Nonequilibrium Thermodynamics for Mathematicians

Hans Christian Öttinger

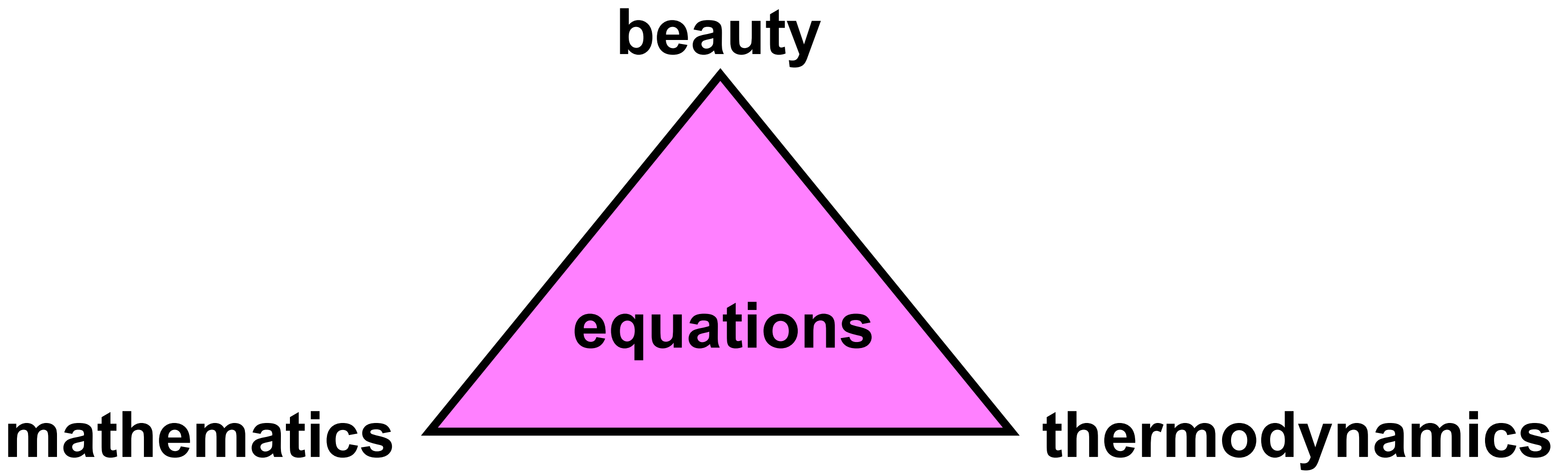
Department of Materials, ETH Zürich, Switzerland

ETH Polymer Physics

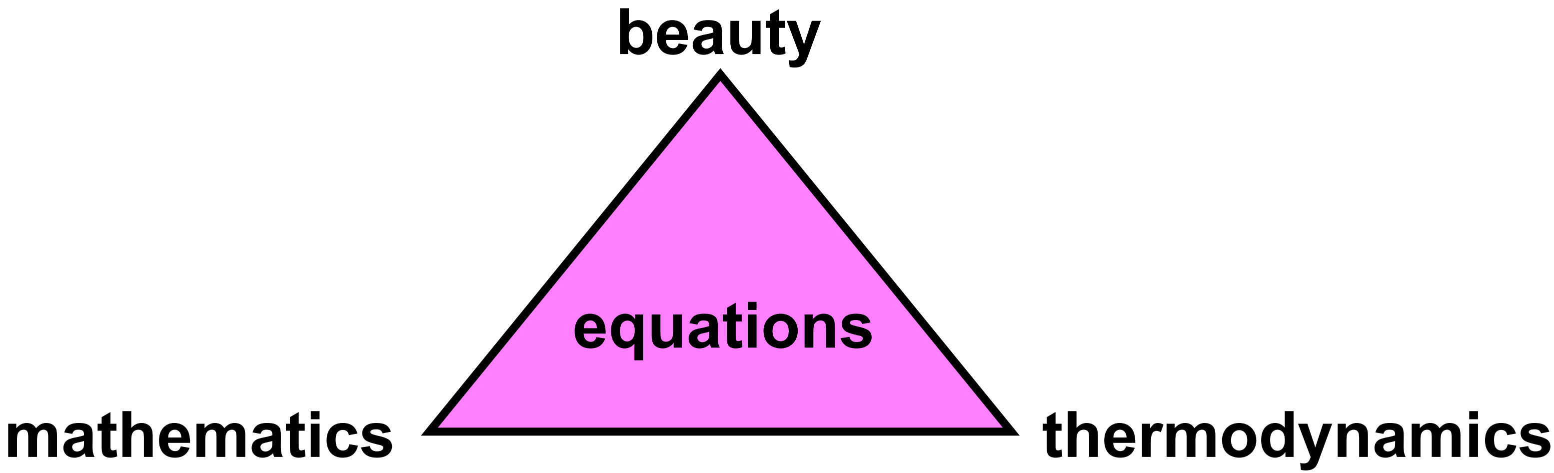
- **Part 1 – Mathematics ⚭ Thermodynamics**
- **Part 2 – Geometric Structure of Thermodynamics**
- **Part 3 – Boundary Thermodynamics**
- **Part 4 – Dissipative Quantum Systems**

