Quantum Dissipation: A Primer

P. Hänggi

Institut für Physik
Universität Augsburg

Dynamics of Open Quantum Systems

P. Hänggi

Institut für Physik
Universität Augsburg

QUANTUM DISSIPATION

$$L = \frac{1}{2} m_0 e^{\gamma t} \dot{x}^2 - \frac{1}{2} m_0 e^{\gamma t} \omega_0^2 x^2$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} = \frac{d}{dt} m_0 e^{\gamma t} \dot{x} = m_0 e^{\gamma t} \ddot{x} + m_0 e^{\gamma t} \gamma \dot{x}$$

$$-\frac{\partial L}{\partial x} = m_0 e^{\gamma t} \omega_0^2 x$$

$$\Rightarrow \cancel{e^{\gamma t}} [m_0 \ddot{x} + m_0 \gamma \dot{x} + m_0 \omega_0^2 x] = 0$$

$$\text{QM: } L \rightarrow H = \frac{p^2}{2m_0} e^{-\gamma t} + \frac{1}{2} m_0 e^{\gamma t} \omega_0^2 x^2$$

QUANTUM DISSIPATION

$$L = \frac{1}{2} m_0 e^{\gamma t} \dot{x}^2 - \frac{1}{2} m_0 e^{\gamma t} \omega_0^2 x^2$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} = \frac{d}{dt} m_0 e^{\gamma t} \dot{x} = m_0 e^{\gamma t} \ddot{x} + m_0 e^{\gamma t} \gamma \dot{x}$$

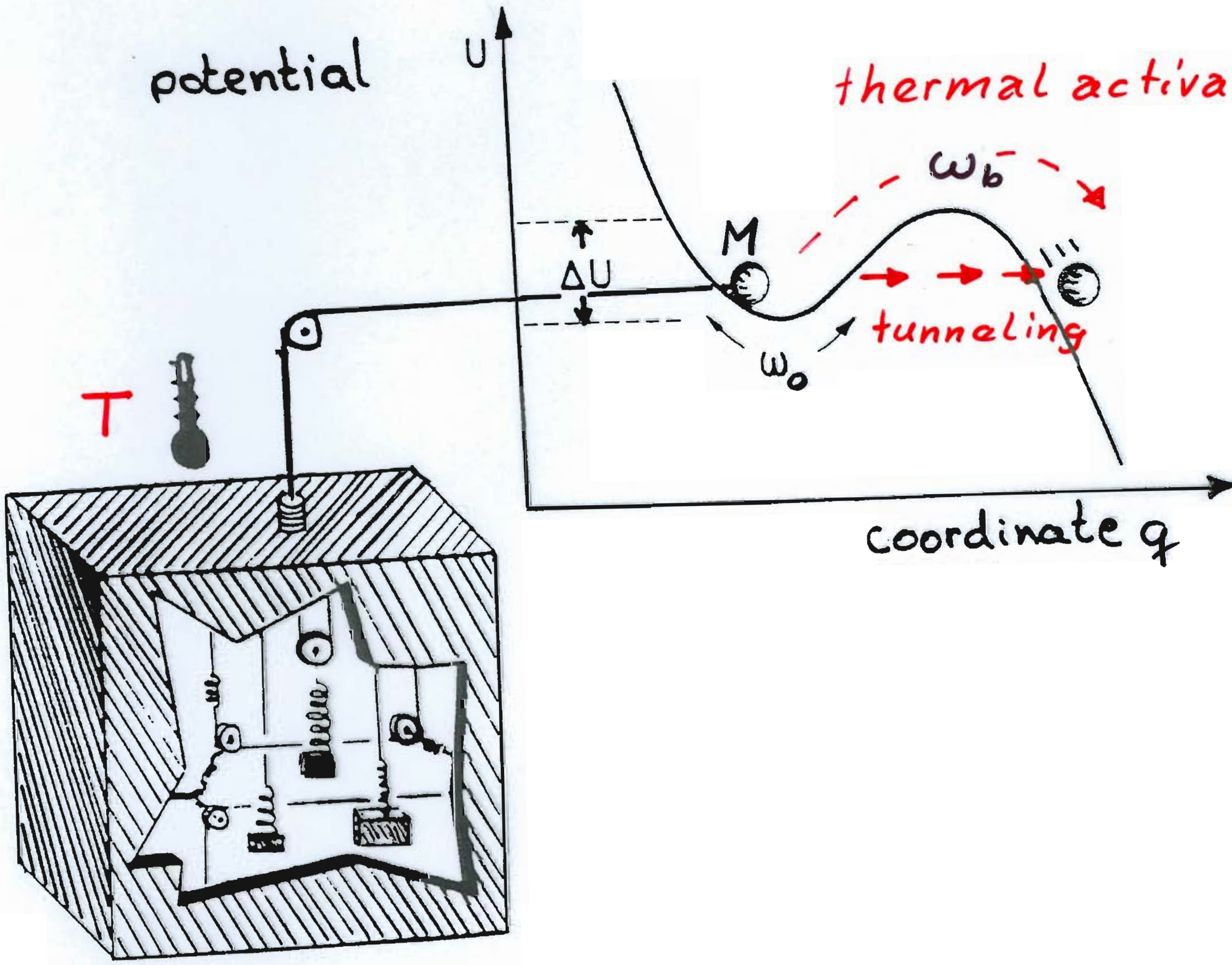
$$-\frac{\partial L}{\partial x} = m_0 e^{\gamma t} \omega_0^2 x$$

$$\Rightarrow \cancel{e^{\gamma t}} [m_0 \ddot{x} + m_0 \gamma \dot{x} + m_0 \omega_0^2 x] = 0$$

$$\text{QM: } L \to H = \frac{p^2}{2m_0} e^{-\gamma t} + \frac{1}{2} m_0 e^{\gamma t} \omega_0^2 x^2$$

¡ $[q, p] = +i\hbar\, e^{-\gamma t}$!

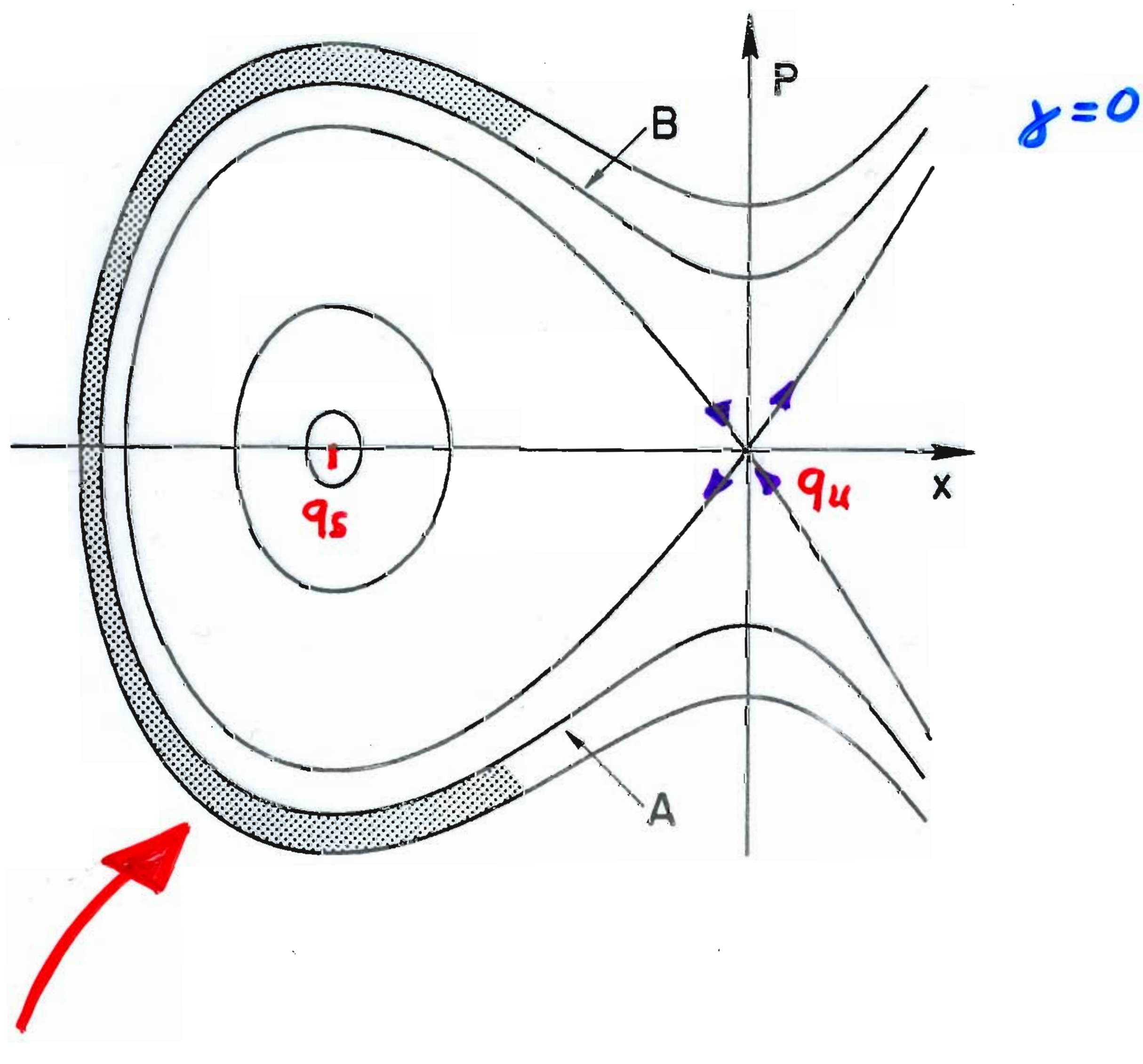
THE PROBLEM



ENVIRONMENT

$$M\ddot{q} + \frac{dU}{dx} + \eta\dot{q} = 0$$

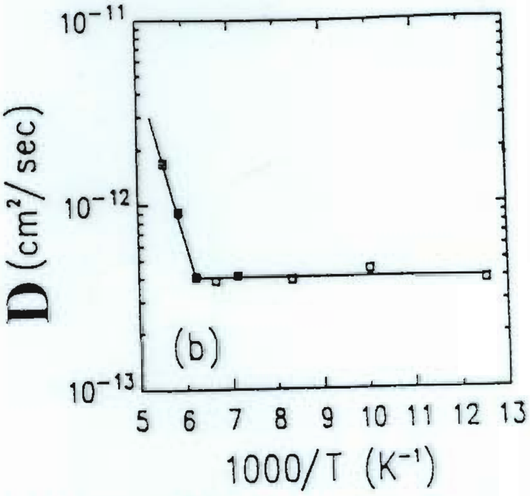
$$\Gamma = \kappa \cdot \underbrace{\frac{\omega_0}{2\pi} \exp(-E_b/kT)}_{\mathrm{TST}}$$



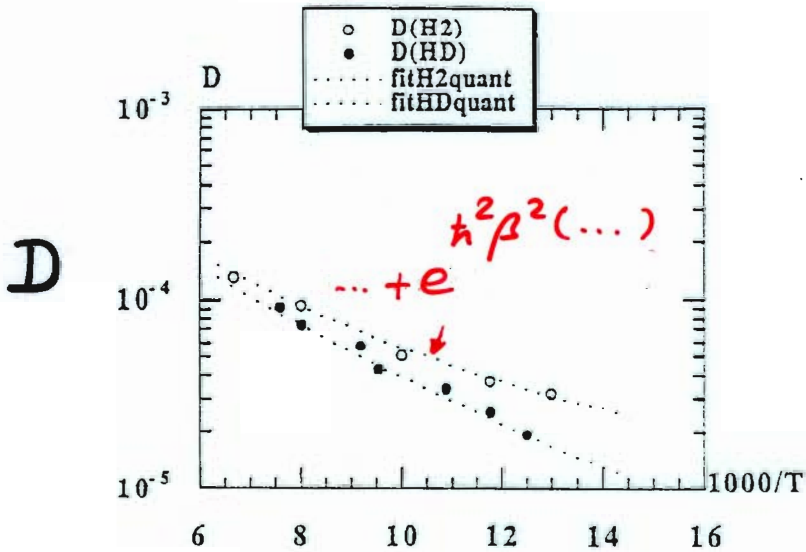
thermal equilibrium

P. H., P. TALKNER, M. BORKOVEC
REV. MOD. PHYS. <u>62</u>: 251 (1990)

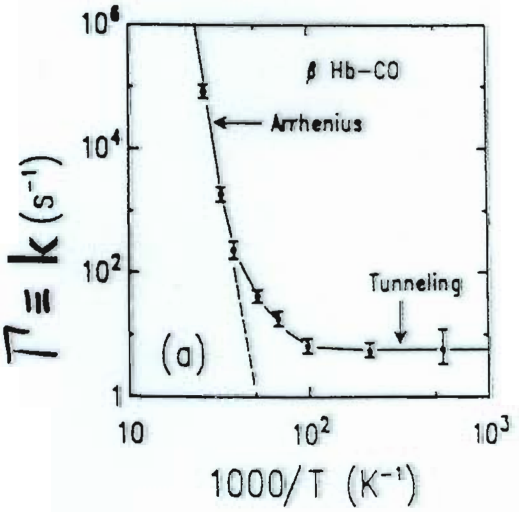
FACTS



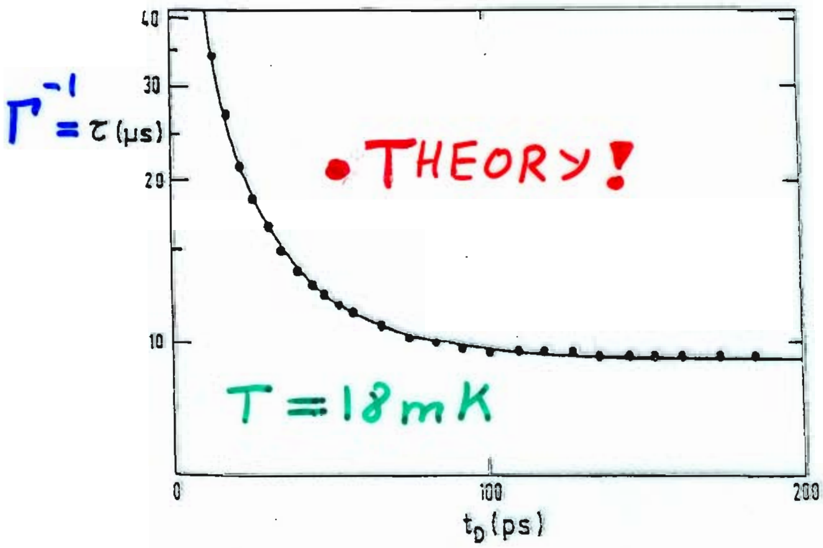
H on (110) tungsten [GOMER(82)]



H_2 & HD sorbed in zeolites [Bouchand et al.(92)]



CO-MIGRATION IN HEMOGLOBIN [Frauenfelder]



TUNNELING IN A JOSEPHSON JUNCTION SUBJECTED TO MEMORY FRICTION [Esteve et. al. (79)]

Results

Quantum Tunneling | Cross-over | Quantum Corrections | thermal activation $\rightarrow T$

Quantum Tunneling

$k = A \exp - B$

$B = S_B(T, \gamma)$

$B(T \neq 0) = B(T=0) - a T^2$!

