = -\nabla V$$

Thermodynamics:

$$dU = TdS - pdV$$

$$\frac{dS}{dt} > 0$$

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→ “Heisenberg Cut” →

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Ergodicity



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Thermodynamics:

$$dU = TdS - pdV$$

$$\frac{dS}{dt} > 0$$

Some Features of Thermodynamical Behavior

2. Law: $\frac{dS}{dt} \geq 0$

- All systems evolve towards equilibrium.
- Equilibrium is characterized by maximum entropy
- If energy is exchanged with the environment, equilibrium is characterized by a Boltzmann distribution.

1. law: $dU = TdS - pdV$

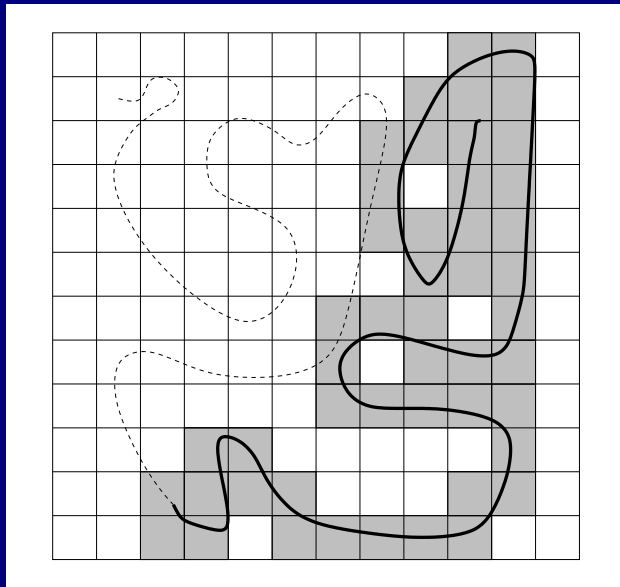
- Description requires very few variables.
- Intensive variables are partial derivatives of energy with respect to the corresponding extensive variables.
- Systems in exchanging contact feature the same intensive variables

How can this be explained on the basis of Newtons or Schrödingers equations, that do not feature any fixpoint?

Even more severly they are invariant with respect to time reversal!

Entropy Dynamics in Phase Space: The Second Law

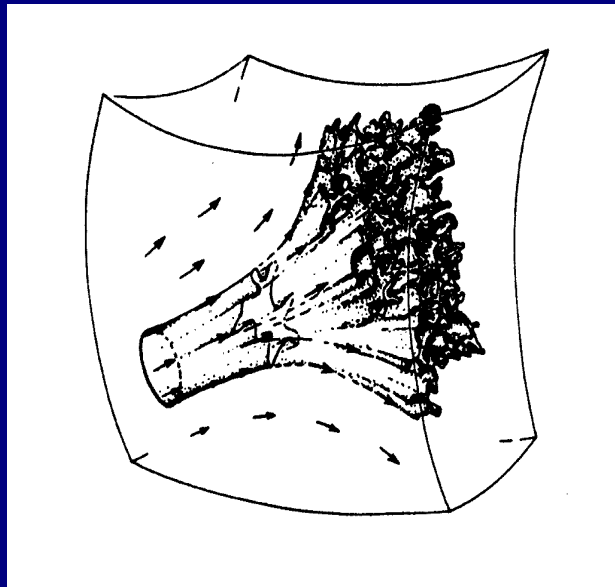
Boltzmann:



Problems:

- Ergodicity
- Cell Size
- Averaging Time

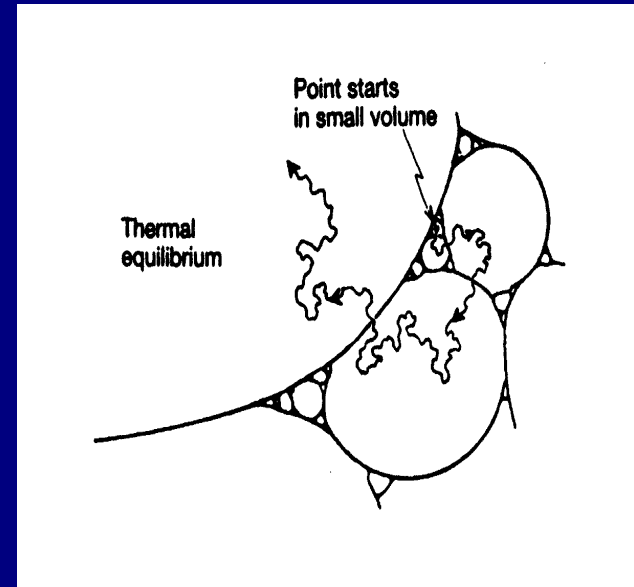
Gibbs:



Problems:

- Liouville's Law
- Mixing
- Cell Size

Ehrenfest:



Problems:

- Definition of Macroscopic Cells
- Phase Space Velocity

Thermodynamics based on Classical Mechanics ?