- **Part 1 – Mathematics ⚭ Thermodynamics**
- **Part 2 – Geometric Structure of Thermodynamics**
- **Part 3 – Boundary Thermodynamics** **useful**
- **Part 4 – Dissipative Quantum Systems** **playful**

- Part 1 – Mathematics ∞ Thermodynamics
- Part 2
- Part 3
- Part 4



P.A.M. Dirac: “This result is too beautiful to be false; it is more important to have beauty in one's equations than to have them fit experiment.” (*Scientific American*, May 1963)



existence & uniqueness of solutions
qualitative behavior of solutions

beauty

equations

mathematics

thermodynamics

existence & uniqueness of solutions
qualitative behavior of solutions
geometric structures

nonequilibrium thermodynamics
provides prerequisites for proofs
via thermodynamic structure

- **Part 1 – Mathematics ⚭ Thermodynamics**
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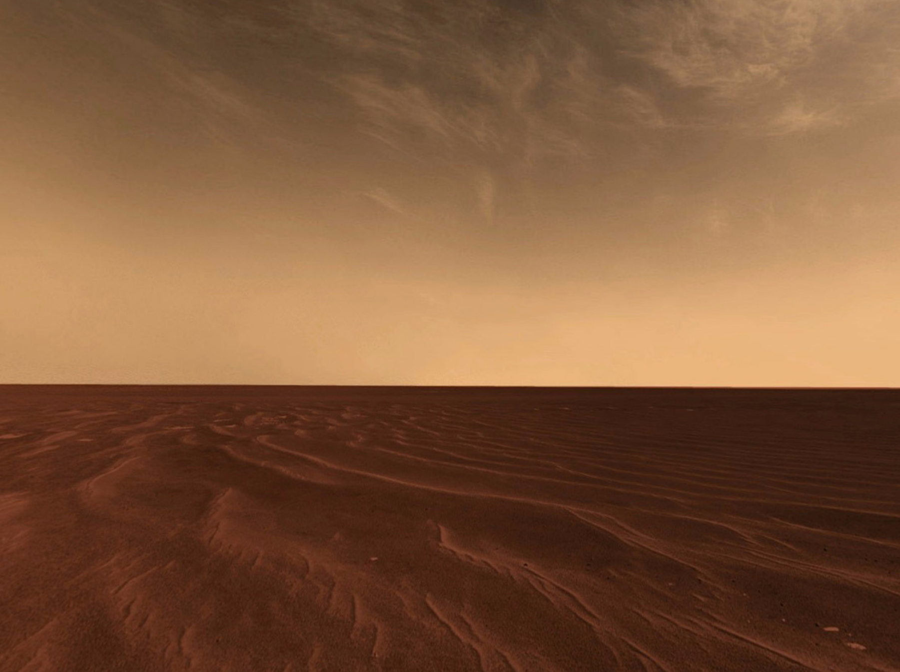
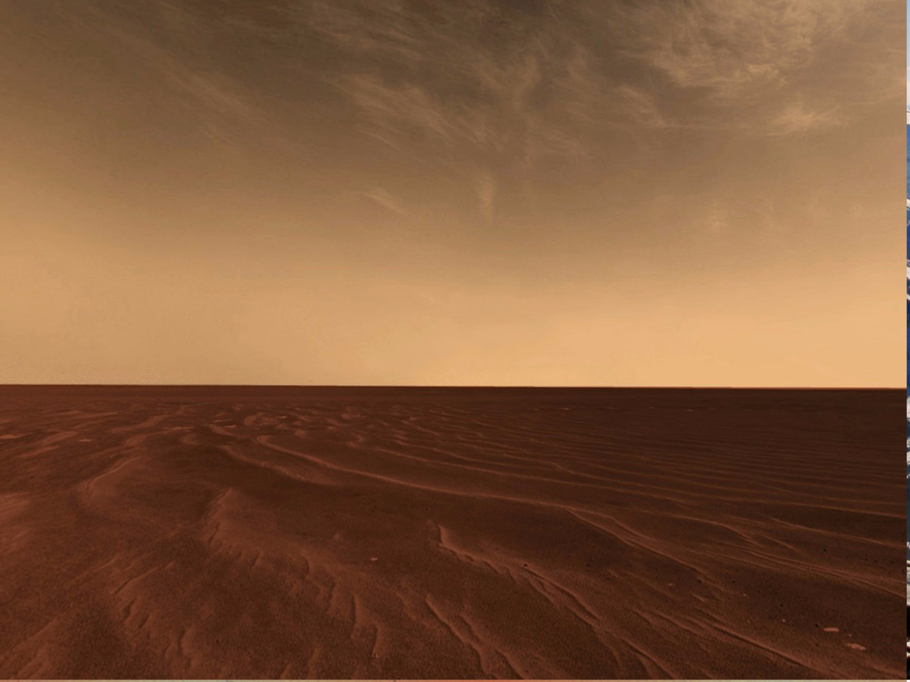
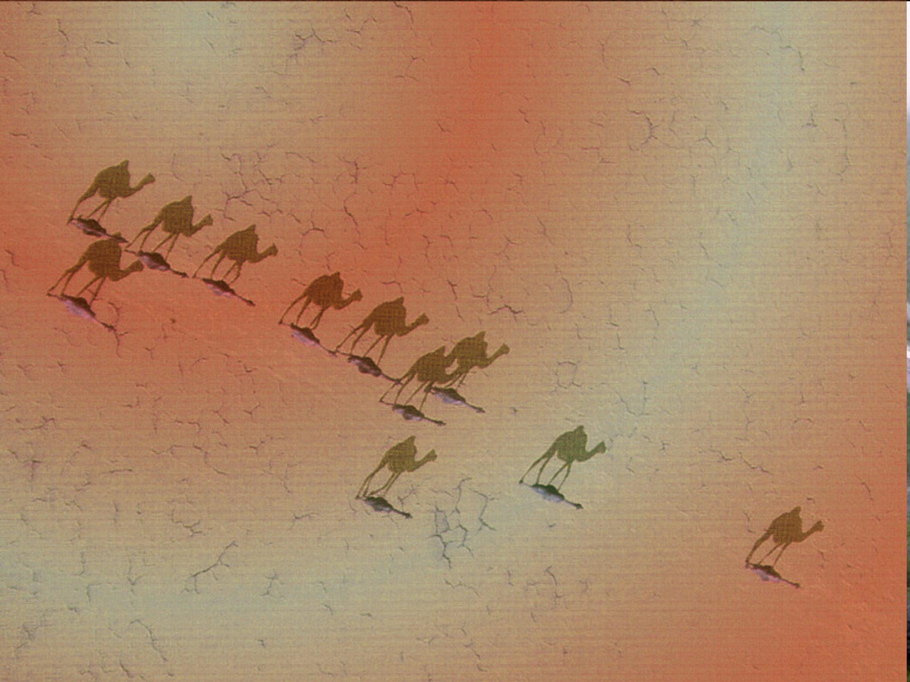
- **Part 3**
- **Part 4**





