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Differences can be negative

in collaboration with:

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Peter Talkner
Universität Augsburg

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

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Laboratoire Kastler Brossel, Paris

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

Motivation I

For the »mutual information« aficionados

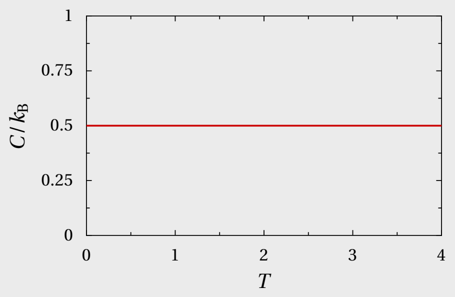
There will be differences of

…specific heats $C_{AB} - C_B$

…and therefore of entropies $S_{AB} - S_B$

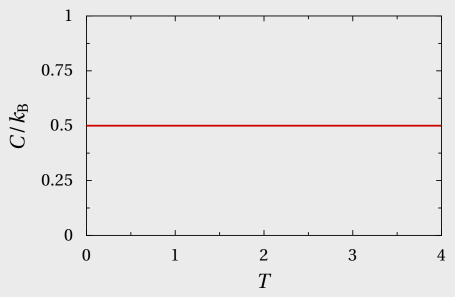
For the »system+environment« aficionados

specific heat of a free particle



For the »system+environment« aficionados

specific heat of a free particle



Does the free particle violate the third law of thermodynamics?

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

We need an energy scale

We need an energy scale

① put particle into a box

let the particle be free (only limited by the size of the observable universe)

$\longrightarrow$ energy scale of $6 \cdot 10^{-70}\,\mathrm{K}$

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 $\dfrac{k_\mathrm{B}T}{\hbar\gamma}$

We need an energy scale

① put particle into a box

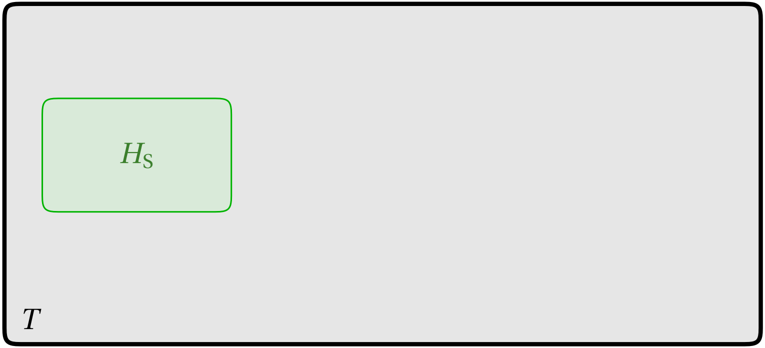
② couple the particle to an environment ✗

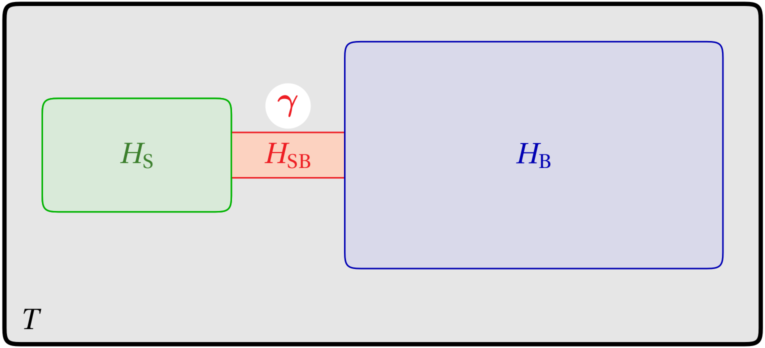
new energy scale $\hbar\gamma \longrightarrow$ relevant quantity $\dfrac{k_\mathrm{B}T}{\hbar\gamma}$

$\gamma \to 0$ corresponds to classical limit $T \to \infty$

Coupling to the environment makes the free particle more quantum! [somewhat in the spirit of J. R. Anglin, J. P. Paz, and W. H. Zurek, *Deconstructing decoherence*, PRA '97]

The problem





What actually do we mean by
»specific heat of a dissipative system«?