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“Over the years enormous effort was invested in proving ergodicity, but for a number of reasons, confidence in the fruitfulness of this approach has waned”

Y.Ben-Menahem, I. Pitowski, Stud. Hist. Phil. Mod. Phys., **32** 503-510, 2001

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Heisenberg cut? \Rightarrow Typical Gas:

Particle masses: $\approx 1 - 100$ Proton masses

Particle sizes: $\approx 10^{-10}$ m

Width of a wavepackage at $t = 0$: 10^{-10} m

Width of a wavepackage at $t = 1$ sek. : 1 m – 100 m

Classical description of thermodynamical systems in general *a priori* arguable.

A Quantum Approach to Thermodynamics

Von Neumann Entropy: $S = -k \text{Tr}\{\hat{\rho} \ln \hat{\rho}\}$

Purity: $P = \sqrt{\text{Tr}\{(\hat{\rho})^2\}}$

Entropy and Purity do not map exactly but: $S_{max} \overset{\approx}{\Leftrightarrow} P_{min}$

entirely isolated system: $i\hbar \frac{d}{dt} \hat{\rho} = [\hat{H}, \hat{\rho}^g] \Rightarrow \frac{dP}{dt} = 0 \Rightarrow \frac{dS}{dt} = 0$

How can entropy possibly change?

Composite Systems

System consisting of considered system (S) and environment (E):

$$i\hbar \frac{d}{dt} |\Psi\rangle = \left(\hat{H}^S + \hat{H}^E + \hat{I} \right) |\Psi\rangle \quad \hat{\rho}^S := \text{Tr}_E \{ |\Psi\rangle \langle \Psi| \}$$

in general: $\hat{I} \neq 0 \quad \Rightarrow \quad \frac{dS}{dt} \neq 0$

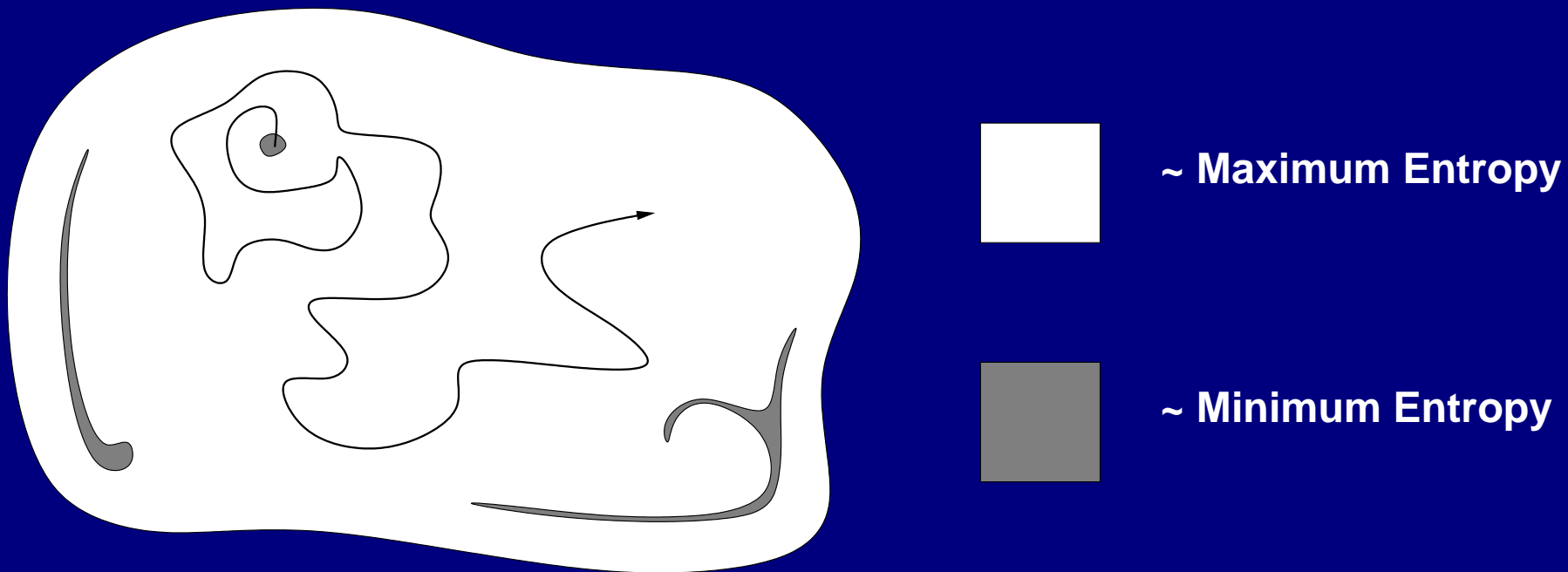
thermally insulated means: $[\hat{H}^S, \hat{I}] = 0$ but not: $\hat{I} = 0$

Entropy may be changed also by interactions that do not exchange energy!

Hilbert space “Landscapes”

Why does entropy increase?

Entropy is defined pointwise on Hilbert space: $S = S(|\Psi\rangle) \Rightarrow$ “Entropy landscape”.



