Doing Small Systems:

concepts, role of ensembles

thermalization & fluctuation theorems

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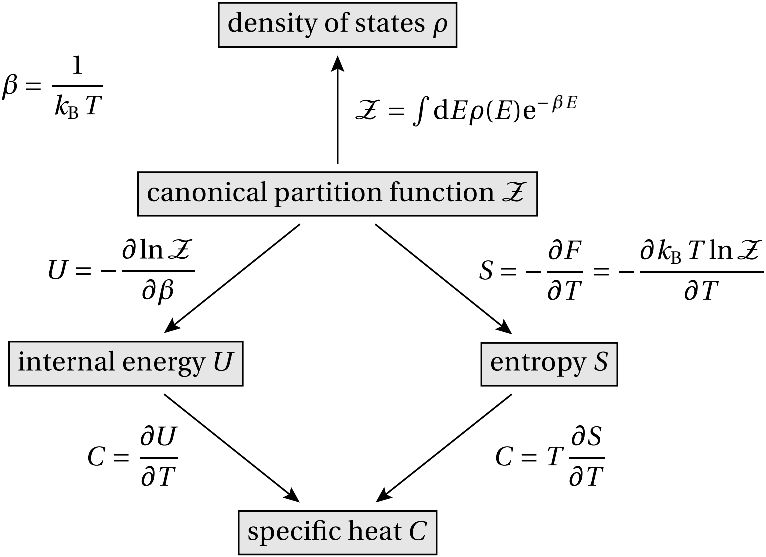
F.-T's:	RMP **83**: 771-791 (2011)
Equilibration:	PRL **106**: 010405 (2011)
Specific heat:	NJP **10**: 115008 (2008); J. Phys. A **42**: 392002 (2009)

A bit of thermodynamics



density of states ρ

$$\mathcal{Z} = \int \mathrm{d}E \rho(E) \mathrm{e}^{-\beta E}$$

$$\beta = \frac{1}{k_\mathrm{B} T}$$

canonical partition function $\mathcal{Z}$

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

$$S = -\frac{\partial F}{\partial T} = -\frac{\partial k_\mathrm{B} T \ln \mathcal{Z}}{\partial T}$$

internal energy U

entropy S

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

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

specific heat C

Four Grand Laws of Thermodynamics

First Law – Energy Conservation

$$\Delta U = \triangle Q + \triangle W$$

ΔU	change in internal energy
$\triangle Q$	heat added on the system
$\triangle W$	work done on the system

H. von Helmholtz: “Über die Erhaltung der Kraft” (1847)

$$\Delta U = (T\Delta S)_{\text{quasi-static}} - (p\Delta V)_{\text{quasi-static}}$$

Thermodynamics of Finite Systems

conventional T.-D.:

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)\,; \quad \text{etc.}$$

Euler-homogenous functions of order “1“

$$\Longrightarrow U = TS - pV + \sum_i \mu_i N_i$$

$$\Longrightarrow G = \sum_i \mu_i N_i$$

Gibbs-Duhem: $$S\mathrm{d}T - V\mathrm{d}p + \sum_i N_i \mathrm{d}\mu_i = 0$$

Finite Size Thermodynamics

Role of density of states:

$$\text{e.g. } G = \mu N + \ldots \underset{\substack{\nearrow \\ \text{surface tension}}}{\sigma} A + \ldots \underset{\substack{\uparrow \\ \text{curvature tension}}}{\lambda} L$$

NOT globally homogeneous

however locally: $\partial G / \partial N = \mu$

Finite Size → important consequences

① Black-Body-Radiation:

$$U_0 = \sigma_{\mathrm{SB}} V T^4$$

- perfectly reflecting walls (lossless cavity): Weyl-problem

$$U(T) = \sum g_i \nu_i \left[\exp\left(h\nu_i / k_{\mathrm{B}} T\right) - 1\right]^{-1}$$

- high T & large volume:

$$U(T) = \sigma_{\mathrm{SB}} V T^4 + \xcancel{0 \cdot T^3} + a_2 V^{1/3} T^2 + a_3 T + a_4 V^{-1/3}$$

