Quantum Dissipation: A Primer

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Dynamics of Open Quantum Systems

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QUANTUM DISSIPATION

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

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

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

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

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

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

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

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

\[ \Rightarrow \quad [m_0 \ddot{x} + m_0 \gamma \dot{x} + m_0 \omega_0^2 x] = 0 \]

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

\[ [q_1, p] = +i \frac{\hbar}{\gamma} e^{-\gamma t} \]
THE PROBLEM

potential

\[ M \ddot{q} + \frac{dU}{dx} + \eta \dot{q} = 0 \]
\[ \Gamma = \pi \frac{\omega_0}{2 \hbar} \exp(-\frac{E_b}{kT}) \]

thermal equilibrium

P.H., P. TALKNER, M. BORKOVEC
REV. MOD. PHYS. 62: 251 (1990)
**F A C T S**

H on (110) tungsten

[**GOMER**(82)]

$D$ (cm$^2$/sec)

1000/T (K$^{-1}$)

10$^{-11}$

10$^{-12}$

10$^{-13}$

10$^{-14}$

10$^{-15}$

10$^{-16}$

H$_2$ & HD sorbed in
Zeolites

[Bouchard et al. 82]

$H^2p^2(...)$

$+e$

$T^{-1}$

$T = 18$ mK

CO-MIGRATION
IN HEMOGLOBIN

[Frauenfelder]

TUNNELING IN A JOSEPHSON
JUNCTION SUBJECTED
TO MEMORY FRICTION

[Esteve et al. (79)]
<table>
<thead>
<tr>
<th>Quantum Tunneling</th>
<th>Cross-over</th>
<th>Quantum Corrections</th>
<th>thermal activation</th>
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</thead>
<tbody>
<tr>
<td>( k = A e^{-B} )</td>
<td>2-0-modes</td>
<td>( k = T ) ( A )</td>
<td>( k = A(\eta) e^{-E_0/\delta T} )</td>
</tr>
<tr>
<td>( B = S_B(T, y) )</td>
<td>( \frac{S_B}{\hbar} = \frac{E_0}{kT_0} )</td>
<td>quantum enhancement</td>
<td>( \uparrow \eta = \frac{\eta}{\eta} )</td>
</tr>
<tr>
<td>( B(T=0) \approx B(0) \approx -aT^2 )</td>
<td>smooth!</td>
<td>( Q \sim \exp \frac{\hbar^2(\omega_0^2+\omega_b^2)}{(kT)^2} )</td>
<td>Kramers</td>
</tr>
<tr>
<td>( A(T,y) = A(y) )</td>
<td>Erfc-behavior</td>
<td>( &gt; 1 )</td>
<td>( { \frac{2}{\pi} \left( \frac{\omega}{\omega_0} + \omega_b \right)^2 - \frac{\omega}{\omega_0} } )</td>
</tr>
<tr>
<td>( \propto \propto )</td>
<td></td>
<td>i.e.</td>
<td>( \omega_0 )</td>
</tr>
<tr>
<td>( \propto \propto (1 + 2.20 y), y \to 0 )</td>
<td></td>
<td>( E_0 \to E_0 - \frac{E}{T} )</td>
<td>( \frac{\omega_0}{2\pi} )</td>
</tr>
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Reaction-rate theory: fifty years after Kramers

Peter Hänggi, Peter Talkner, Michal Borkovec

RMP 62: 251 (90)
VIII. Transition Rates in Nonequilibrium Systems

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   1. Nucleation of a single string
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C. The crossover temperature

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   2. Quantum turnover

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X. Numerical Methods in Rate Theory

