Meaning of temperature in different thermostatistical ensembles

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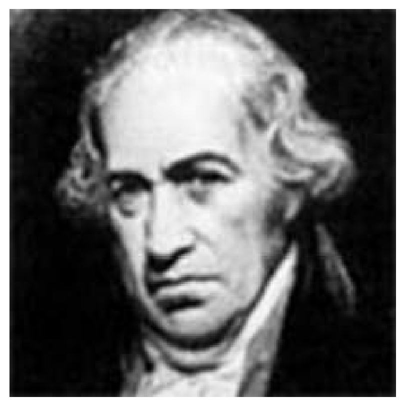
First thermometer & temperature scales

1638: Robert Fludd – air thermometer &scale
~1700: linseed oil thermometer by Newton
1701: red wine as temperature indicator by Rømer
1702: Guillaume Amontons: Absolute zero temperature?
1714: mercury and alcohol thermometer by Fahrenheit

Definition of temperature scales

Sir Isaac Newton
(1643 – 1727)

Olaf Christensen Römer
(1644 – 1710)

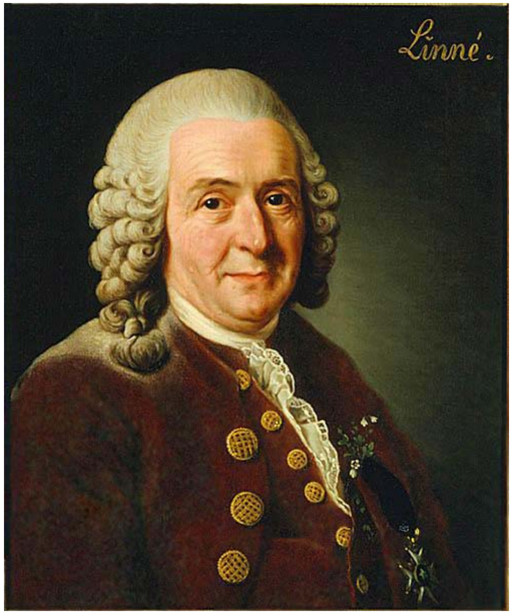


Daniel Gabriel Fahrenheit
(1686 – 1736)

René Antoine Ferchault de Réaumur
(1683 – 1757)

Anders Celsius
(1701 – 1744)

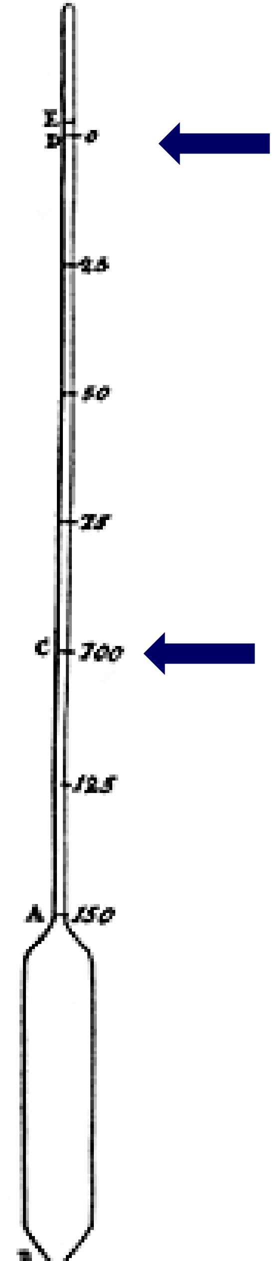
Linneaus thermometer



Carl von Linné
(1707 – 1778)

Reversed the Celsius scale

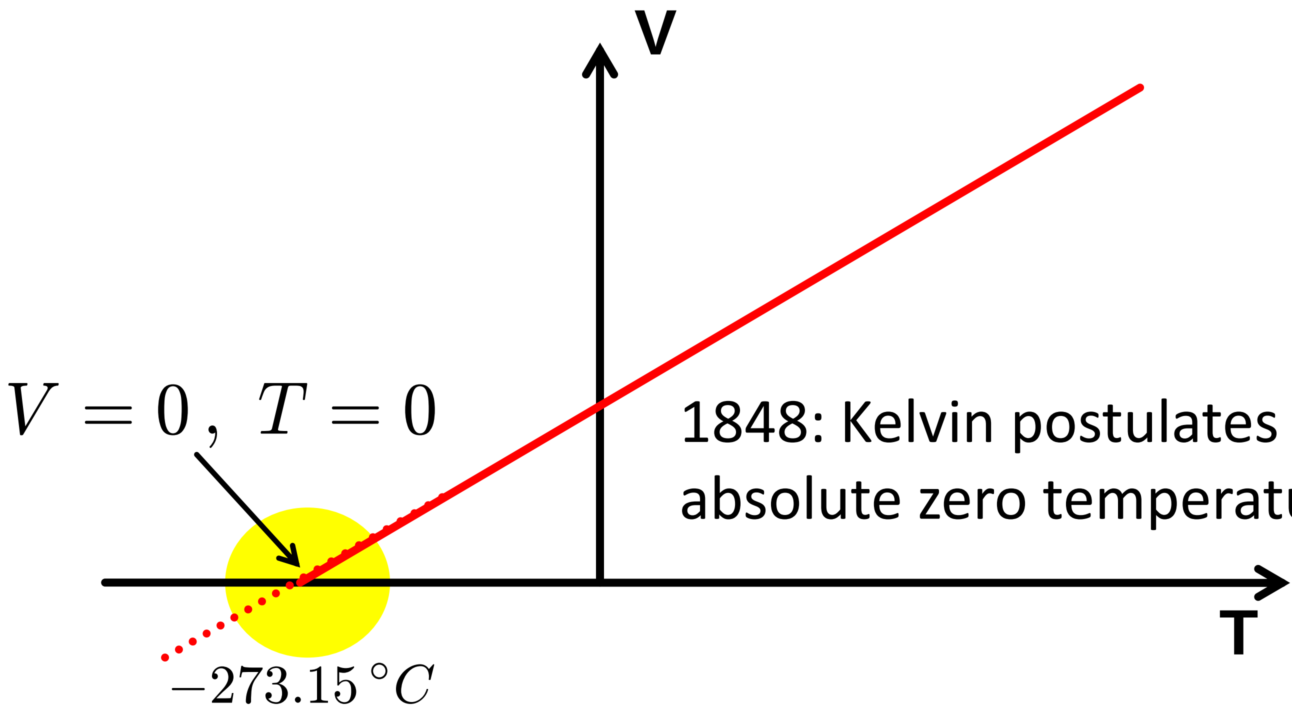
1744: broken on delivery
1745: botanical garden in Uppsala