Conjecture: For “large” environments almost all accessible composite system microstates $|\Psi\rangle$ feature almost maximum local entropy!

Hilbert space Averages

Representation of state spaces:

Classical Mechanics: State definition: $\Gamma = \{x_n, p_n\}$

Phase space, Cartesian coordinates $\{x_n, p_n\}$

Quantum Mechanics: State definition $|\psi\rangle = \sum_n (\phi_n + i\phi'_n) |n\rangle$

Hilbert space, Cartesian coordinates $\{\phi_n, \phi'_n\}$

Energy conservation imposes a condition on the $\{\phi_i\}$, set by the initial state $|\Psi(0)\rangle$
 \Rightarrow Accessible Region (AR)

Hilbert space average: $\langle\langle f \rangle\rangle = \int_{\text{AR}} f(|\Psi\{\phi_i\}\rangle) \prod_i d\phi_i$

Microcanonical and Canonical Conditions

Microcanonical Conditions:

Hilbert space average of the purity over the AR under microcanonical conditions:

$$\langle\langle P^g \rangle\rangle \approx P_{min}^g(|\Psi(0)\rangle) + \frac{\epsilon(|\Psi(0)\rangle)}{N_{rel}^E} \quad N_{rel}^E \gg 1 \quad \Rightarrow \quad \langle\langle S^S \rangle\rangle \approx S_{max}^S$$

N_{rel}^E : Degeneracy of the relevant energy levels of the environment

Canonical conditions

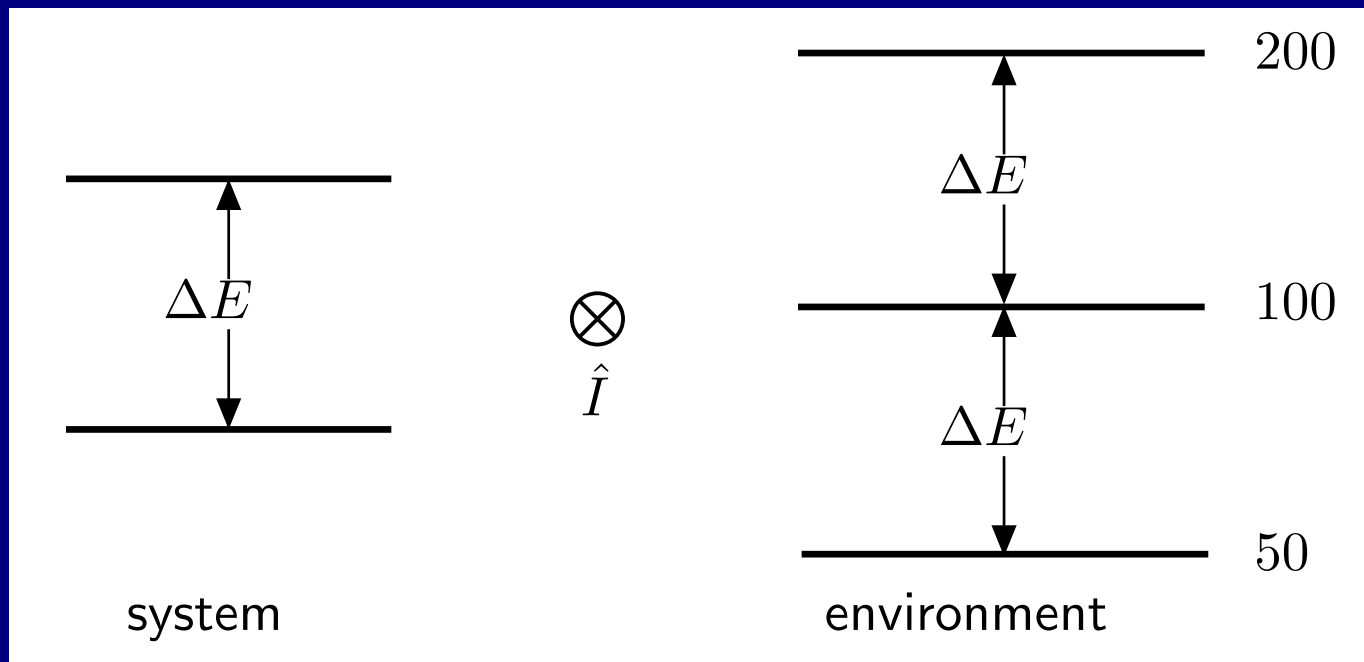
Energy exchange \Rightarrow Occupation number landscape

Hilbert space averages of the occupation numbers over the AR under canonical conditions:

$$\langle\langle W^S(E) \rangle\rangle \propto N^S(E) N^E(U - E)$$

If the system was ergodic, time averaging would yield the same formula!