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Acknowledgments

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References

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 \( (A) \)
\( \mathcal{H} \) Hamiltonian function of the metastable system
\( \mathcal{J} \) complex-valued free energy of a metastable state
\( \mathcal{L}, \mathcal{L}^\dagger \) Fokker-Planck operator, backward operator of a Fokker-Planck process
\( j \) total probability flux of the reaction coordinate
\( h \) Planck's constant
\( h_\hbar \) \( h/(2\pi)^{-1} \)
\( k_B \) Boltzmann constant
\( k \) reaction rate
\( k^+ \) forward rate
\( k^- \) backward rate
\( k_{TST} \) microcanonical transition-state rate, semiclassical cumulative reaction probability
\( k_s \) mass of the semi-classical cumulative reaction probability
\( m_i \) 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 \( \Omega \), 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
\( x_{0\Omega} x_a \) location of well minimum or potential minimum of state \( A \), respectively
\( x_h \) barrier location
\( x_T \) location of the transition state
\( \beta \) inverse temperature \( (k_B T)^{-1} \)
microscopic approach

\[ H_{\text{total}} = \frac{1}{2} M \dot{q}^2 + U(q) \]

system

\[ + \frac{1}{2} \sum_{\alpha} m_\alpha \dot{q}_\alpha^2 + \sum_{\alpha} m_\alpha \omega_\alpha^2 q_\alpha^2 \]

(harmonic) bath

\[ + q \sum_{\alpha} c_\alpha q_\alpha \]

linear coupling

\[ + q^2 \sum_{\alpha} \frac{c^2_\alpha}{2m_\alpha \omega_\alpha^2} \]

compensation of frequency shift

- path integral approach
to density matrix at temperature \( T \)
trace out environment
dissipation

\[ H^T = H_{\text{system}} + H_{\text{bath}} + H_{\text{Int}} \]

\[ \dot{q} = -\frac{1}{M} \frac{\delta U}{\delta q} - \int_0^t y(t-s) \dot{q}(s) \, ds \]

\[ S_E = S_{\text{rev. motion}} + S_{\text{(nonlocal) dissipation}} \]
QUANTUM NOISE
QUANTUM L.-EQ.

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

\[ \downarrow \text{DECOHERENCE} \]
\[ \text{AT } T = 0 \]

\[ H_{S+B} = H_S + H_{S-B} + H_B \]
\[ = \frac{p^2}{2m} + V(x) + \sum_x \left( \frac{p_x^2}{2m_x} + \frac{m_x c_s^2}{2} (q_x - \frac{c_s}{m_x c_s^2} x)^2 \right) \]

\[ \downarrow \quad S_S \neq 2^{-1} \exp \left( - \frac{H_S}{\hbar T} \right) ! \]

\[ S_{\text{Total}} = S_{S+B} = 2^{-1} \exp \left( - \frac{H_{S+B}}{\hbar T} \right) \]
\[ \dot{\mathbf{x}}(t) = [0, \mathbf{H}_T] \]

\[ m \ddot{x} + m \int_0^t ds y(t-s) \dot{x}(s) + \frac{\partial V(x)}{\partial x} = \eta(t) - m y(t-0) \dot{x}(0) \]

**Initial Slip**

\[ y(t-s) = \frac{1}{m} \sum_a \frac{c_a^2}{m_a c_a^2} \cos(\omega_a(t-s)) \]

\[ = y(s-t) \downarrow \]

\[ \eta(t) = \sum_a c_a \left[ q_a(0) \cos(\omega_a t) + \frac{\mu_a}{m_a c_a} \sin(\omega_a t) \right] \]
\[ [\eta^+, \eta^0] = -i \hbar \sum c_{e_\mu} \frac{s_{\mu e_\mu}}{m_{\eta^+}} \sin(\theta_{e_\mu} (t-s)) \neq 0 \]

\[ S_B = 2^{-1} \exp \left\{ -\beta \left[ \frac{1}{2} \left( \frac{\not\! p^2}{2m_e} + \frac{m_e^2}{2} \right) + \not\! q^2 \right] \right\} \]

\[ \langle \eta^+ \rangle \leq 0 \]

\[ \frac{1}{2} \langle \eta^+ \eta^0 + \eta^0 \eta^+ \rangle = C(t-s) \]

\[ C(\tau) = \frac{1}{2} \sum \frac{c_{e_\mu}}{m_{\eta^+}} \coth \left( \frac{\hbar c_{e_\mu}}{2kT} \right) \cos \theta_{e_\mu} \]

\[ \hbar T \gg \hbar c_{e_\mu} \]

\[ \rightarrow kT \gamma(\tau) \]
\[ \hat{\delta}(z) = \int_0^\infty \exp(-zt)j(t)dt \]

\[ \delta(\omega) = \hat{\delta}(z = -i\omega) \]