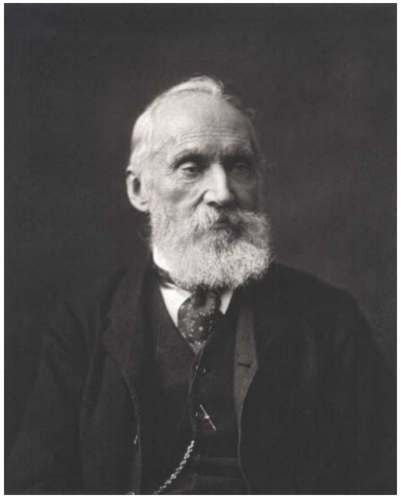
Anders Celsius

Absolute Zero

Ideal gas law: $p\,V = N\,k_{\mathrm{B}}\,T$



1848: Kelvin postulates an absolute zero temperature



William Thomson — Lord Kelvin
(1824 – 1907)

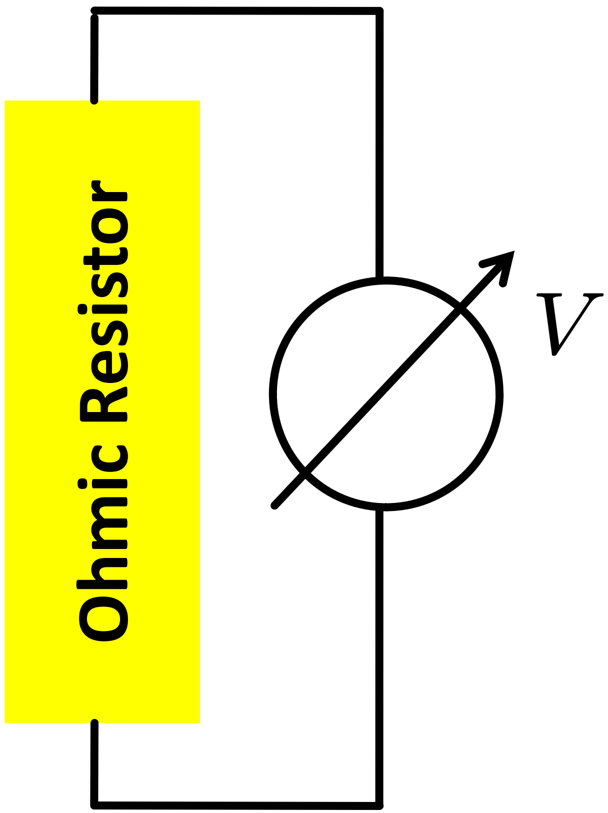
It is impossible by any procedure to reduce the temperature of a system to zero in a finite number of operations.

The highest temperature you can see

Lightning:

