

Quantum Dissipation: A Primer

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Dynamics of Open Quantum Systems

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QUANTUM DISSIPATION

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



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

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

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

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



QUANTUM DISSIPATION



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

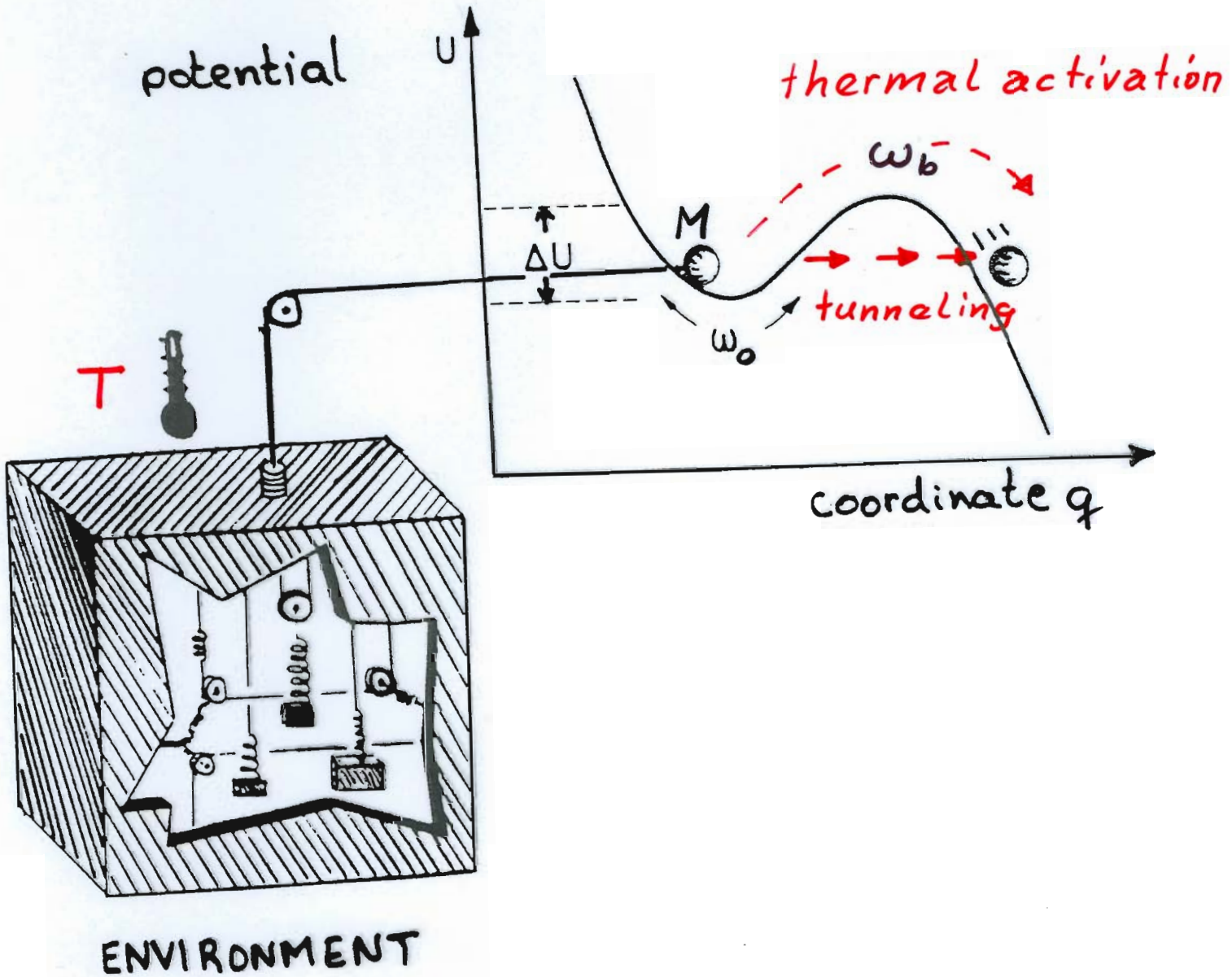
$$\Rightarrow \cancel{e^{\gamma t}} [m_0 \ddot{x} + m_0 \gamma \dot{x} + m_0 \omega_0^2 x] = 0$$

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

$$[q, p] = +i\hbar e^{-\gamma t}$$



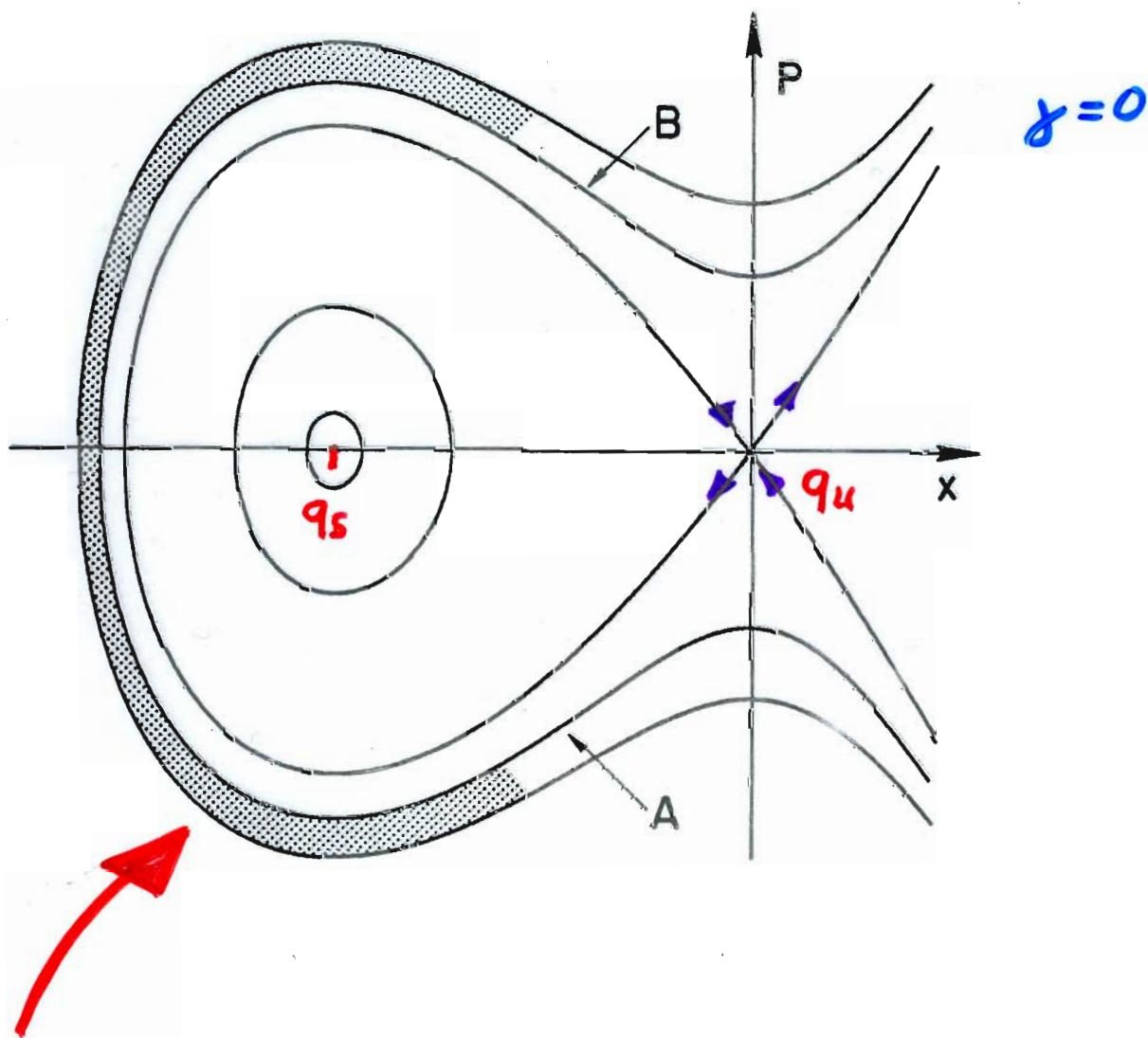
THE PROBLEM



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

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

TST

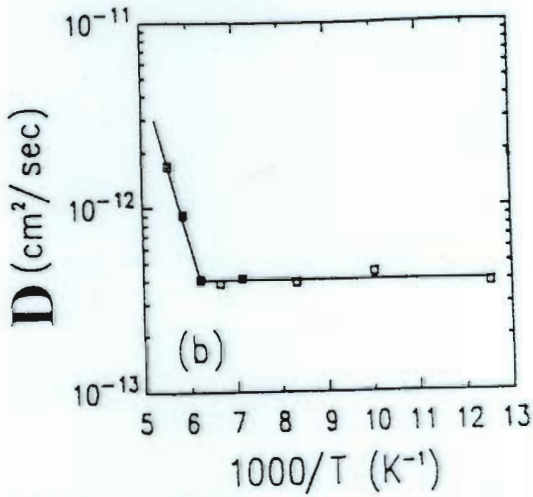


thermal equilibrium

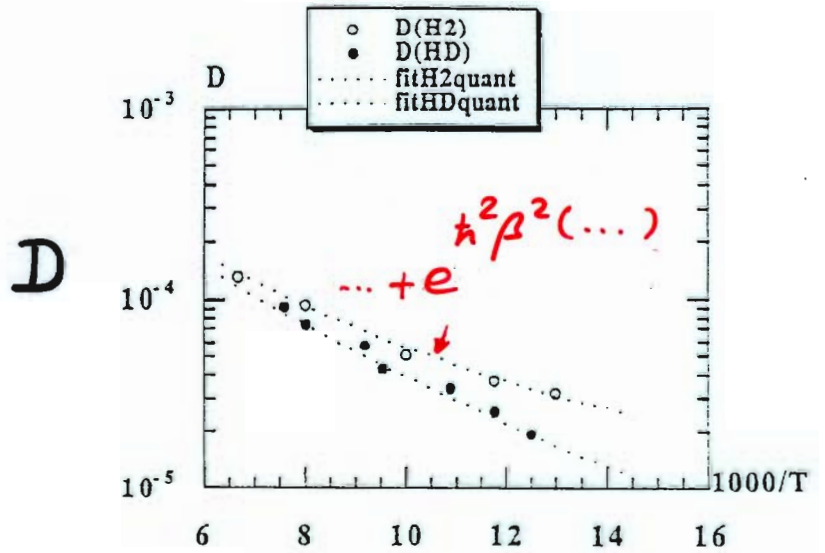
P.H., P. TALKNER, M. BORKOVEC

REV. MOD. PHYS. 62: 251 (1990)