Baltes & Hilf (1976)

not OK for $TV^{1/3} \to 0\,!$

② Specific heat of small grains at low T

$$T < T_{\text{Debye}} :$$

$$C_{\text{Debye}} = \text{const.} \cdot T^3 \quad \text{(Dirichlet b.c.)}$$

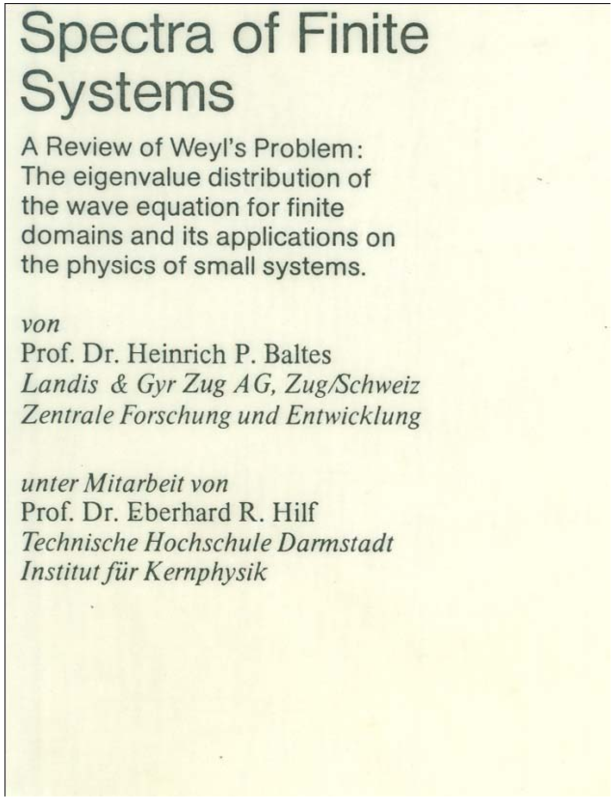
$$C = C_{\text{Debye}} + \ldots \left(\frac{A}{V}\right) T^2 + \ldots \left(\frac{L}{V}\right) T$$

$$\text{OK for } \hbar\omega_1/k_{\text{B}} < T < T_{\text{Debye}}$$

$$\downarrow$$

compare with $C_{\text{electronic}}$

Montroll, Mazo & Onsager, Kubo,
Baltes & Hilf, etc.



Spectra of Finite
Systems

A Review of Weyl's Problem:
The eigenvalue distribution of
the wave equation for finite
domains and its applications on
the physics of small systems.

von
Prof. Dr. Heinrich P. Baltes
Landis & Gyr Zug AG, Zug/Schweiz
Zentrale Forschung und Entwicklung

unter Mitarbeit von
Prof. Dr. Eberhard R. Hilf
Technische Hochschule Darmstadt
Institut für Kernphysik

Ensembles

microcanonical → canonical → grandcanonical

Helmholtz free enery F: $\quad \mathcal{Z} = \exp(-\beta F)$

canonical probability:

$$P(E_\nu) = \exp(\beta F)\, \exp(-\beta E_\nu) \cdot \exp\left\{ -\frac{(U - E_\nu)^2}{2 k_\mathrm{B} T^2 C_\mathrm{bath}} \right\}$$

correction

$S:$ Gibbs-Hertz (1910) ¡ $S = k_\mathrm{B} \ln \Omega(E)$!

$$\Omega(E) = \ldots \int \mathrm{d}\Gamma\, \Theta(E - H(\Gamma))$$

$S:$ Boltzmann $\quad S = k_\mathrm{B} \ln \omega(E)$

$$\omega(E) = \epsilon_\mathrm{scale} \partial \Omega / \partial E$$

$$E = E_1 + E_2$$

$$\Omega(E) = \int \mathrm{d}E_1 \, \Omega_1'(E_1)\Omega_2(E - E_1)$$

$$\ln \Omega(E) \neq \ln \Omega_1(E_1) + \ln \Omega(E_2)$$

not additive !