30 000 °C

Noise Thermometer



Johnson – Nyquist noise

$$\mathrm{PSD}_V(\omega) = 2k_\mathrm{B}TR$$

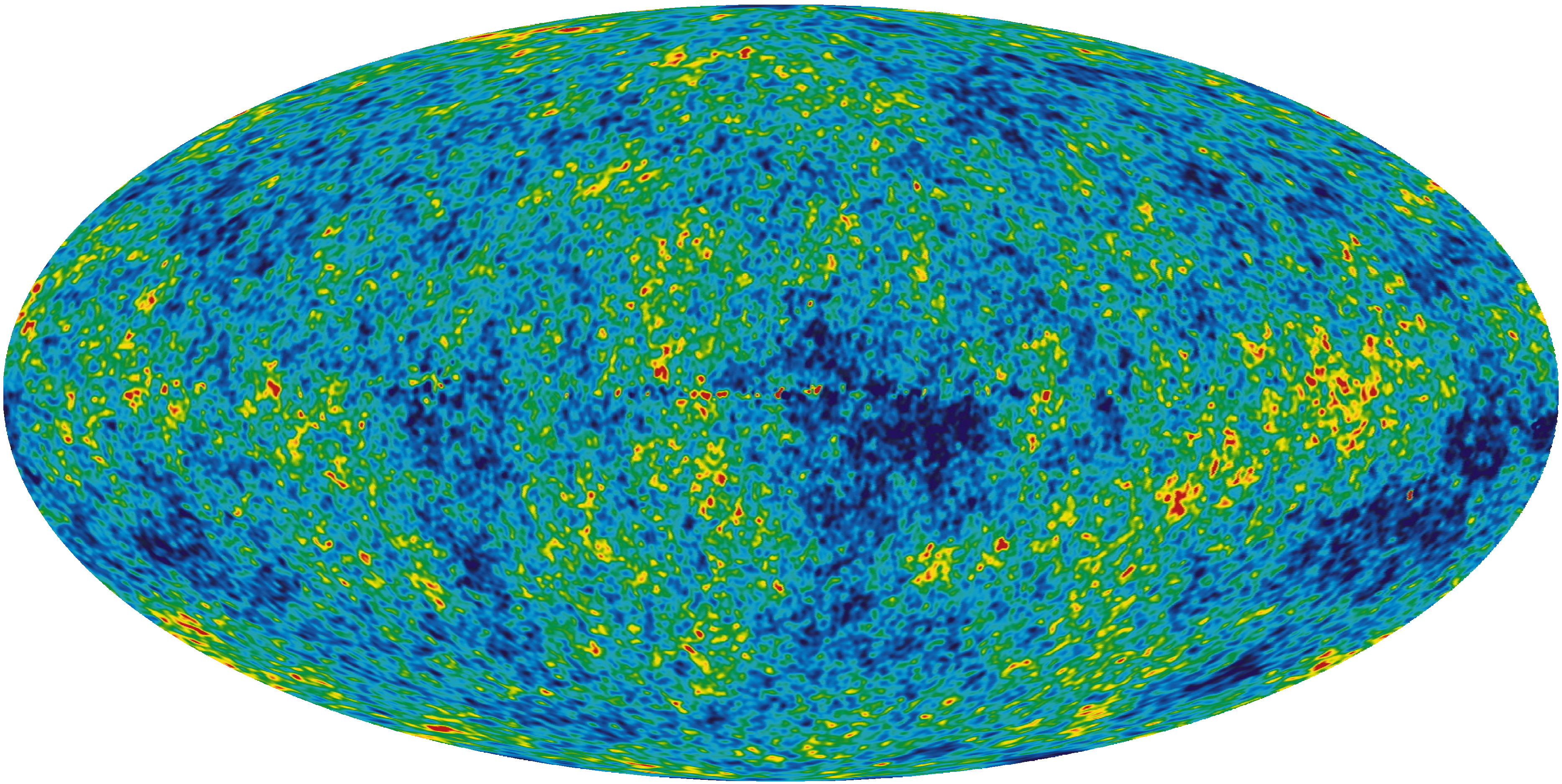
-- classical regime only --

PSD_V : power spectral density of the voltage signal

k_B : Boltzmann constant

R : resistance

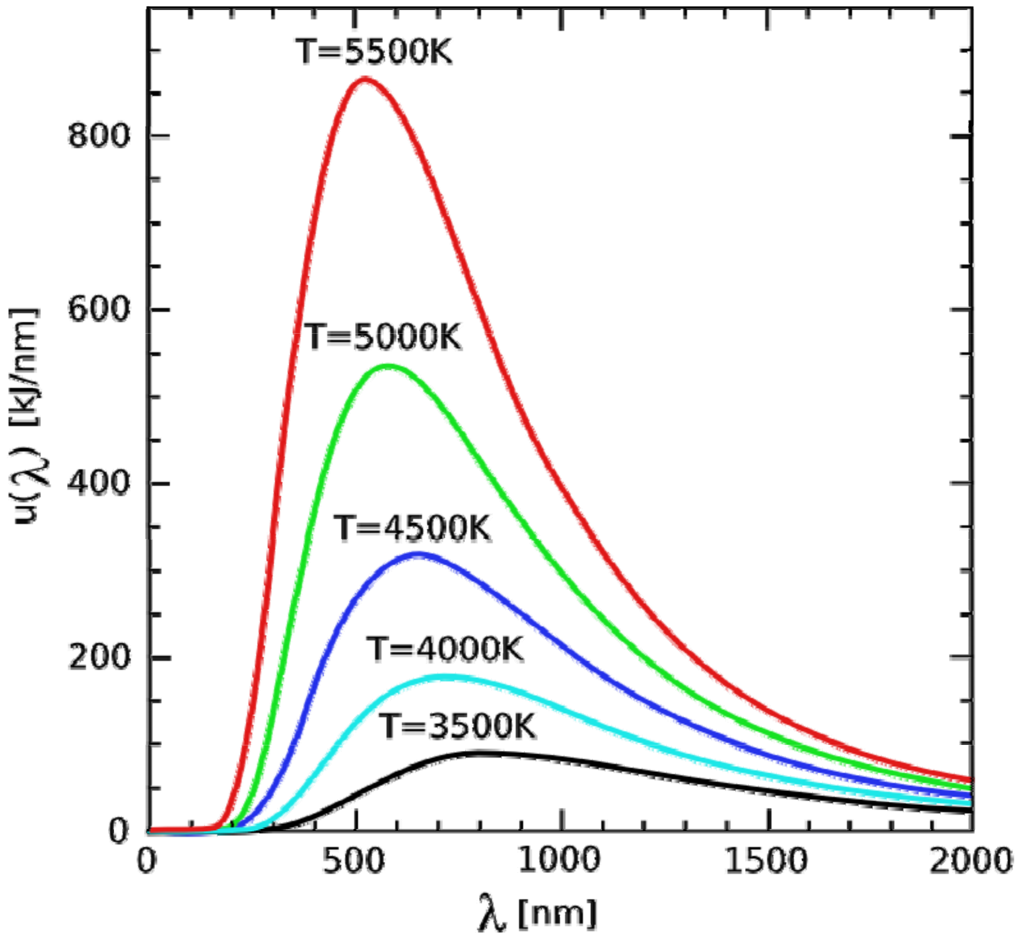
Cosmic background temperature



$T = 2.725 \pm .... \text{ K}$

Black body radiation

Planck's law [1901]: $$u(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp(\frac{hc}{\lambda k_B T}) - 1}$$



$u(\lambda, T)$: spectral energy density

λ : wavelength

h : Planck constant

c : speed of light

k_B : Boltzmann constant

Stefan – Boltzmann law:

$$E \propto T^4$$

Thermometer !

The famous Laws

Equilibrium Principle -- minus first Law

An isolated, macroscopic system which is placed in an arbitrary initial state within a finite fixed volume will attain a unique state of equilibrium.

Second Law (Clausius)

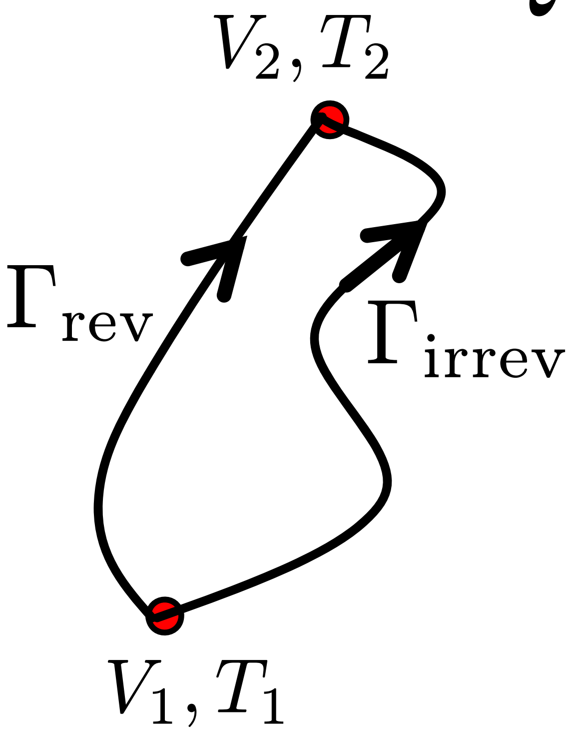
For a non-quasi-static process occurring in a thermally isolated system, the entropy change between two equilibrium states is non-negative.

Second Law (Kelvin)

[redacted]

Entropy S – content of *transformation* „Verwandlungswert“

$$d\,S = \delta Q^{\mathrm{rev}}/T\,; \qquad \delta Q^{\mathrm{irrev}} < \delta Q^{\mathrm{rev}}$$



$$\oint_C \frac{\delta Q}{T} \leq 0$$

$$C = \Gamma_{\mathrm{rev}}^{-1} + \Gamma_{\mathrm{irrev}}$$

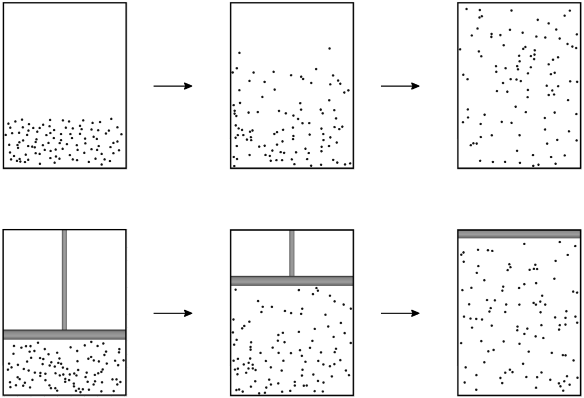
$$S(V_2,T_2) - S(V_1,T_1) \geq \int_{\Gamma_{\mathrm{irrev}}} \frac{\delta Q}{T}$$

$$S(V_2,T_2) - S(V_1,T_1) = \int_{\Gamma_{\mathrm{rev}}} \frac{\delta Q^{\mathrm{rev}}}{T}$$

$$\frac{\partial S}{\partial t} \geq 0$$

NO !

MINUS FIRST LAW vs. SECOND LAW



-1st Law

2nd Law

SECOND LAW

Quote by Sir Arthur Stanley Eddington:

“If someone points out to you that your pet theory of the universe is in disagreement with Maxwell’s equations – then so much the worse for Maxwell’s equations. If it is found to be contradicted by observation – well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation.“

Freely translated into German:

Falls Ihnen jemand zeigt, dass Ihre Lieblingstheorie des Universums nicht mit den Maxwellgleichungen übereinstimmt - Pech für die Maxwellgleichungen. Falls die Beobachtungen ihr widersprechen - nun ja, diese Experimentatoren bauen manchmal Mist. -- Aber wenn Ihre Theorie nicht mit dem zweiten Hauptsatz der Thermodynamik übereinstimmt, dann kann ich Ihnen keine Hoffnung machen; ihr bleibt nichts übrig als in tiefster Schande aufzugeben.