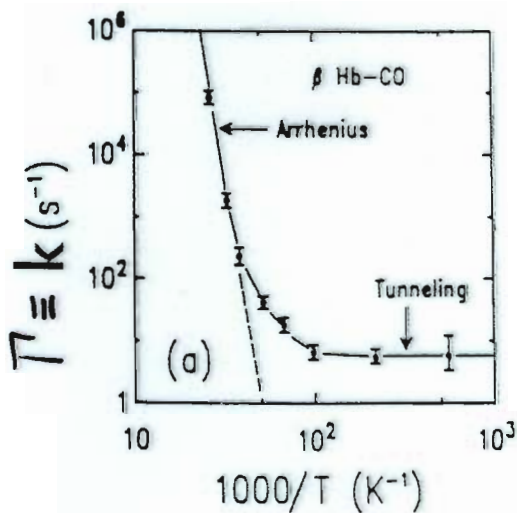
FACTS



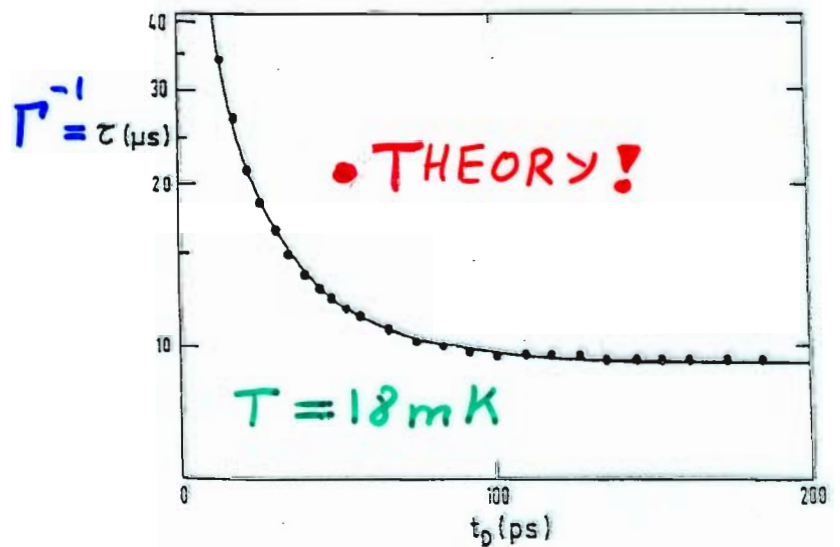
H on (110) tungsten
[GOMER(82)]



H₂ & HD sorbed in
zeolites [Bouchand et al. (82)]



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 T

$$k = A \exp(-B)$$

$$B = S_B(T, \gamma)$$

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

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

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

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

2-0-modes

$$\frac{S_B}{\hbar} = \frac{E_b}{\hbar\omega_0}$$

smooth!

Erfc-behavior

$$k = \Gamma_{CP} Q$$

quantum enhancement

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

$$> 1$$

i.e.

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

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

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

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)

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LIST OF SYMBOLS

$A(T)$	temperature-dependent quantum rate prefactor	$K(x, x')$	transition probability kernel
$C(t)$	correlation function	M	mass of reactive particle
D	diffusion coefficient	$P(E)$	period of oscillation in the classically allowed region
E	energy function	$P(E, E')$	classical conditional probability of finding the energy E , given initially the energy E'
E_b	activation energy (=barrier energy with the energy at the metastable state set equal to zero)	Q	quantum correction to the classical prefactor
$E^{(A)}$	Hessian matrix of the energy function at the stable state	S_b	dissipative bounce action
$E^{(S)}$	Hessian matrix of the energy function around the saddle-point configuration	T	temperature
I	action variable of the reaction coordinate	T_0	crossover temperature
J	Jacobian	$T(E)$	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 i th 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 $(k_B T)^{-1}$

microscopic approach

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

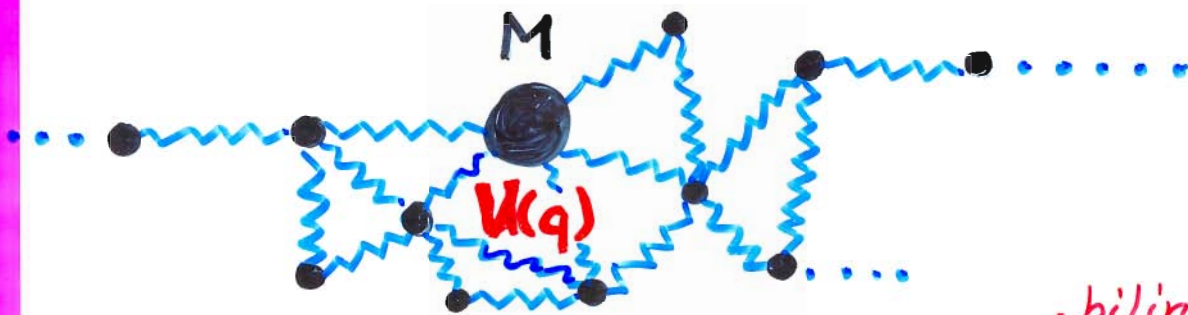
$$+ \underbrace{\frac{1}{2} \sum_{\alpha} m_{\alpha} \dot{q}_{\alpha}^2 + \sum_{\alpha} m_{\alpha} \omega_{\alpha}^2 q_{\alpha}^2}_{\text{(harmonic) bath}}$$

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

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

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

dissipation



$$H^T = H_{\text{system}} + H_{\text{bath}} + H_{\text{Int}} \quad \swarrow \text{bilinear}$$

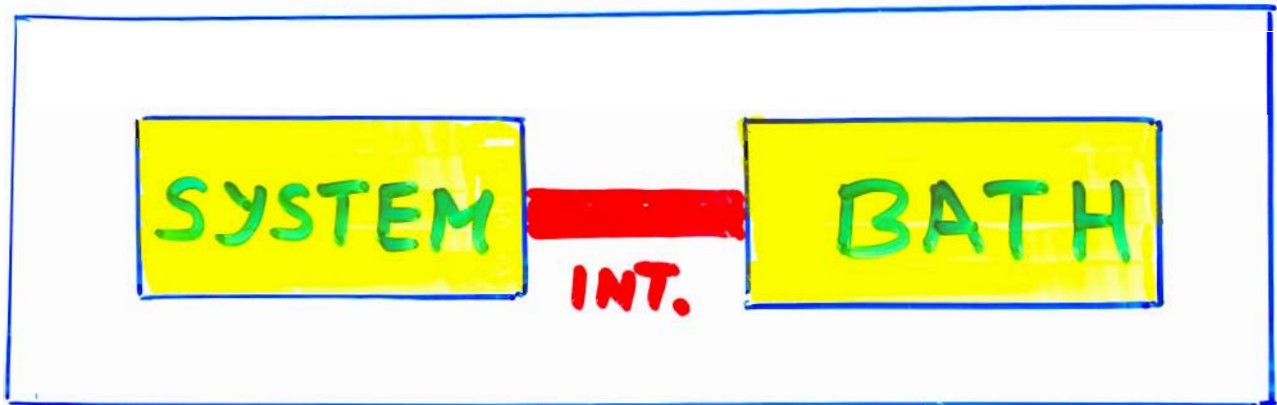
$$\ddot{q} = -\frac{1}{M} \frac{\delta U}{\delta q} - \int_0^t \gamma(t-s) \dot{q}(s) ds$$



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

QUANTUM NOISE

QUANTUM L.-EQ.



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

↳ DECOHERENCE
AT $T = 0$

$$H_{S+B} = H_S + H_{S-B} + H_B$$

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

! $S_S \neq 2^{-1} \exp\left(-\frac{H_S}{kT}\right)$!