GENERIC Structure

General equation for the nonequilibrium reversible-irreversible coupling

metriplectic structure (P. J. Morrison, 1986)

$$\boxed{\frac{dA}{dt} = \{A, H\} + [A, S]}$$

$H(x)$ energy

$S(x)$ entropy

Poisson bracket

$\{A,B\}$ antisymmetric, Jacobi identity

$$\{S, A\} = 0$$

Dissipative bracket

$[A,B]$ Onsager/Casimir symmetric, positive-semidefinite

$$[H, A] = 0$$

Physics of the Dissipative Bracket

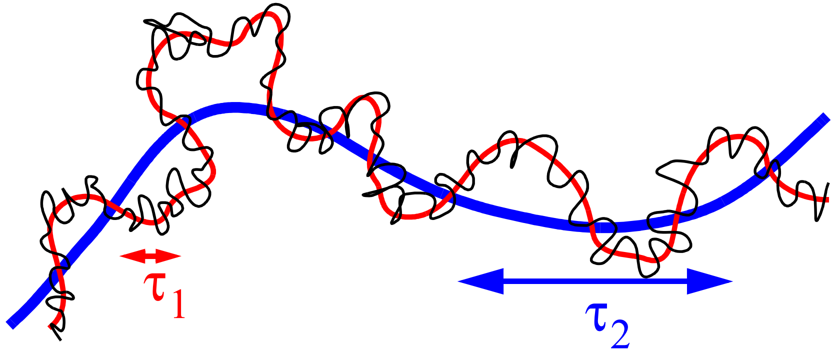
$$\frac{dS}{dt} = [S, S]$$

Frictional properties are related to time-dependent fluctuations:

$$\boxed{\text{cf.} \quad D = \frac{1}{2\Delta t}\langle(\Delta x)^2\rangle}$$

Einstein

$$[A, B] = \frac{1}{2k_B\tau}\langle \Delta_\tau A^{\mathrm{f}}\, \Delta_\tau B^{\mathrm{f}}\rangle$$



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- Part 4

References/Acknowledgments

PHYSICAL REVIEW E **80**, 021606 (2009)

Nonequilibrium thermodynamics of transport through moving interfaces with application to bubble growth and collapse

Hans Christian Öttinger*
Department of Materials, Polymer Physics, ETH Zürich, HCI H 543, CH-8093 Zürich, Switzerland