The Smallest Thermodynamical System

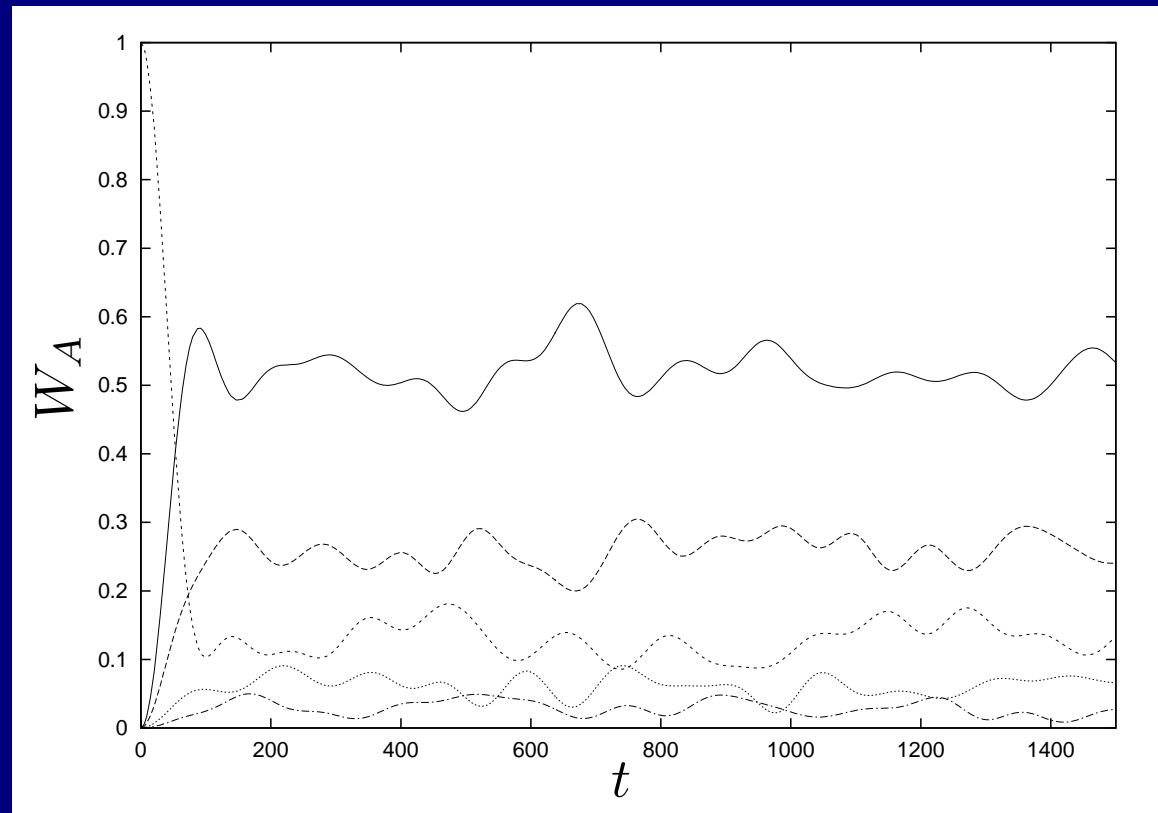
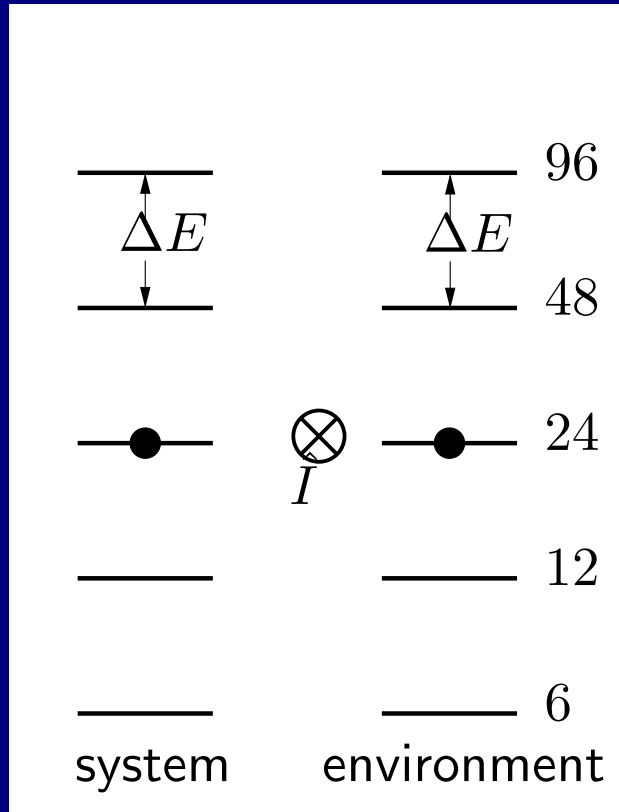


$$\hat{I}_{can} = \sum_i c_i \hat{\sigma}^+ \hat{a}_i^- + c_i^* \hat{\sigma}^- \hat{a}_i^+ \quad \hat{I}_{mic} = \sum_i (c_i^0 \hat{\sigma}^+ \hat{\sigma}^- + c_i^1 \hat{\sigma}^- \hat{\sigma}^+) (\hat{b}_i^- + \hat{b}_i^+)$$