dito: for

$$\omega(E) = \int \mathrm{d}E_1 \, \omega_1(E_1)\omega_2(E - E_1)$$

additive vs. extensive

H. Touchette, Physica A **305**, 84-88 (2002)

$$x^n \equiv \{x_1, ..., x_n\}$$

Additivity: $Q(x^n) = Q(x^m) + Q(x^{n-m})$, for $m \leq n$

Extensivity: $Q(x^n)/n \longrightarrow$ reaches a constant as $n \to \infty$

additivity $\not\longrightarrow$ extensivity (often - but not always)

extensivity $\not\longrightarrow$ additivity

Q: non-extensive: then typically non-additive (long range forces)

→ rescaling → extensive (Kac's prescription)

Q: non-additive: pseudo-additive if

$$Q(x^n) = \sum \tilde{Q}(x_i)\,, \quad \text{e.g. } T = \sum \frac{p_i^2}{2\,m_{\text{eff}}}$$

Size of Fluctuations

$$x = x_1 + x_2 + ... + x_n$$

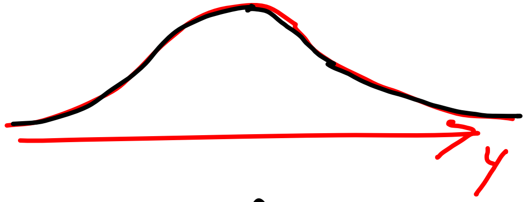
$$\langle x \rangle = \langle x_1 \rangle + \langle x_2 \rangle ... + \langle x_n \rangle$$

$$\sigma = \sigma_1 + \sigma_2 + ... + \sigma_n$$

$$p(x) = p_1 * p_2 * ... * p_n \,; \quad f * g \equiv \int f(x-u) g(u) \mathrm{d}u$$

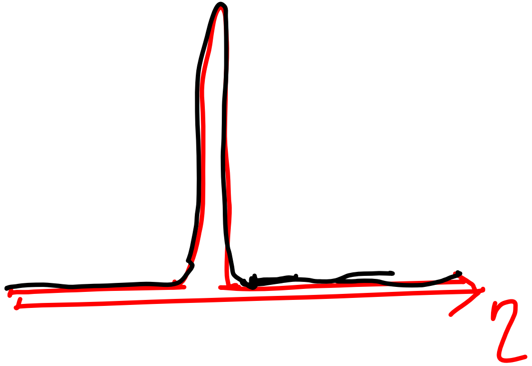
$$\text{(i)} \; y = \frac{x}{\sqrt{n}} \longrightarrow p(y) = (2\pi\bar{\sigma})^{-1/2} \exp\left(-\frac{(y - \langle y \rangle^2}{2\,\bar{\sigma}} \right)$$

$$\bar{\sigma} = \lim_{n\to\infty} \sigma/n$$



$$\text{(ii)} \eta = \frac{x}{n} = O(n^{-1/2})$$

$$\longrightarrow p(\eta) \propto \exp\left(-\frac{(\eta - \langle \eta \rangle^2}{2\,\bar{\sigma}/n} \right)$$



Small system – single realizations

1-st law: $\Delta E_\omega = \triangle Q_\omega + \triangle W_\omega$

! random quantities ¡

$$\langle \ldots \rangle \Rightarrow \Delta U = \triangle Q + \triangle W$$

Note: $\triangle Q = \Delta U - \triangle W$

$\Delta U = ?$ & $\triangle W = ?$

weak coupling: $\triangle Q = -\triangle Q_{\text{bath}}$

2-nd law: $\Delta S^{\text{REV}}_{A\to B} \geq \dfrac{\triangle Q}{T}$

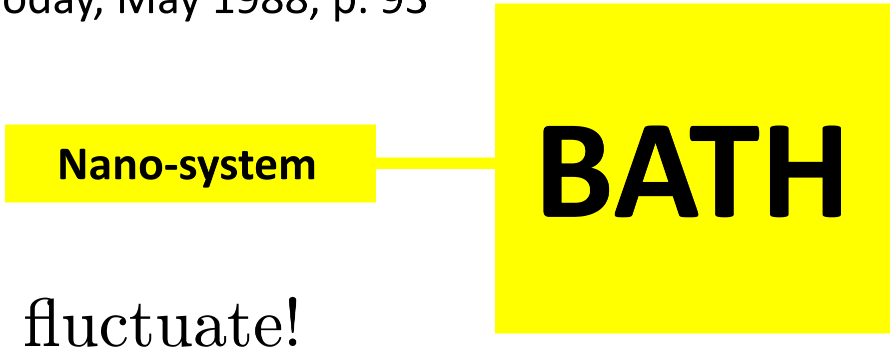
$$\Delta S^{\text{REV}}_{A\to B} = \frac{\triangle Q}{T} + \sum^{\text{IRREV}} (\geq 0)$$

$$= \frac{\Delta U - \triangle W}{T} + \sum^{\text{IRREV}}$$

$$= \frac{-\triangle Q_{\text{bath}}}{T} + \sum^{\text{IRREV}}$$; for weak coupling