$A(T,\gamma) \simeq A(\gamma)$

$\propto \gamma^{7/2}, \; \gamma \to \infty$

$\propto A_0 \left(1 + \frac{2.80\gamma}{2M\omega_0}\right), \; \gamma \to 0$

Cross-over

2-0-modes

$\frac{S_B}{\hbar} = \frac{E_b}{k T_0}$

smooth!

Erfc-behavior

Quantum Corrections

$k = \Gamma_{cl} Q$

quantum enhancement

$Q \sim \exp \frac{\hbar^2(\omega_0^2 + \omega_b^2)}{(kT)^2}$

> 1

i.e.

$E_b \rightarrow E_b - \frac{c}{T}$

thermal activation

$k = A(\eta) e^{-E_b/kT}$

$\uparrow \; \gamma = \eta/M$

Kramers

$\left\{ \left(\frac{\gamma^2}{4} + \omega_b^2 \right)^{1/2} - \frac{\gamma}{2} \right\}$

$\cdot \frac{\omega_0}{2\pi}$

Reaction-rate theory: fifty years after Kramers

Peter Hänggi, Peter Talkner, Michal Borkovec

RMP 62: 251 (90)

LIST OF SYMBOLS

$A(T)$	temperature-dependent quantum rate prefactor
$C(t)$	correlation function
D	diffusion coefficient
E	energy function
E_b	activation energy (=barrier energy with the energy at the metastable state set equal to zero)
$E^{(A)}$	Hessian matrix of the energy function at the stable state
$E^{(S)}$	Hessian matrix of the energy function around the saddle-point configuration
I	action variable of the reaction coordinate
J	Jacobian
$K(x,x')$	transition probability kernel
M	mass of reactive particle
$P(E)$	period of oscillation in the classically allowed region
$P(E,E')$	classical conditional probability of finding the energy E, given initially the energy E'
Q	quantum correction to the classical prefactor
S_b	dissipative bounce action
T	temperature
T_0	crossover temperature
$T(E)$	period in the classically forbidden regime
$U(x)$	metastable potential function for the reaction coordinate
V	volume of a reacting system
Z	partition function, inverse normalization
Z_0, Z_A	partition function of the locally stable state (A)
$Z^{\neq}$	partition function of the transition rate
$\mathcal{H}$	Hamiltonian function of the metastable system
$\mathcal{F}$	complex-valued free energy of a metastable state
$\mathcal{L}$	Fokker-Planck operator
$\mathcal{L}^{\dagger}$	backward operator of a Fokker-Planck process
j	total probability flux of the reaction coordinate
h	Planck's constant
$\hbar$	$h(2\pi)^{-1}$
k_B	Boltzmann constant
k	reaction rate
k^+	forward rate
k^-	backward rate
k_{TST}	transition-state rate
$k(E)$	microcanonical transition-state rate, semiclassical cumulative reaction probability
k_S	spatial-diffusion-limited Smoluchowski rate
m_i	mass of ith degree of freedom
$p(x,t)$	probability density
$p_0(x)$	stationary nonequilibrium probability density for the reaction coordinate
p_i	momentum degree of freedom
q_i	configurational degree of freedom
$r(E)$	quantum reflection coefficient
$s(x)$	density of sources and sinks
$t(E)$	quantum transmission coefficient
$t_\Omega(x)$	mean first-passage time to leave the domain Ω, with the starting point at x
t_{MFPT}	constant part of the mean first-passage time to leave a metastable domain of attraction
$v=\dot{x}$	velocity of the reaction coordinate
x	reaction coordinate
x_0, x_a	location of well minimum or potential minimum of state A, respectively
x_b	barrier location
x_T	location of the transition state
β	inversion temperature $(k_BT)^{-1}$

microscopic approach

$$H^{total} = \underbrace{\frac{1}{2} M \dot{q}^2 + U(q)}_{\text{system}}$$

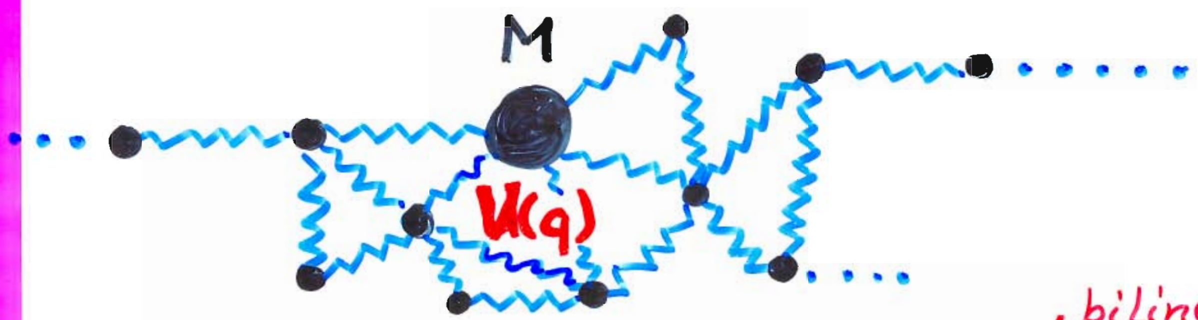
$$+ \underbrace{\frac{1}{2} \sum_\alpha m_\alpha \dot{q}_\alpha^2 + \sum_\alpha m_\alpha \omega_\alpha^2 q_\alpha^2}_{\text{(harmonic) bath}}$$

$$+ \underbrace{q \sum_\alpha c_\alpha q_\alpha}_{\text{linear coupling}}$$

$$+ \underbrace{q^2 \sum_\alpha \frac{c_\alpha^2}{2 m_\alpha \omega_\alpha^2}}_{\text{compensation of frequency shift}}$$

- path integral approach to density matrix at temperature T
- trace out environment

dissipation



$$H^T = H_{system} + H_{bath} + H_{Int}$$

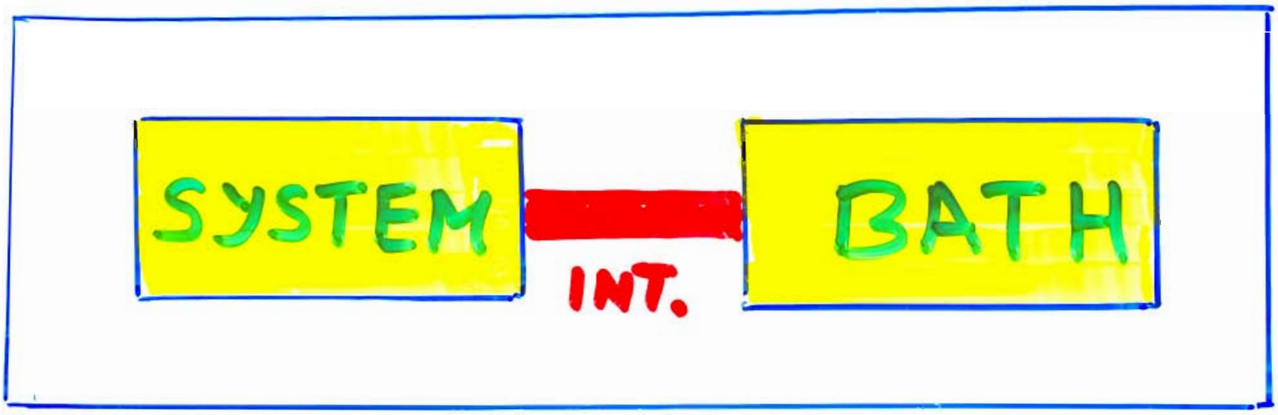
bilinear

$$\ddot{q} = -\frac{1}{M}\frac{\partial U}{\partial q} - \int_0^t \gamma(t-s)\,\dot{q}(s)\,ds$$

$$S_E = S_{rev.\ motion} + S_{dissipation}\ \text{(nonlocal)}$$

QUANTUM NOISE

QUANTUM L.-EQ.



$$|0\rangle_{S+B} \neq |0\rangle_S \, |0\rangle_B$$

↳ DECOHERENCE AT $T=0$

$$\mathbb{H}_{S+B} = \mathbb{H}_S + \mathbb{H}_{S-B} + \mathbb{H}_B$$

$$= \frac{p^2}{2m} + V(x) + \sum_\alpha \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{m_\alpha \omega_\alpha^2}{2}\left(q_\alpha - \frac{c_\alpha}{m_\alpha \omega_\alpha^2} x\right)^2 \right]$$

$$¡\ \rho_S \neq Z^{-1} \exp\left(-\frac{\mathbb{H}_S}{kT}\right)\ !$$

$$\rho_{Total} = \rho_{S+B} = Z^{-1} \exp\left(-\frac{\mathbb{H}_{S+B}}{kT}\right)$$

Q L E

$$i\hbar \dot{O} = [O, H_T]$$

$$m\ddot{x} + m\int_0^t ds\,\gamma(t-s)\,\dot{x}(s) + \frac{\partial V(x)}{\partial x}$$

$$= \eta(t) \underbrace{- m\gamma(t-0)\,x(0)}_{\text{INITIAL SLIP}}$$

$$! \; \gamma(t-s) = \frac{1}{m}\sum_\alpha \frac{c_\alpha^2}{m_\alpha \omega_\alpha^2}\cos(\omega_\alpha(t-s))$$

$$= \gamma(s-t) \; ¡$$

$$\eta(t) = \sum_\alpha c_\alpha \Big[q_\alpha(0)\cos(\omega_\alpha t) + \frac{p_\alpha}{m_\alpha \omega_\alpha}\sin(\omega_\alpha t) \Big]$$

- $$[\eta(t), \eta(s)] = -i\hbar \sum_\alpha \frac{c_\alpha^2}{m_\alpha \omega_\alpha} \sin(\omega_\alpha(t-s)) \neq 0$$

$$\rho_B = Z^{-1} \exp\left\{-\beta\left[\sum_\alpha \left(\frac{p_\alpha^2}{2m_\alpha} + \frac{m\omega_\alpha^2}{2} q_\alpha^2\right)\right]\right\}$$

- $$\langle \eta(t) \rangle_{\rho_B} = 0$$

- $$\frac{1}{2}\langle \eta(t)\eta(s) + \eta(s)\eta(t) \rangle = C(t-s)$$

$$= C(\tau) = \frac{\hbar}{2} \sum_\alpha \frac{c_\alpha^2}{m_\alpha \omega_\alpha} \coth\left(\frac{\hbar\omega_\alpha}{2kT}\right) \cos(\omega_\alpha \tau)$$

$$\xrightarrow{kT \gg \hbar\omega_\alpha} kT\gamma(\tau)$$

$$\hat{\gamma}(z) = \int_0^\infty \exp(-zt)\,\gamma(t)\,dt$$

$$\tilde{\gamma}(\omega) = \hat{\gamma}(z = -i\omega)$$

OHMIC DISSIPATION

$$J(\omega) = \gamma\,\omega \exp(-\omega/\omega_c)$$

cut-off frequency

$\omega_c \gg \omega_0, \omega_b$

KONDO-PARAMETER

$$= \underbrace{(2\pi\hbar/a^2)\,\boxed{\alpha}}_{=\gamma}\,\omega \exp(-\omega/\omega_c)$$

$a = 2q_a$: tunneling length

REMARKS

1.

QLE OPERATES IN FULL HILBERT SPACE OF $S \oplus B$

2.

$$\hat{\gamma}(z) = \int_0^\infty e^{izt}\gamma(t)dt = \frac{i}{2m}\sum_\alpha \frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\left[\frac{1}{z-\omega_\alpha} + \frac{1}{z+\omega_\alpha}\right]$$

$\operatorname{Im} z > 0$

$$\frac{1}{x+i0^+} = P\left(\frac{1}{x}\right) - i\pi\delta(x)$$

$$\operatorname{Re}\hat{\gamma}(z=\omega+i0^+) = \frac{\pi}{2m}\sum_\alpha \frac{c_\alpha^2}{m_\alpha\omega_\alpha^2}\left[\delta(\omega-\omega_\alpha) + \delta(\omega+\omega_\alpha)\right]$$

$$\Rightarrow \boxed{C(\tau) = \frac{m}{\pi}\int_0^\infty d\omega \operatorname{Re}\hat{\gamma}(\omega+i0^+)\cos(\omega\tau) \times \coth\left(\frac{\hbar\omega}{2kT}\right)}$$

3. with $\xi(t) = \eta(t) - m\gamma(t)x(0)$

$$\hat{\rho}_B = Z^{-1}\exp -\beta\left[\sum_\alpha\left(\frac{p_\alpha^2}{2m_\alpha} + \frac{m_\alpha\omega_\alpha^2}{2}\left(q_\alpha - \frac{c_\alpha}{m_\alpha\omega_\alpha^2}x\right)^2\right)\right]$$

$$\Rightarrow \langle \xi(t)\rangle_{\hat{\rho}} = 0$$

$$\frac{1}{2}\langle \xi(\tau)\xi(0) + \xi(0)\xi(\tau)\rangle_{\hat{\rho}} = C(\tau)$$

$\boxed{4.}$ ¡ DEPHASING AT $T=0$!

$$\langle \mathbb{X}(0)\,\xi(t)\rangle_{\hat{\beta}} \neq 0$$

$$\langle \mathbb{H}_{INT}\rangle_{\hat{\beta}} \neq 0$$

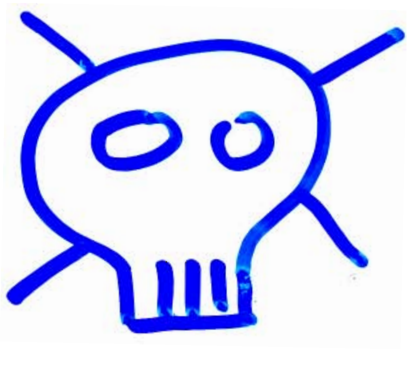
$\boxed{5.}$

$\xi(t) \longrightarrow$ C-NOISE $\xi(t)$

WITH CORRELATION

$C(\tau)$

IS INCONSISTENT



SYNOPSIS

LINEAR RESPONSE THEORY & QUANTUM-FDT

$$\hat{H}(t) = \hat{H}_0 - F(t)\hat{A} \; ; \; \varrho_\beta = Z^{-1}\exp(-\beta \hat{H}_0)$$

$$\langle \hat{B}(t)\rangle - \langle \hat{B}(t)\rangle_\beta = \langle \delta\hat{B}(t)\rangle = \int_{t_0}^{t} \chi_{BA}(t-s)\, F(s)\, ds$$

KUBO: $$\chi_{BA}(\tau) = \Theta(\tau)\frac{i}{\hbar}\langle[\hat{B}(\tau), \hat{A}(0)]\rangle_\beta$$

$$= -\Theta(\tau)\int_0^\beta \langle \hat{A}(-i\hbar\lambda)\dot{\hat{B}}(\tau)\rangle_\beta \, d\lambda$$

classical limit $\longrightarrow -\Theta(\tau)\,\beta\,\langle \dot{B}(\tau) A(0)\rangle_\beta$

SYNOPSIS

LINEAR RESPONSE THEORY & QUANTUM-FDT

$$\hat{H}(t) = \hat{H}_0 - \mathcal{F}(t)\hat{A} \; ; \; \varrho_\beta = Z^{-1}\exp(-\beta\hat{H}_0)$$

$$\langle\hat{B}(t)\rangle - \langle\hat{B}(t)\rangle_\beta = \langle\delta\hat{B}(t)\rangle = \int_{t_0}^{t}\chi_{BA}(t-s)\,\mathcal{F}(s)\,ds$$