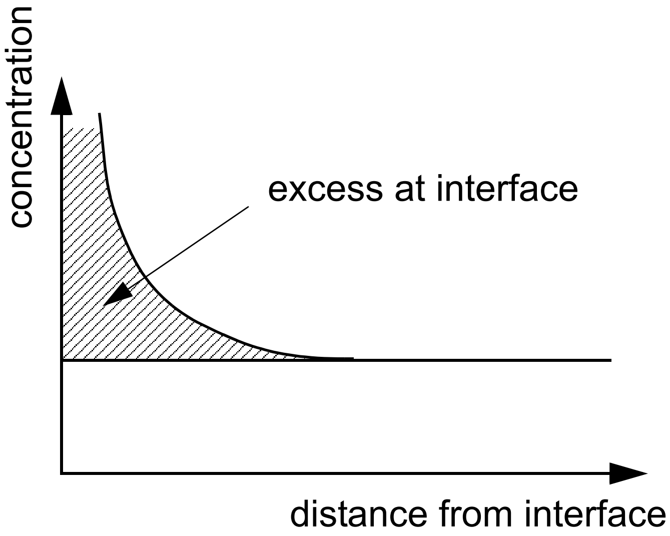
Dick Bedeaux†
Department of Chemistry, Norwegian University of Science and Technology, Trondheim 7491, Norway and Department of Process and Energy, Technical University of Delft, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

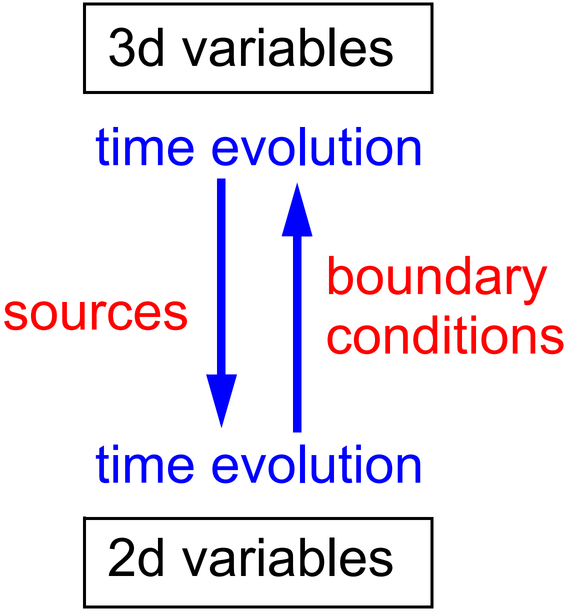
David C. Venerus‡
Department of Chemical & Biological Engineering, Illinois Institute of Technology, 10 West 33rd Street, Chicago, Illinois 60616, USA
(Received 23 March 2009; published 21 August 2009)

See also:

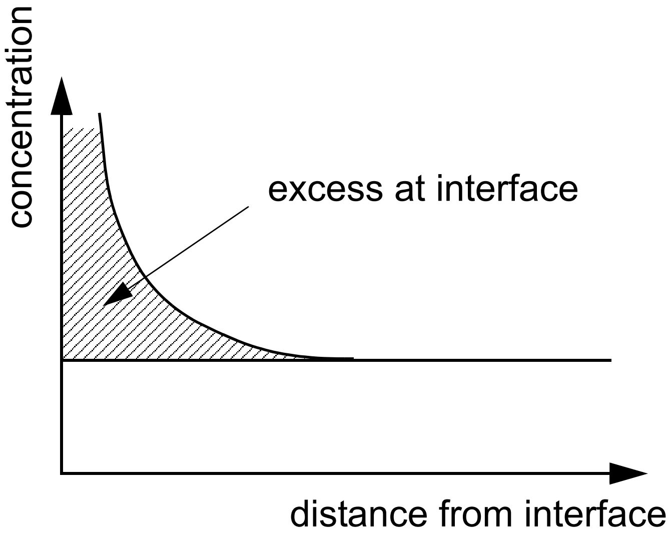
hco, Phys. Rev. E 73 (2006) 036126
A.N. Beris & hco, J. Non-Newtonian Fluid Mech. 152 (2008) 2
hco, J. Non-Newtonian Fluid Mech. 152 (2008) 66