Temperature Fluctuations – An Oxymoron

Ch. Kittel, Physics Today, May 1988, p. 93



Nano-system

BATH

$$\beta = \frac{1}{k_\mathrm{B} T}$$

T does NOT fluctuate!

$$|\Delta U|\,|\Delta\beta| = 1 \leftrightarrow |\Delta U|\,|\Delta T| = k_\mathrm{B} T^2 \quad \textbf{NO!}$$

"…Temperature is precisely defined only for a system in thermal equilibrium with a heat bath: The temperature of a system A, however small, is defined as equal to the temperature of a very large heat reservoir B with which the system is in equilibrium and in thermal contact. Thermal contact means that A and B can exchange energy, although insulated from the outer World. …"

DOES T FLUCTUATE ?

I SAY **NO**

$$\left(\frac{\partial S}{\partial E}\right) = \frac{1}{T} \quad ; \quad \langle(\Delta E)^2\rangle = k_B T^2 C$$

$$\left(\frac{\partial^2 S}{\partial E^2}\right) = -\frac{1}{T^2}\left(\frac{dT}{dE}\right) = \frac{-1}{C T^2} \qquad (*)$$

$$\Delta\left(\frac{1}{T}\right)\Delta\left(\frac{1}{T}\right) = -\frac{1}{T^2}(\Delta T) - \frac{1}{T^2}(\Delta T) = \frac{(\Delta T)^2}{T^4} \text{ ; with } (*)$$

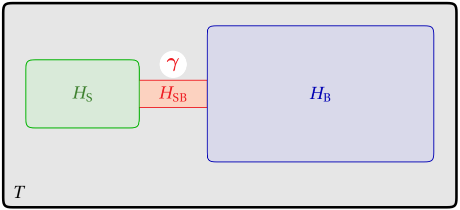
$$= \left(\frac{\partial^2 S}{\partial E^2}\right)\left(\frac{\partial^2 S}{\partial E^2}\right)(\Delta E)^2 = \frac{1}{C^2 T^4} \cdot k_B T^2 C$$

$$\Rightarrow \langle(\Delta T)^2\rangle = \underset{\substack{\downarrow \\ \text{"}(\Delta E)^2\text{"}/C^2}}{\frac{k_B T^2 C}{C^2}} = \boxed{\frac{k_B T^2}{C}}$$

$C\,$"ΔT" = "ΔE"

A 'SYMBOL' FOR "ΔE"'s

Finite bath coupling



The definition of thermodynamic quantities for systems coupled to a bath with finite coupling strength is not unique.

P. Hänggi, GLI, Acta Phys. Pol. B **37**, 1537 (2006)

Effective description of the system

Reduced partition function

$$\mathcal{Z} = \frac{\mathcal{Z}_{\mathrm{S+B}}}{\mathcal{Z}_{\mathrm{B}}} \longrightarrow \ln(\mathcal{Z}) = \ln(\mathcal{Z}_{\mathrm{S+B}}) - \ln(\mathcal{Z}_{\mathrm{B}})$$

This quantity answers questions of the form:
How does a thermodynamic quantity change when the system degree of freedom is coupled to the bath?

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)

An important difference

Route I

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

Route II

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

$$\begin{aligned} \Rightarrow U &= \langle H \rangle - \langle H_{\mathrm{B}} \rangle_{\mathrm{B}} \\ &= E_{\mathrm{S}} + \Big[\langle H_{\mathrm{SB}} \rangle + \boxed{\langle H_{\mathrm{B}} \rangle - \langle H_{\mathrm{B}} \rangle_{\mathrm{B}}} \Big] \end{aligned}$$

For finite coupling E and U differ!