$$S_{\text{Total P}} = S_{S+B} = 2^{-1} \exp\left(-\frac{H_{S+B}}{kT}\right)$$



Q L E

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

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

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

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

$$= \gamma(s-t) \triangle$$

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

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

$\neq 0$

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

- $\langle \eta(t) \rangle_{\mathcal{S}_B} = 0$

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

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

$kT \gg \hbar\omega_{\alpha}$

$\longrightarrow kT \gamma(\tau)$

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

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

OHMIC DISSIPATION

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

cut-off frequency

$\omega_c \gg \omega_0, \omega_b$

KONDO-PARAMETER

$$= (2\pi\hbar/a^2) \alpha \omega \exp(-\omega/\omega_c)$$

~~~~~ =  $\gamma$

$a = 2q_a$ : tunneling length



# REMARKS

1.

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

2.

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

$$\frac{1}{x + i0^+} = P\left(\frac{1}{x}\right) - i\pi \delta(x) \quad \text{Im } z > 0$$

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

$$\rightarrow C(\tau) = \frac{m}{\pi} \int_0^{\infty} d\omega \text{Re } \hat{y}(\omega + i0^+) \cos(\omega\tau) \cdot \coth\left(\frac{\hbar\omega}{2kT}\right)$$

3.

with  $\hat{y}(t) = \eta(t) - m\gamma(t) * (0)$

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

$$\rightarrow \langle \hat{y}(t) \rangle_{\hat{S}} = 0$$

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

4. DEPHASING AT  
 $T=0$  !

$$\langle x(0) \xi(t) \rangle_{\mathcal{P}} \neq 0$$

$$\langle H_{INT} \rangle_{\mathcal{P}} \neq 0$$

5.

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

WITH CORRELATION

$C(\tau)$

IS INCONSISTENT



# SYNOPSIS

## LINEAR RESPONSE THEORY & QUANTUM-FDT

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

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

$$\begin{aligned} \text{KUBO: } \chi_{BA}(\tau) &= \Theta(\tau) \frac{i}{\hbar} \langle [\hat{B}(\tau), \hat{A}(0)] \rangle_\beta \\ &= -\Theta(\tau) \int_0^\beta \langle \hat{A}(-i\hbar\lambda) \dot{\hat{B}}(\tau) \rangle_\beta d\lambda \end{aligned}$$

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



# SYNOPSIS

## LINEAR RESPONSE THEORY & QUANTUM-FDT

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

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

$$\begin{aligned} \text{KUBO: } \chi_{BA}(\tau) &= \Theta(\tau) \frac{i}{\hbar} \langle [\hat{B}(\tau), \hat{A}(0)] \rangle_\beta \\ &= -\Theta(\tau) \int_0^\beta \langle \hat{A}(-i\hbar\lambda) \dot{\hat{B}}(\tau) \rangle_\beta d\lambda \end{aligned}$$

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

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

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

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

# QUANTUM-FDT

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

$$\chi_{BA}(\tau) = \chi'_{BA}(\tau) + i \chi''_{BA}(\tau)$$
$$\frac{1}{2} [\chi_{BA}(\tau) + \chi_{AB}(-\tau)] \quad -\frac{i}{2} [\chi_{BA}(\tau) - \chi_{AB}(-\tau)]$$

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

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

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

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