KUBO: $$\chi_{BA}(\tau) = \Theta(\tau)\frac{i}{\hbar}\langle[\hat{B}(\tau),\hat{A}(0)]\rangle_\beta$$

$$= -\Theta(\tau)\int_0^\beta\langle\hat{A}(-i\hbar\lambda)\dot{\hat{B}}(\tau)\rangle_\beta\,d\lambda$$

classical limit $\longrightarrow -\Theta(\tau)\beta\langle\dot{B}(\tau)A(0)\rangle_\beta$

$$\hat{B} = \hat{A} = \hat{q} \; ; \; \mathcal{F}(t) = A\cos\Omega t$$

$$\langle\delta\hat{q}(t)\rangle = P_1 e^{-i\Omega t} + P_{-1} e^{-i\Omega t}$$

$$P_{1,-1} = \frac{A}{2}\,e^{\mp i\Omega t}\chi(\pm\Omega)$$

QUANTUM-FDT

$$S_{BA}(\tau) = \frac{1}{2}\Big\langle \big(\hat{B}(t) - \langle \hat{B}\rangle_\beta\big)\big(\hat{A}(0) - \langle \hat{A}\rangle_\beta\big) + \big(\hat{A}(0) - \langle \hat{A}\rangle_\beta\big)\big(\hat{B}(\tau) - \langle \hat{B}\rangle_\beta\big)\Big\rangle_\beta$$

$$\chi_{BA}(\tau) = \underbrace{\chi'_{BA}(\tau)}_{\frac{1}{2}[\chi_{BA}(t) + \chi_{AB}(-t)]} + i\,\underbrace{\chi''_{BA}(\tau)}_{-\frac{i}{2}[\chi_{BA}(t) - \chi_{AB}(-t)]}$$

$$\chi_{BA}(\omega) = \int_{\cancel{-\infty}\;0}^{\infty} \chi_{BA}(t)\, e^{i\omega t}\, dt$$

$$\Rightarrow \quad \chi''_{BA}(\omega) = \frac{1}{\hbar}\tanh(\hbar\omega\beta/2)\, S_{BA}(\omega)$$

$$S_{BA}(\omega) = \hbar \coth(\hbar\omega\beta/2)\, \chi''_{BA}(\omega)$$

$$\xrightarrow{\hbar\omega\beta \ll 1} \quad 2\chi''_{BA}(\omega)/(\beta\Omega)$$

<u>NOTE:</u> $\chi''_{BA}(\omega) = \frac{i}{2}\left[\chi^*_{AB}(\omega) - \chi_{BA}(\omega)\right]$

$\neq \mathrm{Im}\,\chi_{BA}(\omega)$; except $\hat{A} = \hat{B}$

$\hat{A} = \hat{B} = \hat{q}$: $\underline{\underline{S_{qq}(\Omega) = \hbar \coth(\hbar\Omega\beta/2)\, \mathrm{Im}\,\chi_{qq}(\Omega)}}$

EQ.-CURRENT NOISE

$\mathbb{A} = \mathbb{B}$ $\qquad \mathbb{I} := \frac{d\mathbb{B}}{dt}$; $\langle \delta I(t) \rangle = \int_{-\infty}^{t} Z(t-s) F(s) ds$

$$Z(t-s=\tau) = \frac{d\chi(\tau)}{d\tau}$$

$$\chi''_{AA}(\omega) = \frac{1}{\omega} \mathrm{Im}\left(\frac{Z(\omega)}{i}\right) = -\frac{1}{\omega} \mathrm{Re}\, Z(\omega)$$

$$S_{II}(\omega) = -\omega^2 S_{BB}(\omega)$$

$$S_{II}(\omega) = (\hbar\omega) \coth\left(\frac{\hbar\omega}{2kT}\right) \mathrm{Re}\, Z(\omega)$$

$kT \gg \hbar\omega$: $S_{II}(\omega) \rightarrow 2kT\, \mathrm{Re}\, Z(\omega)$

$$\xrightarrow{\text{MARKOV}} \underline{2kT/R}$$

JOHNSON-NYQUIST (1928)

$kT \ll \hbar\omega \longrightarrow \hbar\omega\, \mathrm{Re}\, Z(\omega)$

quantum-zero point fluct.

$S_{II}(\omega=0) = 0$ at $\omega = 0$

1900-1951

J.B. Johnson

Thermal agitation of electricity in conductors.

Phys. Rev. (1928) 32 (July) 97-109

H. Nyquist

Thermal agitation of electric charge in conductors.

Phys. Rev. (1928) 32 (July) 110-113

L. Onsager

Reciprocal relation in irreversible process.

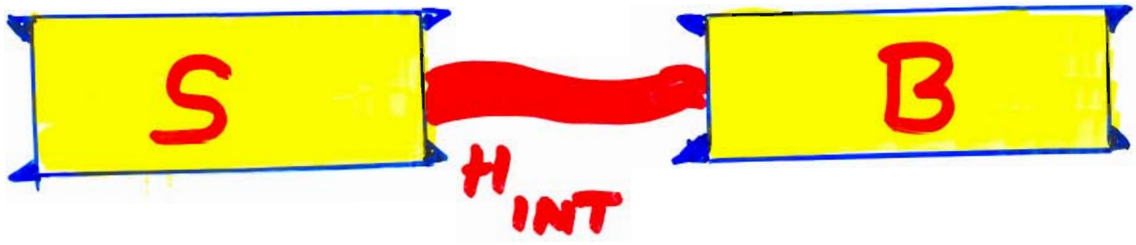
Phys. Rev. (1931) 32 (February) 405-426

H.B. Callen, T.A. Welton

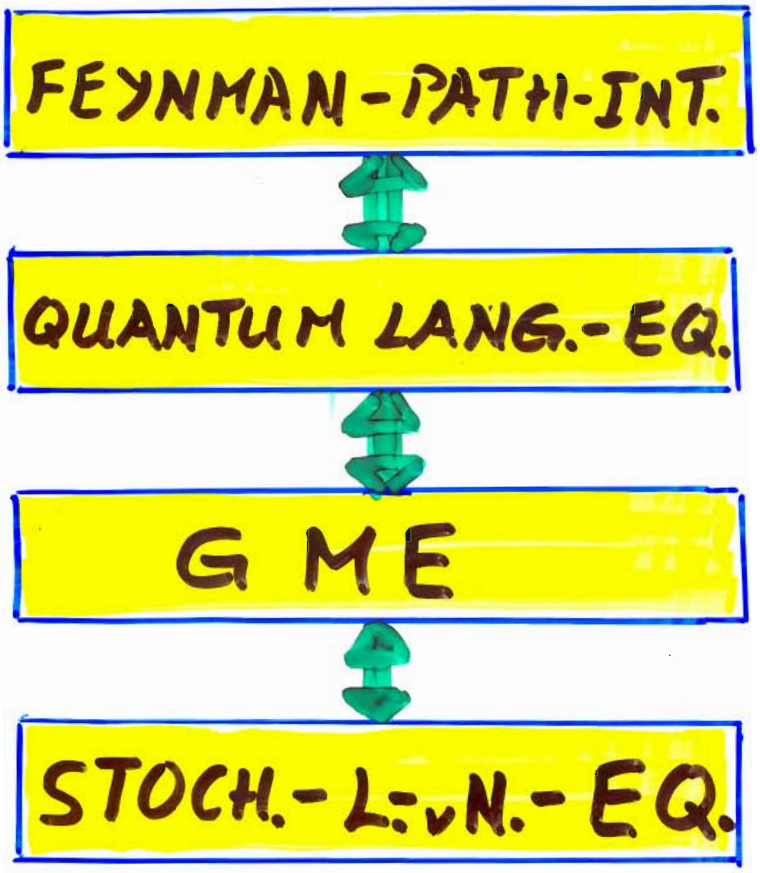
Irreversibility and Generalized Noise.

Phys. Rev. (1951) 83 (1) 34-40

QUANTUM NOISE



NO QUANTUM EQ.-PARTITION-TH.



$$\rho := |\psi_1(t)\rangle\langle\psi_2(t)| \; ; \; \mu := \frac{2}{\pi}\int_0^\infty d\omega \, \frac{J(\omega)}{\omega}$$

$$i\hbar\dot{\rho} = [H_0, \rho] + \frac{\mu}{2}[X^2, \rho] - \xi(t)[X, \rho] - \frac{\hbar}{2}\nu(t)\{X, \rho\}_+$$

COMPLEX VALUED NOISE

$$\langle \xi(t)\xi(t')\rangle = \mathrm{Re}\, L(t-t') \; ; \; \langle \xi(t)\nu(t')\rangle = \frac{2i}{\hbar}\,\theta(t-t')\,\mathrm{Im}\, L(t-t')$$

$$\langle \nu(t)\nu(t')\rangle = 0$$

 PITFALLS

MARKOV MASTER EQ

$$\frac{d}{dt}\rho = -\frac{i}{\hbar} L \rho - \Gamma \rho + I(t)$$

BLOCH-REDFIELD

i.g. NO DET. BALANCE

ROTATING WAVE APPROX.

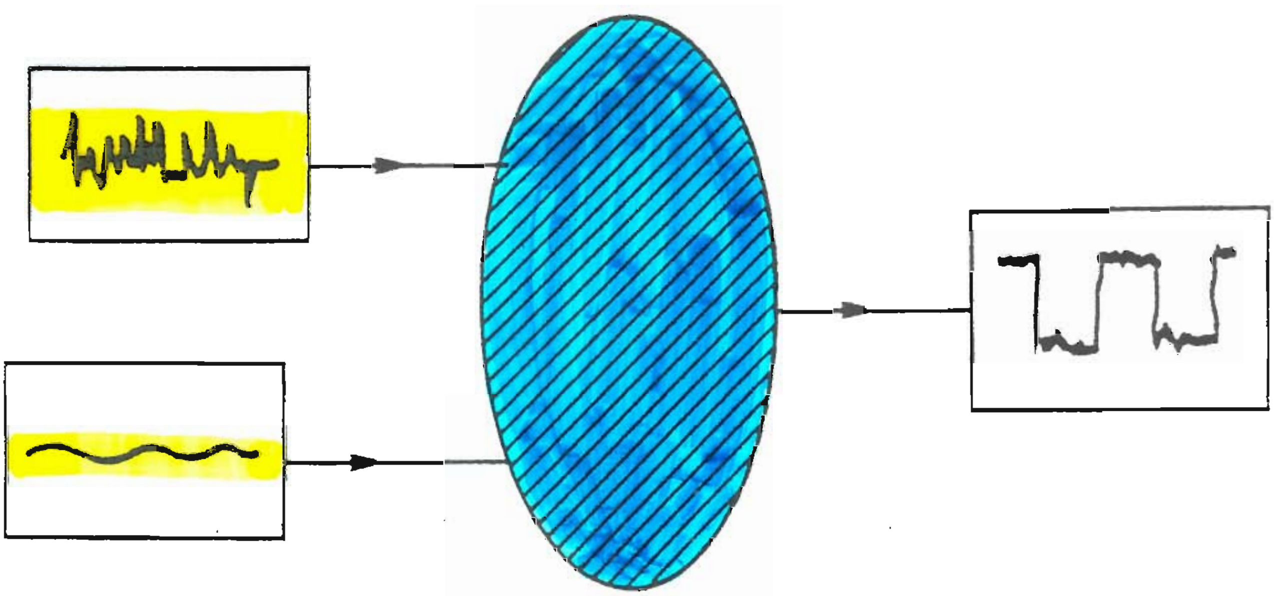
(LINDBLAD: DAVIES-APPROX.)

DET. BALANCE ✓ O.K.

BUT

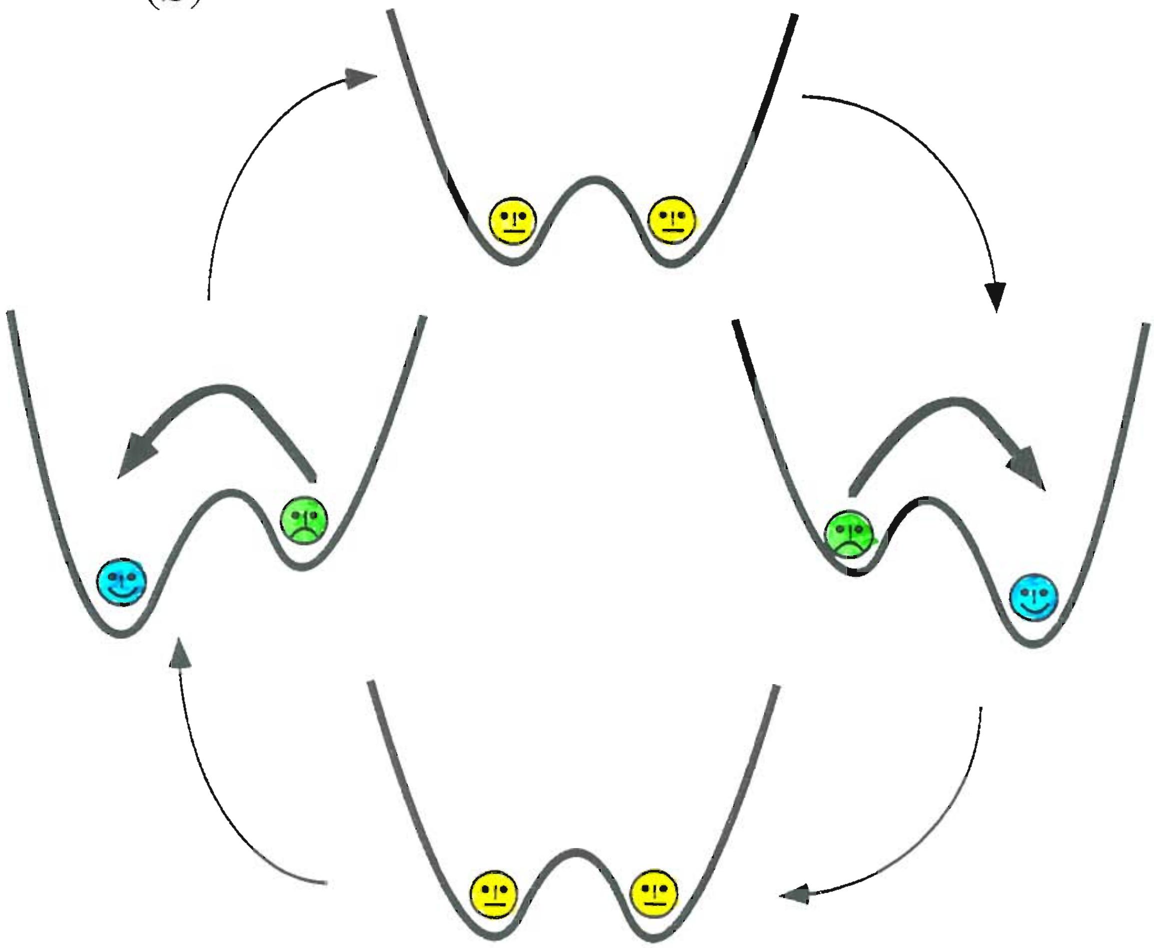
- WRONG EHRENFEST EQ.
- NO FDT
- NO KMS-COND. $\langle u(t)\, v \rangle_\beta = \langle v\, u(t + i\hbar\beta) \rangle_\beta$

SR



Schematic of stochastic resonance . The cross-hatched oval represents a black-box system which receives two inputs: one weak and periodic, the other strong and random. The output is relatively regular with small fluctuations.