Thermodynamic Temperature

$$\delta Q^{\mathrm{rev}} = T\,dS \leftarrow \text{thermodynamic entropy}$$

$$S = S(E, V, N_1, N_2, ...; M, P, ...)$$

$S(E, ...)$: (continuous) & differentiable and

monotonic function of the internal energy E

$$\left(\frac{\partial S}{\partial E}\right)_{...} = \frac{1}{T}$$

microcanonical ensemble

Entropy in Stat. Mech.

$$S = k_{\mathrm{B}} \ln \Omega(E, V, \ldots)$$

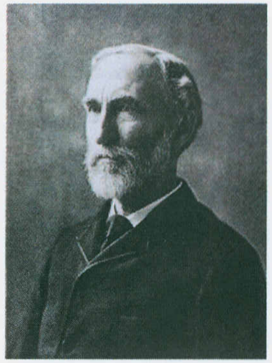
QM: $\Omega_{\mathrm{G}}(E, V, \ldots) = \sum_{0 \le E_i \le E} 1$

classical

Gibbs: $\Omega_{\mathrm{G}} = \left(\frac{1}{N!\, h^{\mathrm{DOF}}}\right) \int \mathrm{d}\Gamma\, \Theta\left(E - H(\underline{q}, \underline{p}; V, \ldots)\right)$

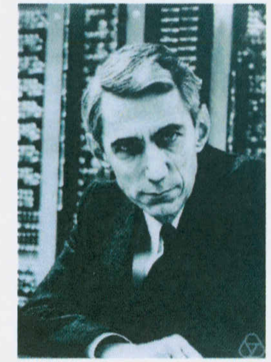
Boltzmann: $\Omega_{\mathrm{B}} = \epsilon_0 \frac{\partial\, \Omega_{\mathrm{G}}}{\partial E} \propto \int \mathrm{d}\Gamma\, \delta\left(E - H(\underline{q}, \underline{p}; V, \ldots)\right)$

density of states



J. W. Gibbs

L. Boltzmann



C. E. Shannon

$$H_G = \int W_N \ln W_N \, d\Gamma_N$$

$$S_G = k_B \ln \Omega_G$$

$$H_B = N \int W_1 \ln W_1 \, d\Gamma_1$$

$$S_B = k_B \ln \left(\frac{\partial \Omega_G}{\partial E} \right) \delta E$$

$$S_S = - \sum_i p_i \log_2 p_i$$

+

200

Renyi

Relative-

Kullback-Leibler

v. NEUMANN

KOLMOGOROV-SINAI

CONDITIONAL

CLAUSIUS

FISHER

Daroczy-Harvda-Charvat-Tsallis

WEHRL

Hartley-chaitin

ETC.

Entropy in Stat. Mech.

$$S = k_{\mathrm{B}} \ln \Omega(E, V, \ldots)$$

Gibbs: $\Omega_{\mathrm{G}} = \left(\dfrac{1}{N!\, h^{\mathrm{DOF}}} \right) \displaystyle\int \mathrm{d}\Gamma\, \Theta\left(E - H(\underline{q}, \underline{p}; V, \ldots)\right)$

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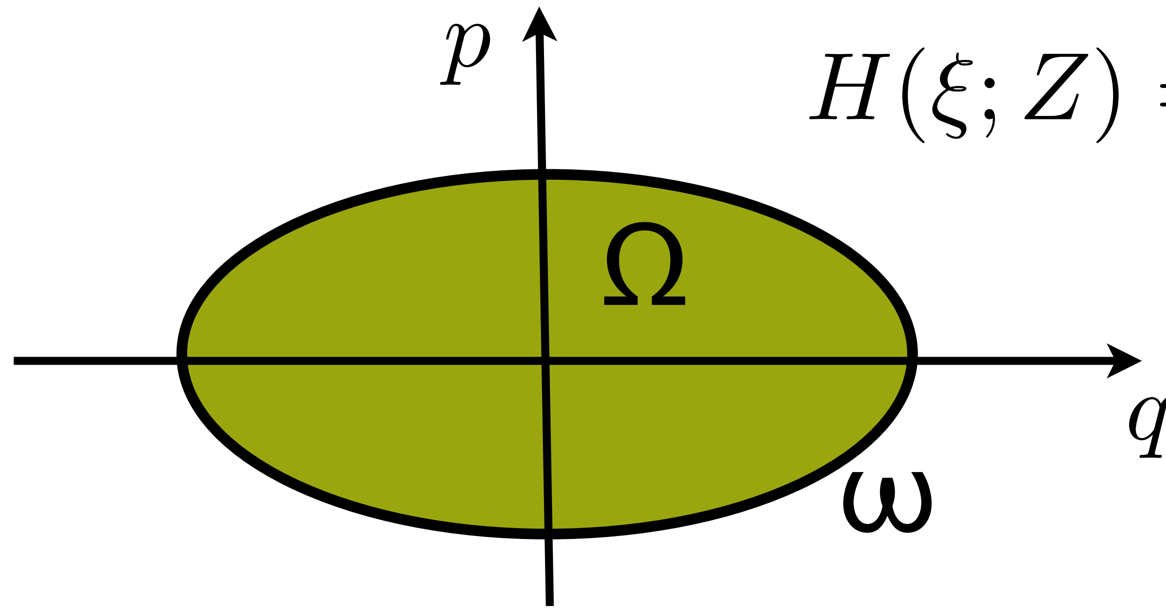
density of states