Statistical physics 101

$$\beta = \frac{1}{k_B T}$$

density of states ρ

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

canonical partition function $\mathcal{Z}$

$$U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \qquad\qquad S = -\frac{\partial F}{\partial T} = -\frac{\partial k_B T \ln \mathcal{Z}}{\partial T}$$

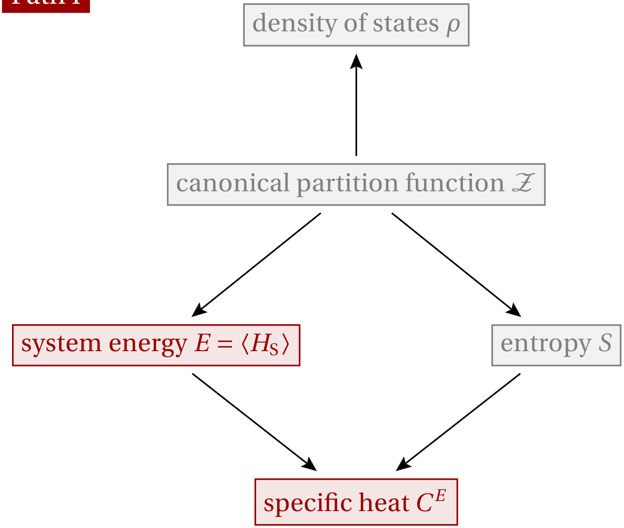
internal energy U | **entropy S**

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

specific heat C

From system energy to specific heat

Path I



From partition function to specific heat

Path II

$$\begin{tikzcd}
& \boxed{\text{density of states } \rho} & \\
& \boxed{\text{canonical partition function } \mathcal{Z} = \dfrac{\mathrm{Tr}_{\mathrm{S+B}}\left(\mathrm{e}^{-\beta H}\right)}{\mathrm{Tr}_{\mathrm{B}}\left(\mathrm{e}^{-\beta H_{\mathrm{B}}}\right)}} \arrow[u] \arrow[dl] \arrow[dr] & \\
\boxed{\text{internal energy } U} \arrow[dr] & & \boxed{\text{entropy } S} \arrow[dl] \\
& \boxed{\text{specific heat } C^{Z}} &
\end{tikzcd}$$

An important difference

Path I

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

Path II

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

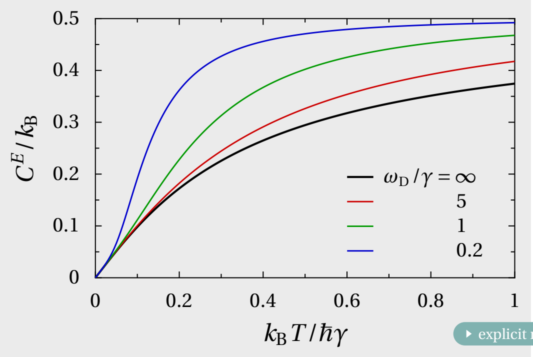
$$\Rightarrow U = \langle H \rangle - \langle H_\mathrm{B} \rangle_\mathrm{B}$$

$$= E + \left[\langle H_\mathrm{SB} \rangle + \langle H_\mathrm{B} \rangle - \langle H_\mathrm{B} \rangle_\mathrm{B} \right]$$

For finite coupling to the bath, E and U differ!
⇒ There is no unique way to define a specific heat.

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

Path I

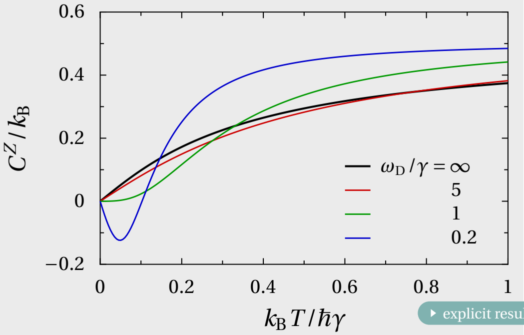


explicit results

- $T \to \infty$: classical value $k_B/2$
  Damping constant γ determines temperature scale
- Third Law saved by coupling to the environment
- more damping makes the system more quantum