(b)



NOISE-ASSISTED

SYNCHRONIZED

HOPPING

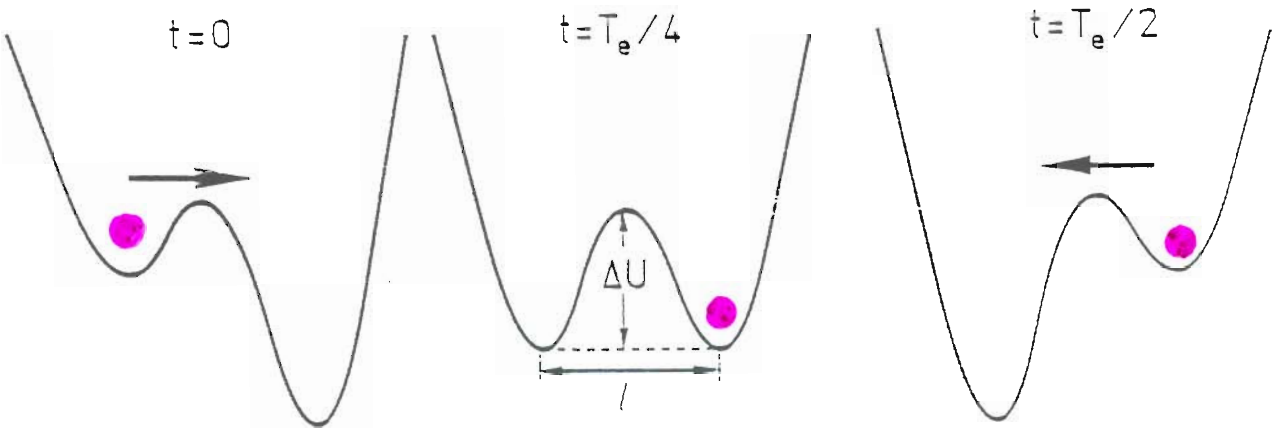
Fig 1b

Bistable Model

$$\dot{x}=x-x^3+A\cos(\Omega t+\varphi)+\xi(t)$$

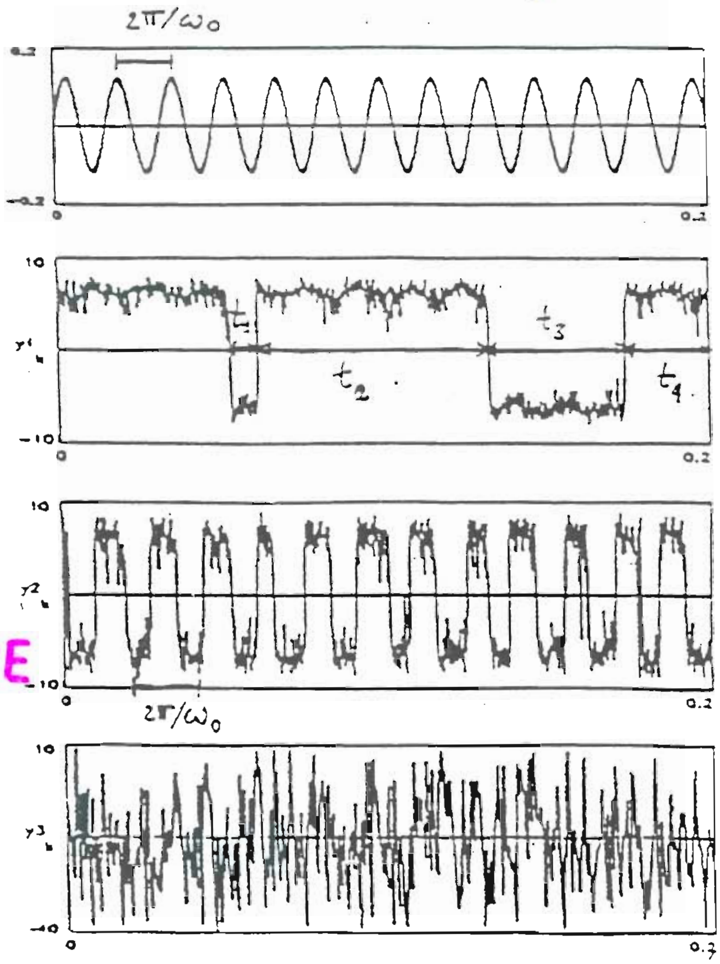
$$\langle\xi(t)\rangle=0$$

$$\langle\xi(t)\xi(t')\rangle=2D\,\delta(t-t')$$



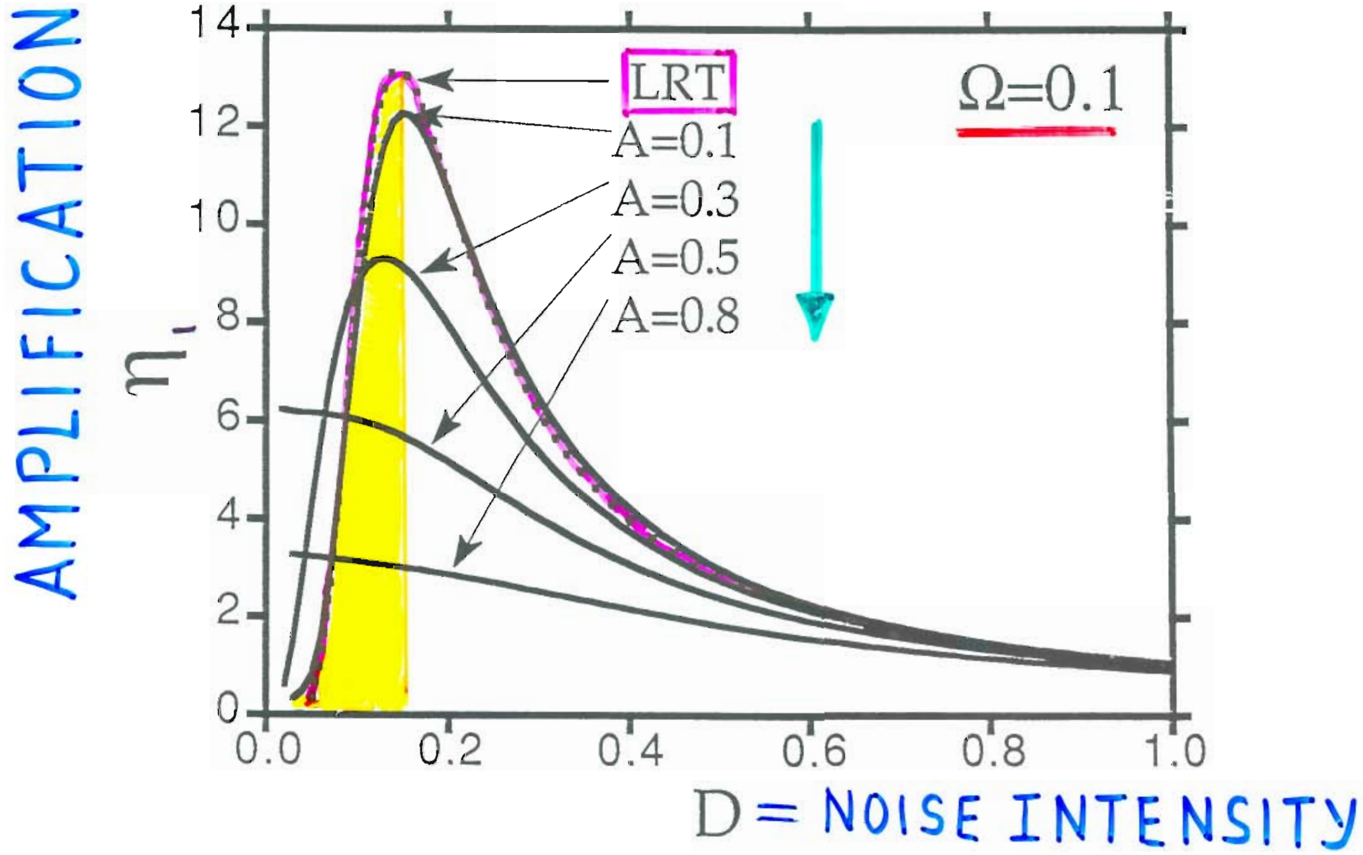
$$T_e = 2\pi/\Omega$$

SIGNAL



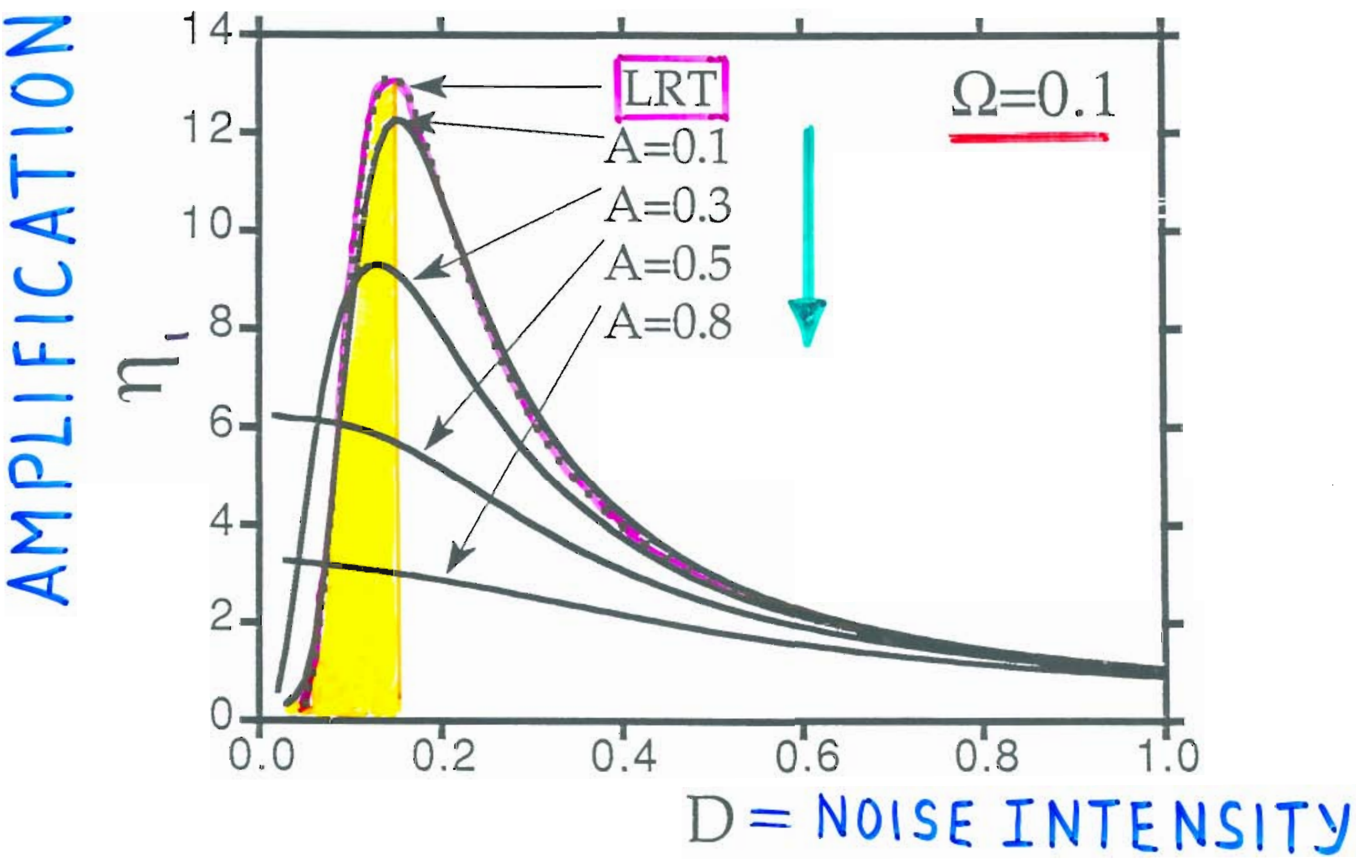
$$T_e \sim 2\Gamma^{-1}_{ESCAPE}$$

P. JUNG + P. H., PHYS. REV. A44: 8032 (91)



MORE NOISE → MORE SIGNAL

P. JUNG + P. H., PHYS. REV. A44: 8032 (91)



MORE NOISE → MORE SIGNAL

$$M_1 \sim \chi(\tau) = -\frac{1}{D}\frac{d}{d\tau}\langle \delta x(\tau)\,\delta \xi(0)\rangle$$

$$|M_1|^2 \propto \quad 1/D^2 \qquad \exp(-2\Delta U/D)$$

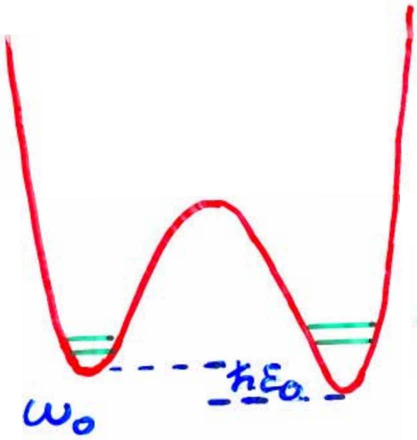
S R

IN QUANTUM MECHANICS

Q S R

$$V_0 \gg \hbar\omega_0 \gg \hbar\varepsilon_0,\, kT$$

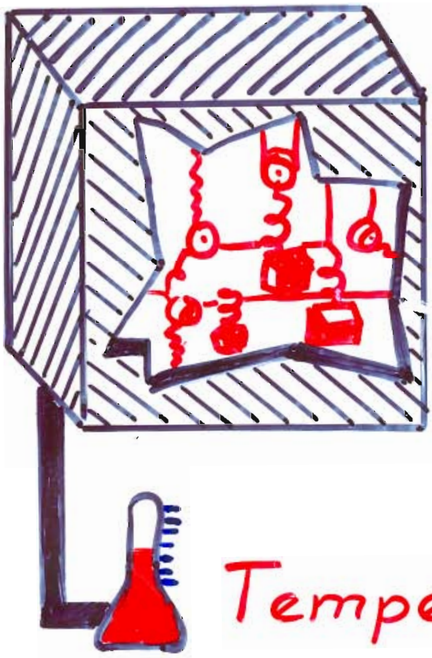
TS



$$-\frac{\hbar}{2}\left(\varepsilon_0\sigma_z + \Delta\sigma_x\right)$$

$\oplus$

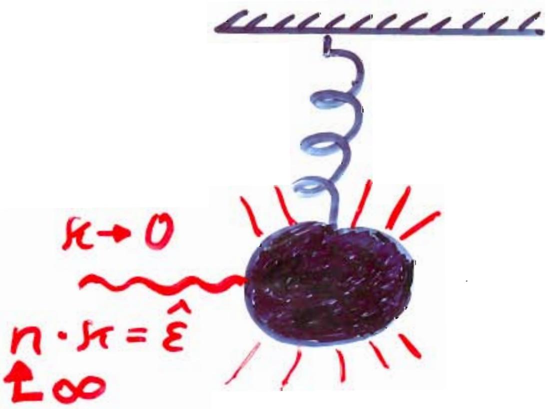
BATH
T, γ



$$\frac{1}{2}\sum_\alpha\left(\frac{p_\alpha^2}{m_\alpha} + m_\alpha\omega_\alpha^2 x_\alpha^2 - c_\alpha x_\alpha \sigma_z\right)$$

$\oplus$

DRIVE
$\Omega, \hat{\varepsilon}$



$$\frac{\hbar\hat{\varepsilon}}{2}\cos(\Omega t)\,\sigma_z$$

LINEAR RESPONSE & QSR

with $P_1 = \frac{A}{2}\chi_{qq}(\Omega) \equiv \frac{A}{2}\chi(\Omega)$

$$\eta_1 = 4\pi |P_1|^2 = \pi A^2 |\chi(\Omega)|^2$$

$$\mathrm{SNR} = \frac{\pi A^2 |\chi(\Omega)|^2}{S_{qq}(\Omega, A=0)} = \frac{\pi A^2 |\chi(\Omega)|^2}{\mathrm{Im}\,\chi(\Omega)\,\hbar\coth(\hbar\Omega\beta/2)}$$

¡valid at all temperatures!