Specific heat of a damped free particle

NJP **10**: 115008 (2008)
Also: J. Phys. A **42**: 392002 (2009)

Free particle made quantum

We need an energy scale

① put particle into a box

② couple the particle to an environment

new energy scale $\hbar\gamma \longrightarrow$ relevant quantity $\dfrac{k_\mathrm{B}T}{\hbar\gamma}$

- zero-temperature limit and zero-damping limit do not commute

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

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

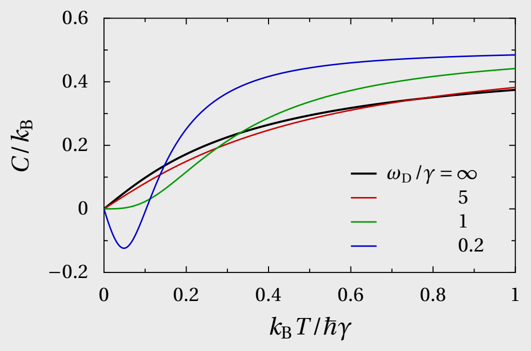
$$\frac{C^Z}{k_\mathrm{B}} = \frac{1}{2} - \frac{\hbar^2\gamma\omega_\mathrm{D}}{12(k_\mathrm{B}T)^2} + \mathrm{O}(T^{-3})$$

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

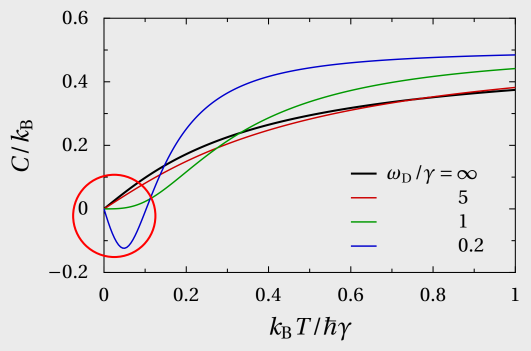


P. Hänggi, GLI, P. Talkner, New J. Phys. **10**, 115008 (2008)

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

$$\hat{\gamma}(z) = \frac{\gamma\omega_D}{z + \omega_D}$$

Specific heat of a damped free particle



P. Hänggi, GLI, P. Talkner, New J. Phys. **10**, 115008 (2008)

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Thermal equilibration between two quantum systems

Peter Hänggi

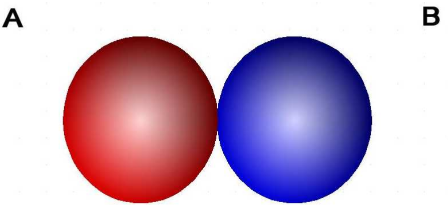
University of Augsburg

A. Ponomarev, S. Denisov, and P. H., PRL **106**, 010405 (2011)

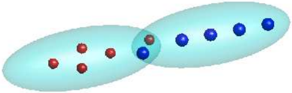
Introduction

OUR SET-UP

(II)



Exact numerical calculations for two different models

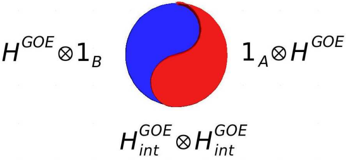


1. Cold atoms in two traps

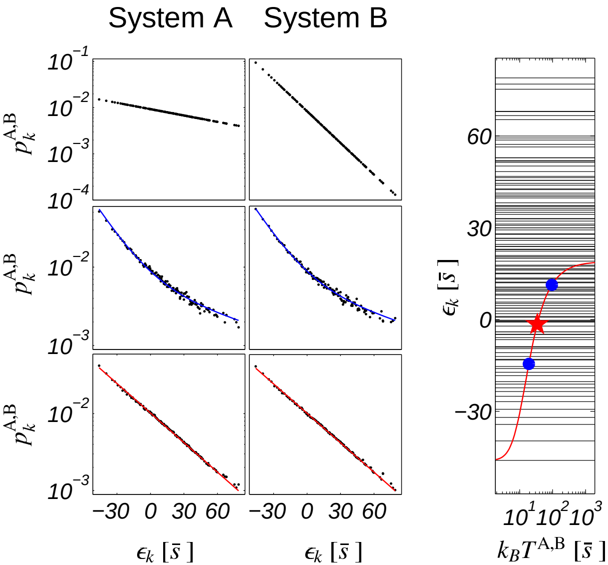
- 2 x Bose-Hubbard Hamiltonian, $N = 5$ (Hilbert space size 15876)
- Contact coupling, $n_{j_\mathrm{A}=L} \otimes n_{j_\mathrm{B}=1}$