Path II

▸ Partition function

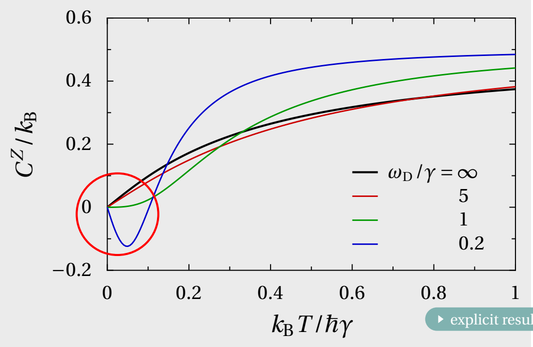


▸ explicit results

- already the leading high temperature corrections for C^E and C^Z differ

Path II

Partition function



explicit results

- already the leading high temperature corrections for C^E and C^Z differ
- **The specific heat can become negative*!?***

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

reduced partition function

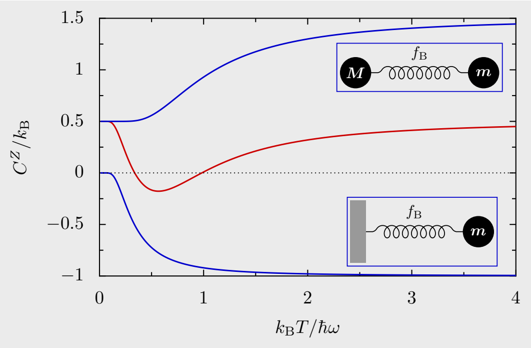
$$\mathcal{Z} = \frac{\mathcal{Z}_{\mathrm{S+B}}}{\mathcal{Z}_{\mathrm{B}}}$$

In order to obtain the entropy or the specific heat, one needs to take the logarithm.
$\Rightarrow$ The reduced partition function leads to differences of entropies or of specific heats:

$$C^Z = C^Z_{\mathrm{S+B}} - C^Z_{\mathrm{B}}$$

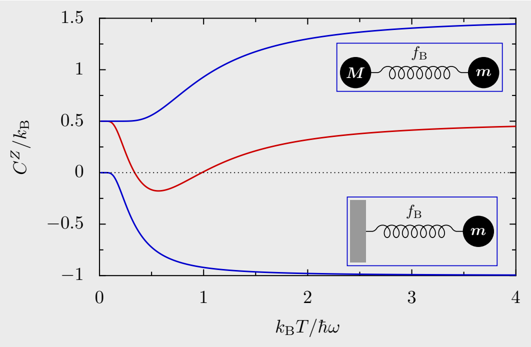
i. e., how does the specific heat change if the system degree of freedom is coupled to the bath?
The difference of two positive numbers can be negative.

Path II



GLI, P. Hänggi, P. Talkner Phys. Rev. E **79**, 061105 (2009)

Path II



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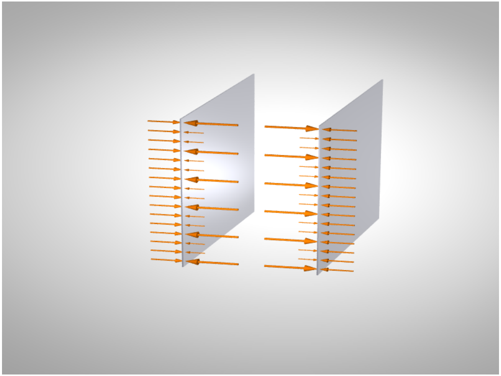
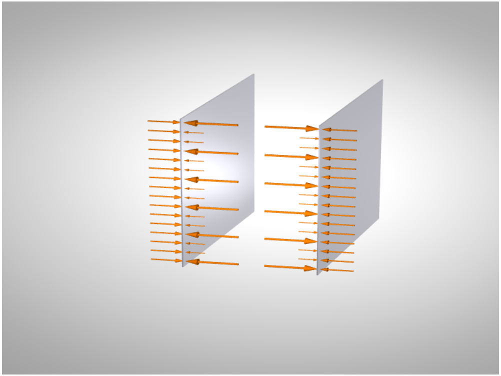
Coupling of a degree of freedom to an environment can lead to a reduction of the specific heat.