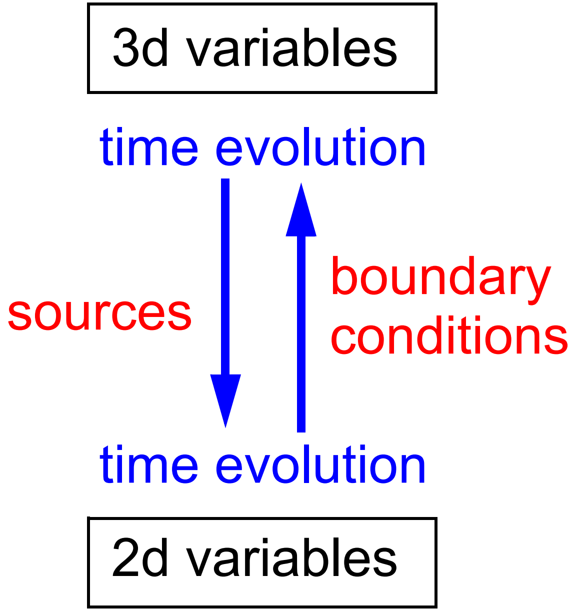
Boundary Thermodynamics





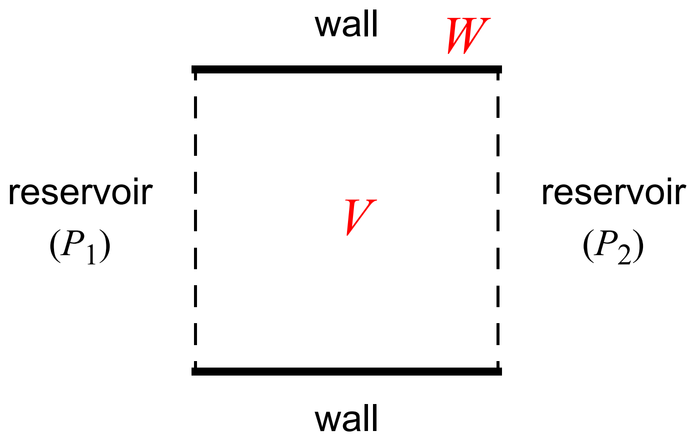
Boundary Thermodynamics





Conditions at the boundary vs. boundary conditions!

Example: Diffusion Cell



System: Solute particle number densities

- P in the bulk
- p at the wall

Brenner & Ganesan, Phys. Rev. E 61 (2000) 6879
hco, Phys. Rev. E 73 (2006) 036126

$$\frac{\delta S}{\delta P} = -k_{\mathrm{B}} \ln \frac{P}{P_0}, \qquad \frac{\delta S}{\delta p} = -k_{\mathrm{B}} \ln \frac{p}{p_0}$$

$$k_{\mathrm{B}}[A, B] = \int_V D_{\mathrm{b}} \left[\frac{\partial}{\partial \boldsymbol{r}} \frac{\delta A}{\delta P}\right] \cdot \left[\frac{\partial}{\partial \boldsymbol{r}} \frac{\delta B}{\delta P}\right] P\, d^3 r + \int_W D_{\mathrm{s}} \left[\frac{\partial}{\partial \boldsymbol{r}} \frac{\delta A}{\delta p}\right] \cdot \left[\frac{\partial}{\partial \boldsymbol{r}} \frac{\delta B}{\delta p}\right] p\, d^2 r$$
$$+ \int_W \nu_{\mathrm{s}} \left[\frac{\delta A}{\delta p} - \Omega \frac{\delta A}{\delta P}\right]\left[\frac{\delta B}{\delta p} - \Omega \frac{\delta B}{\delta P}\right] p\, d^2 r$$

$\Omega = 1$

ν_{s}: ad/desorption rate

Diffusion Cell: Results

$$[A, S] = \int_V \frac{\delta A}{\delta P} \cdot \left[\frac{\mathrm{d}P}{\mathrm{d}t}\right]_{\mathrm{irr}} d^3 r + \int_W \frac{\delta A}{\delta p} \cdot \left[\frac{\mathrm{d}p}{\mathrm{d}t}\right]_{\mathrm{irr}} d^2 r + \int_{\partial V} J^A_{\mathrm{irr}} d^2 r$$

open boundaries: $J^A_{\mathrm{irr}} = -\frac{\delta A}{\delta P}\boldsymbol{n} \cdot D_{\mathrm{b}} \frac{\partial P}{\partial \boldsymbol{r}}$

wall: $J^A_{\mathrm{irr}} = 0$

evolution equations:

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{\partial}{\partial \boldsymbol{r}} \cdot D_{\mathrm{b}} \frac{\partial P}{\partial \boldsymbol{r}}$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{\partial}{\partial \boldsymbol{r}} \cdot D_{\mathrm{s}} \frac{\partial p}{\partial \boldsymbol{r}} - \boldsymbol{n} \cdot D_{\mathrm{b}} \frac{\partial P}{\partial \boldsymbol{r}}$$

boundary condition on wall:

$$-\boldsymbol{n} \cdot D_{\mathrm{b}} \frac{\partial P}{\partial \boldsymbol{r}} = \nu_{\mathrm{s}} p \ln \frac{HP}{p}$$

$$H = p_0 / P_0$$

characteristic length scale

Moving Boundaries

Challenge: How to match the chain rule and thermodynamic evolution equations?