PROBLEM: QUANTUM $\chi_{qq}(\Omega) \overset{FDT}{\rightsquigarrow} S_{qq}(\Omega)$

$$S_{qq}(t) = \frac{1}{2}\langle \delta\hat{q}(t)\delta\hat{q}(0) + \delta\hat{q}(0)\delta\hat{q}(t)\rangle_\beta$$

¡DIFFICULT!

LINEAR RESPONSE & QSR

with $P_1 = \frac{A}{2}\chi_{qq}(\Omega) \equiv \frac{A}{2}\chi(\Omega)$

$$\eta_1 = 4\pi |P_1|^2 = \pi A^2 |\chi(\Omega)|^2$$

$$SNR = \frac{\pi A^2 |\chi(\Omega)|^2}{S_{qq}(\Omega; A=0)} = \frac{\pi A^2 |\chi(\Omega)|^2}{\mathrm{Im}\,\chi(\Omega)\,\hbar \coth(\hbar\Omega\beta/2)}$$

¡valid at all temperatures!

PROBLEM: QUANTUM $\chi_{qq}(\Omega) \overset{FDT}{\leftrightarrow} S_{qq}(\Omega)$

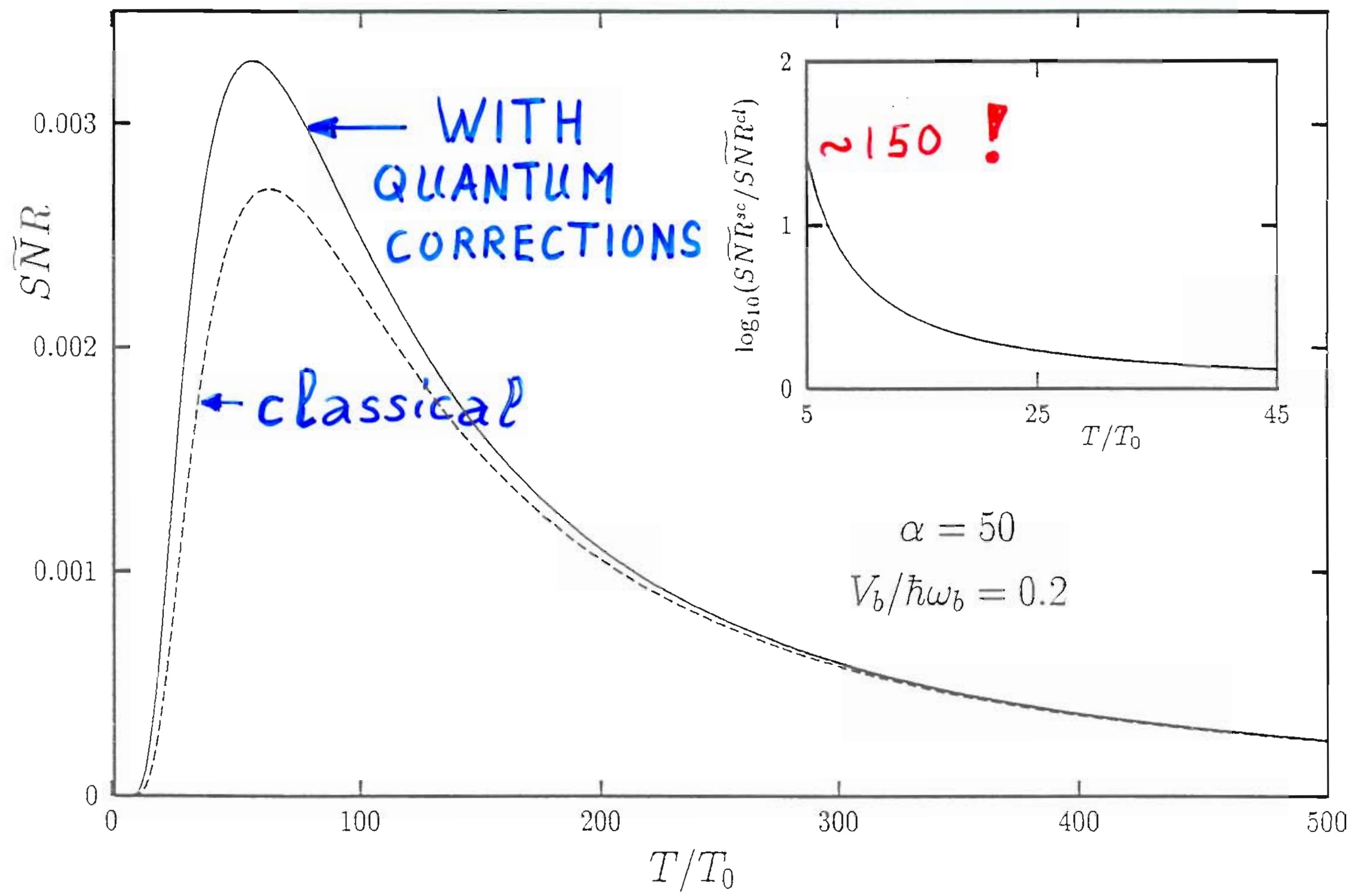
$$S_{qq}(t) = \frac{1}{2}\langle \delta\hat{q}(t)\delta\hat{q}(0) + \delta\hat{q}(0)\delta\hat{q}(t)\rangle_\beta$$

¡DIFFICULT!

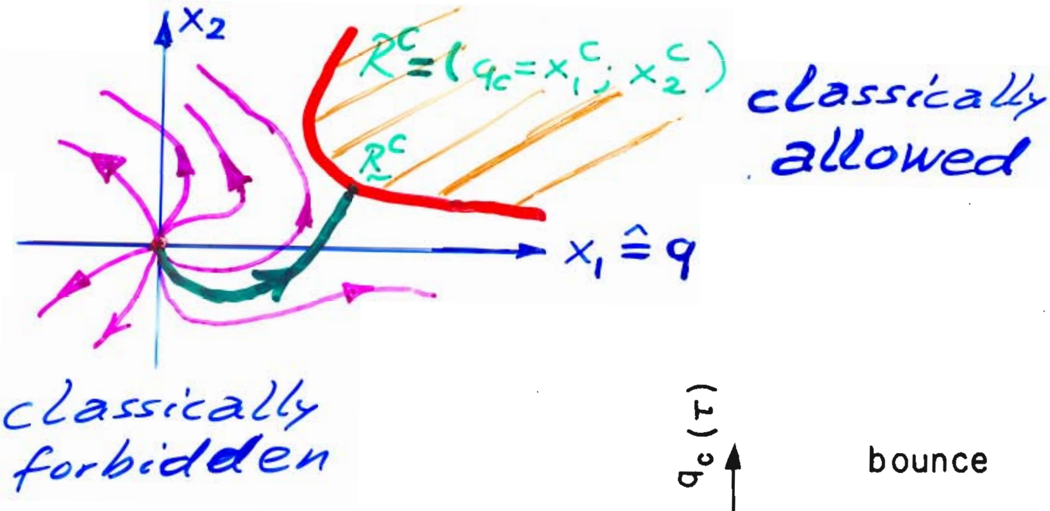
2 LIMITS

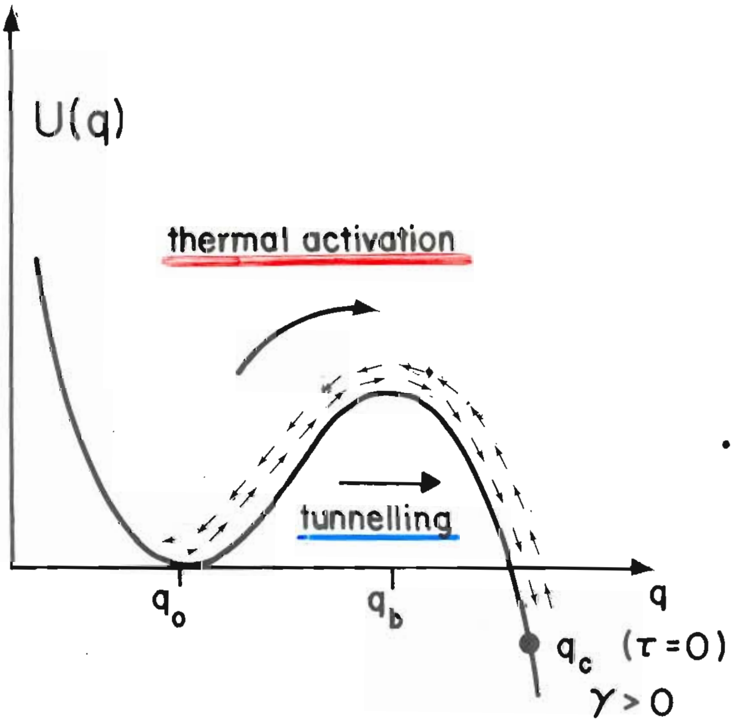
above ~ near crossover to thermal hopping

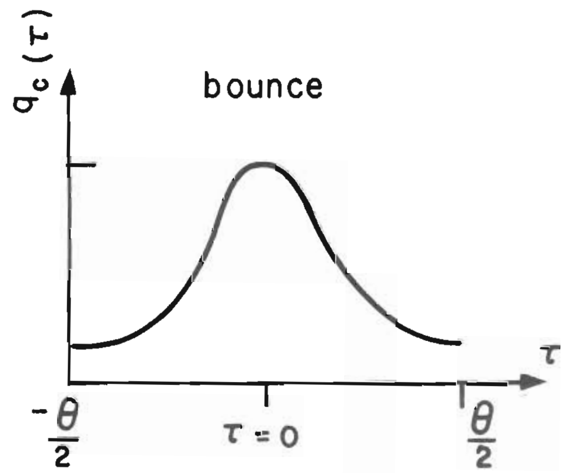
AT LOW T

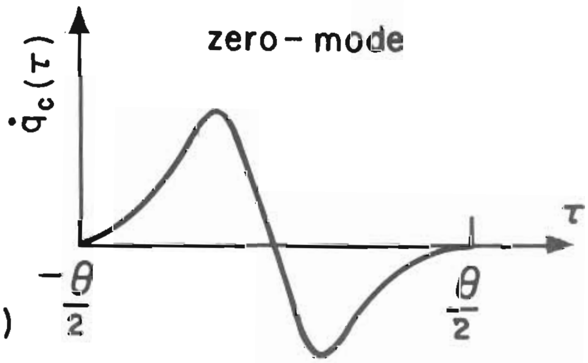

$\widetilde{SNR}$
0.003
0.002
0.001
0
0
100
200
300
400
500
T/T_0
WITH QUANTUM CORRECTIONS
classical
$\log_{10}(\widetilde{SNR}^{sc}/\widetilde{SNR}^{cl})$
2
1
0
5
25
45
T/T_0
~150 !
$\alpha = 50$
$V_b/\hbar\omega_b = 0.2$

$T=0$





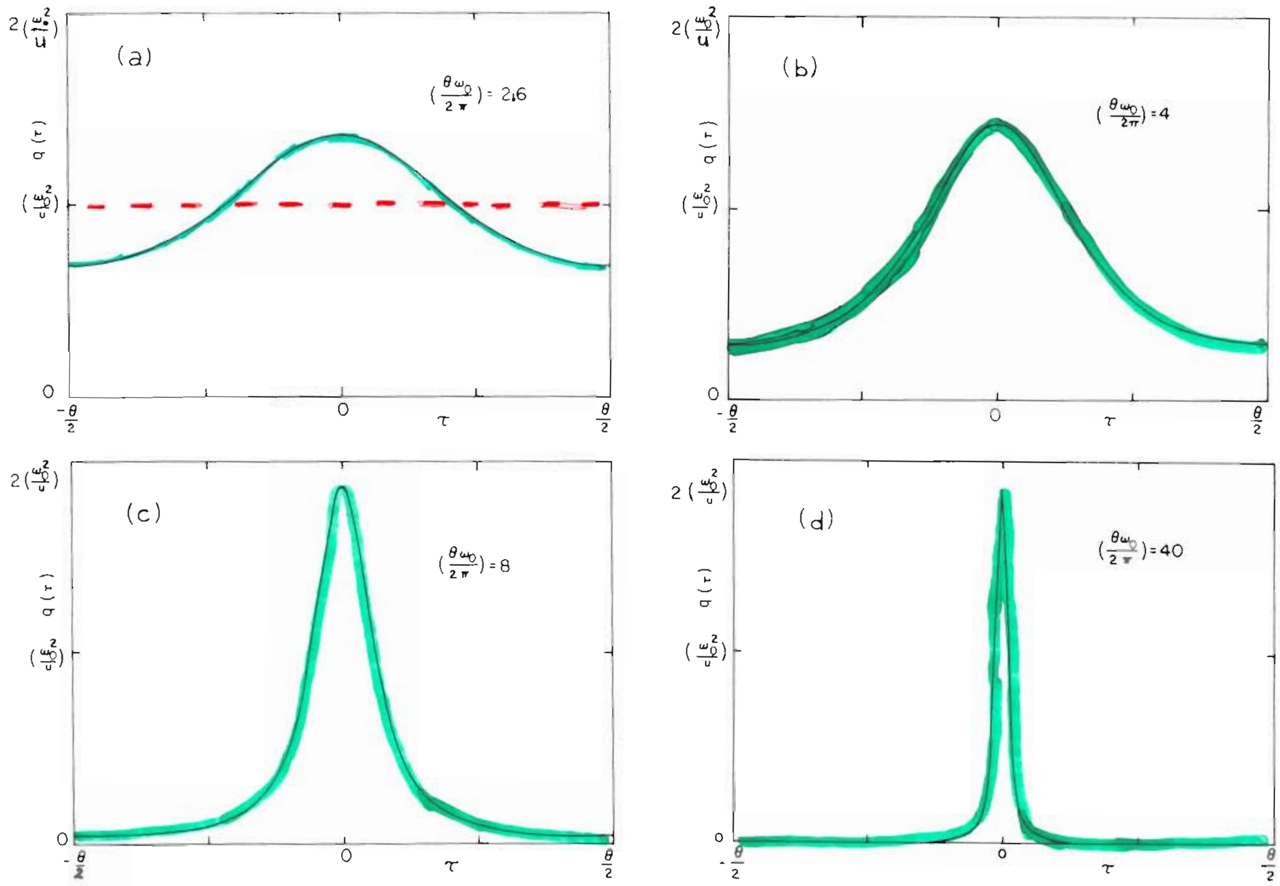




$\gamma = 0$:

$$M \frac{d^2}{d\tau^2} q_B(\tau) = \frac{\partial U}{\partial q_B}$$

$$- M \frac{d^2}{d\tau^2} \dot{q}_B(\tau) + \left(\frac{\partial^2 U}{\partial q_B^2} \right) \dot{q}_B(\tau) = 0$$