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

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

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

# EQ.-CURRENT NOISE

$$A = B$$

$$I := \frac{dB}{dt}$$

$$\langle \delta I(t) \rangle = \int_{-\infty}^t Z(t-s) F(s) ds$$
$$Z(t-s) = \frac{dX(\tau)}{d\tau}$$

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

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

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

---

---

$$kT \gg \hbar \omega : S_{II}(\omega) \rightarrow 2kT \text{Re} Z(\omega)$$
$$\xrightarrow{\text{MARKW}} \underline{2kT/R}$$

JOHNSON-NYQUIST (1928)

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

quantum-zero point fluct.

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



**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.**

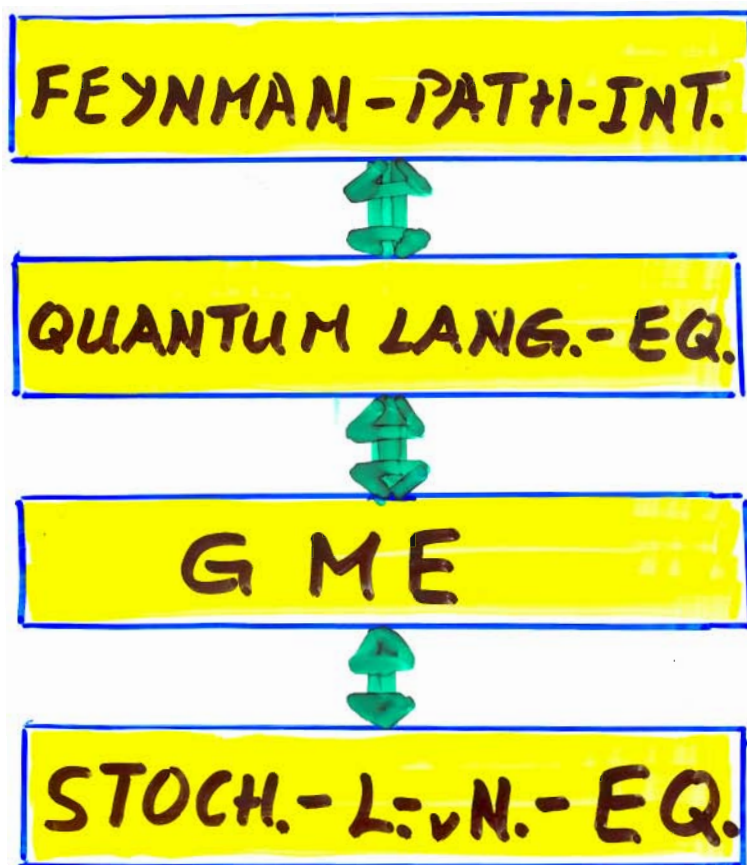
**Phys. Rev. (1951) 83 (1) 34-40**



# QUANTUM NOISE



NO QUANTUM EQ.-PARTITION-TH.



$$S := |4_1(t)\rangle \langle 4_2(t)|, \quad \mu := \frac{2}{\pi} \int_0^\infty d\omega \frac{\gamma(\omega)}{\omega}$$

$$i\hbar \dot{S} = [H_0, S] + \frac{\mu}{2} [X^2, S] - \gamma(t) [X, S] - \frac{\hbar}{2} \nu(t) \{X, S\} + \text{COMPLEX VALUED NOISE}$$

$$\langle \gamma(t) \gamma(t') \rangle = \text{Re } L(t-t'), \quad \langle \gamma(t) \nu(t') \rangle = \frac{2}{\hbar} \theta(t-t') \text{Im } L(t-t')$$

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



# PIT FALLS

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.

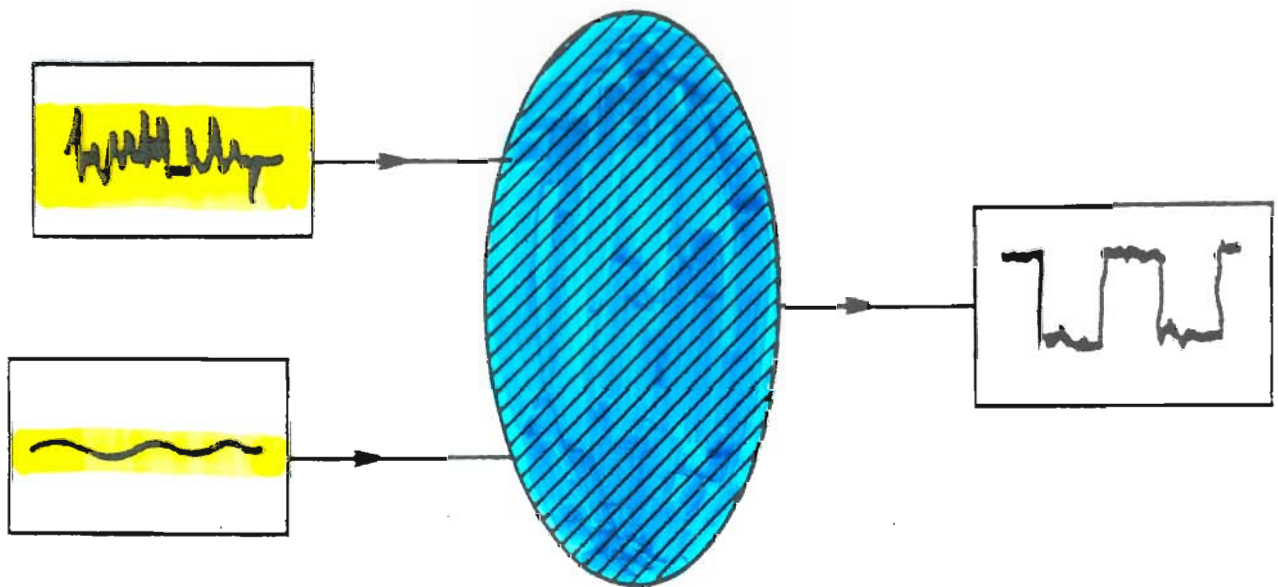
BUT

● WRONG EHRENFEST EQ.

● NO FDT

● NO KMS-COND.  $\langle U(t) V \rangle_{\beta} = \langle V U(t + i\hbar\beta) \rangle_{\beta}$

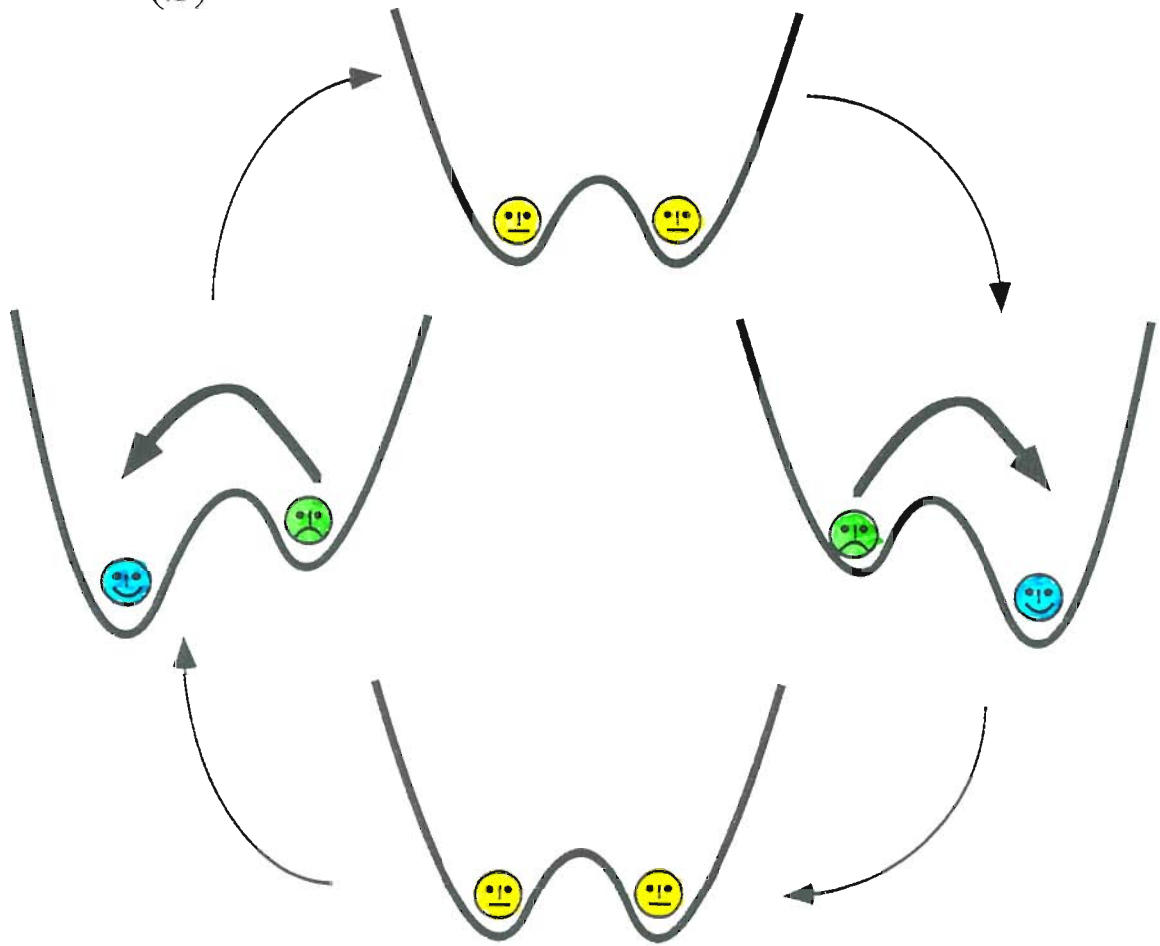
# SR



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

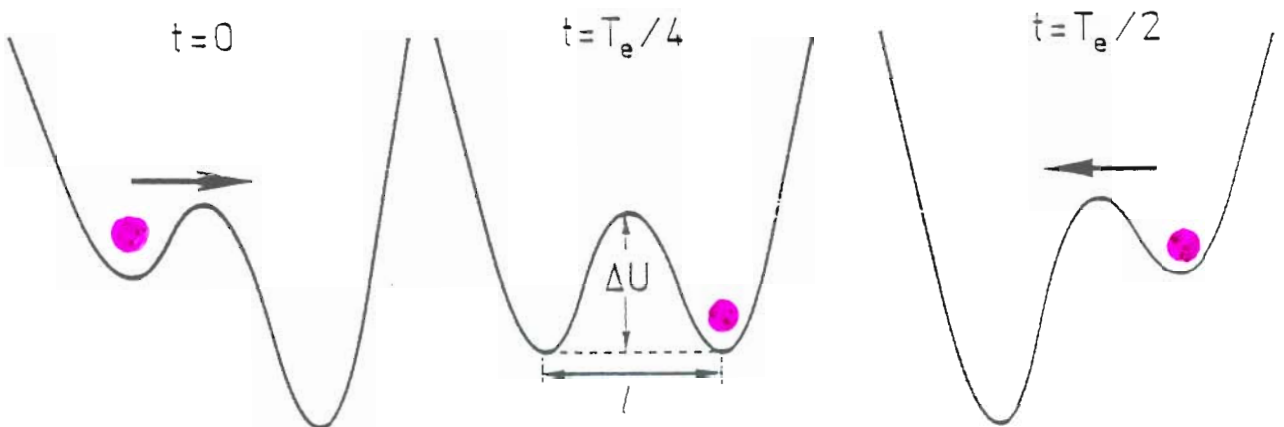


# Bistable Model

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

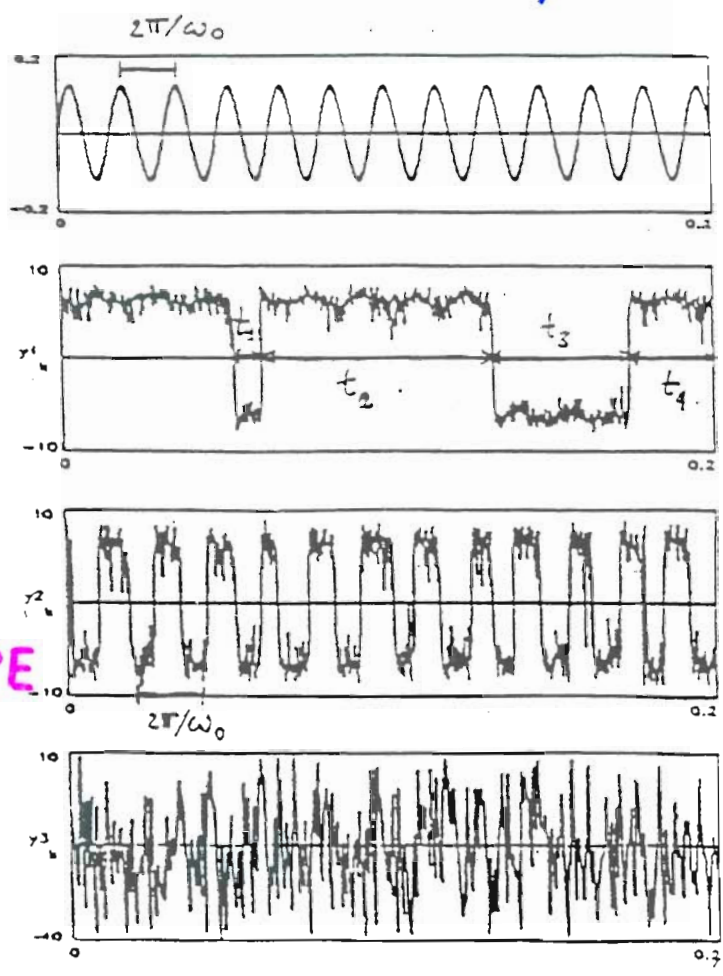
$$\langle \xi(t) \rangle = 0$$

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



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

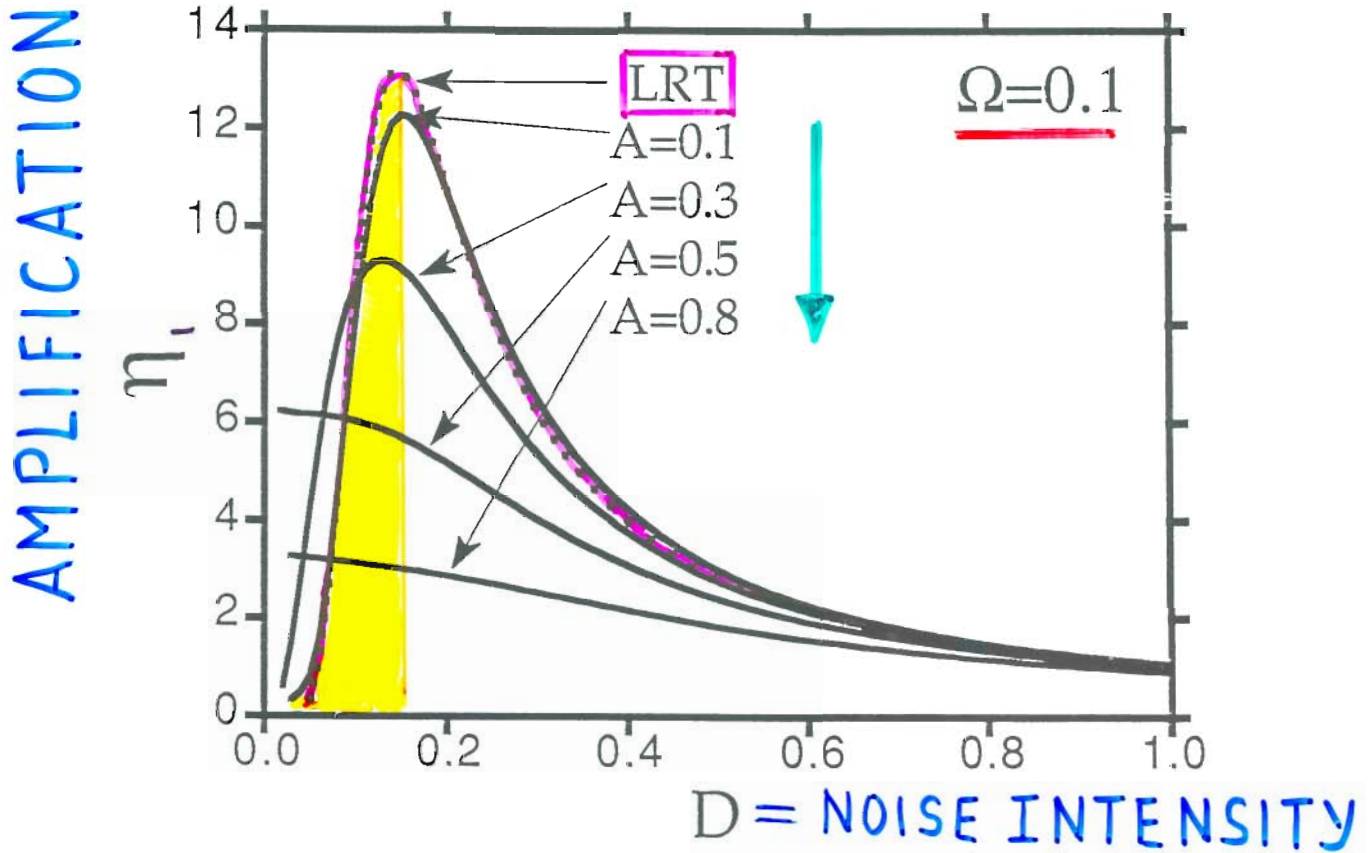
SIGNAL



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

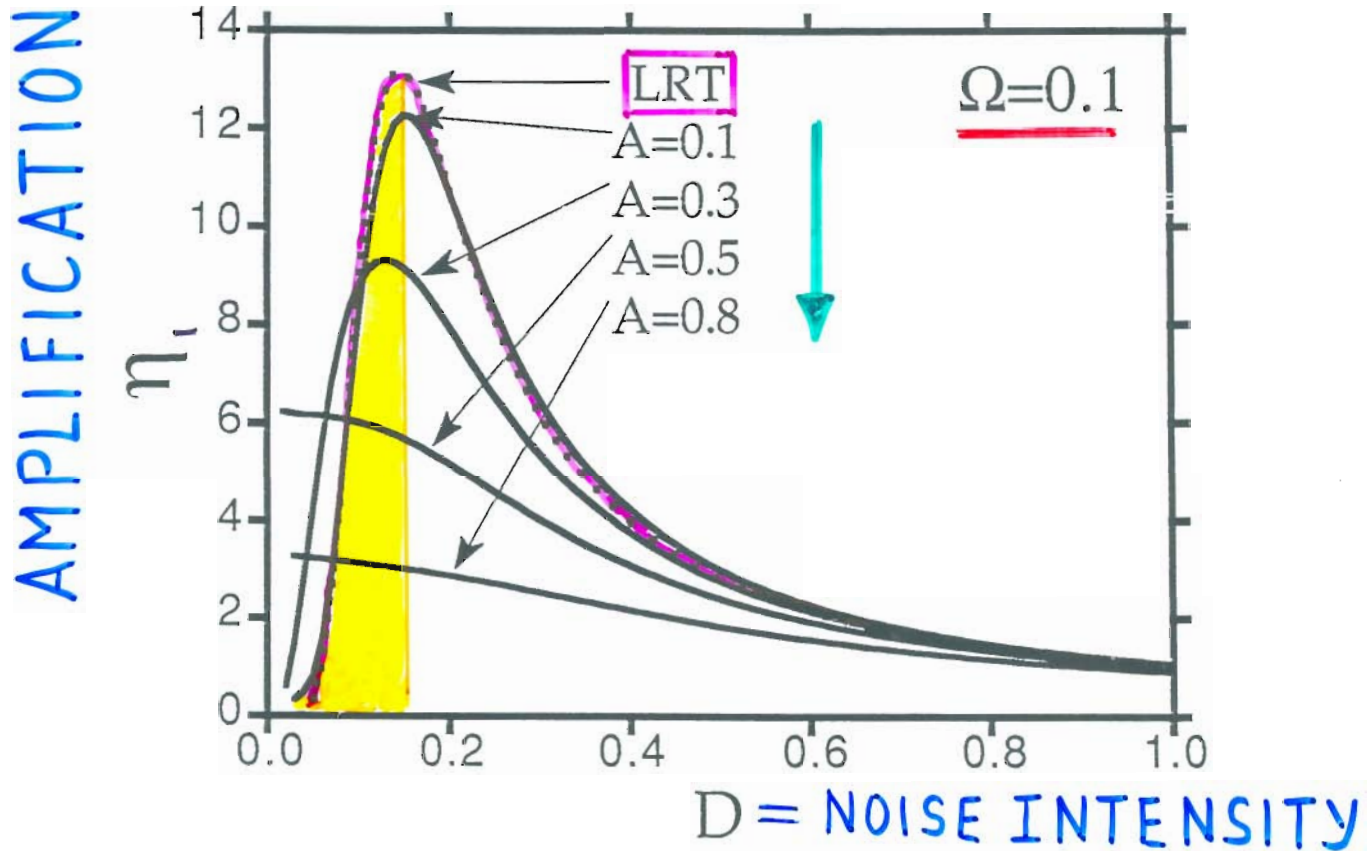
ESCAPE

P. JUNG + P. H., PHYS. REV. A44:8032(191)



MORE NOISE  $\rightarrow$  MORE SIGNAL

P. JUNG + P. H., PHYS. REV. A44:8032(191)



MORE NOISE  $\rightarrow$  MORE SIGNAL

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

$$|M_1|^2 \propto \frac{1}{D^2} \quad \downarrow \quad \downarrow \quad \exp(-2\alpha U/D)$$

**S R**

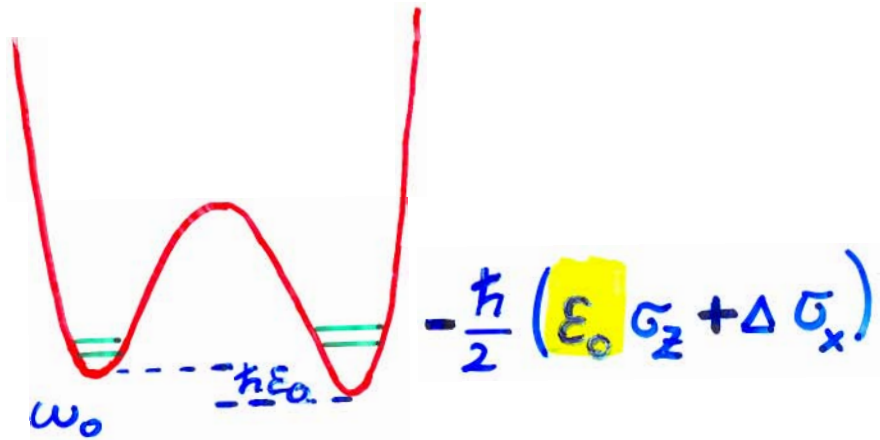
**IN QUANTUM MECHANICS**

**Q S R**



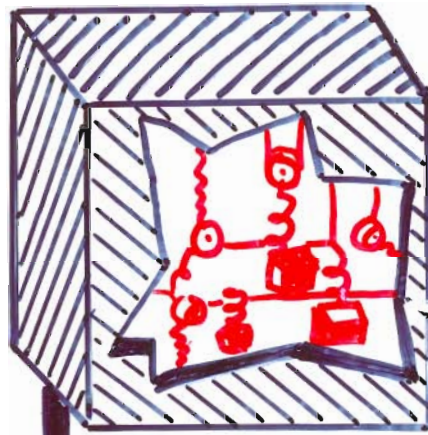
$$V_0 \gg \hbar\omega_0 \gg \hbar\epsilon_0, kT$$

TS



+

BATH  
 $T, \gamma$



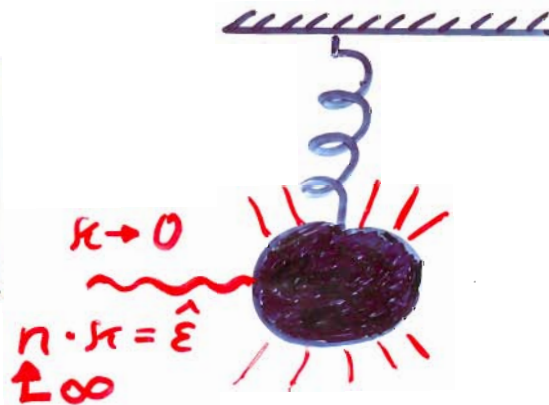
$$\frac{1}{2} \sum_{\alpha} \left( \frac{p_{\alpha}^2}{m_{\alpha}} + m_{\alpha} \omega_{\alpha}^2 x_{\alpha}^2 - c_{\alpha} x_{\alpha} G_z \right)$$

+



Temperature

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



$$\frac{\hbar \hat{\epsilon}}{2} \cos(\Omega t) G_z$$

# LINEAR RESPONSE & QSR

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

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

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

! Valid at all temperatures!

PROBLEM: QUANTUM  $\chi_{qq}(\Omega) \stackrel{\text{FDT}}{\sim} S_{qq}(\Omega)$

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

! DIFFICULT !

# LINEAR RESPONSE & QSR

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! DIFFICULT !