Moving Boundaries

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$$\{A, B\}^{\text{mint}} = \int_I \frac{\partial a^{\text{s}}}{\partial \boldsymbol{M}^{\text{s}}} \cdot \boldsymbol{n} \left[(\tilde{b}^{\text{g}} - b^{\text{g}}) - (\tilde{b}^{1} - b^{1}) + (\tilde{b}^{\text{s}} - b^{\text{s}}) \frac{\partial}{\partial \boldsymbol{r}_{\parallel}} \cdot \boldsymbol{n} \right] \mathrm{d}^2 r - (A \leftrightarrow B)$$

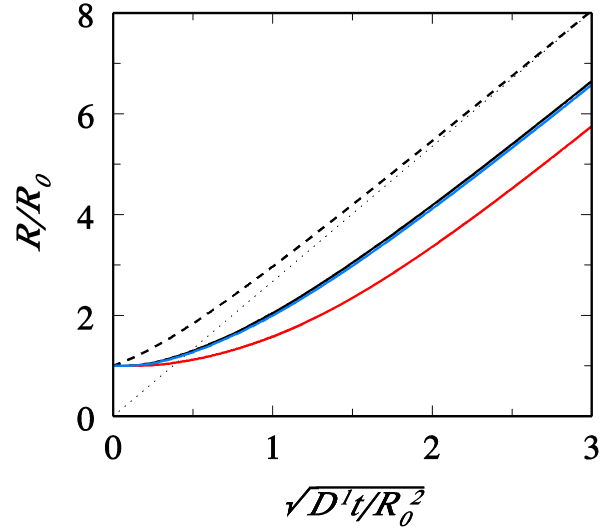
$$\tilde{b}^{\text{g}} = \left(\rho^{\text{g}} \frac{\partial}{\partial \rho^{\text{g}}} + \boldsymbol{M}^{\text{g}} \cdot \frac{\partial}{\partial \boldsymbol{M}^{\text{g}}} + s^{\text{g}} \frac{\partial}{\partial s^{\text{g}}} \right) b^{\text{g}}$$

mass momentum entropy

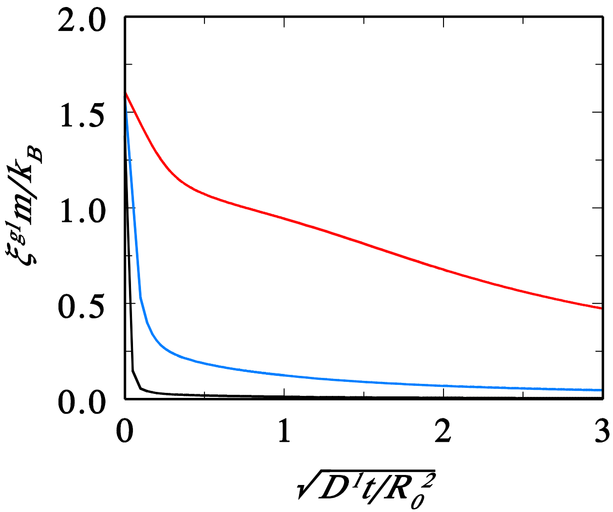
b^{g}	$\tilde{b}^{\text{g}}$
ρ^{g}	ρ^{g}
$\boldsymbol{M}^{\text{g}}$	$\boldsymbol{M}^{\text{g}}$
s^{g}	s^{g}
ε^{g}	$\varepsilon^{\text{g}} + p^{\text{g}}$

Bubble growth in a supersaturated liquid for different solute release rates

bubble size



interfacial driving force



deviation from Henry's law: $c(R) = Kp^{g}\exp\left\{\xi^{gl}m/k_{B}\right\}$

hco, D. Bedeaux, and D.C. Venerus, Phys. Rev. E 80 (2009) 021606

Next Steps

- Local equilibrium and gauge invariance
- Free boundaries
- Viscoelastic interfaces
- More general relations between bulk and boundary variables
- Variables characterizing the geometry of interfaces
- Functional calculus
- Statistical mechanics

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References

PHYSICAL REVIEW A **82**, 052119 (2010)

Nonlinear thermodynamic quantum master equation: Properties and examples

Hans Christian Öttinger*
ETH Zürich, Department of Materials, Polymer Physics, HCI H 543, CH-8093 Zürich, Switzerland
(Received 5 April 2010; revised manuscript received 26 August 2010; published 29 November 2010)

The quantum master equation obtained from two different thermodynamic arguments is seriously nonlinear. We argue that, for quantum systems, nonlinearity occurs naturally in the step from reversible to irreversible equations and we analyze the nature and consequences of the nonlinear contribution. The thermodynamic nonlinearity naturally leads to canonical equilibrium solutions and extends the range of validity to lower temperatures. We discuss the Markovian character of the thermodynamic quantum master equation and introduce a solution strategy based on coupled evolution equations for the eigenstates and eigenvalues of the density matrix. The general ideas are illustrated for the two-level system and for the damped harmonic oscillator. Several conceptual implications of the nonlinearity of the thermodynamic quantum master equation are pointed out, including the absence of a Heisenberg picture and the resulting difficulties with defining multitime correlations.

See also:

hco, Europhys. Lett. 93 (2011) in press, epl13417

Quantum dissipation is a hot topic!

But:

How can quantum degrees of freedom appear in thermodynamics?