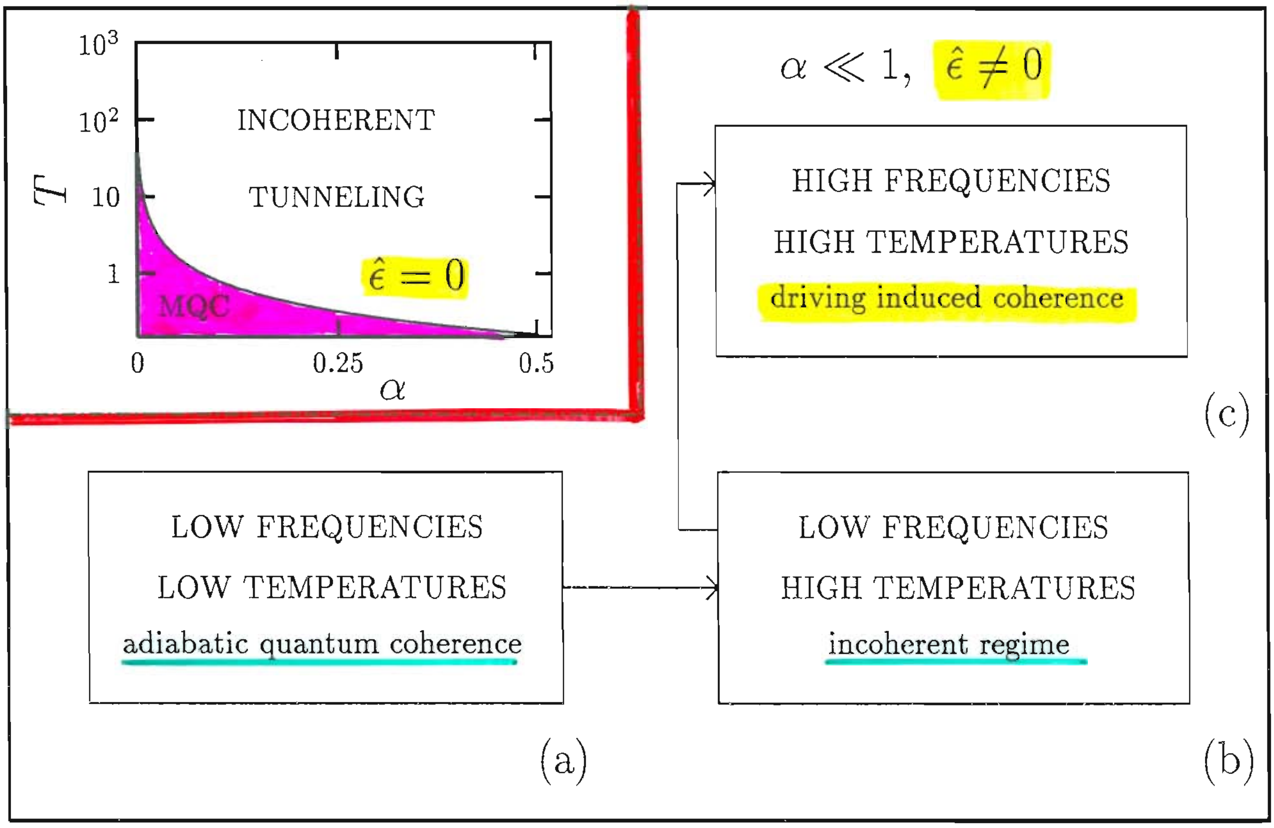


$$-M\ddot{q}_B + \frac{\partial U(q_B)}{\partial q_B} + \int_{-\Theta/2}^{\Theta/2} k(\tau-\tau')\,q_B(\tau')\,d\tau' = 0$$

$$\Theta = \hbar/kT$$

$$q_B(\tau+\Theta) = q_B(\tau)$$

QUANTUM SR



10^3
10^2
10
1
T
INCOHERENT
TUNNELING
$\hat{\epsilon} = 0$
MQC
0
0.25
0.5
α
$\alpha \ll 1$, $\hat{\epsilon} \neq 0$
HIGH FREQUENCIES
HIGH TEMPERATURES
driving induced coherence
(c)
LOW FREQUENCIES
LOW TEMPERATURES
adiabatic quantum coherence
(a)
LOW FREQUENCIES
HIGH TEMPERATURES
incoherent regime
(b)

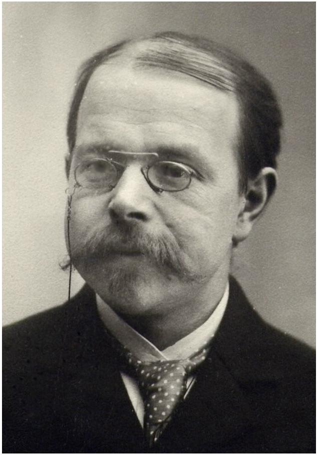
DRIVEN QUANTUM TUNNELING

M. GRIFONI, P.H. PHYS. REP. **304**: 229 – 358 (98)

FREE COPY

http://www.physik.uni-augsburg.de/theo1/hanggi/

Third Law of thermodynamics



Walter Hermann NERNST
(1864 - 1941)

„mein Wärmesatz"
(during his lecture August 15, 1905)

$$\frac{\Delta H - \Delta G}{T} = \Delta S \longrightarrow 0 \quad \text{as} \quad T \longrightarrow 0$$

Famous exceptions to the Third Law

classical ideal gas

$$S = N\left[c_V \ln(T) + k_B \ln(V/N) + \sigma\right]$$

Moreover:
classical statistical mechanics: n-vector model with n-dimensional vectors > 1 violates third law.
(e.g. planar Heisenberg ($n = 2$) or the $n = 3$ Heisenberg model)

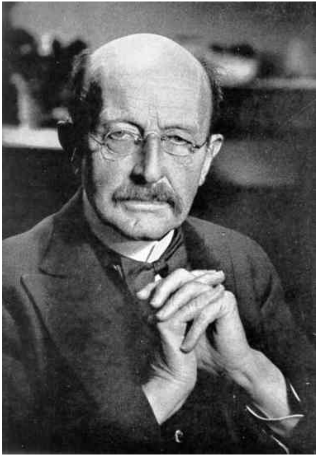
Quantum Brownian motion and the Third Law of thermodynamics

Peter Hänggi, Michele Campisi,
Gert-Ludwig Ingold, and Peter Talkner

Uni Augsburg

Acta Phys. Pol. B **37**, 1537 (2006)
New J. Phys. **10**, 115008 (2008)
Phys. Rev. E **79**, 061105 (2009)
J. Phys. A (Fast Track) **42**, 392002 (2009)

…and Planck's version

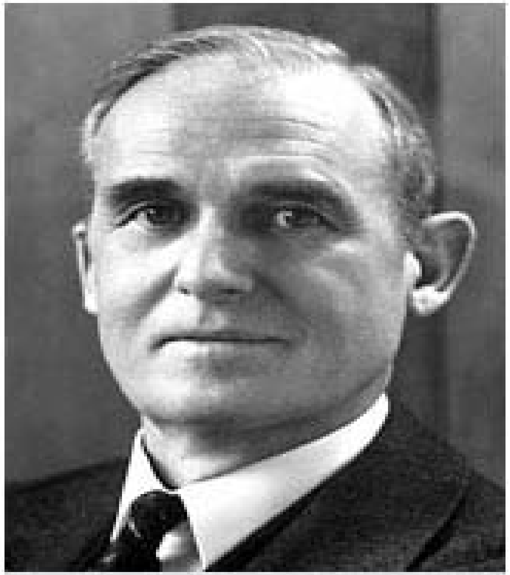


Max PLANCK
(1858 - 1947)

The entropy $s = S/N$ per particle approaches at $T = 0$ a constant ($s_0 = k_B \ln g(N)/N$) value that possibly depends on the chemical composition of the system. This limiting value can generally be set to zero.

The Nobel Prize in Chemistry 1949

"for his contributions in the field of chemical thermodynamics, particularly concerning the behaviour of substances at extremely low temperatures"



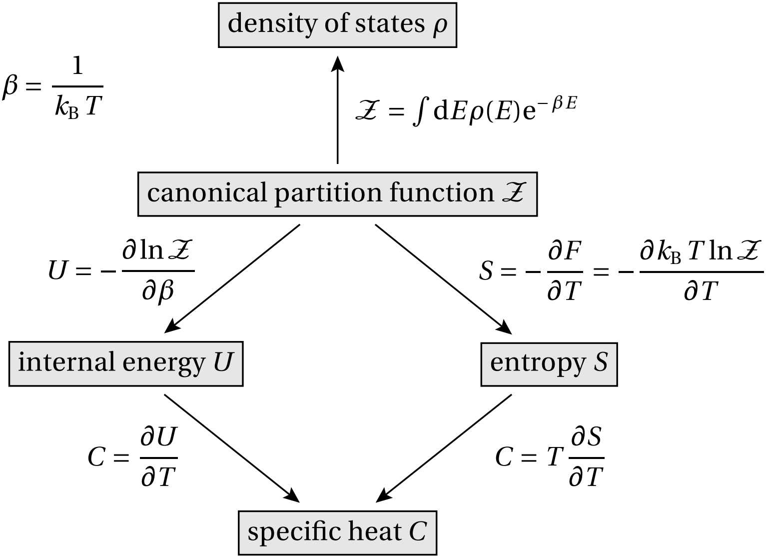
William Francis Giauque

USA

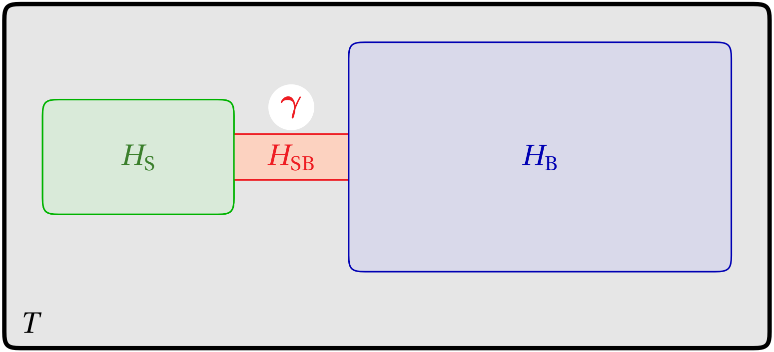
University of California
Berkeley, CA, USA

b. 1895
d. 1982

A bit of thermodynamics



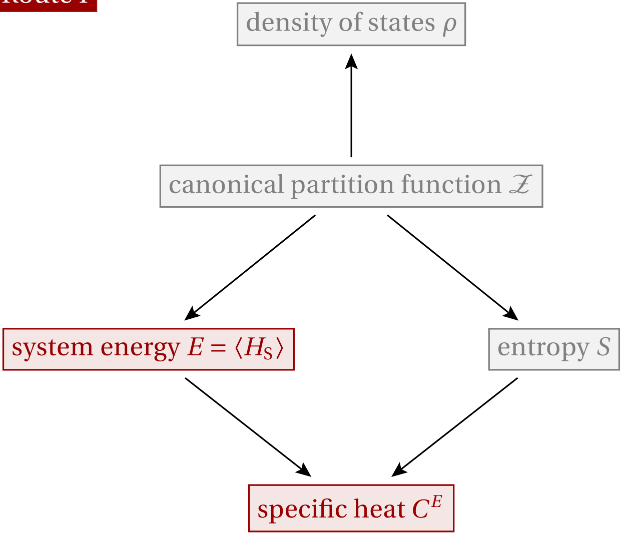
The problem



What is the specific heat of a damped system?

Specific heat from the system energy

Route I



Specific heat from the partition function

Route II

density of states ρ

$\uparrow$

canonical partition function $\mathcal{Z} = \dfrac{\mathrm{Tr}_{\mathrm{S+B}}\left(\mathrm{e}^{-\beta H}\right)}{\mathrm{Tr}_{\mathrm{B}}\left(\mathrm{e}^{-\beta H_{\mathrm{B}}}\right)}$

$\swarrow \qquad \searrow$

internal energy U | entropy S

$\searrow \qquad \swarrow$

specific heat C^{Z}

Free energy of a system strongly coupled to an environment

Thermodynamic argument:

$$\mathcal{Z} = \frac{\mathrm{Tr}_{\mathrm{S+B}}(\mathrm{e}^{-\beta H})}{\mathrm{Tr}_{\mathrm{B}}(\mathrm{e}^{-\beta H_{\mathrm{B}}})} \qquad \longrightarrow \qquad F_{\mathrm{S}} = F - F_{\mathrm{B}}^{0}$$

F total system free energy

F_{B} bare bath free energy

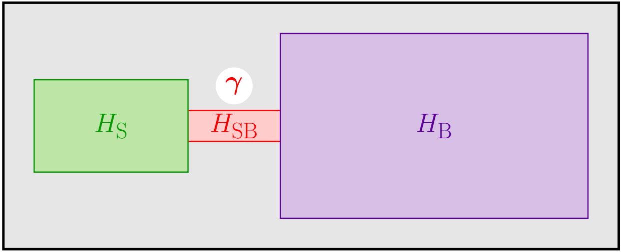
With this form of free energy the three laws of thermodynamics are fulfilled.

G. W. Ford, J. T. Lewis, R. F. O'Connell, Phys. Rev. Lett. **55**, 2273 (1985)

P. Hänggi, G.-L. Ingold, P. Talkner, New J. Phys. **10**, 115008 (2008)

G.-L. Ingold, P. Hänggi, P. Talkner, Phys. Rev. E **79**, 061105 (2009)

The role of quantum dissipation



energy of damped harmonic oscillator

$$E = \langle H_S \rangle = \frac{\langle p^2 \rangle}{2M} + \frac{M}{2}\omega_0^2 \langle q^2 \rangle$$

expectation value of system operator

$$\langle O_S \rangle = \frac{\mathrm{Tr}\left[O_S \exp(-\beta H)\right]}{\mathrm{Tr}\left[\exp(-\beta H)\right]}$$

An important difference

Route I

$$E \doteq E_S = \langle H_S \rangle = \frac{\mathrm{Tr}_{S+B}(H_S e^{-\beta H})}{\mathrm{Tr}_{S+B}(e^{-\beta H})}$$

Route II

$$\mathcal{Z} = \frac{\mathrm{Tr}_{S+B}(e^{-\beta H})}{\mathrm{Tr}_B(e^{-\beta H_B})} \qquad U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$$

$$\begin{aligned} \Rightarrow U &= \langle H \rangle - \langle H_B \rangle_B \\ &= E_S + \Big[\langle H_{SB} \rangle + \boxed{\langle H_B \rangle - \langle H_B \rangle_B} \Big] \end{aligned}$$

For finite coupling E and U differ!