Microcanonical thermostatistics



$$H(\xi;Z) = E$$

D-Operator

$$\rho(\boldsymbol{\xi}|E,Z) = \frac{\delta(E-H)}{\omega}$$

DoS

$$\omega(E,Z) = \mathrm{Tr}[\delta(E-H)] \geq 0$$

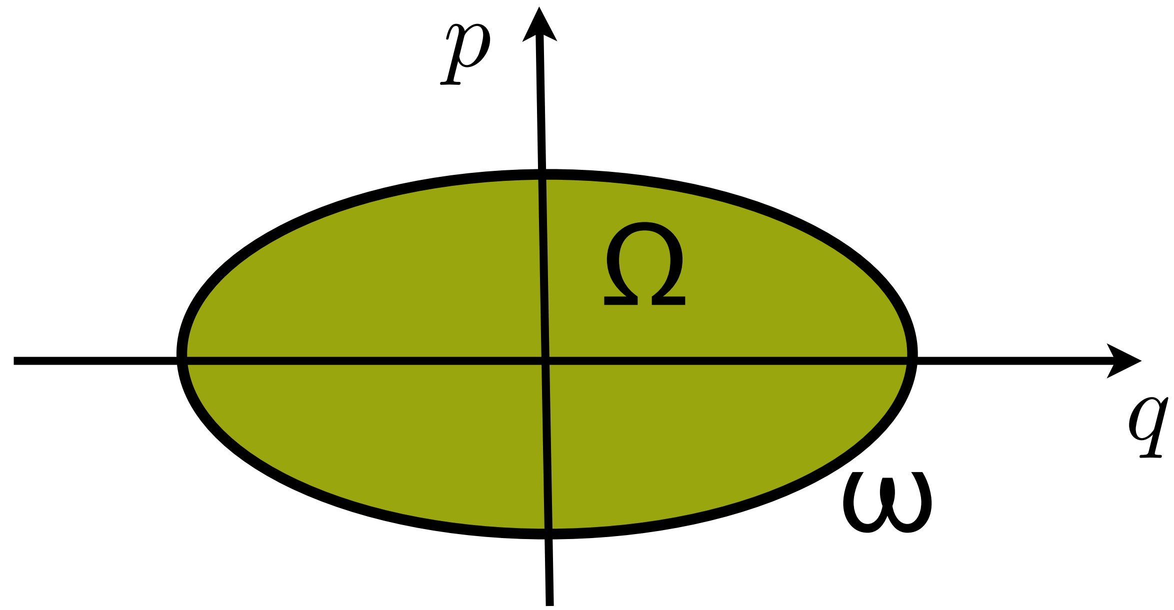
$$\Omega(E,Z) = \mathrm{Tr}[\Theta(E-H)]$$

IntDoS

Thermodynamic Entropy ?

$S_{\mathrm{B}}(E) = \ln(\epsilon\,\omega)$	vs.	$S_{\mathrm{G}}(E) = \ln\Omega$
Boltzmann (?)		Gibbs (1902), Hertz (1910)

Boltzmann *vs.* Gibbs

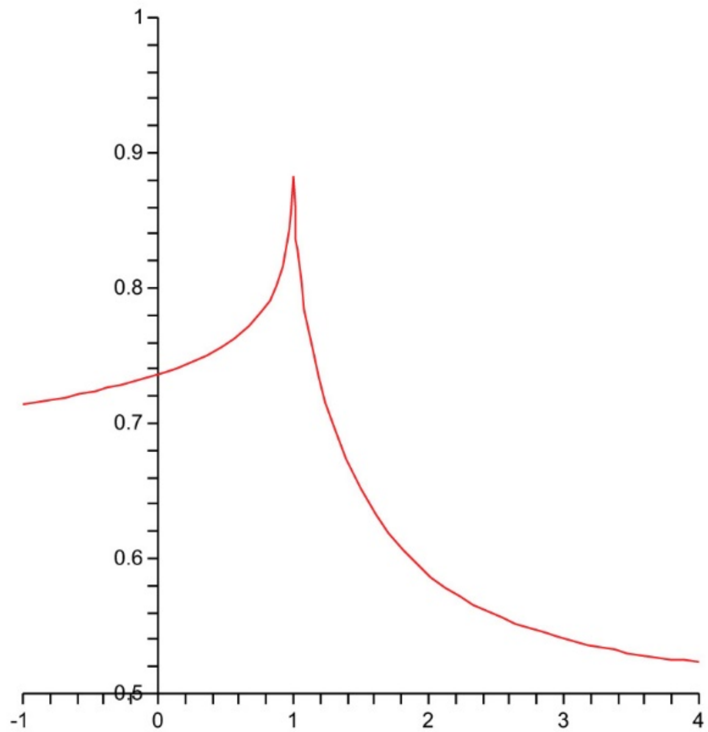


$$S_{\mathrm{B}}(E) = \ln(\epsilon\,\omega) \qquad\qquad S_{\mathrm{G}}(E) = \ln\Omega$$

$$T(E,Z) \equiv \left(\frac{\partial S}{\partial E}\right)^{-1}$$

$$T_{\mathrm{B}}(E) = \frac{\omega}{\nu} \gtrless 0 \qquad\qquad T_{\mathrm{G}}(E) = \frac{\Omega}{\omega} \geq 0$$

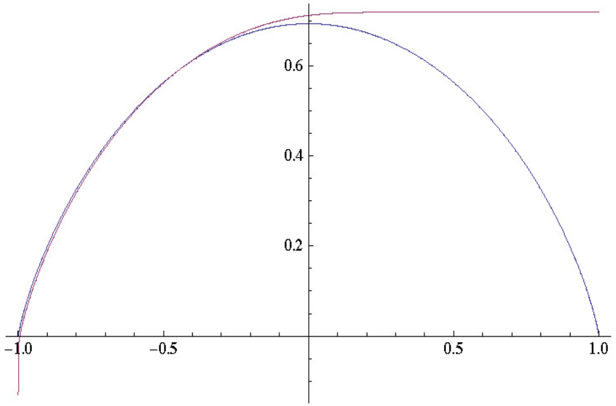
$$\nu(E,Z) = \partial\omega/\partial E,$$



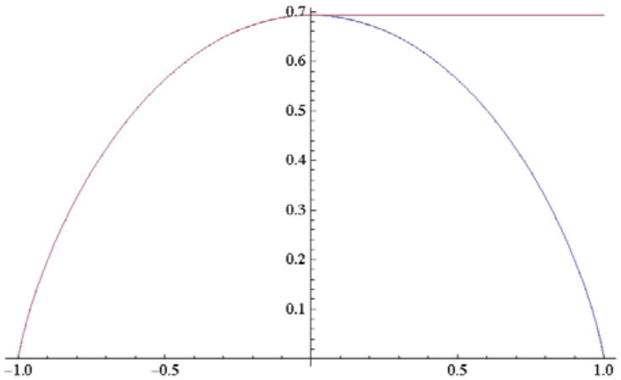
Density of states of the pendulum in reduced units (complete elliptic integrals of the first kind). Fig. 1 in reference: M. Baeten and J. Naudts, Entropy, 13, 1186-1199 (2011).

N Spins $|\vec{S}| = 1/2$

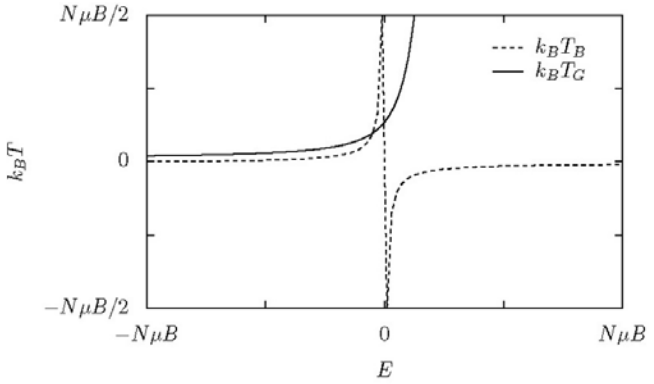
Entropy for N = 100
(magenta: S_G ; blue: S_B