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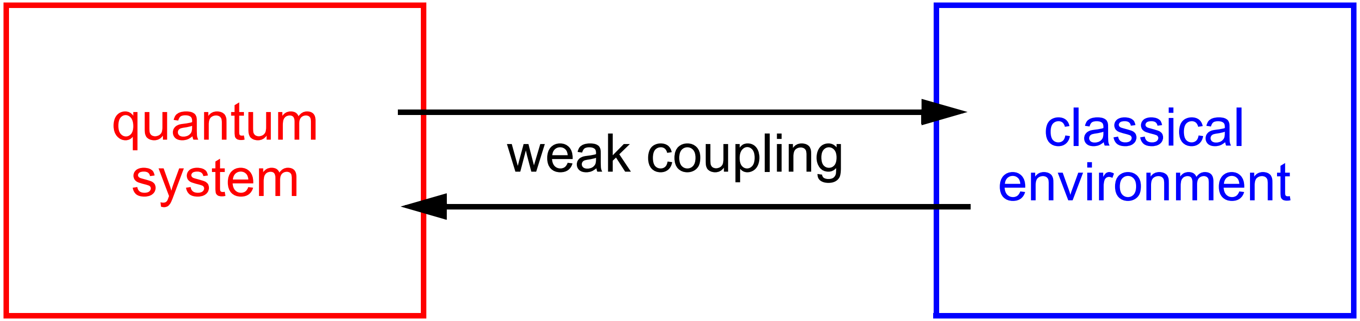
How can quantum degrees of freedom appear in thermodynamics?



P.A.M. Dirac: "We should thus expect to find that important concepts in classical mechanics correspond to important concepts in quantum mechanics, and, from an understanding of the general nature of the analogy between classical and quantum mechanics, we may hope to get laws and theorems in quantum mechanics appearing as simple generalizations of well-known results in classical mechanics"
(*The Principles of Quantum Mechanics*)

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(*The Principles of Quantum Mechanics*)

The order of performing measurements matters
Observables do not commute
Commutators matter in quantum mechanics

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(*The Principles of Quantum Mechanics*)

The order of performing measurements matters
Observables do not commute
Commutators matter in quantum mechanics

$$i\hbar \{A, B\} = [A, B]_q = AB - BA$$

Poisson bracket   commutator

GENERIC: From Classical to Quantum Systems

Poisson bracket

$$\{A, B\}$$

$$\downarrow$$

commutator

$$[A, B]_{\mathrm{q}} = AB - BA$$

GENERIC: From Classical to Quantum Systems

Poisson bracket

$$\{A, B\}$$

$$\downarrow$$

commutator

$$[A, B]_{\mathrm{q}} = AB - BA$$

dissipative bracket

$$[A, B]$$

$$\downarrow$$

?

GENERIC: From Classical to Quantum Systems

Poisson bracket

$$\{A, B\}$$

$\downarrow$

commutator

$$[A, B]_{\mathrm{q}} = AB - BA$$

dissipative bracket

$$[A, B]$$

$\downarrow$

canonical correlation
of commutators

$$\langle [A, Q]_{\mathrm{q}} ; [B, Q]_{\mathrm{q}} \rangle_{\rho}$$

GENERIC: From Classical to Quantum Systems

Poisson bracket

$$\{A, B\}$$

$$\downarrow$$

commutator

$$[A, B]_q = AB - BA$$

dissipative bracket

$$[A, B]$$

$$\downarrow$$

canonical correlation
of commutators

$$\langle [A, Q]_q ; [B, Q]_q \rangle_\rho$$

canonical correlation (Kubo): $\langle A ; B \rangle_\rho = \int_0^1 \mathrm{tr}(\rho^\lambda A \rho^{1-\lambda} B) d\lambda$

Nonlinear Thermodynamic Quantum Master Equation

Quantum subsystem:

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] - \qquad [Q, [Q, H]_\rho] - \qquad [Q, [Q, \rho]]$$

Nonlinear Thermodynamic Quantum Master Equation

Quantum subsystem:

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] - \qquad [Q, [Q, H]_\rho] - \qquad [Q, [Q, \rho]]$$

nonlinearity

$$A_\rho = \int_0^1 \rho^\lambda A \rho^{1-\lambda} d\lambda$$

Nonlinear Thermodynamic Quantum Master Equation

Quantum subsystem:

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] - \frac{1}{k_\mathrm{B}}[H_\mathrm{e}, S_\mathrm{e}]_x\,[Q, [Q, H]_\rho] - [H_\mathrm{e}, H_\mathrm{e}]_x\,[Q, [Q, \rho]]$$

Nonlinear Thermodynamic Quantum Master Equation

Quantum subsystem:

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] - \frac{1}{k_{\mathrm{B}}}[H_{\mathrm{e}}, S_{\mathrm{e}}]_x \, [Q, [Q, H]_\rho] - [H_{\mathrm{e}}, H_{\mathrm{e}}]_x \, [Q, [Q, \rho]]$$

Heat bath: *H. Grabert, Z. Phys. B 49 (1982) 161*

Nonlinear Thermodynamic Quantum Master Equation

Quantum subsystem:

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] - \frac{1}{k_B}[H_e, S_e]_x\ [Q, [Q, H]_\rho] - [H_e, H_e]_x\ [Q, [Q, \rho]]$$