**Ohmic Dissipation**

\[ j(\omega) = \gamma \omega \exp(-\omega/\omega_c) \]

**Kondo-Parameter**

\[ \gamma = (2\pi \hbar / a^2) \times \omega \exp(-\omega/\omega_c) \]

\[ a = 2q_a : \text{tunneling length} \]
1. QLE OPERATES IN FULL HILBERT SPACE OF $S \oplus B$

$$\tilde{\phi}(\tau) = \sum_{n=0}^{\infty} \frac{1}{2m} \sum_{\alpha} \frac{\epsilon_{\alpha}^2}{m_{\alpha} c_{\alpha}^2} \left[ \frac{1}{2c_{\alpha}} + \frac{1}{2c_{\alpha}} \right]$$

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

$$\text{Re}_{\tau}(\tau = \omega + i0^+) = \frac{\pi}{2m} \sum_{\alpha} \frac{\epsilon_{\alpha}^2}{m_{\alpha} c_{\alpha}^2} \left[ d(\omega - c_{\alpha}) + d(\omega + c_{\alpha}) \right]$$

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

3. with $\tilde{\Phi}(t) = \Phi(t) - m \gamma(t) \times \Phi(0)$

$$\tilde{S}_B = 2^{-1} \exp(-\beta \left[ \frac{\epsilon_{\alpha}^2}{2m_{\alpha}} + \frac{m_{\alpha} c_{\alpha}^2}{2} (\vec{x} - \frac{\epsilon_{\alpha}^2}{m_{\alpha} c_{\alpha}^2} \vec{x}) \right]$$

$$\langle \Phi(t) \Phi(0) + \Phi(0) \Phi(t) \rangle = C(\tau)$$
4. DEPHASING AT $T = 0$?

$\langle x(t) \delta(t) \rangle_\beta \neq 0$

$\langle H_{\text{INT}} \rangle_\beta \neq 0$

5. $\delta(t) \rightarrow C$-NOISE $\delta(t)$

WITH CORRELATION $C(\tau)$

IS INCONSISTENT
\[ \hat{H}(t) = \hat{H}_0 - F(t)\hat{A} \]
\[ s = Z^{-1} \exp(-\beta \hat{H}_0) \]
\[ \langle \hat{B}(t) \rangle - \langle \hat{B}(t) \rangle_0 = \langle \delta \hat{B}(t) \rangle = \int_{t_0}^{t} \chi(t-s) F(s) ds \]

**Kubo:**
\[ \chi_{BA}(\tau) = \Theta(\tau) \frac{i}{\hbar} \left\langle [\hat{B}(\tau), \hat{A}(0)] \right\rangle_\beta \]
\[ = -\Theta(\tau) \int_0^{\beta} \left\langle \hat{A}(-i\hbar \lambda) \hat{B}(\tau) \right\rangle d\lambda \]

*classical limit*  
\[ \rightarrow -\Theta(\tau) \beta \left\langle \hat{B}(t) \hat{A}(0) \right\rangle \]
\[ \hat{H}(t) = \hat{H}_0 - F(t) \hat{A} \; ; \; g_\beta = Z^{-1} \exp(-\beta \hat{H}_0) \]

\[ \langle \hat{B}(t) \rangle - \langle \hat{B}(t) \rangle = \langle \delta \hat{B}(t) \rangle = \int_{t_0}^{t} \chi(t-s) F(s) ds \]

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

\[ = -\Theta(\tau) \int_{0}^{\tau} \langle \hat{A}(-i\hbar \lambda) \hat{B}(\lambda) \rangle d\lambda \]

classical limit \[ \rightarrow -\Theta(\tau) \beta \langle \hat{B}(\tau) \hat{A}(0) \rangle \]