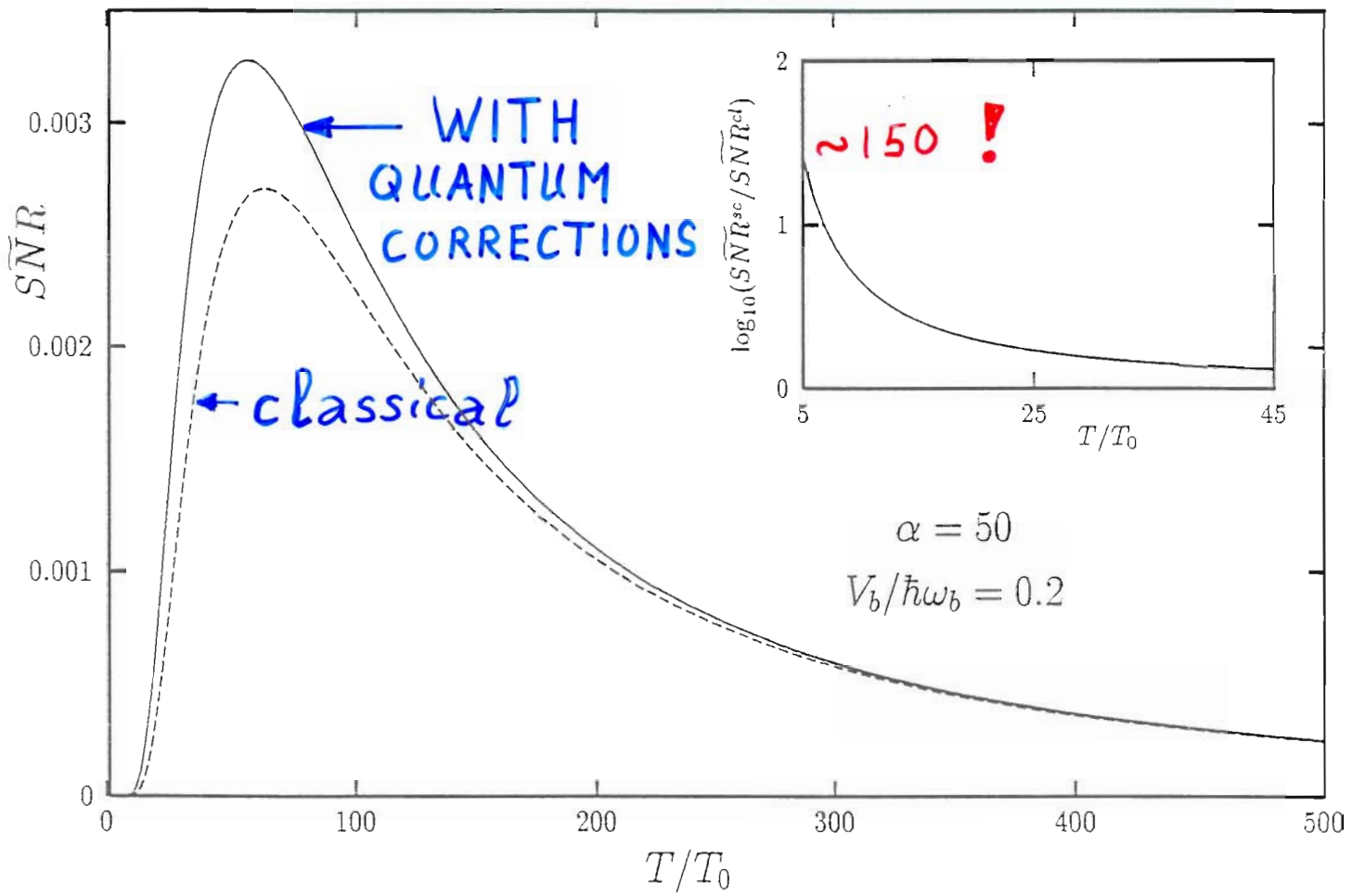
2 LIMITS



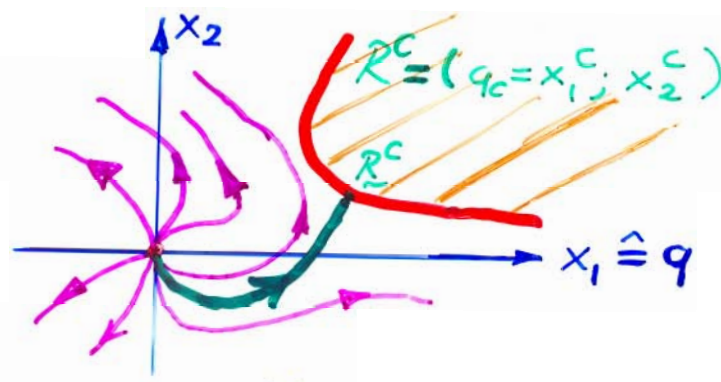
AT LOW T

above ~ near  
crossover to  
thermal hopping



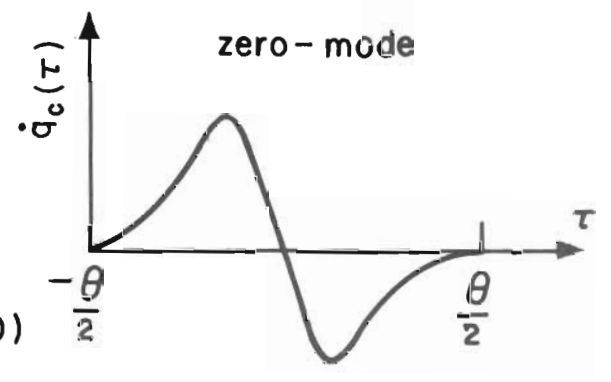
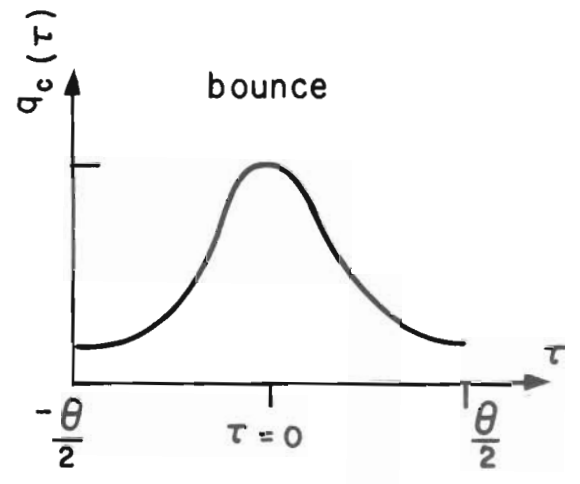
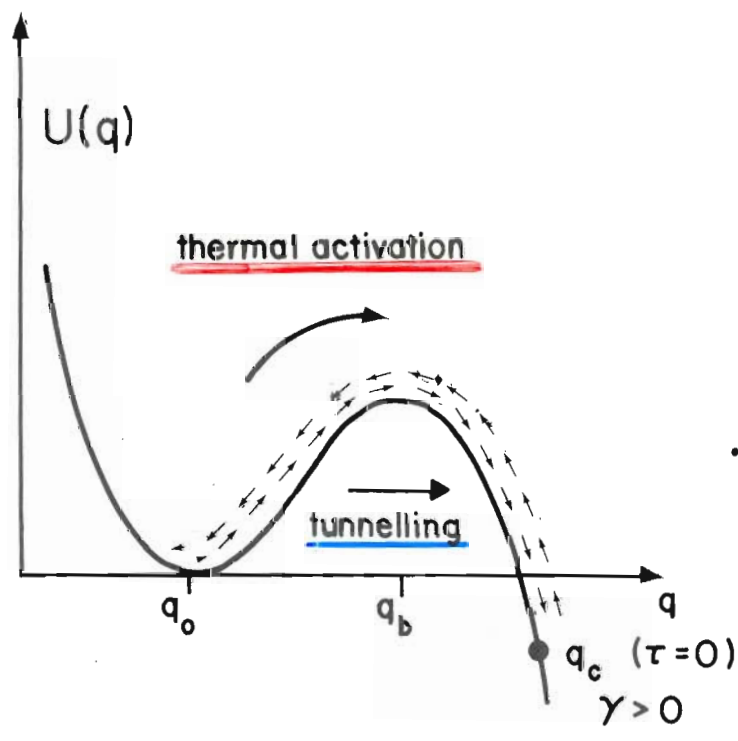


$T=0$



classically allowed

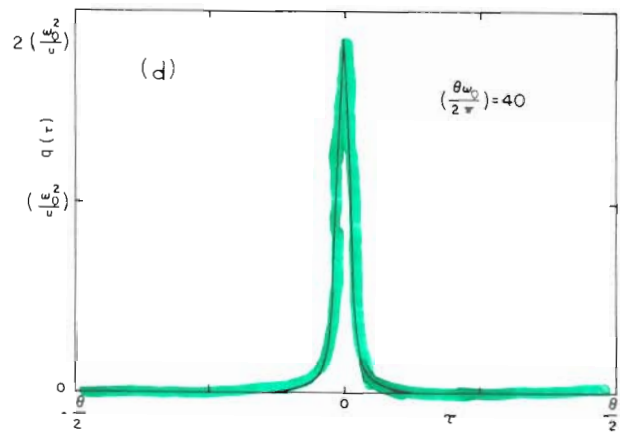
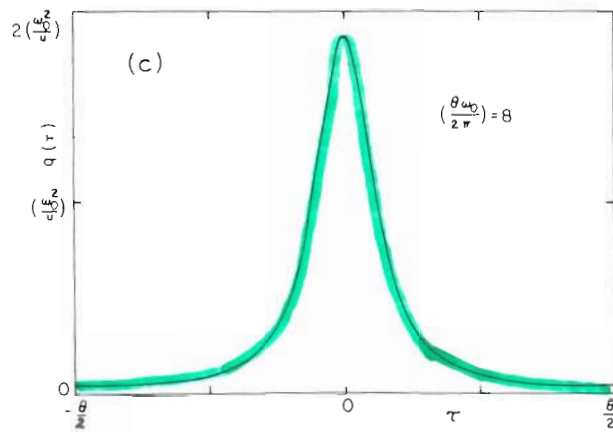
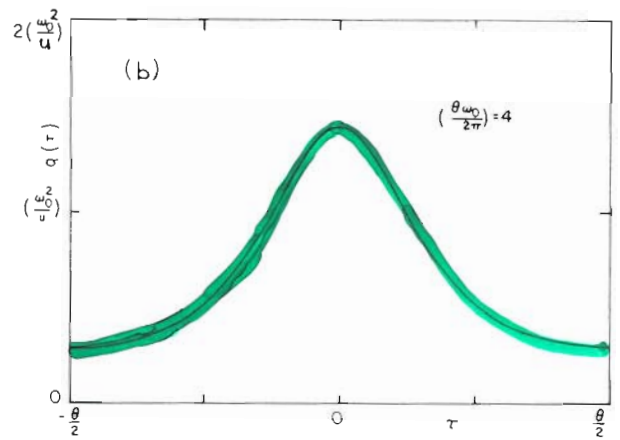
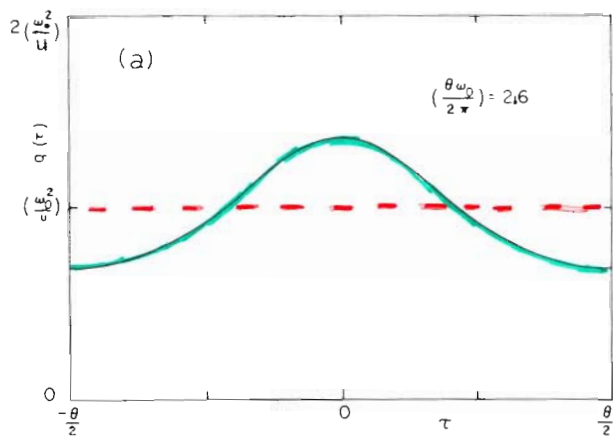
classically forbidden



$\gamma=0$ :

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

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



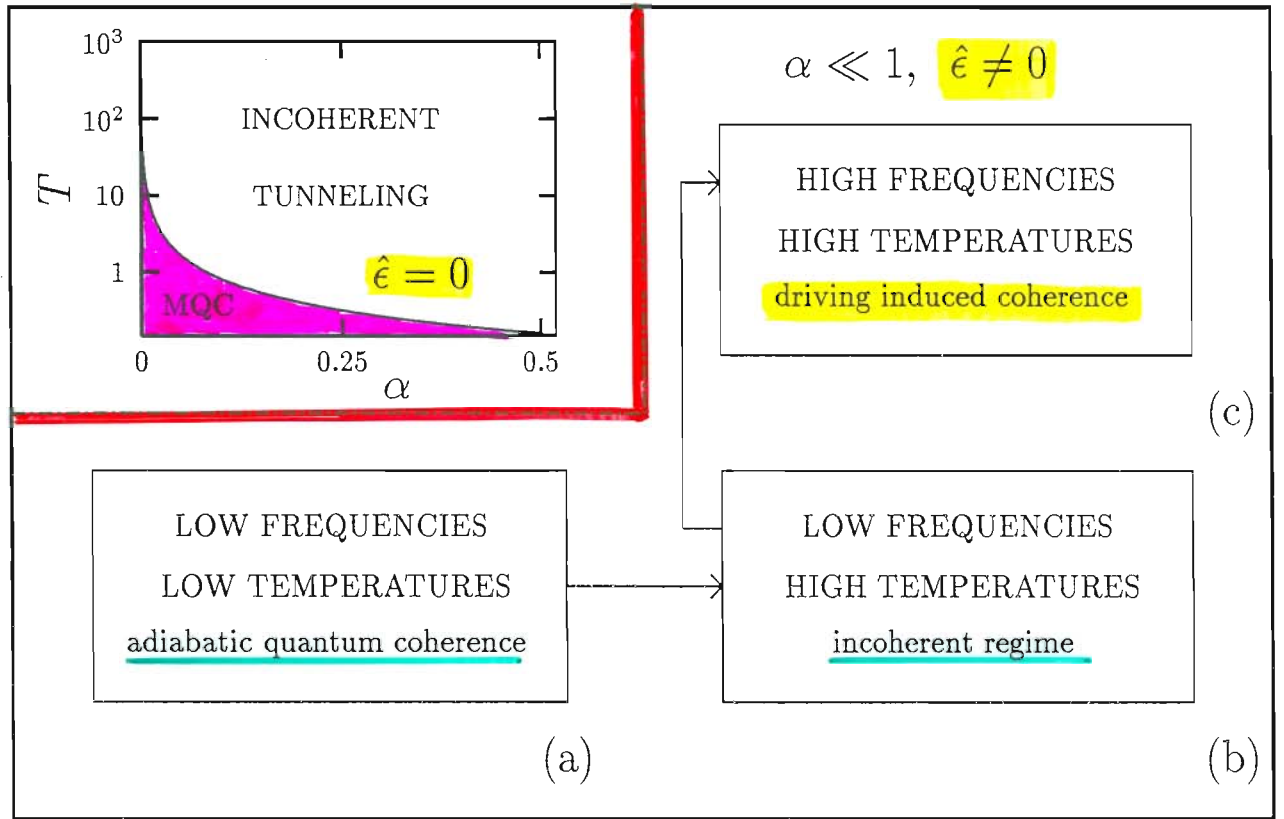
$$-M\ddot{q}_B + \frac{\partial U(q_B)}{\partial q_B} + \int_{-\Theta/2}^{\Theta/2} k(\tau - \tau') q_B(\tau') d\tau' = 0$$

$$\Theta = \hbar/kT$$

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



# QUANTUM SR



# DRIVEN QUANTUM TUNNELING

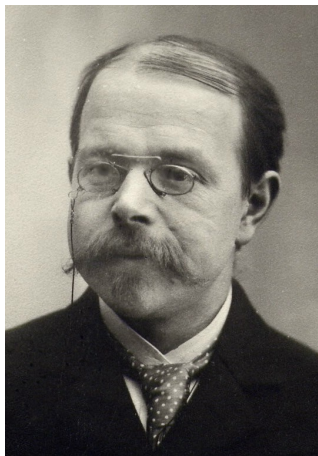
M. GRIFONI, P.H. PHYS. REP.

304: 229 - 358 (98)

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[http://www.physik.uni-augsburg.  
de/theo1/hanggi/](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)

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

Third Law

Harmonic oscillator

Dissipative systems

Harmonic oscillator

Free Brownian particle





# Famous exceptions to the Third Law



classical ideal gas

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

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)

Third Law

Harmonic oscillator

Dissipative systems

Harmonic oscillator

Free Brownian particle



# Quantum Brownian motion and the Third Law of thermodynamics

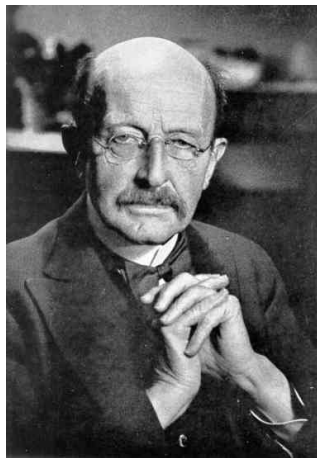
Peter Hänggi, Michele Campisi,  
Gert-Ludwig Ingold, and Peter Talkner  
Uni Augsburg

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)



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.

Third Law

Harmonic oscillator

Dissipative systems

Harmonic oscillator

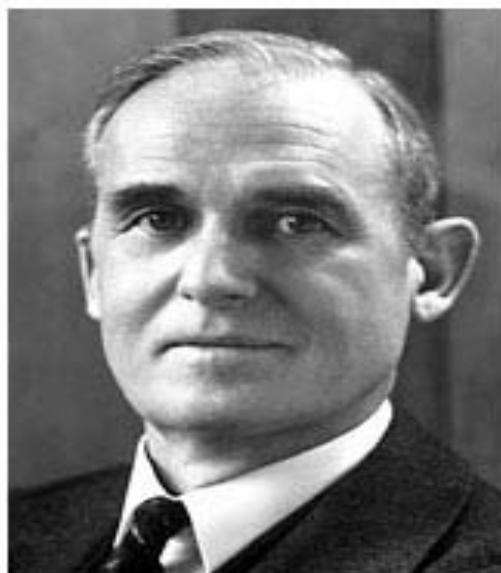
Free Brownian particle





## 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  
Giaque**

USA

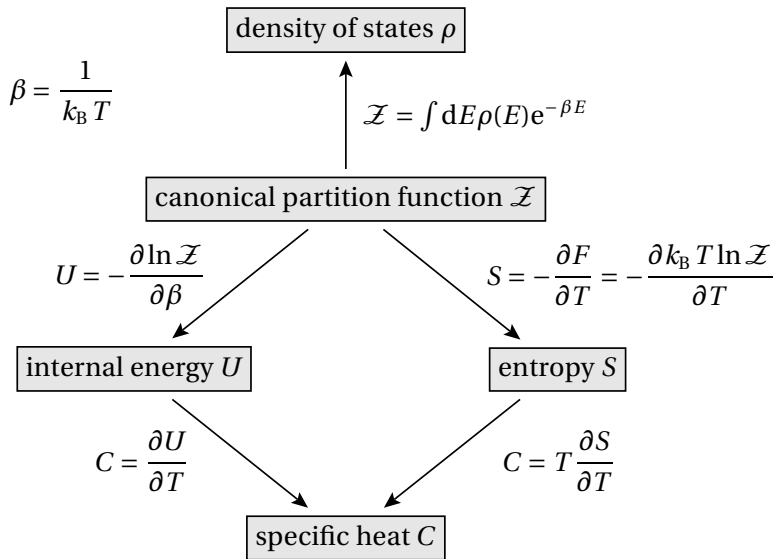
University of California  
Berkeley, CA, USA

b. 1895  
d. 1982

# A bit of thermodynamics



Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law



Specific heat and  
dissipation

Two approaches  
Microscopic model

Route I

Route II  
specific heat  
density of states

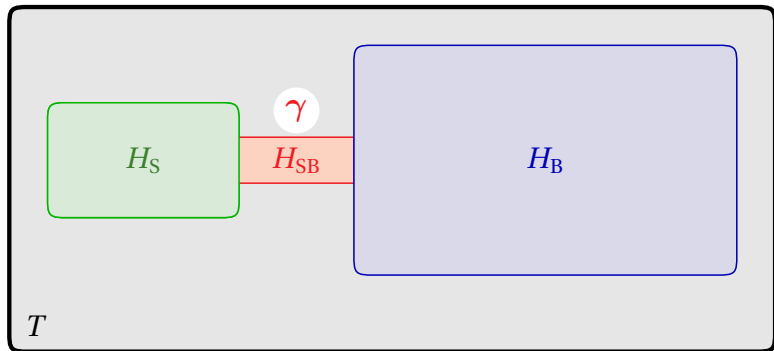
Conclusions



# The problem



Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law



Specific heat and  
dissipation

Two approaches  
Microscopic model

Route I

Route II  
specific heat  
density of states

Conclusions

What is the specific heat of a damped system?



# Specific heat from the system energy



Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

Specific heat and  
dissipation

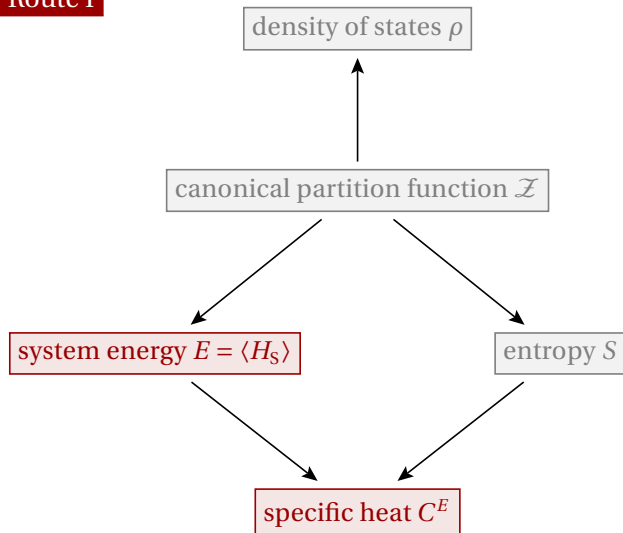
Two approaches  
Microscopic model

Route I

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specific heat  
density of states

Conclusions

Route I





# Specific heat from the partition function



Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

Specific heat and  
dissipation

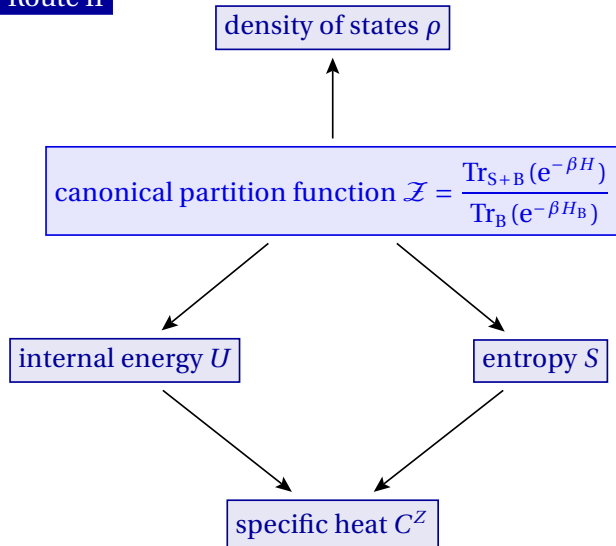
Two approaches  
Microscopic model

Route I

Route II  
specific heat  
density of states

Conclusions

Route II





Thermodynamic argument:

$$\mathcal{Z} = \frac{\text{Tr}_{S+B}(e^{-\beta H})}{\text{Tr}_B(e^{-\beta H_B})} \longrightarrow F_S = F - F_B^0$$

$F$  total system free energy

$F_B$  bare bath free energy