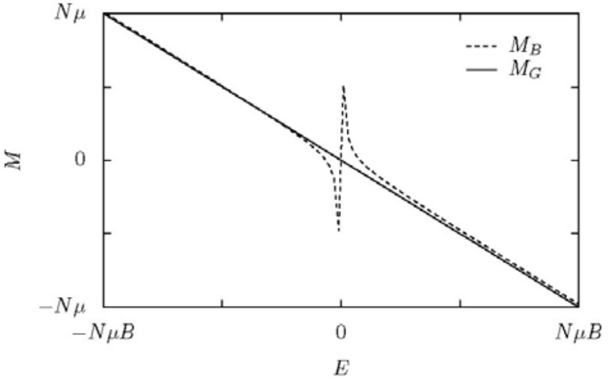


N = 10^8



N = 100





$\Delta = M_B - M = - k_B T_B / B$

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Negative Absolute Temperature for Motional Degrees of Freedom

S. Braun,[1,2] J. P. Ronzheimer,[1,2] M. Schreiber,[1,2] S. S. Hodgman,[1,2] T. Rom,[1,2]
I. Bloch,[1,2] U. Schneider[1,2]*

Because negative temperature systems can absorb entropy while releasing energy, they give rise to several counterintuitive effects, such as Carnot engines with an efficiency greater than unity (*4*). Through a stability analysis for thermodynamic equilibrium, we showed that negative temperature states of motional degrees of freedom necessarily possess negative pressure (*9*) and are thus of fundamental interest to the description of dark energy in cosmology, where negative pressure is required to account for the accelerating expansion of the universe (*10*).

✓ Carnot efficiencies >1

✓ Dark Energy

Recent Experiments

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- fit to 1-particle level occupation
  $\Rightarrow$ negative temperature
- Carnot efficiencies $\eta > 1$
- $T < 0$ & $p < 0 \Rightarrow$ model for dark energy

Recent Experiments

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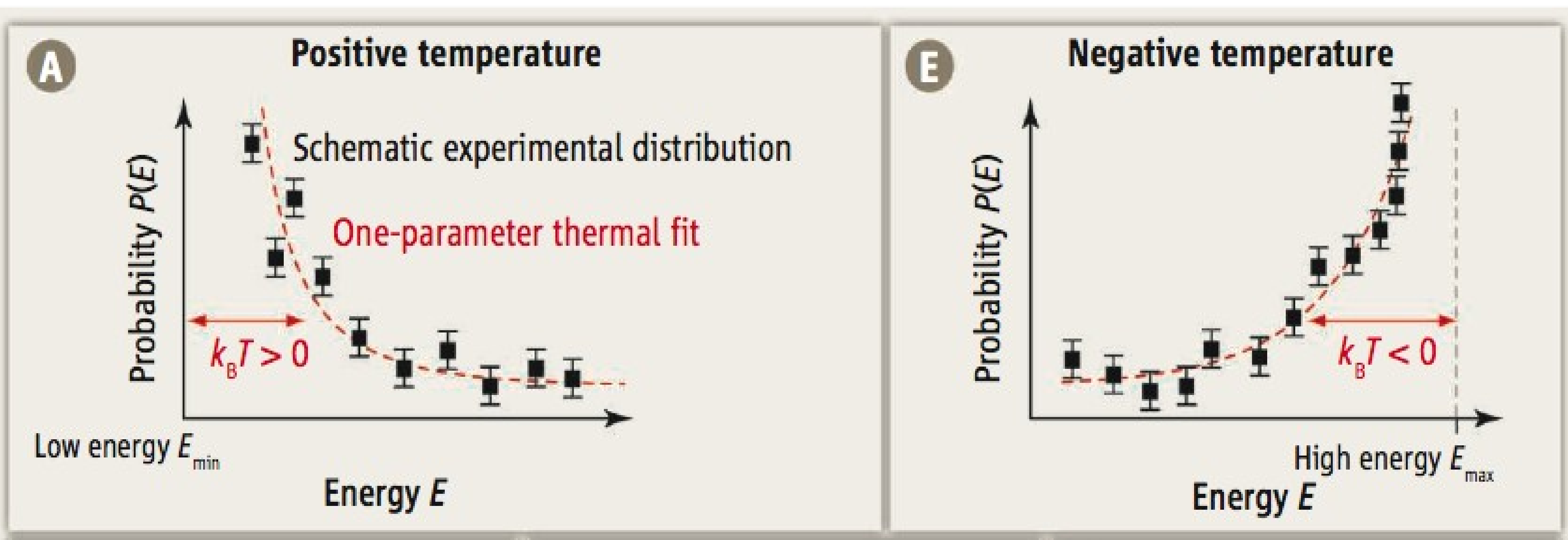

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Thermodynamic laws in isolated systems

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**** 23 pages ****

Joint Work with

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Massachusetts Institute of Technology

and

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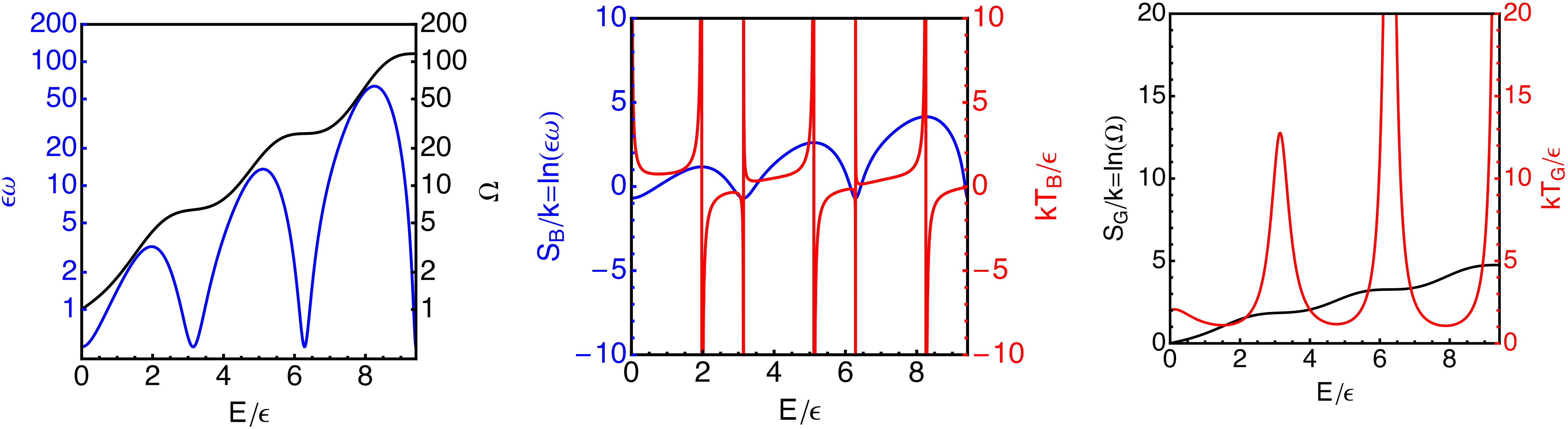
Excellence Cluster Universe,
Ludwig-Maximilians-Universität, Munich

'Non-uniqueness' of temperature

$$\Omega(E) = \exp\left[\frac{E}{2\epsilon} - \frac{1}{4}\sin\left(\frac{2E}{\epsilon}\right)\right] + \frac{E}{2\epsilon},$$



Temperature does NOT determine direction heat flow.
Energy is primary control parameter of MCE.