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

\[ \langle \delta q(t) \rangle = P_1 e^{-i\Omega t} + P_1 e^{-i\Omega t} \]

\[ P_{1-1} = \frac{A}{2} e^{\pm i\Omega t} \chi(\pm \Omega) \]
QUANTUM - FDT

\[ S_{BA}(\tau) = \frac{1}{2} \langle (\hat{B}(t) - \langle \hat{B} \rangle_\beta) (\hat{A}(0) - \langle \hat{A} \rangle_\beta) \rangle + \langle (\hat{A}(0) - \langle \hat{A} \rangle_\beta) (\hat{B}(t) - \langle \hat{B} \rangle_\beta) \rangle_\beta \]

\[ x'_{BA}(\tau) = x'_{BA}(\tau) + i x''_{BA}(\tau) \]
\[ \frac{1}{2} [ x_{BA}^+(t) + x_{BA}^-(t^-) ] - \frac{i}{2} [ x_{BA}^+(t) - x_{BA}^-(t^-) ] \]

\[ x_{BA}(\omega) = \sum_{-\infty}^{\infty} x_{BA}(t) e^{i \omega t} dt \]

\[ x''_{BA}(\omega) = \frac{1}{\hbar} \tanh (\hbar \omega \beta / 2) S_{BA}(\omega) \]

\[ S_{BA}(\omega) = \hbar \coth (\hbar \omega \beta / 2) x''_{BA}(\omega) \]

\[ \hbar \omega \ll 1 \rightarrow 2 x''_{BA}(\omega) / (\beta S_\hbar) \]

**NOTE:** \[ x''_{BA}(\omega) = \frac{1}{2} [ x^*_{AB}(\omega) - x_{BA}(\omega) ] \]

\[ \neq \text{Im } x_{BA}(\omega), \text{ except } \lambda = \beta \]

\[ \hat{A} = \hat{B} = \hat{a}: \quad S_{qq}(\omega) = \hbar \coth (\hbar \omega \beta / 2) \text{Im } x_{qq}(\omega) \]
**EQ.-CURRENT NOISE**

\[ I = \frac{dI}{dt} \]

\[ \chi_{AA}^{ii}(\omega) = \frac{1}{\omega} \text{Im} \left( \frac{Z(\omega)}{i} \right) = -\frac{1}{\omega} \text{Re} Z(\omega) \]

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

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

---

\[ kT \gg \hbar \omega : S_{II}(\omega) \rightarrow 2kT \text{Re} Z(\omega) \]

\[ \frac{2kT}{R} \]

**JOHNSON-NYQUIST (1928)**

\[ kT < \hbar \omega \rightarrow \hbar \omega \text{ Re} Z(\omega) \]

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

quantum-zero point fluct.
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.

FEYNMAN-PATH-INT.

QUANTUM LANG.-EQ.

GME

STOCH.-L.-V.N.-EQ.

\[ s := 14 \langle 1 \vert \langle 12 \vert s \rangle \langle 12 \vert s \rangle \langle 1 \vert \], \quad \mu := \frac{2}{\hbar} \int dt \langle 12, \chi\rangle \langle \chi, 12 \rangle \]

\[ i \hbar \dot{s} = [H_{\text{in}}, s] + \frac{\hbar}{2} \left[ x, \langle 12, \chi \rangle \right] - \frac{1}{2} \nabla (\langle 12, \chi \rangle \left[ x, \langle 12, \chi \rangle \right] + \text{complex valued noise}) \]

\[ \langle 1 \vert 1 \rangle = 2, \quad \langle 12 \vert 12 \rangle = \frac{2}{\hbar} \theta (12) \text{Im} (12) \quad \langle 1 \vert 2 \rangle = 0 \]
PITFALLS

**MARKOV MASTER EQ**

\[
\frac{d}{dt} \rho = -\frac{i}{\hbar} [H, \rho] - \Gamma \rho + I(t)
\]

**BLOCH-REDFIELD**

i.e. **NO DET. BALANCE**

**ROTATING WAVE APPROX.**

(LINDBLAD; DAVIES-APPROX.)