\hat{a} : Interband Transition \hat{b} : Innerband Transition c_i : Randomly distributed small complex numbers

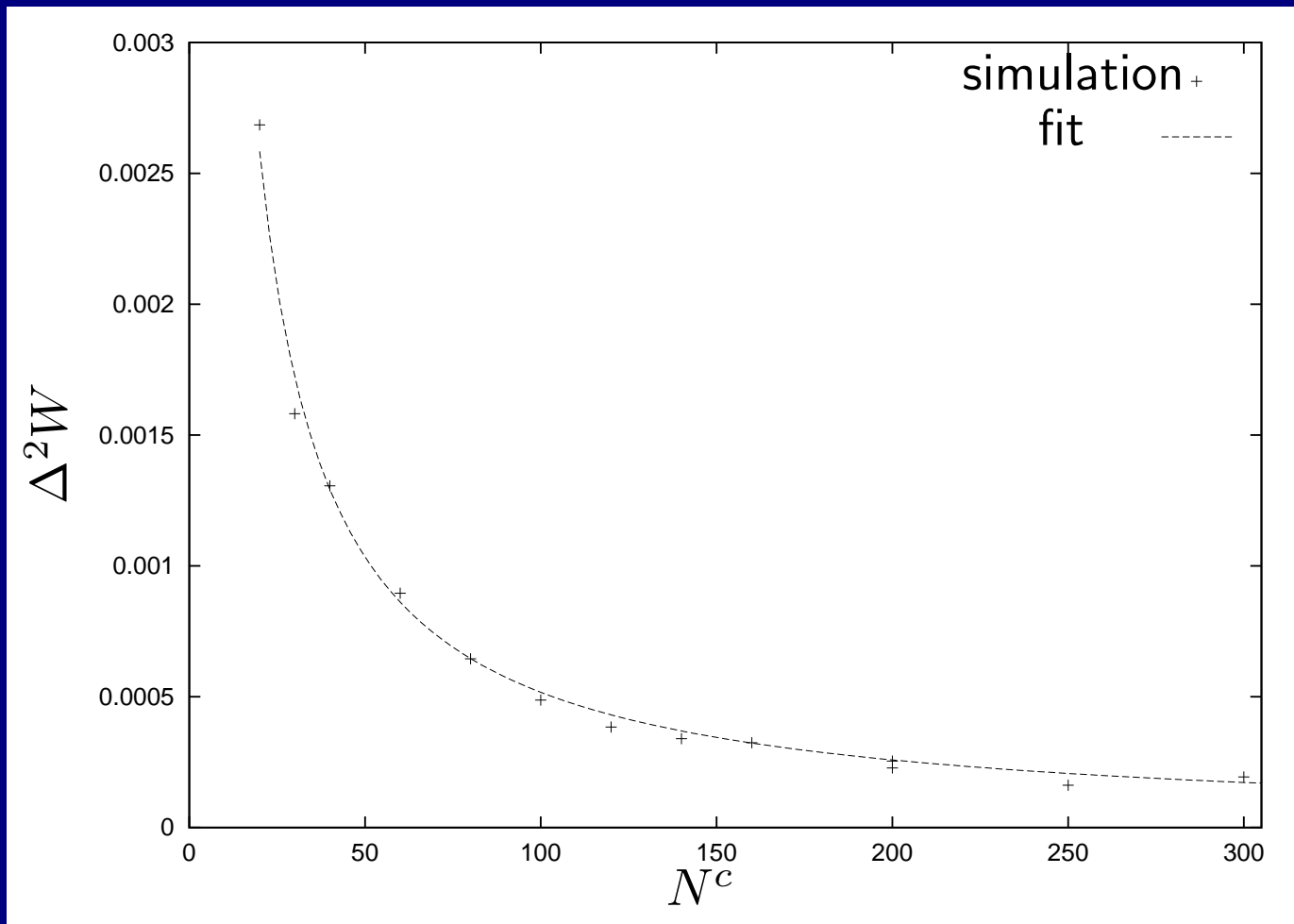
Solve the Schrödinger equation \Rightarrow Thermodynamics!