Entropy of the damped harmonic oscillator

$$S = k_{\mathrm{B}}\left[1 - \ln(\hbar\beta\omega_0) + \frac{\hbar\beta\gamma}{2\pi} + g(\lambda_+) + g(\lambda_-)\right]$$

$$\text{with}\quad g(z) = \ln[\Gamma(1+z)] - z\psi(1+z)$$

leading low-temperature behavior

$$S = \frac{\pi}{3}\frac{\gamma}{\omega_0}\frac{k_{\mathrm{B}}^2 T}{\hbar\omega_0} + O(T^3)$$

third Law is satisfied ✔

The concept of a partition function…

…for dissipative quantum systems

$$Z = \frac{\mathrm{Tr}\left[\exp(-\beta H)\right]}{\mathrm{Tr_B}\left[\exp(-\beta H_\mathrm{B})\right]}$$

harmonic oscillator

$$Z = \frac{1}{\hbar\beta\omega_0}\prod_{n=1}^{\infty}\frac{\nu_n^2}{\nu_n^2+\nu_n\hat{\gamma}(\nu_n)+\omega_0^2} \qquad \text{with} \quad \nu_n = \frac{2\pi}{\hbar\beta}n$$

$$\begin{aligned}\langle E\rangle_Z &= -\frac{\partial}{\partial\beta}\ln(Z)\\ &= \frac{1}{\beta}\left[1+\sum_{n=1}^{\infty}\frac{2\omega_0^2+\nu_n\hat{\gamma}(\nu_n)-\nu_n^2\hat{\gamma}'(\nu_n)}{\nu_n^2+\nu_n\hat{\gamma}(\nu_n)+\omega_0^2}\right]\end{aligned}$$

The fundamental relation

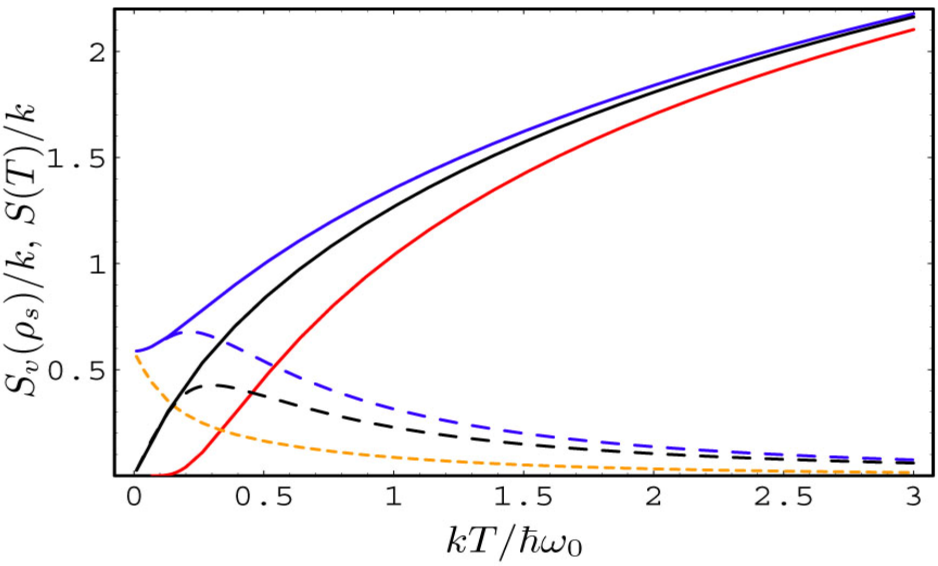
$$\langle E\rangle_Z = -\frac{\partial}{\partial\beta}\ln(Z) = \frac{1}{\beta}\left[1+\sum_{n=1}^{\infty}\frac{2\omega_0^2+\nu_n\hat{\gamma}(\nu_n)-\nu_n^2\hat{\gamma}'(\nu_n)}{\nu_n^2+\nu_n\hat{\gamma}(\nu_n)+\omega_0^2}\right]$$

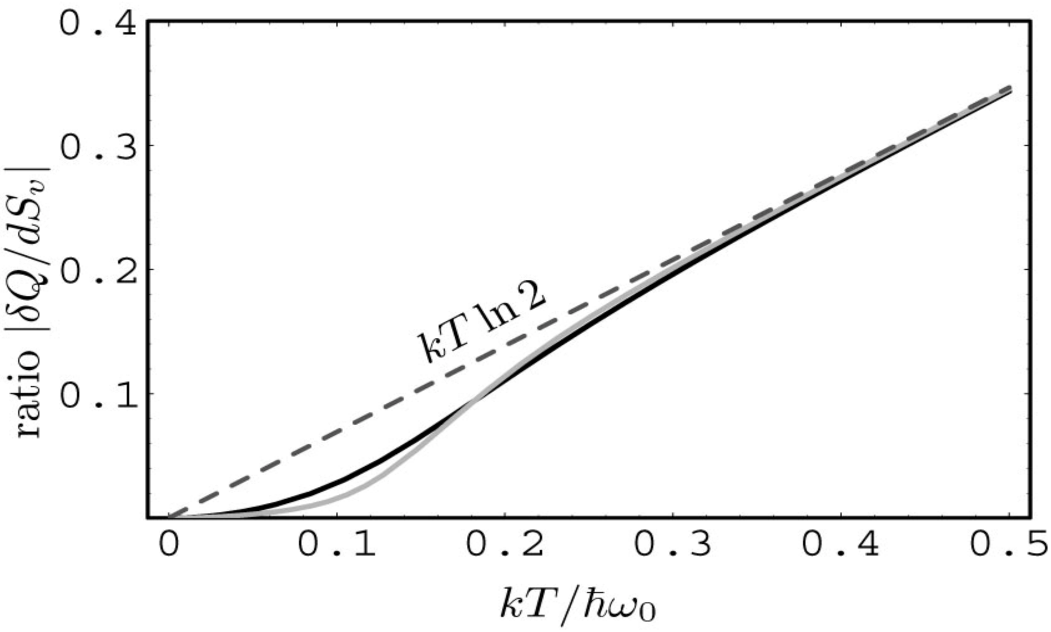
$$\stackrel{?}{=} \frac{1}{\beta}\left[1+\sum_{n=1}^{\infty}\frac{2\omega_0^2+\nu_n\hat{\gamma}(\nu_n)}{\nu_n^2+\nu_n\hat{\gamma}(\nu_n)+\omega_0^2}\right] = \langle E\rangle$$

in general: NO

$$\begin{aligned}\langle E\rangle_Z &= \langle H\rangle - \langle H_\mathrm{B}\rangle_\mathrm{B}\\ &= \underbrace{\langle E\rangle}_{=\langle H_\mathrm{S}\rangle} + [\langle H_\mathrm{SB}\rangle + \langle H_\mathrm{B}\rangle - \langle H_\mathrm{B}\rangle_\mathrm{B}]\\ &\neq \langle H_\mathrm{S}\rangle\end{aligned}$$

$$S_{vN} = - k \, \mathrm{Tr} \, (\rho_s \ln \rho_s) \geq S\,(T)$$





C. Hörhammer & H. Büttner, arXiv:0710.1716

Temperature dependence of the ratio $|\delta Q/dS_v|$ (in bits) with the heat defined by $\delta Q = TdS(T)$ for quasi-static variations of the oscillator frequency $d\omega_0$. The system-bath-couplings are chosen to be $\gamma = m\omega_0^2/\Gamma = 0.1$ (dark line) and $\gamma = m\omega_0^2/\Gamma = 0.5$ (gray line). At low T deviations from the Landauer bound $kT \ln 2$ (dashed line) occur.

$$? \quad |\,\delta Q/dS_{vN}| \geq k\,T \ln 2 \quad ?$$

Drude model

damping kernel

$$\gamma(t) = \gamma\omega_{\mathrm{D}}\mathrm{e}^{-\omega_{\mathrm{D}} t}$$

Quantum Langevin equation

$$M\frac{\mathrm{d}^2}{\mathrm{d}t^2}q + M\gamma\omega_{\mathrm{D}}\int_{t_0}^{t}\mathrm{d}s\,\mathrm{e}^{-\omega_{\mathrm{D}}(t-s)}\frac{\mathrm{d}}{\mathrm{d}s}q = \xi(t)$$

equivalent equations of motion

$$\dot{q} = v$$

$$\dot{v} = z$$

$$\dot{z} = -\omega_{\mathrm{D}} z - \gamma\omega_{\mathrm{D}} v$$

oscillations occur for $\omega_{\mathrm{D}} < 4\gamma$

Model for a damped free particle

Hamiltonian

$$H = H_{\mathrm{S}} + H_{\mathrm{B}} + H_{\mathrm{SB}}$$

$$= \frac{p^2}{2M} + \sum_{n=1}^{\infty}\left(\frac{p_n^2}{2m_n} + \frac{m_n}{2}\omega_n^2 x_n^2\right) + \sum_{n=1}^{\infty}\left(-c_n x_n q + \frac{c_n^2}{2m_n\omega_n^2}q^2\right)$$

translational invariance: $c_n = m_n\omega_n^2$

$$= \frac{p^2}{2M} + \sum_{n=1}^{\infty}\left(\frac{p_n^2}{2m_n} + \frac{m_n}{2}\omega_n^2 (x_n - q)^2\right)$$

Quantum Langevin equation

$$M\frac{\mathrm{d}^2}{\mathrm{d}t^2}q + M\int_{t_0}^{t}\mathrm{d}s\gamma(t-s)\frac{\mathrm{d}}{\mathrm{d}s}q = \xi(t)$$

damping kernel and noise

Damping kernel and noise

damping kernel

$$\gamma(t) = \frac{1}{M}\sum_{n=1}^{\infty}\frac{c_n^2}{m_n\omega_n^2}\cos(\omega_n t)$$
$$= \frac{1}{M}\sum_{n=1}^{\infty} m_n\omega_n^2\cos(\omega_n t)$$

noise operator

$$\xi(t) = -M\gamma(t-t_0)q(t_0) + \sum_{n=1}^{\infty}\Big[c_n x_n(t_0)\cos\big(\omega_n(t-t_0)\big) + \frac{c_n}{m_n\omega_n}p_n(t_0)\sin\big(\omega_n(t-t_0)\big)\Big]$$
$$= -M\gamma(t-t_0)q(t_0) + \sum_{n=1}^{\infty}\Big[m_n\omega_n^2 x_n(t_0)\cos\big(\omega_n(t-t_0)\big) + \omega_n p_n(t_0)\sin\big(\omega_n(t-t_0)\big)\Big]$$

return

A gas of free Brownian particles

energy

$$E = \frac{\langle p^2 \rangle}{2M} = \frac{1}{2\beta}\left[1 + 2\sum_{n=1}^{\infty}\frac{\hat{\gamma}(\nu_n)}{\nu_n + \hat{\gamma}(\nu_n)}\right]$$

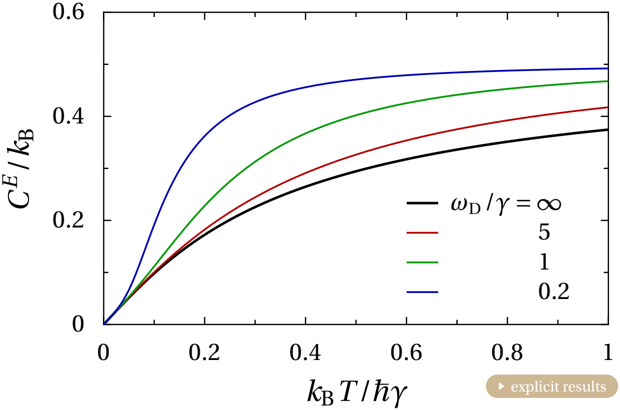
specific heat

$$C^E = \frac{1}{2} + \sum_{n=1}^{\infty}\frac{\hat{\gamma}^2(\nu_n) + \nu_n^2\hat{\gamma}'(\nu_n)}{(\nu_n + \hat{\gamma}(\nu_n))^2}$$

return

Specific heat of a damped free particle

Route I



explicit results

- $T \to \infty$: classical value $k_B/2$
  damping constant γ sets the temperature scale
- coupling to the environment ensures 3^{rd} law
- less damping makes the system more classical

Specific heat from system energy

$$\frac{C^E}{k_\mathrm{B}} = \frac{x_1 x_2}{x_1 - x_2}\left[x_2\psi'(x_2) - x_1\psi'(x_1)\right] - \frac{1}{2}$$

with

$$x_{1,2} = \frac{\hbar\beta\omega_\mathrm{D}}{4\pi}\left(1 \pm \sqrt{1 - \frac{4\gamma}{\omega_\mathrm{D}}}\right)$$

high-temperature expansion

$$\frac{C^E}{k_\mathrm{B}} = \frac{1}{2} - \frac{\hbar^2\gamma\omega_\mathrm{D}}{24(k_\mathrm{B}T)^2} + \mathrm{O}(T^{-3})$$

low-temperature expansion

$$\frac{C^E}{k_\mathrm{B}} = \frac{\pi}{3}\frac{k_\mathrm{B}T}{\hbar\gamma} - \frac{4\pi^3}{15}\left(\frac{k_\mathrm{B}T}{\hbar\gamma}\right)^3\left(1 - 2\frac{\gamma}{\omega_\mathrm{D}}\right) + \mathrm{O}(T^5)$$

return

Partition function and internal energy

undamped case

$$Z_0 = \frac{L}{\hbar}\left(\frac{2\pi m}{\beta}\right)^{1/2}$$

with damping

$$Z = Z_0 \prod_{n=1}^{\infty} \frac{\nu_n}{\nu_n + \hat{\gamma}(\nu_n)}$$

internal energy

compare with energy E

$$U = \frac{1}{2\beta}\left[1 + 2\sum_{n=1}^{\infty} \frac{\hat{\gamma}(\nu_n) - \nu_n \hat{\gamma}'(\nu_n)}{\nu_n + \hat{\gamma}(\nu_n)}\right]$$

$$= \frac{\hbar\omega_\mathrm{D}}{2\pi}\psi\left(\frac{\hbar\beta\omega_\mathrm{D}}{2\pi}\right) - \frac{x_+}{\beta}\psi(x_+) - \frac{x_-}{\beta}\psi(x_-) - \frac{1}{2\beta}$$

Specific heat from partition function

$$\frac{C^Z}{k_\mathrm{B}} = x_1^2\psi'(x_1) + x_2^2\psi'(x_2) - \left(\frac{\hbar\beta\omega_\mathrm{D}}{2\pi}\right)^2 \psi'\left(\frac{\hbar\beta\omega_\mathrm{D}}{2\pi}\right) - \frac{1}{2}$$

with

$$x_{1,2} = \frac{\hbar\beta\omega_\mathrm{D}}{4\pi}\left(1 \pm \sqrt{1 - \frac{4\gamma}{\omega_\mathrm{D}}}\right)$$

high-temperature expansion

$$\frac{C^Z}{k_\mathrm{B}} = \frac{1}{2} - \frac{\hbar^2\gamma\omega_\mathrm{D}}{12(k_\mathrm{B}T)^2} + \mathrm{O}(T^{-3})$$

low-temperature expansion

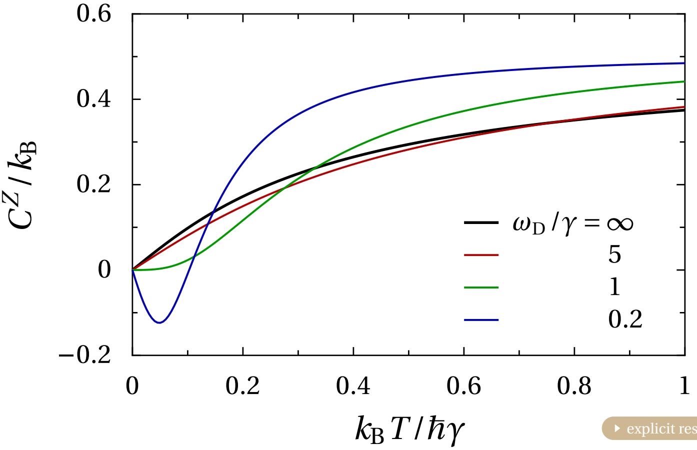
$$\frac{C^Z}{k_\mathrm{B}} = \frac{\pi}{3}\frac{k_\mathrm{B}T}{\hbar\gamma}\left(1 - \frac{\gamma}{\omega_\mathrm{D}}\right) - \frac{4\pi^3}{15}\left(\frac{k_\mathrm{B}T}{\hbar\gamma}\right)^3\left[1 - 3\frac{\gamma}{\omega_\mathrm{D}} - \left(\frac{\gamma}{\omega_\mathrm{D}}\right)^3\right] + \mathrm{O}(T^5)$$

return

Specific heat of a damped free particle

Route II

▸ partition function



▸ explicit results

The specific heat can be negative!?