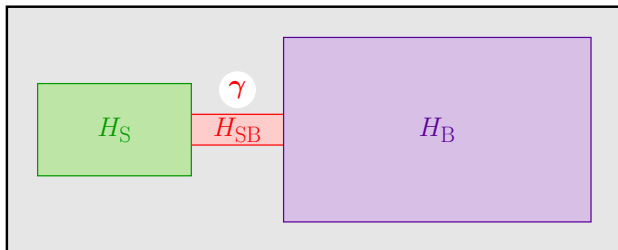
With this form of free energy the three laws of thermodynamics are fulfilled.

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



Third Law

Harmonic oscillator

Dissipative systems

Harmonic oscillator

Free Brownian particle

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

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



# An important difference



Route I

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

Route II

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

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

For finite coupling  $E$  and  $U$  differ!

Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

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Route II

specific heat  
density of states

Conclusions





# Entropy of the damped harmonic oscillator



Third Law

Harmonic oscillator

Dissipative systems

Harmonic oscillator

Free Brownian particle

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

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

leading low-temperature behavior

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

third Law is satisfied ✓



# The concept of a partition function...



...for dissipative quantum systems

$$Z = \frac{\text{Tr} [\exp(-\beta H)]}{\text{Tr}_B [\exp(-\beta H_B)]}$$

harmonic oscillator

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

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

Third Law

Harmonic oscillator

Dissipative systems

Harmonic oscillator

Free Brownian particle



# The fundamental relation



Third Law

Harmonic oscillator

Dissipative systems

Harmonic oscillator

Free Brownian particle

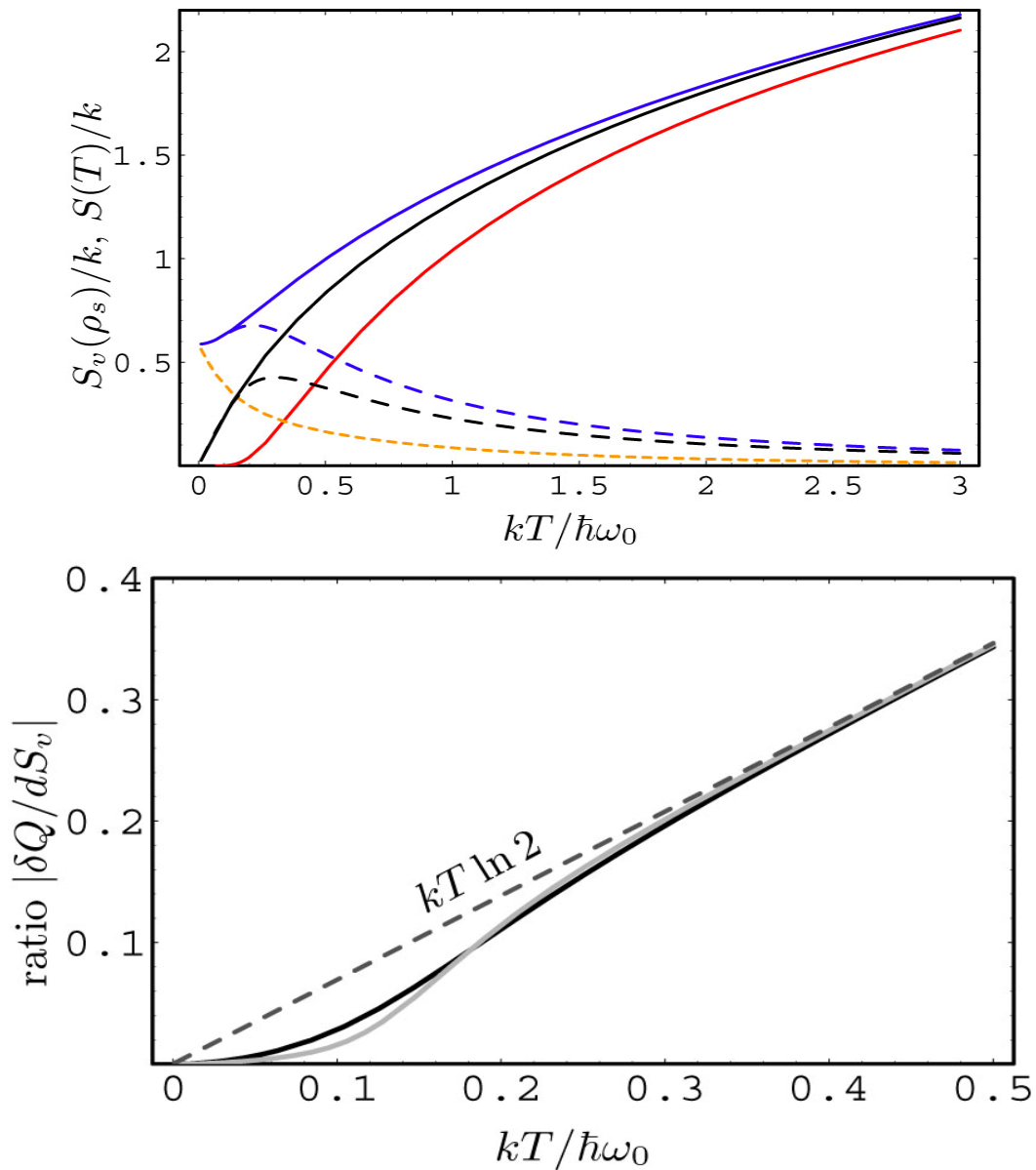
$$\langle E \rangle_Z = -\frac{\partial}{\partial \beta} \ln(Z) = \frac{1}{\beta} \left[ 1 + \sum_{n=1}^{\infty} \frac{2\omega_0^2 + \nu_n \hat{\gamma}(\nu_n) - \nu_n^2 \hat{\gamma}'(\nu_n)}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n) + \omega_0^2} \right]$$
$$\stackrel{?}{=} \frac{1}{\beta} \left[ 1 + \sum_{n=1}^{\infty}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

in general: NO

$$\begin{aligned} \langle E \rangle_Z &= \langle H \rangle - \langle H_B \rangle_B \\ &= \langle E \rangle + [\langle H_{SB} \rangle + \langle H_B \rangle - \langle H_B \rangle_B] \\ &\quad \parallel \\ &\quad \langle H_S \rangle \\ &\neq \langle H_S \rangle \end{aligned}$$



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



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

$$\gamma(t) = \gamma\omega_D e^{-\omega_D t}$$

Quantum Langevin equation

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

equivalent equations of motion

$$\dot{q} = v$$

$$\dot{v} = z$$

$$\dot{z} = -\omega_D z - \gamma\omega_D v$$

oscillations occur for  $\omega_D < 4\gamma$



Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

Specific heat and  
dissipation

Two approaches

Microscopic model

Route I

Route II

specific heat

density of states

Conclusions



# Model for a damped free particle

## Hamiltonian

$$\begin{aligned} H &= H_S + H_B + H_{SB} \\ &= \frac{p^2}{2M} + \sum_{n=1}^{\infty} \left( \frac{p_n^2}{2m_n} + \frac{m_n}{2} \omega_n^2 x_n^2 \right) + \sum_{n=1}^{\infty} \left( -c_n x_n q + \frac{c_n^2}{2m_n \omega_n^2} q^2 \right) \end{aligned}$$

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

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

▶ damping kernel and noise



Quantum  
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# Damping kernel and noise