Boltzmann Distribution



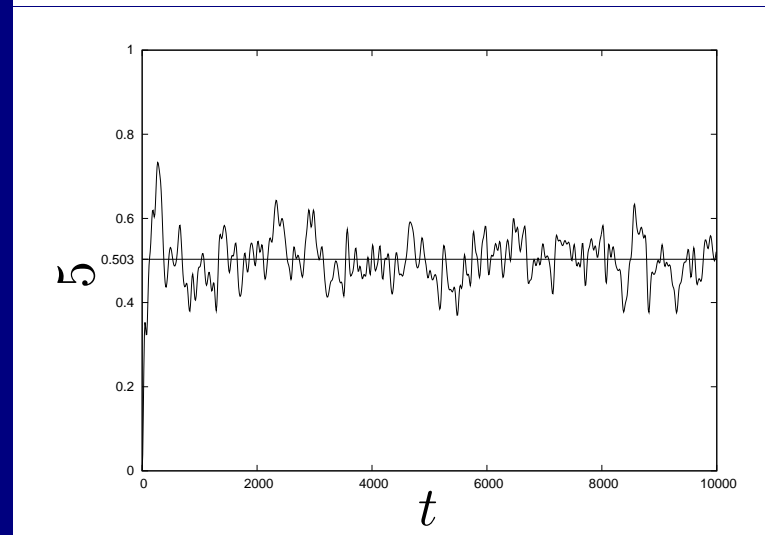
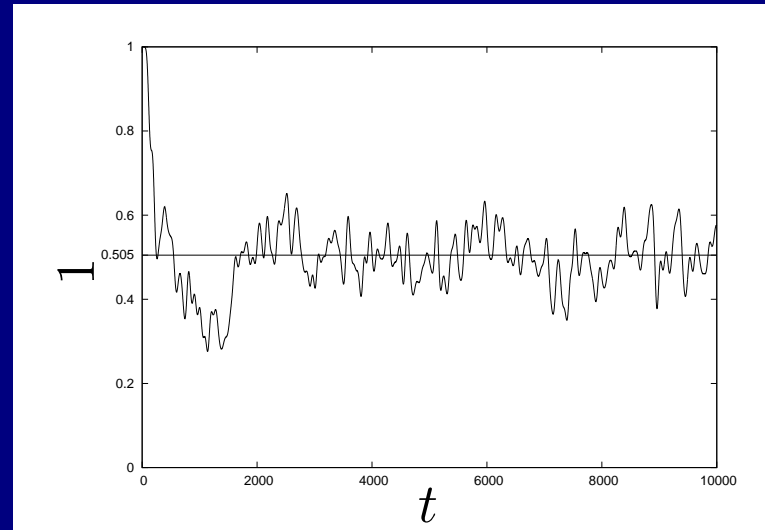
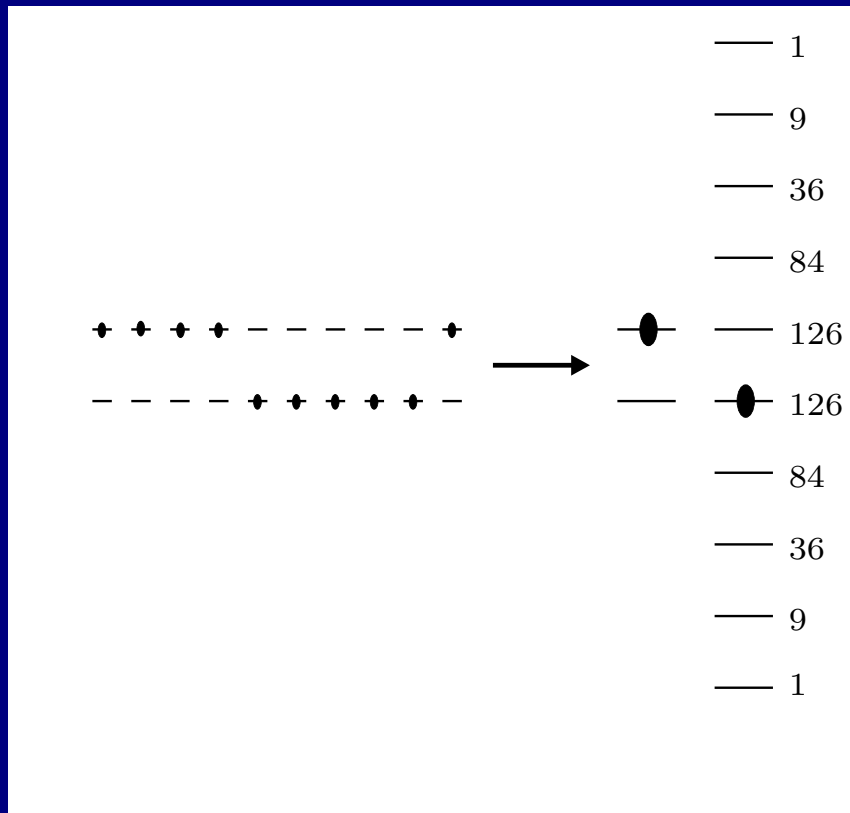
Systems may evolve into a Boltzmann distribution without the environment being in a thermal state.

Fluctuations



Fluctuations vanish like $\sqrt{\frac{1}{NE}}$ with the environment size.

Heisenberg Spin Chain in Strong Magnetic Field



Equilibrium may be enforced onto subunits by the considered system itself.

The Route to Equilibrium

How can statistical, exponential relaxation processes be explained?

Fermis Golden Rule: *Der unbestreitbare Erfolg der Goldenen Regel muss bei genau-erem Hinsehen allerdings mehr als verblüffen, da wir zu ihrer Ableitung mehrere sich zum Teil eklatant widersprechende Voraussetzung benützt haben. (Nolting 5/2)*

Weisskopf Wigner Theory: Explains the decay of an excitation in an atom coupled to the electromagnetic field at $T = 0$. Hard to generalize!