**DET. BALANCE \lor O.K.**

**BUT**

- **WRONG EHRENFEST EQ.**
- **NO FDT**
- **NO KMS-COND.**

\[
\langle \varphi(t) \varphi \rangle = \langle \varphi \varphi(t+\sqrt{t}) \rangle
\]
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.
NOISE-ASSISTED SYNCHRONIZED HOPPING
Bistable Model

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

\[ \langle \xi(t) \rangle = 0 \]

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

\[ T_e = \frac{2\pi}{\Omega} \]

 SIGNAL

 \[ T_e \approx 2T^{-1}_{\text{ESCAPE}} \]
More noise → More signal
P. JUNG + P. H., PHYS. REV. A44: 8032 (91)

More noise $\rightarrow$ more signal

$$\mathcal{M}_1 \sim \chi(\tau) = -\frac{1}{D} \frac{d}{dr} \langle \psi(x(r)) | \psi(0) \rangle$$

$$|\mathcal{M}_1|^2 \propto \frac{1}{D^2} e^{-2\omega U(1)}$$
\[ V_0 \gg \hbar \omega_0 \gg \hbar \epsilon_0, kT \]

\[ \omega_0 \quad -\frac{\hbar}{2} \left( \epsilon_0 \sigma_2 + \Delta \sigma_1 \right) \]

\[ \frac{1}{2} \sum_{\alpha} \left( \frac{p_\alpha^2}{m_\alpha} + m_\alpha \omega_\alpha^2 x_\alpha^2 - c_\alpha x_\alpha \sigma_2 \right) \]

\[ \frac{\hbar \hat{\epsilon}}{2} \cos (\Omega t) \sigma_2 \]

\[ \text{Temperature} \]

\[ n \cdot \vec{v} = \hat{\epsilon} \]

\[ t \to \infty \]

\[ \text{DRIVE} \quad \omega, \hat{\epsilon} \]

\[ \text{BATH} \quad T, \sigma \]

\[ \text{TS} \]
\[ \eta = 4\pi |P_1|^2 = \pi A^2 |\chi(\Omega)|^2 \]

\[ \text{SNR} = \frac{\pi A^2 |\chi(\Omega)|^2}{S_{\theta\theta}(\Omega, A=0)} = \frac{\pi A^2 |\chi(\Omega)|^2}{\text{Im} \chi(\Omega) \text{sech}(\hbar \Omega / 2)} \]

- Valid at all temperatures!

**PROBLEM: QUANTUM** \[ \chi_{\theta\theta}^\text{FDT} S_{\theta\theta}(\Omega) \]

\[ S_{\theta\theta}(t) = \frac{1}{2} \langle d\theta(t) d\theta(0) + d\bar{\theta}(0) d\bar{\theta}(t) \rangle_B \]

- **DIFFICULT!**
LINEAR RESPONSE & QSR

with \( P_1 = \frac{A}{2} \chi_{99}(\omega) = \frac{A}{2} \chi(\Omega) \)

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

\[
\text{SNR} = \frac{\pi A^2 |\chi(\Omega)|^2}{S_{99}(\omega, A=0)} = \frac{\pi A^2 |\chi(\Omega)|^2}{\text{Im} \chi(\Omega) \coth(\hbar \beta/2)}
\]

\text{Valid at all temperatures!}

**PROBLEM:** QUANTUM \( \chi_{99}(\omega) \) vs. \( S_{99}(\omega) \)

\[
S_{99}(\tau) = \frac{1}{2} \langle \delta q(\tau) \delta q(0) + \delta q(0) \delta q(\tau) \rangle
\]

\text{DIFFICULT!}

\[\text{2 LIMITS} \]

\text{above ~ near crossover to thermal hopping}

\text{AT LOW T}
\[ \frac{\alpha}{\hbar \omega_b} = 0.2 \]
\[ T = 0 \]

Classically allowed

Classically forbidden

\[ U(q) \]

Thermal activation

Tunnelling

\[ \gamma > 0 \]

\[ M \frac{d^2}{d\tau^2} q_B(\tau) = \frac{\delta U}{\delta q_B} \]

\[ - M \frac{d^2}{d\tau^2} \dot{q}_B(\tau) + \left( \frac{\delta^2 U}{\delta q_B^2} \right) \ddot{q}_B(\tau) = 0 \]
\[-\dot{M} \dot{q}_B + \frac{\partial U(q_B)}{\partial q_B} + \int_{-\frac{\Theta}{2}}^{\frac{\Theta}{2}} k(\tau - \tau') q_B(\tau') d\tau' = 0\]

\[\Theta = \hbar/kT\]

\[q_B(\tau + \Theta) = q_B(\tau)\]
QUANTUM SR

(a) LOW FREQUENCIES
LOW TEMPERATURES
adiabatic quantum coherence

(b) LOW FREQUENCIES
HIGH TEMPERATURES
incoherent regime

(c) $\alpha \ll 1$, $\bar{\epsilon} \neq 0$
HIGH FREQUENCIES
HIGH TEMPERATURES
driving induced coherence
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/
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

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.