2. Random matrix model

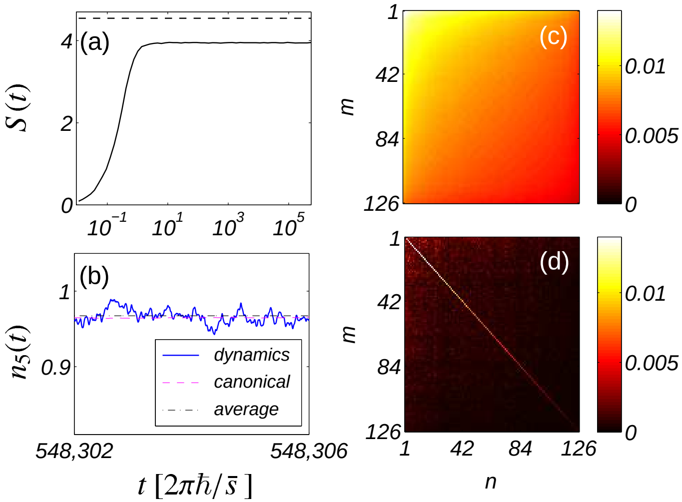
- 2 x Random matrix (RM) GOE Hamiltonian, $\mathcal{N} = 192$ (Hilbert space size 36864)
- $\mathrm{A} \leftrightarrow \mathrm{B}$ invariant RM GOE coupling term, $H^{GOE}\,\mathrm{int} \otimes H^{GOE}_{\mathrm{int}}$



Arithmetic vs. Thermal equilibration (cold atoms)



Typicality and growth of entanglement entropy



Evolution of initially pure state.

Take-Home-Messages:
T.D. of finite systems

- Use Gibbs-Hertz- Entropy

- finite system-bath coupling

partition function: $\mathcal{Z} = \mathcal{Z}_{S+B}/\mathcal{Z}_B$

Then, all Grand Laws of T.D. are obeyed!

- temperature of a nanosystem does not fluctuate

Effective description of the system

Reduced partition function

$$\mathcal{Z} = \frac{\mathcal{Z}_{\mathrm{S+B}}}{\mathcal{Z}_{\mathrm{B}}} \longrightarrow \ln(\mathcal{Z}) = \ln(\mathcal{Z}_{\mathrm{S+B}}) - \ln(\mathcal{Z}_{\mathrm{B}})$$

This quantity answers questions of the form:
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Partition function and internal energy

undamped case

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

with damping

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

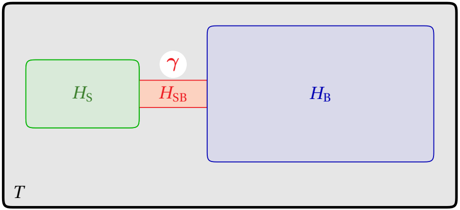
internal energy

▸ compare with energy E

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

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

Finite bath coupling



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P. Hänggi, GLI, Acta Phys. Pol. B **37**, 1537 (2006)

Strong coupling: Example

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

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

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

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

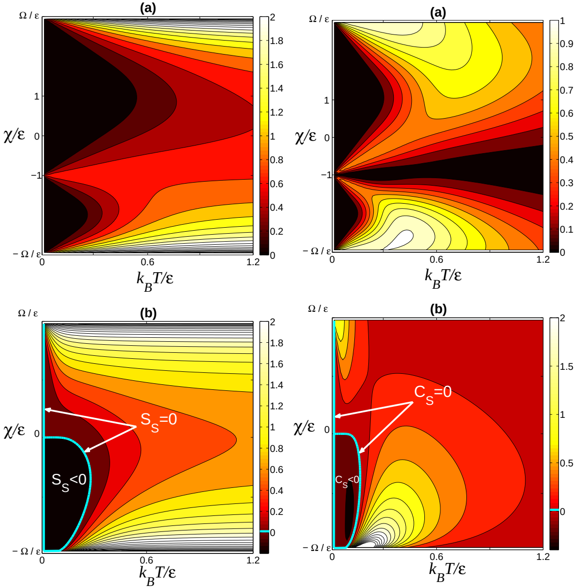
$$\gamma = \frac{1}{2\beta}\ln\left(\frac{1 - 2e^{-\beta\Omega}\cosh(\beta\chi) + e^{-2\beta\Omega}}{(1 - e^{-\beta\Omega})^2}\right)$$