Origin of a negative density of states

a simple model:

- system
- one single bath oscillator with frequency ω

➠ total system with eigenenergies E_n and degeneracies g_n

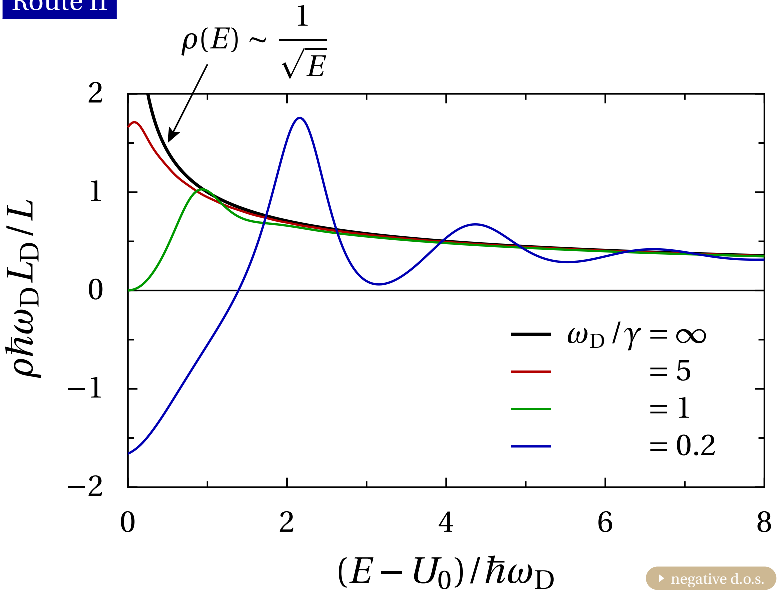
$$Z = \frac{\mathrm{Tr}_{\mathrm{S+osc}}(\mathrm{e}^{-\beta H})}{\mathrm{Tr}_{\mathrm{osc}}(\mathrm{e}^{-\beta H_{\mathrm{osc}}})} = \sum_n g_n \mathrm{e}^{-\beta E_n}\left(\mathrm{e}^{\hbar\beta\omega/2} - \mathrm{e}^{-\hbar\beta\omega/2}\right)$$

$$\rho(E) = \sum_n g_n \delta(E - E_n + \hbar\omega/2) - \sum_n g_n \delta(E - E_n - \hbar\omega/2)$$

return

Density of states of a damped free particle

Route II



negative d.o.s.

Strong coupling: Example

Peter Hänggi, Michele Campisi, and Peter Talkner

System: Two-level atom; "bath": Harmonic oscillator

$$H = \frac{\epsilon}{2}\sigma_z + \Omega\left(a^\dagger a + \frac{1}{2}\right) \quad + \chi\sigma_z\left(a^\dagger a + \frac{1}{2}\right)$$

$$H^* = \frac{\epsilon^*}{2}\sigma_z + \gamma$$

$$\epsilon^* = \epsilon + \chi + \frac{2}{\beta}\mathrm{artanh}\left(\frac{e^{-\beta\Omega}\sinh(\beta\chi)}{1 - e^{-\beta\Omega}\cosh(\beta\chi)}\right)$$

$$\gamma = \frac{1}{2\beta}\ln\left(\frac{1 - 2e^{-\beta\Omega}\cosh(\beta\chi) + e^{-2\beta\Omega}}{(1 - e^{-\beta\Omega})^2}\right)$$

$$Z_S = \mathrm{Tr} e^{-\beta H^*} \quad F_S = -k_b T \ln Z_S$$

$$S_S = -\frac{\partial F_S}{\partial T} \quad C_S = T\frac{\partial S_S}{\partial T}$$

M. Campisi, P. Talkner, P. Hänggi, J. Phys. A: Math. Theor. **42** 392002 (2009)

Strong coupling: Example

System: Two-level atom; “bath”: Harmonic oscillator

$$H = \frac{\epsilon}{2}\sigma_z + \Omega\left(a^\dagger a + \frac{1}{2}\right) \quad + \chi\sigma_z\left(a^\dagger a + \frac{1}{2}\right)$$

$$H^* = \frac{\epsilon^*}{2}\sigma_z + \gamma$$

$$\epsilon^* = \epsilon + \chi + \frac{2}{\beta}\mathrm{artanh}\left(\frac{e^{-\beta\Omega}\sinh(\beta\chi)}{1 - e^{-\beta\Omega}\cosh(\beta\chi)}\right)$$

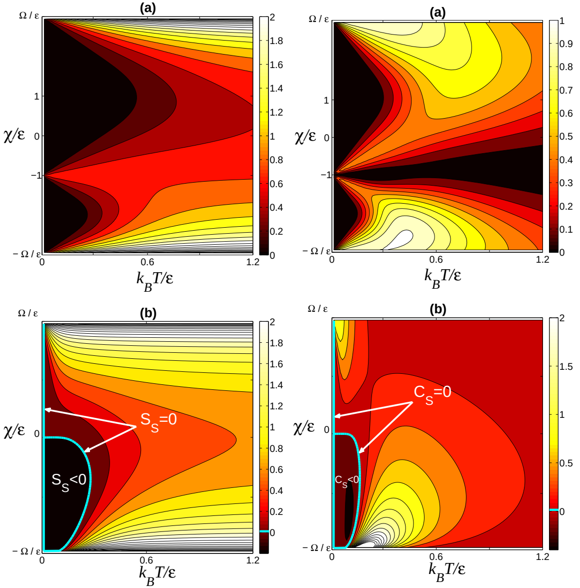
$$\gamma = \frac{1}{2\beta}\ln\left(\frac{1 - 2e^{-\beta\Omega}\cosh(\beta\chi) + e^{-2\beta\Omega}}{(1 - e^{-\beta\Omega})^2}\right)$$

$$Z_S = \mathrm{Tr}e^{-\beta H^*} \quad F_S = -k_b T \ln Z_S$$

$$S_S = -\frac{\partial F_S}{\partial T} \quad C_S = T\frac{\partial S_S}{\partial T}$$

M. Campisi, P. Talkner, P. Hänggi, J. Phys. A: Math. Theor. **42** 392002 (2009)

Entropy and specific heat



$\Omega/\epsilon = 3$

$\Omega/\epsilon = 1/3$

Conclusions

- specific heat depends on friction strength
- finite damping restores third Law for the free Brownian particle

$$C \propto \frac{k_B T}{\hbar\gamma}$$

- dependence on prescription
  H_{SB} part of "S" and/or part of "B"
  exception: strict ohmic damping

References:

Acta Phys. Pol. B **37**, 1537 (2006)
http://th-www.if.uj.edu.pl/acta/vol37/pdf/v37p1537.pdf
New J. Phys. **10**, 115008 (2008)
Phys. Rev. E **79**, 061105 (2009)
J. Phys. A (Fast Track) **42**, 392002 (2009)
Phys. Rev. E **80**, 041113 (2009)

Low temperature behaviour of the specific heat

Route II

Free damped particle

$$\frac{C^Z}{k_\mathrm{B}} = \frac{\pi}{3}\,\frac{1+\hat{\gamma}'(0)}{\hat{\gamma}(0)}\,\frac{k_\mathrm{B}T}{\hbar} + \mathrm{O}(T^3)$$

Damped harmonic oscillator

$$\frac{C^Z}{k_\mathrm{B}} = \frac{\pi}{3}\,\frac{\hat{\gamma}(0)}{\omega_0^2}\,\frac{k_\mathrm{B}T}{\hbar} + \mathrm{O}(T^3)$$

for the damped harmonic oscillator the specific heat is always positive

HOMEPAGE
„HANGGI“

GO TO : FEATURE ARTICLES

- **Quantum Dissipation**
  and
  Quantum Transport

http://www.physik.uni-augsburg.de/theo1/hanggi/Quantum.html

DRIVEN - TUNNELING - ZOO

SUPPR. vs. ENH.

CDT

EHG

CHAOS-ASSISTED

QSR

COHERENT

TUNNELING CONTROL

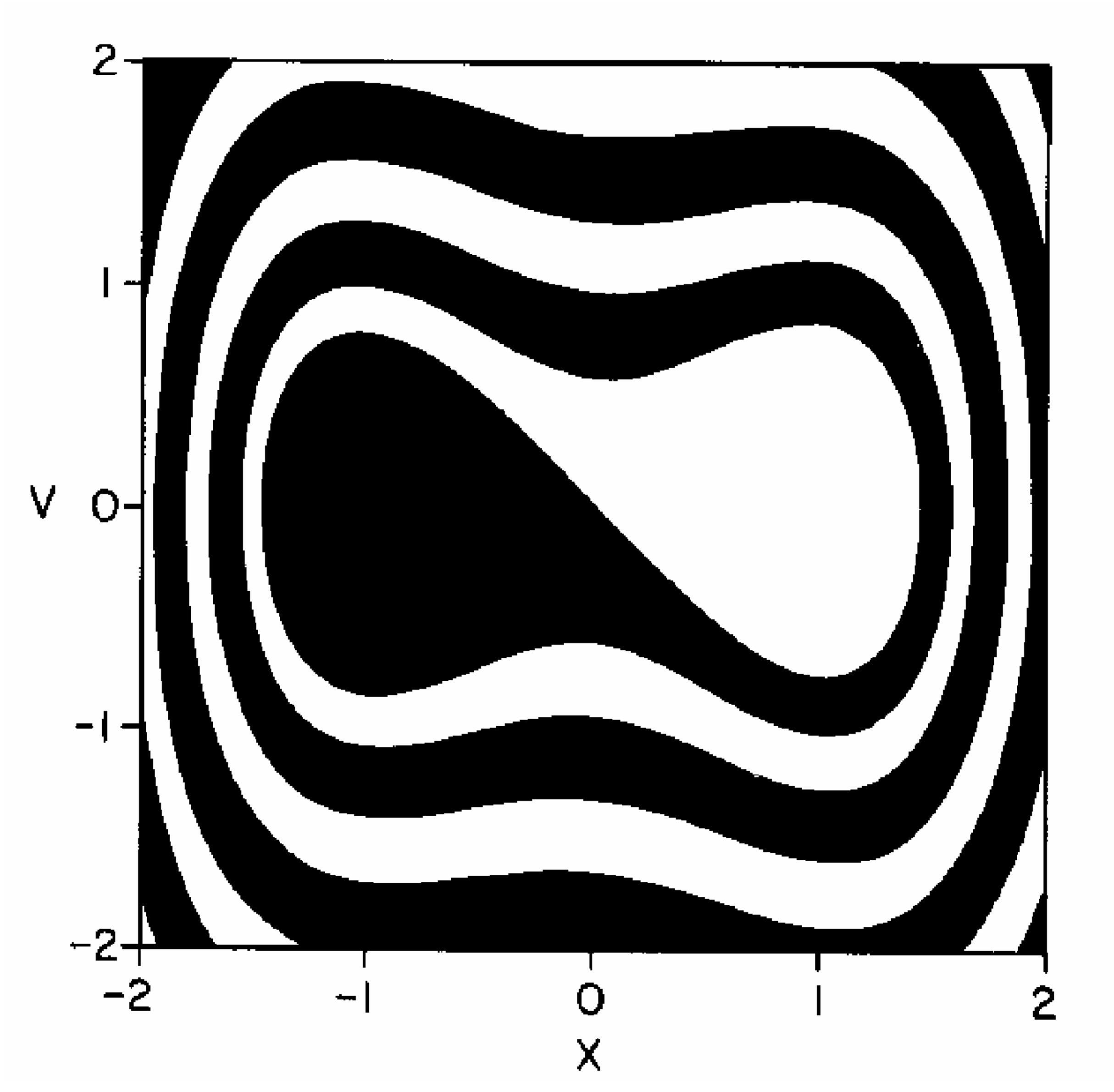
- DRIVING (Ω, A, ..)
- BATH SPECTRUM
- NOISE INPUT

Quantum Dissipation: A Primer

P. Hänggi

Institut für Physik
Universität Augsburg

NOISE-INDUCED ESCAPE



$$\text{rate} = A(\gamma)\,\frac{\omega_0}{2\pi}\exp(-\Delta U/D)$$

RMP $\underline{62}$: 251 (90)

Reaction-rate theory: fifty years after Kramers

Peter Hänggi

Lehrstuhl für Theoretische Physik, University of Augsburg, D-8900 Augsburg, Federal Republic of Germany

Peter Talkner*

Department of Physics, University of Basel, CH-4056 Basel, Switzerland

Michal Borkovec

Institut für Lebensmittelwissenschaft, ETH-Zentrum, CH-8092 Zürich, Switzerland

The calculation of rate coefficients is a discipline of nonlinear science of importance to much of physics, chemistry, engineering, and biology. Fifty years after Kramers' seminal paper on thermally activated barrier crossing, the authors report, extend, and interpret much of our current understanding relating to theories of noise-activated escape, for which many of the notable contributions are originating from the communities both of physics and of physical chemistry. Theoretical as well as numerical approaches are discussed for single- and many-dimensional metastable systems (including fields) in gases and condensed phases. The role of many-dimensional transition-state theory is contrasted with Kramers' reaction-rate theory for moderate-to-strong friction; the authors emphasize the physical situation and the close connection between unimolecular rate theory and Kramers' work for weakly damped systems. The rate theory accounting for memory friction is presented, together with a unifying theoretical approach which covers the whole regime of weak-to-moderate-to-strong friction on the same basis (turnover theory). The peculiarities of noise-activated escape in a variety of physically different metastable potential configurations is elucidated in terms of the mean-first-passage-time technique. Moreover, the role and the complexity of escape in driven systems exhibiting possibly multiple, metastable stationary nonequilibrium states is identified. At lower temperatures, quantum tunneling effects start to dominate the rate mechanism. The early quantum approaches as well as the latest quantum versions of Kramers' theory are discussed, thereby providing a description of dissipative escape events at all temperatures. In addition, an attempt is made to discuss prominent experimental work as it relates to Kramers' reaction-rate theory and to indicate the most important areas for future research in theory and experiment.

CONTENTS

---

*Present address: Paul Scherrer Institut, CH-5232 Villigen, Switzerland.