Heat bath: *H. Grabert, Z. Phys. B 49 (1982) 161*

Quantum regression hypothesis:

$$\frac{d\rho}{dt} = -i\mathcal{L}\rho$$

Heisenberg picture $\Rightarrow$ $\langle [A(t), B] \rangle_\rho = \mathrm{tr}(A e^{-i\mathcal{L}t}[B, \rho])$

fluctuation-dissipation theorem $\Rightarrow$ $\langle [A(t), B] \rangle_\rho = \frac{\hbar}{kT_e}\mathrm{tr}(A e^{-i\mathcal{L}t}\mathcal{L}B_\rho)$

Nonlinear Thermodynamic Quantum Master Equation

Quantum subsystem:

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] - \frac{1}{k_{\mathrm{B}}}[H_{\mathrm{e}}, S_{\mathrm{e}}]_x \; [Q, [Q, H]_\rho] - [H_{\mathrm{e}}, H_{\mathrm{e}}]_x \; [Q, [Q, \rho]]$$

plus feedback equation
for the evolution of the classical environment

ETH Polymer Physics

Dissipative Quantum Sytems

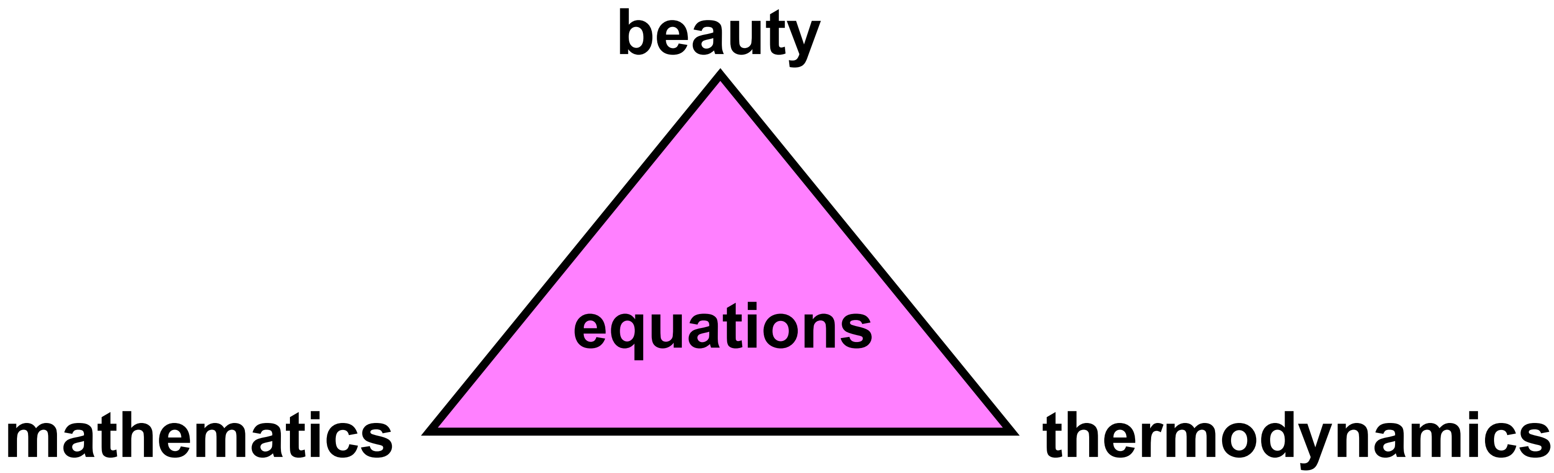
Nonlinear master equation for the quantum subsystem

Feedback contribution for the evolution of the classical environment

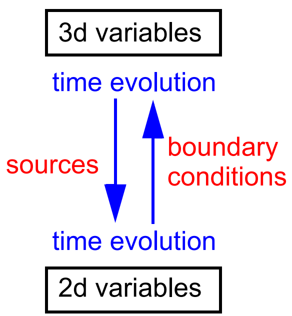
- $\rho(t)$ stays symmetric and positive-semidefinite
- Canonical equilibrium solutions
- Validity at low temperatures (for weak dissipation)
- Modifies the usual but incorrect “quantum regression hypothesis” (H. Grabert, 1982)

Take-Home Messages

- There exists a (beautiful) *geometric formulation* of classical *nonequilibrium thermodynamics* (far away from equilibrium!)
- *Boundary thermodynamics* allows us to model conditions (physics) at the boundaries (and provides boundary conditions)
- The generalization to *dissipative quantum systems* by Dirac's *method of classical analogy* is supported nicely by the geometric formulation
- We obtain a (beautiful) nonlinear *quantum master equation* (plus an equation for the environment)
- Environments and couplings of enormous *generality* can be handled, including open environments



$$\boxed{\frac{dA}{dt} = \{A, H\} + [A, S]}$$



$$ih\{A, B\} = [A, B]_q = AB - BA$$

$$\langle (A, Q); (B, Q) \rangle_\rho$$