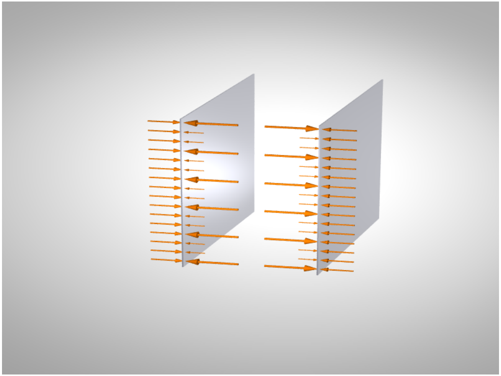
Differences can be negative



Casimir effect



finite temperature
finite permittivity
geometry
surface roughness
finite thickness



finite temperature
finite permittivity
geometry
surface roughness
finite thickness

ideal mirrors

$$\varepsilon(\omega) = -\infty$$

From ideal to real mirrors

ideal mirrors

$$\varepsilon(\omega) = -\infty$$

plasma model

$$\varepsilon(\omega) = 1 - \frac{\omega_\mathrm{P}^2}{\omega^2}$$

ideal mirrors

$$\varepsilon(\omega) = -\infty$$

plasma model

$$\varepsilon(\omega) = 1 - \frac{\omega_\mathrm{P}^2}{\omega^2}$$

Drude model

$$\varepsilon(\omega) = 1 - \frac{\omega_\mathrm{P}^2}{\omega(\omega + \mathrm{i}\gamma)}$$

From ideal to real mirrors

Differences can be negative

ideal mirrors

$$\varepsilon(\omega) = -\infty$$

plasma model

$$\varepsilon(\omega) = 1 - \frac{\omega_P^2}{\omega^2}$$

Drude model ✗ negative entropy !

$$\varepsilon(\omega) = 1 - \frac{\omega_P^2}{\omega(\omega + i\gamma)}$$

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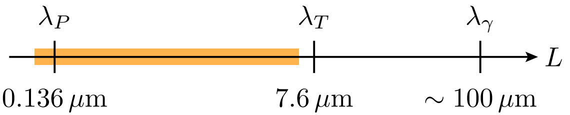
Length scales

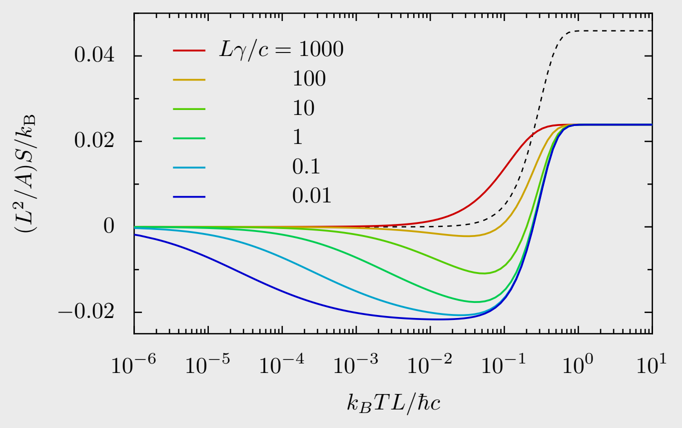
$$\varepsilon(\omega) = 1 - \frac{\omega_{\mathrm{P}}^2}{\omega(\omega + \mathrm{i}\gamma)} \qquad \lambda_{\mathrm{P}} = \frac{2\pi c}{\omega_{\mathrm{P}}} \qquad \lambda_{\mathrm{T}} = \frac{\hbar c}{k_{\mathrm{B}} T}$$



$$\boxed{\Delta S_{\mathrm{TE}} \sim f\left(\frac{\hbar\gamma}{k_{\mathrm{B}} T}\right)}$$

Casimir entropy

Differences can be negative



GLI, A. Lambrecht, S. Reynaud, Phys. Rev. E **80**, 041113 (2009)

Conclusions

- Dissipation can save the Third Law of thermodynamics.
- For nonnegligible coupling to the bath, specific heat is not uniquely defined.
- The reduced partition function can lead to negative values of the (difference of) specific heat(s).
- This scenario finds an application in the Casimir effect.

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

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

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

back

Partition function of the damped free particle

$$\mathcal{Z} = \frac{L}{\hbar}\left(\frac{2\pi m}{\beta}\right)^{1/2} \prod_{n=1}^{\infty} \frac{\nu_n}{\nu_n + \hat{\gamma}(\nu_n)}$$

back

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

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

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

back