Quantum Master Equations:

- Systems must be Markovian
- Initial state must factorize
- Bath state must be thermal
- Often systems are assumed to remain uncorrelated
- Backactions onto the bath are ignored

Hilbert space Average Method (HAM)

For a short time-step τ , second order time-dependent perturbation theory yields:

$$|\Psi(t + \tau)\rangle \approx \hat{U}(t, \tau)|\Psi(t)\rangle$$

Short time evolutions of matrix elements of the density matrix of the considered system read

$$\langle \Psi(t + \tau) | i \rangle \langle j | \Psi(t + \tau) \rangle = \langle \Psi(t) | \hat{U}^+(t, \tau) | i \rangle \langle j | \hat{U}(t, \tau) | \Psi(t) \rangle := \rho_{ij}(|\Psi\rangle, t, \tau)$$

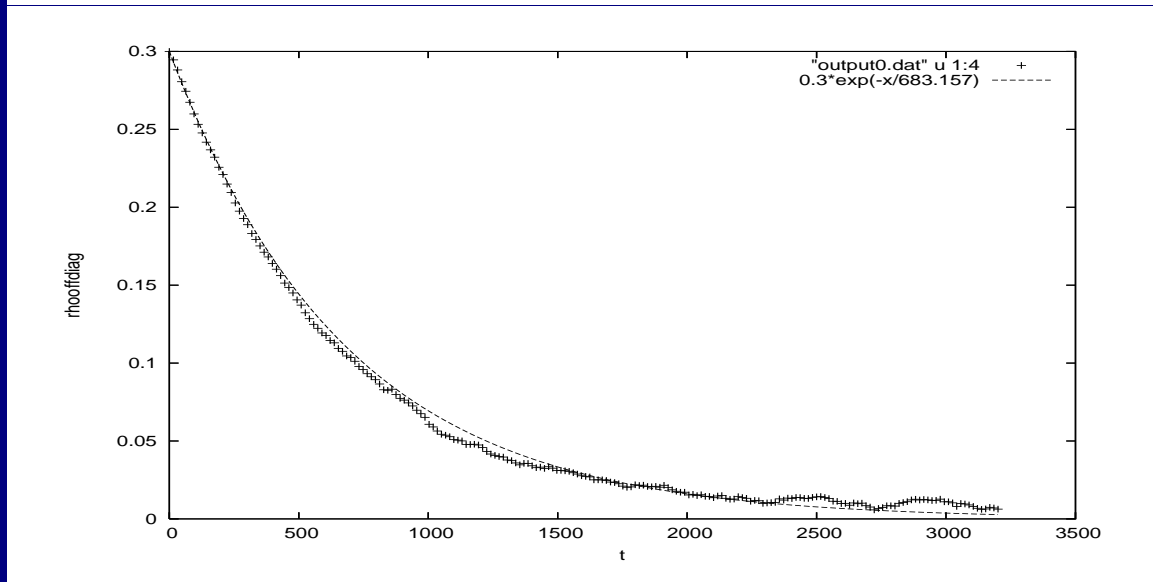
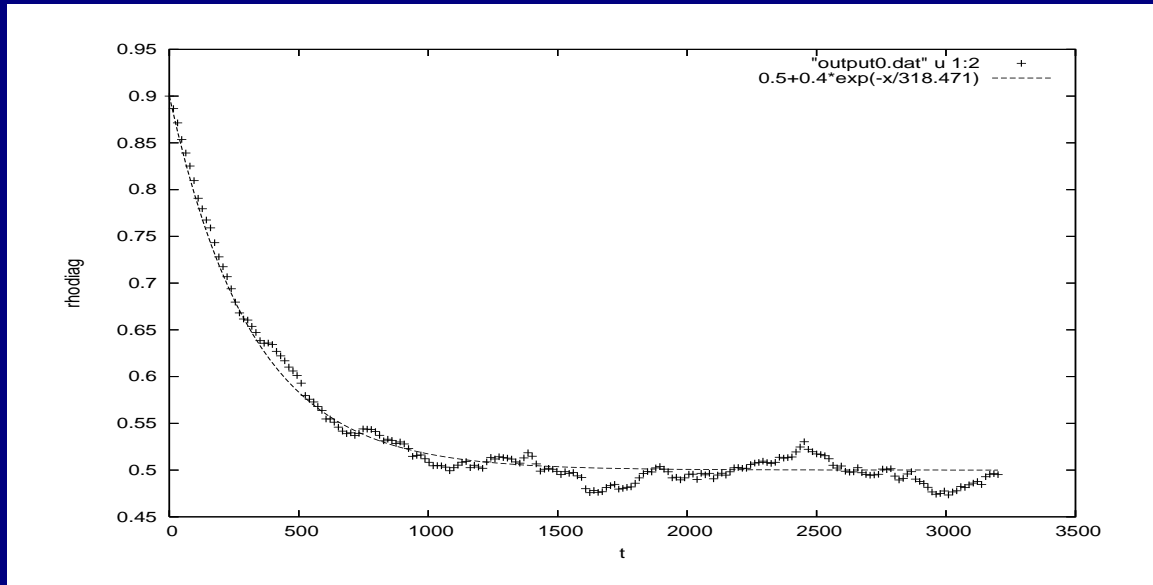
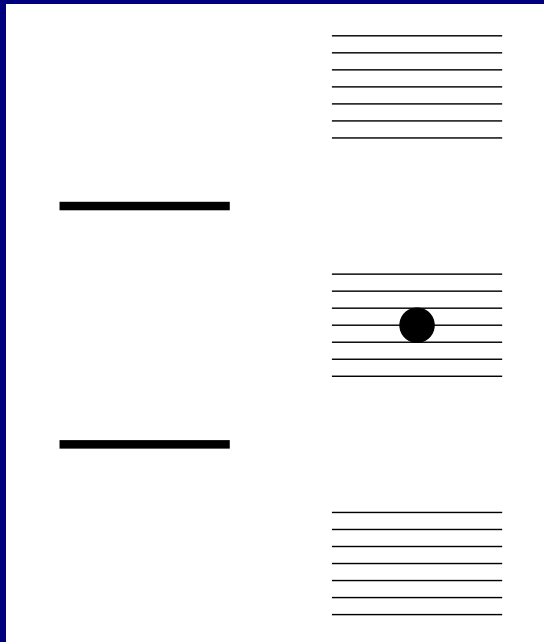
Markovian Systems: Computing the Hilbert space average of ρ_{ij} over an appropriate region yields