## damping kernel

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

## noise operator

$$\begin{aligned}\xi(t) &= -M\gamma(t-t_0)q(t_0) + \sum_{n=1}^{\infty} \left[ c_n x_n(t_0) \cos(\omega_n(t-t_0)) \right. \\ &\quad \left. + \frac{c_n}{m_n \omega_n} p_n(t_0) \sin(\omega_n(t-t_0)) \right] \\ &= -M\gamma(t-t_0)q(t_0) + \sum_{n=1}^{\infty} \left[ m_n \omega_n^2 x_n(t_0) \cos(\omega_n(t-t_0)) \right. \\ &\quad \left. + \omega_n p_n(t_0) \sin(\omega_n(t-t_0)) \right]\end{aligned}$$

Quantum  
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▶ return



# A gas of free Brownian particles



energy

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

specific heat

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

▶ return

Third Law

Harmonic oscillator

Dissipative systems

Harmonic oscillator

Free Brownian particle

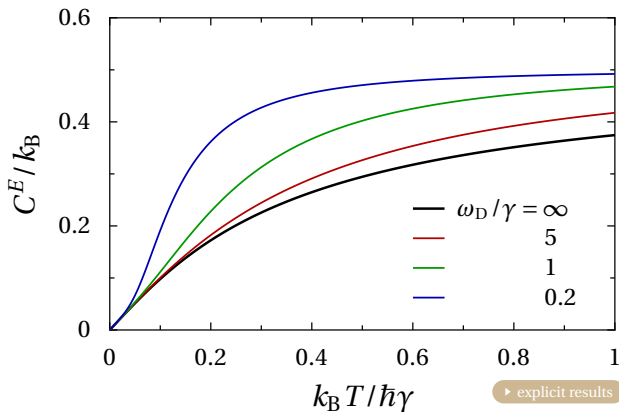




# Specific heat of a damped free particle



## Route I



- $T \rightarrow \infty$ : classical value  $k_B/2$   
damping constant  $\gamma$  sets the temperature scale
- coupling to the environment ensures 3<sup>rd</sup> law
- less damping makes the system more classical

Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

Specific heat and  
dissipation

Two approaches  
Microscopic model

Route I

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specific heat  
density of states

Conclusions



# Specific heat from system energy



Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

$$\frac{C^E}{k_B} = \frac{x_1 x_2}{x_1 - x_2} [x_2 \psi'(x_2) - x_1 \psi'(x_1)] - \frac{1}{2}$$

with

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

high-temperature expansion

$$\frac{C^E}{k_B} = \frac{1}{2} - \frac{\hbar^2 \gamma \omega_D}{24(k_B T)^2} + O(T^{-3})$$

low-temperature expansion

$$\frac{C^E}{k_B} = \frac{\pi}{3} \frac{k_B T}{\hbar \gamma} - \frac{4\pi^3}{15} \left( \frac{k_B T}{\hbar \gamma} \right)^3 \left( 1 - 2 \frac{\gamma}{\omega_D} \right) + O(T^5)$$

Specific heat and  
dissipation

Two approaches  
Microscopic model

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specific heat  
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Conclusions

▶ 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

$$\begin{aligned} U &= \frac{1}{2\beta} \left[ 1 + 2 \sum_{n=1}^{\infty} \frac{\hat{\gamma}(\nu_n) - \nu_n \hat{\gamma}'(\nu_n)}{\nu_n + \hat{\gamma}(\nu_n)} \right] \\ &= \frac{\hbar\omega_D}{2\pi} \psi \left( \frac{\hbar\beta\omega_D}{2\pi} \right) - \frac{x_+}{\beta} \psi(x_+) - \frac{x_-}{\beta} \psi(x_-) - \frac{1}{2\beta} \end{aligned}$$

Third Law

Harmonic oscillator

Dissipative systems

Harmonic oscillator

Free Brownian particle



# Specific heat from partition function

$$\frac{C^Z}{k_B} = x_1^2 \psi'(x_1) + x_2^2 \psi'(x_2) - \left( \frac{\hbar\beta\omega_D}{2\pi} \right)^2 \psi' \left( \frac{\hbar\beta\omega_D}{2\pi} \right) - \frac{1}{2}$$

with

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

## high-temperature expansion

$$\frac{C^Z}{k_B} = \frac{1}{2} - \frac{\hbar^2 \gamma \omega_D}{12(k_B T)^2} + O(T^{-3})$$

## low-temperature expansion

$$\frac{C^Z}{k_B} = \frac{\pi}{3} \frac{k_B T}{\hbar\gamma} \left( 1 - \frac{\gamma}{\omega_D} \right) - \frac{4\pi^3}{15} \left( \frac{k_B T}{\hbar\gamma} \right)^3 \left[ 1 - 3 \frac{\gamma}{\omega_D} - \left( \frac{\gamma}{\omega_D} \right)^3 \right] + O(T^5)$$



Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

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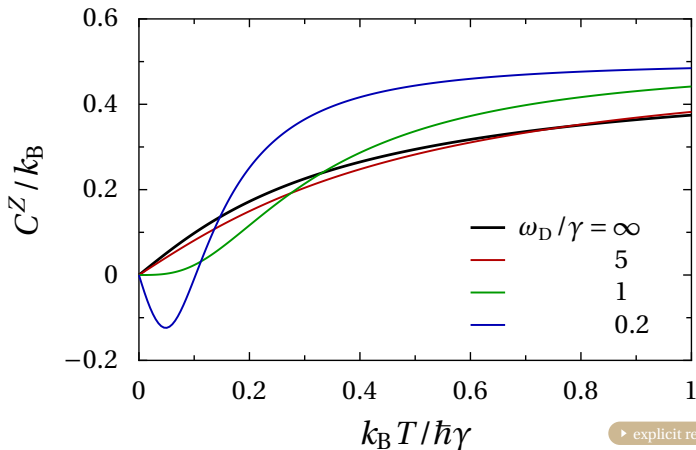


# Specific heat of a damped free particle



## Route II

► partition function