Thermodynamic Entropy

- $\mathrm{d}E = \delta Q + \delta W$
- W and Q not state functions
  $\Rightarrow$ differentials δW and δQ not total
- but $\mathrm{d}S = \dfrac{\delta Q}{T}$ total differential

if $\dfrac{1}{T} = \left(\dfrac{\partial f\left[\Omega\left(E,Z\right)\right]}{\partial E}\right)_Z$!

Mech. Adiabatic Processes

$$\mathrm{d}E = \delta Q + \delta W = T\,\mathrm{d}S - \sum_n p_n \mathrm{d}Z_n$$

$$p_i = T\left(\frac{\partial S}{\partial Z_i}\right)_{E,Z_{n\neq j}}$$

$$\mathrm{d}E = \sum_n \left\langle \frac{\partial H}{\partial Z_n} \right\rangle_\rho \mathrm{d}Z_n$$

Mech. Adiab. = Thermod. Adiab.

$$\mathrm{d}E = \delta Q + \delta W = T\,\mathrm{d}S - \sum_n p_n \mathrm{d}Z_n$$

$$p_i = T\left(\frac{\partial S}{\partial Z_i}\right)_{E,Z_{n\neq j}}$$

$$\mathrm{d}E = \sum_n \left\langle \frac{\partial H}{\partial Z_n} \right\rangle_{\rho} \mathrm{d}Z_n$$

$$\mathrm{d}S = 0$$

First Law

$$\mathrm{d}E = \delta Q + \delta W = T\,\mathrm{d}S - \sum_n p_n \,\mathrm{d}Z_n$$

$$\Rightarrow \quad p_i = T\left(\frac{\partial S}{\partial Z_i}\right)_{E,Z_{n\neq j}} \stackrel{!}{=} -\left\langle \frac{\partial H}{\partial Z_i} \right\rangle_\rho$$

$$\Rightarrow \quad S(E,\ldots) \stackrel{!}{=} f\left[\Omega(E,\ldots)\right]$$

$f(\cdot) = k_\mathrm{B} \ln(\cdot)$ from additional constraints (e.g. gas thermometer)

First law

$$dE \;=\; \delta Q + \delta A \;=\; T\,dS - \sum_n p_n dZ_n$$

$$p_j = T\left(\frac{\partial S}{\partial Z_j}\right)_{E,Z_n \neq Z_j} \stackrel{!}{=} -\left\langle \frac{\partial H}{\partial Z_j} \right\rangle_E$$

Gibbs ✓ $\Rightarrow$ Boltzmann ✗

see also Campisi, Physica A 2007

Second Law

$$\sum_i^{\text{after}} S_i \overset{!}{\geq} \sum_j^{\text{before}} S_j$$

Second law

Gibbs

$$S_{\mathrm{G}}(E) = \ln \Omega$$

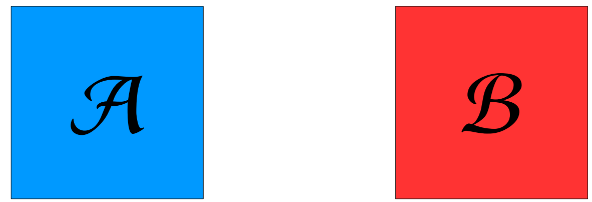
$$
\begin{aligned}
&\Omega(E_{\mathcal{A}} + E_{\mathcal{B}}) \\
&= \int_0^{E_{\mathcal{A}}+E_{\mathcal{B}}} \mathrm{d}E' \, \Omega_{\mathcal{A}}(E')\omega_{\mathcal{B}}(E_{\mathcal{A}} + E_{\mathcal{B}} - E') \\
&= \int_0^{E_{\mathcal{A}}+E_{\mathcal{B}}} \mathrm{d}E' \int_0^{E'} \mathrm{d}E''\omega_{\mathcal{A}}(E'')\omega_{\mathcal{B}}(E_{\mathcal{A}} + E_{\mathcal{B}} - E') \\
&\geq \int_{E_{\mathcal{A}}}^{E_{\mathcal{A}}+E_{\mathcal{B}}} \mathrm{d}E' \int_0^{E_{\mathcal{A}}} \mathrm{d}E''\omega_{\mathcal{A}}(E'')\omega_{\mathcal{B}}(E_{\mathcal{A}} + E_{\mathcal{B}} - E') \\
&= \int_0^{E_{\mathcal{A}}} \mathrm{d}E''\omega_{\mathcal{A}}(E'') \int_0^{E_{\mathcal{B}}} \mathrm{d}E'''\omega_{\mathcal{B}}(E''') \\
&= \Omega_{\mathcal{A}}(E_{\mathcal{A}})\,\Omega_{\mathcal{B}}(E_{\mathcal{B}}).
\end{aligned}
$$

$$\Rightarrow \quad S_{\mathrm{G}\mathcal{A}\mathcal{B}}(E_{\mathcal{A}} + E_{\mathcal{B}}) \geq S_{\mathrm{G}\mathcal{A}}(E_{\mathcal{A}}) + S_{\mathrm{G}\mathcal{B}}(E_{\mathcal{B}})$$

Second Law

before coupling

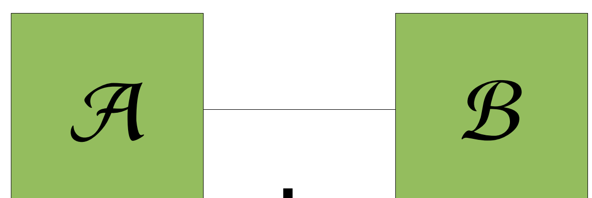
$$H_{\mathcal{A}} = E_{\mathcal{A}} \qquad H_{\mathcal{B}} = E_{\mathcal{B}}$$



$$S_{\mathcal{A}}(E_{\mathcal{A}}) \qquad S_{\mathcal{B}}(E_{\mathcal{B}})$$

after coupling

$$H_{\mathcal{AB}} = H_{\mathcal{A}} + H_{\mathcal{B}} = E_{\mathcal{A}} + E_{\mathcal{B}} = E_{\mathcal{AB}}$$