$$\langle\langle \rho_{ij}(|\Psi\rangle, t, \tau) \rangle\rangle \approx \rho_{ij}(t) - \tau \sum_{lm} \gamma_{ijlm} \rho_{lm}(t)$$

Replace actual value by Hilbert space average and iterate \Rightarrow

$$\dot{\rho}_{ij} = - \sum_{lm} \gamma_{ijlm} \rho_{lm}(t)$$

From Schrödingerian to Statistical Dynamics

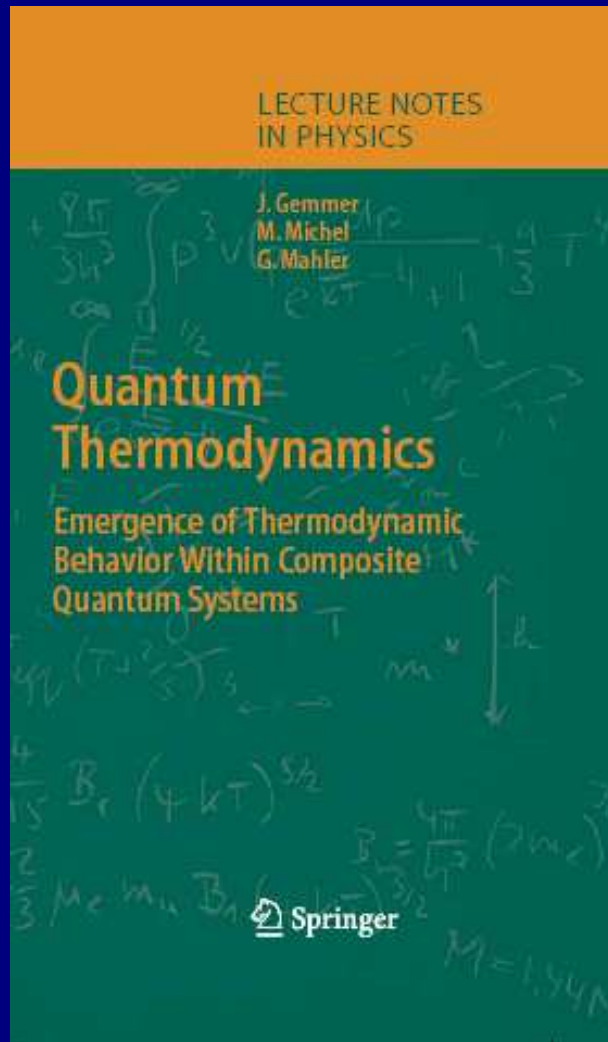


Pure state Schrödinger dynamics may give rise to an exponential decay.

Summary and Conclusion

- Quantum systems, that are weakly coupled to larger systems, show, under pure Schrödingerian dynamics, a strong tendency towards thermodynamical equilibrium, even if no energy is exchanged.
- The occurrence of thermodynamical behavior depends on various conditions, but there is no minimum size or particle number.
- Energy exchange between moderate sized quantum systems may appear merely statistical. This might lead to an improved understanding of thermal transport.

Buy Now!



Quantum Thermodynamics

Emergence of Thermodynamic Behavior Within Composite Quantum Systems

Lecture Notes in Physics, Vol 657

Gemmer J., Michel M., Mahler G.

ISBN 3-540-22911-6

Less costly:

Google:

Quantenthermodynamik, Gemmer

(English site under construction.)

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