Max PLANCK
(1858 - 1947)
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

\[ \beta = \frac{1}{k_B T} \]

\[ \mathcal{Z} = \int dE \rho(E) e^{-\beta E} \]

\[ U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \]

\[ S = -\frac{\partial F}{\partial T} = -\frac{\partial k_B T \ln \mathcal{Z}}{\partial T} \]

\[ C = \frac{\partial U}{\partial T} \]

\[ C = T \frac{\partial S}{\partial T} \]
What is the specific heat of a damped system?
Quantum Brownian motion and the 3rd law

Specific heat and dissipation

Two approaches
Microscopic model

Route I
Route II
specific heat
density of states

Conclusions

Specific heat from the system energy

Route I

density of states $\rho$

canonical partition function $Z$

system energy $E = \langle H_S \rangle$

entropy $S$

specific heat $C^E$

$Z = \int dE \rho(E) e^{-\beta E}$

$U = -\frac{\partial \ln Z}{\partial \beta}$

$S = -\frac{\partial F}{\partial T} = -\frac{\partial k_B T \ln Z}{\partial T}$

$C = \frac{\partial U}{\partial T}$

$C = T \frac{\partial S}{\partial T}$

$\beta = \frac{1}{k_B T}$
Specific heat from the partition function

Route II

density of states $\rho$

canonical partition function $\mathcal{Z} = \frac{\text{Tr}_{S+B}(e^{-\beta H})}{\text{Tr}_{B}(e^{-\beta H_B})}$

internal energy $U$

entropy $S$

specific heat $C^Z$

$\text{Tr}_{S+B}(e^{-\beta H})$

$\text{Tr}_{B}(e^{-\beta H_B})$

$\int dE \rho(E) e^{-\beta E}$

$U = -\frac{\partial \ln Z}{\partial \beta}$

$S = -\frac{\partial F}{\partial T} = -\frac{\partial k_B T \ln Z}{\partial T}$

$C^Z = \frac{\partial U}{\partial T}$

$C^Z = T \frac{\partial S}{\partial T}$

$\beta = \frac{1}{k_B T}$
Free energy of a system strongly coupled to an environment

Thermodynamic argument:

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

\( F \) total system free energy
\( F_B \) bare bath free energy

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

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

\[ \langle O_S \rangle = \frac{\text{Tr} [ O_S \exp(-\beta H)]}{\text{Tr} [ \exp(-\beta H)]} \]
Quantum Brownian motion and the 3rd law

Specific heat and dissipation

Two approaches

Microscopic model

Route I

Route II

An important difference

For finite coupling $E$ and $U$ differ!
Entrophy of the damped harmonic oscillator

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

with \( g(z) = \ln[\Gamma(1 + z)] - z\psi(1 + z) \)

leading low-temperature behavior

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

third Law is satisfied ✔
The concept of a partition function...

...for dissipative quantum systems

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

harmonic oscillator

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

$$\langle E \rangle_Z = -\frac{\partial}{\partial \beta} \ln(Z)$$

$$= \frac{1}{\beta} \left[ 1 + \sum_{n=1}^{\infty} \frac{2\omega_0^2 + \nu_n \gamma(v_n) - v_n^2 \gamma'(v_n)}{v_n^2 + \nu_n \gamma(v_n) + \omega_0^2} \right]$$
The fundamental relation

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

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

in general: NO

\[ \langle E \rangle_Z = \langle H \rangle - \langle H_B \rangle_B \]

\[ = \langle E \rangle + [\langle H_{SB} \rangle + \langle H_B \rangle - \langle H_B \rangle_B] \]

\[ \parallel \]

\[ \langle H_S \rangle \]

\[ \neq \langle H_S \rangle \]
\[ S_{VN} = -k \text{ Tr } (\rho_s \ln \rho_s) \geq S(T) \]


Temperature dependence of the ratio \(|\delta Q/dS_v|\) (in bits) with the heat defined by \(\delta Q = T dS(T)\) for quasi-static variations of the oscillator frequency \(d\omega_0\). The system-bath-couplings are chosen to be \(\gamma = m\omega^2_0/\Gamma = 0.1\) (dark line) and \(\gamma = m\omega^2_0/\Gamma = 0.5\) (gray line). At low T deviations from the Landauer bound \(kT \ln 2\) (dashed line) occur.