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

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

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

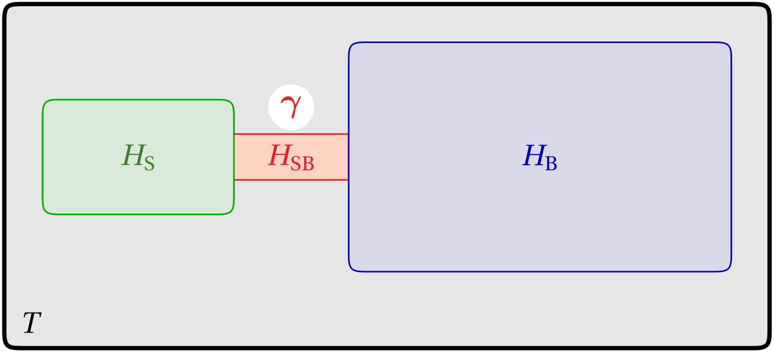
Entropy and specific heat



$\Omega/\epsilon = 3$

$\Omega/\epsilon = 1/3$

The problem

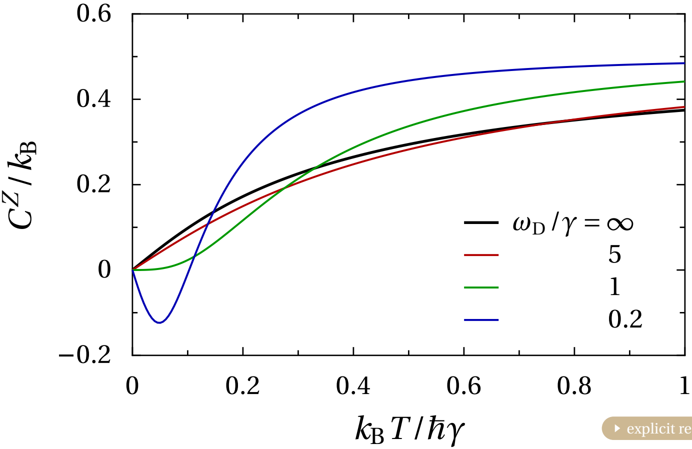


What is the specific heat of a damped system?

Specific heat of a damped free particle

Route II

partition function

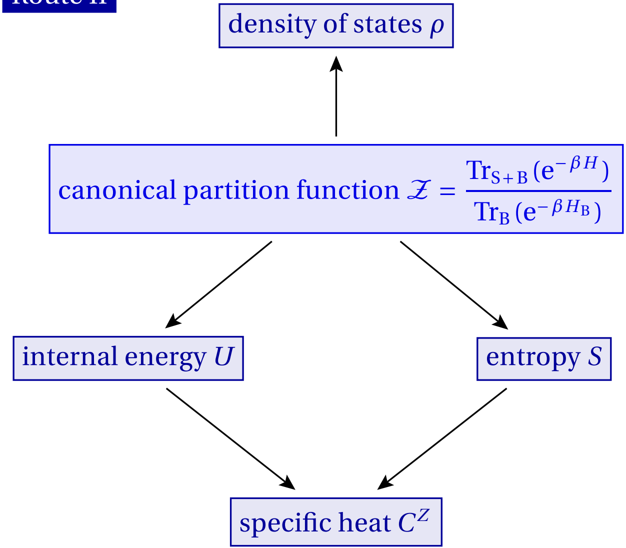


explicit results

The specific heat can be negative!?

Specific heat from the partition function

Route II



density of states ρ

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

internal energy U

entropy S

specific heat C^{Z}