► explicit results

**The specific heat can be negative!?**

Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

Specific heat and  
dissipation

Two approaches  
Microscopic model

Route I

Route II

specific heat  
density of states

Conclusions





# Origin of a negative density of states



Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

a simple model:

- system
- one single bath oscillator with frequency  $\omega$
- ⇒ total system with eigenenergies  $E_n$  and degeneracies  $g_n$

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

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

▶ return

Specific heat and  
dissipation

Two approaches  
Microscopic model

Route I

Route II  
specific heat  
density of states

Conclusions



# Density of states of a damped free particle



Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

Specific heat and  
dissipation

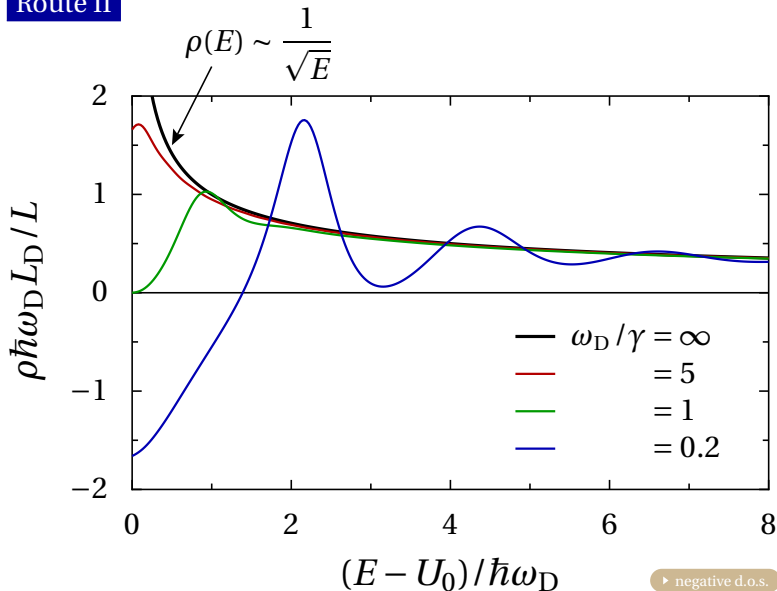
Two approaches  
Microscopic model

Route I

Route II  
specific heat  
density of states

Conclusions

Route II



# Strong coupling: Example

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

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

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

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

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

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

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

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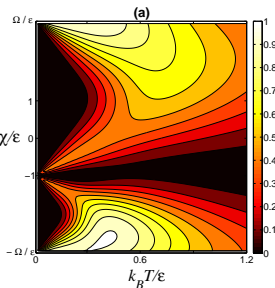
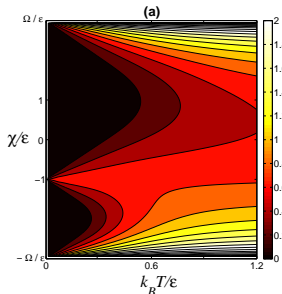
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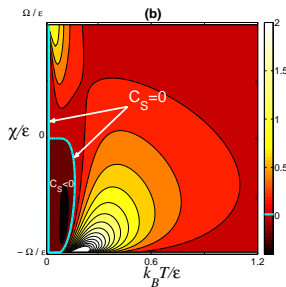
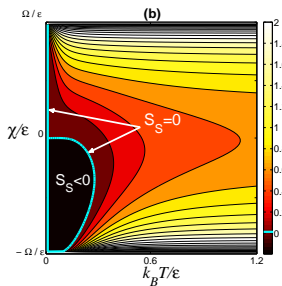
# Entropy and specific heat

Fluctuation  
Theorem for  
Arbitrary  
Open  
Quantum  
Systems

Peter Hänggi,  
Michele  
Campisi, and  
Peter Talkner



$$\Omega/\epsilon = 3$$



$$\Omega/\epsilon = 1/3$$



# 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

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Phys. Rev. E **80**, 041113 (2009)



Quantum  
Brownian  
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# Low temperature behaviour of the specific heat



## Route II

### Free damped particle

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

### Damped harmonic oscillator

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

for the damped harmonic oscillator the specific heat is always positive

Quantum  
Brownian  
motion and  
the 3<sup>rd</sup> law

Specific heat and  
dissipation

Two approaches  
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Route II

specific heat  
density of states

Conclusions





# **HOMEPAGE „HANGGI“**

**GO TO : [FEATURE ARTICLES](#)**

- **Quantum Dissipation  
and  
Quantum Transport**

**[http://www.physik.uni-augsburg.de/  
theo1/hanggi/Quantum.html](http://www.physik.uni-augsburg.de/theo1/hanggi/Quantum.html)**

# DRIVEN - TUNNELING - ZOO



SUPPR. vs. ENH.



CDT



CHAOS-ASSISTED

EHG



QSR



COHERENT

TUNNELING CONTROL

- DRIVING ( $\Omega, A, \dots$ )
- BATH SPECTRUM
- NOISE INPUT



# Quantum Dissipation: A Primer

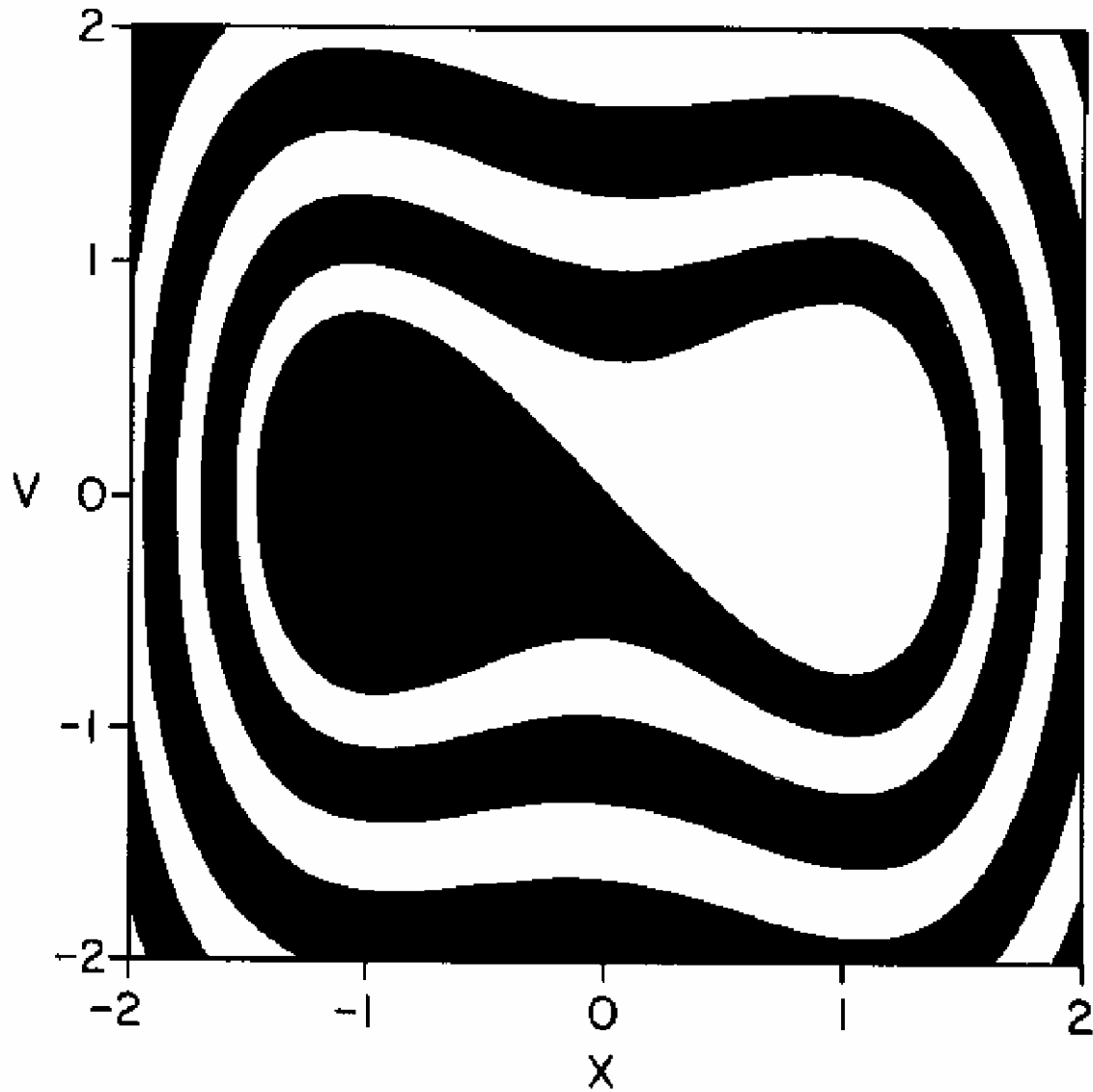
*P. Hänggi*

*Institut für Physik  
Universität Augsburg*





# NOISE-INDUCED ESCAPE



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

RMP 62: 251 (90)

# Reaction-rate theory: fifty years after Kramers

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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.

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