\(? \quad |\delta Q/dS_{VN}| \geq kT \ln 2 \quad ?\)
Drude model

damping kernel

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

Quantum Langevin equation

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

equivalent equations of motion

\[ \dot{q} = v \]
\[ \dot{v} = z \]
\[ \dot{z} = -\omega_D z - \gamma \omega_D v \]

oscillations occur for \( \omega_D < 4\gamma \)
Model for a damped free particle

Hamiltonian

\[ H = H_S + H_B + H_{SB} \]

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

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

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

\[
\xi(t) = -M \gamma(t-t_0) q(t_0) + \sum_{n=1}^{\infty} \left[ c_n x_n(t_0) \cos(\omega_n(t-t_0))
\right.
\]

\[
+ \frac{c_n}{m_n \omega_n} p_n(t_0) \sin(\omega_n(t-t_0)) \right]
\]

\[
= -M \gamma(t-t_0) q(t_0) + \sum_{n=1}^{\infty} \left[ m_n \omega_n^2 x_n(t_0) \cos(\omega_n(t-t_0))
\right.
\]

\[
+ \omega_n p_n(t_0) \sin(\omega_n(t-t_0)) \right]
\]
A gas of free Brownian particles

energy

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

specific heat

\[ C^E = \frac{1}{2} + \sum_{n=1}^{\infty} \frac{\gamma^2(v_n) + v_n^2 \gamma'(v_n)}{(v_n + \gamma(v_n))^2} \]
Specific heat of a damped free particle

**Route I**

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

Explicit results

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

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

with

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

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

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

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

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

\[
\frac{C^Z}{k_B} = \frac{\pi}{3} \frac{k_B T}{\hbar \gamma} \left( 1 - \frac{\gamma}{\omega_D} \right) - \frac{4\pi^3}{15} \left( \frac{k_B T}{\hbar \gamma} \right)^3 \left[ 1 - 3 \frac{\gamma}{\omega_D} - \left( \frac{\gamma}{\omega_D} \right)^3 \right] + O(T^5)
\]
Specific heat of a damped free particle

The specific heat can be negative!??
Origin of a negative density of states

a simple model:

• system

• one single bath oscillator with frequency $\omega$

$\Rightarrow$ total system with eigenenergies $E_n$ and degeneracies $g_n$

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

$$\rho(E) = \sum_n g_n \delta(E - E_n + \hbar \omega/2) - \sum_n g_n \delta(E - E_n - \hbar \omega/2)$$
Density of states of a damped free particle

Route II

\[ \rho(E) \sim \frac{1}{\sqrt{E}} \]

\[ \rho(\hbar \omega_D L_D / L) \]

\[ (E - U_0) / \hbar \omega_D \]

\[ \omega_D / \gamma = \infty \]

\[ = 5 \]

\[ = 1 \]

\[ = 0.2 \]

negative d.o.s.
Strong coupling: Example

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

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

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

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

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

\[ Z_S = \text{Tr} e^{-\beta H^*} \quad F_S = -k_b T \ln Z_S \]

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

Strong coupling: Example

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

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

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

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

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

\[ Z_S = \text{Tr} e^{-\beta H^*} \quad F_S = -k_b T \ln Z_S \]

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

Fluctuation Theorem for Arbitrary Open Quantum Systems

Peter Hänggi, Michele Campisi, and Peter Talkner

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”
  \textit{exception:} strict ohmic damping

References:

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
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 (R, A,)
- BATH SPECTRUM
- NOISE INPUT
Quantum Dissipation: A Primer

P. Hänggi

Institut für Physik
Universität Augsburg
NOISE-INDUCED ESCAPE

\[
\text{rate} = A(y) \frac{\omega_0}{2\pi} \exp(-\alpha \Pi/\Gamma)
\]

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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