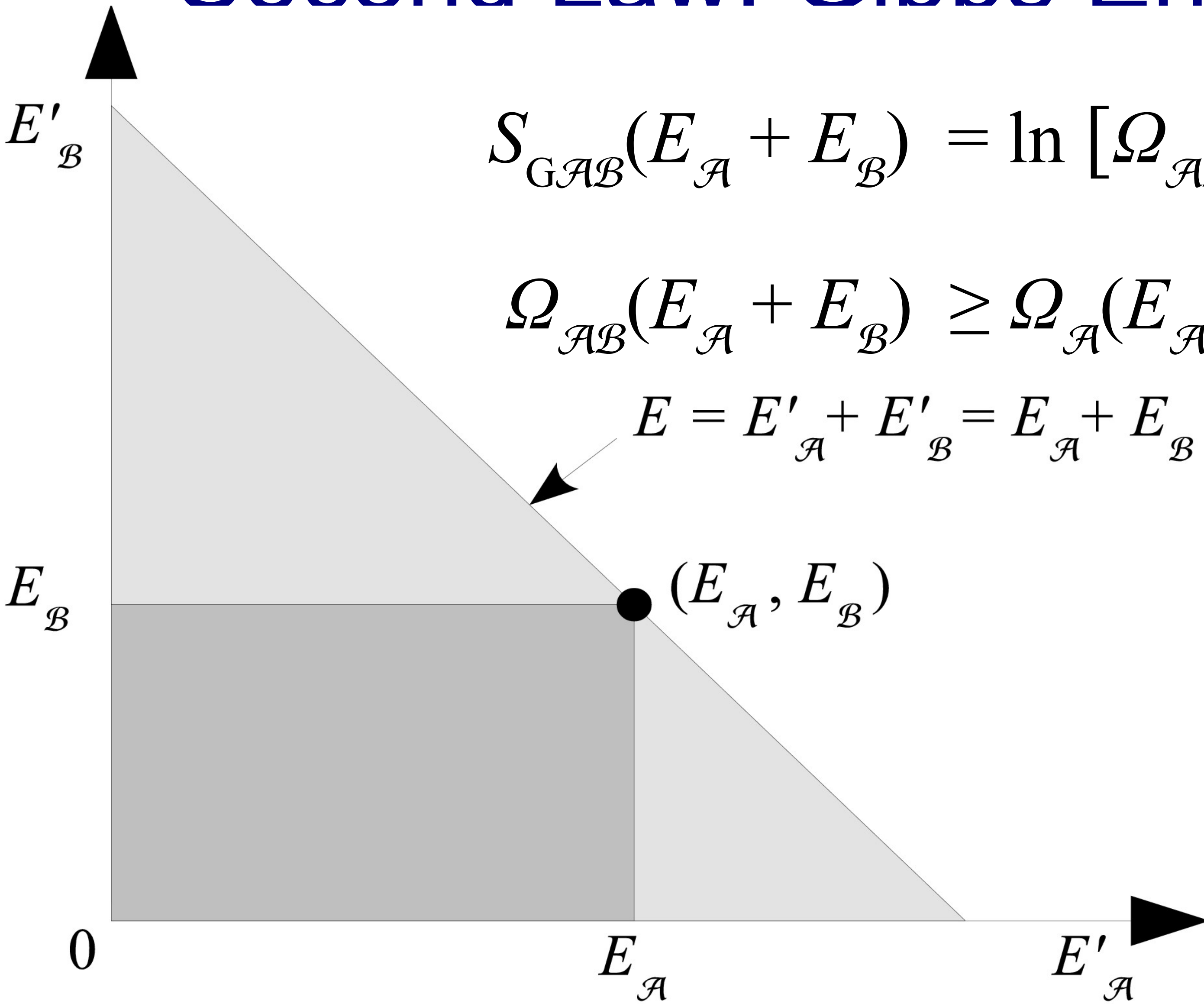


$$S_{\mathcal{AB}}(E_{\mathcal{AB}}) \overset{!}{\geq} S_{\mathcal{A}}(E_{\mathcal{A}}) + S_{\mathcal{B}}(E_{\mathcal{B}})$$

Second Law: Gibbs Entropy

$$S_{\mathrm{G}\mathcal{AB}}(E_{\mathcal{A}} + E_{\mathcal{B}}) = \ln\left[\Omega_{\mathcal{AB}}(E_{\mathcal{A}} + E_{\mathcal{B}})\right]$$

$$\Omega_{\mathcal{AB}}(E_{\mathcal{A}} + E_{\mathcal{B}}) \geq \Omega_{\mathcal{A}}(E_{\mathcal{A}})\ \Omega_{\mathcal{B}}(E_{\mathcal{B}})$$



Second law

Boltzmann $$S_{\mathrm{B}}(E) = \ln(\epsilon\,\omega)$$

$$\epsilon\omega(E_{\mathcal{A}} + E_{\mathcal{B}}) = \epsilon \int_0^{E_{\mathcal{A}}+E_{\mathcal{B}}} \mathrm{d}E'\omega_{\mathcal{A}}(E')\omega_{\mathcal{B}}(E_{\mathcal{A}} + E_{\mathcal{B}} - E')$$

$$\cancel{\geq} \quad \epsilon^2\omega_{\mathcal{A}}(E_{\mathcal{A}})\omega_{\mathcal{B}}(E_{\mathcal{B}})$$

Second Law

$$\sum_i^{\text{after}} S_i \overset{!}{\geq} \sum_j^{\text{before}} S_j$$

$$S_{\mathrm{B}\mathcal{A}\mathcal{B}}(E_{\mathcal{A}} + E_{\mathcal{B}}) \ngeq S_{\mathrm{B}\mathcal{A}}(E_{\mathcal{A}}) + \mathrm{S}_{\mathrm{B}\mathcal{B}}(E_{\mathcal{B}})$$

$$S_{\mathrm{G}\mathcal{A}\mathcal{B}}(E_{\mathcal{A}} + E_{\mathcal{B}}) \geq S_{\mathrm{G}\mathcal{A}}(E_{\mathcal{A}}) + \mathrm{S}_{\mathrm{G}\mathcal{B}}(E_{\mathcal{B}})$$

Erunt multi qui, postquam mea scripta legerint, non ad contemplandum utrum vera sint quae dixerim, mentem convertent, sed solum ad disquirendum quomodo, vel iure vel iniuria, rationes meas labefactare possent.

G. Galilei, *Opere* (Ed. Naz., vol. I, p. 412)

There will be many who, when they will have read my paper, will apply their mind, not to examining whether what I have said is true, but only to seeking how, by hook or by crook, they could demolish my arguments.

Example: Classical Ideal Gas

$$\Omega(E, V, N) = \alpha(D, N) V^N E^{DN/2}$$

$$S_\mathrm{B}(E, \ldots) = k_\mathrm{B} \ln \epsilon \omega(E, \ldots)$$

$$E = \left(\frac{DN}{2} - 1\right) k_\mathrm{B} T_\mathrm{B}$$

for $DN = 1$ or $DN = 2$?

$$S_\mathrm{G}(E, \ldots) = k_\mathrm{B} \ln \Omega(E, \ldots)$$

$$E = \frac{DN}{2} k_\mathrm{B} T_\mathrm{G}$$

Example 1: Classical ideal gas

$$\Omega(E,V) = \alpha E^{dN/2} V^N, \qquad \alpha = \frac{(2\pi m)^{dN/2}}{N! h^d \Gamma(dN/2+1)}$$

$$S_{\mathrm{B}}(E,V,A) = k_{\mathrm{B}} \ln[\epsilon\omega(E)]$$

$$E = \left(\frac{dN}{2} - 1\right) k_{\mathrm{B}} T_{\mathrm{B}}$$

vs.

$$S_{\mathrm{G}}(E,V,A) = k_{\mathrm{B}} \ln[\Omega(E)]$$

$$E = \frac{dN}{2} k_{\mathrm{B}} T_{\mathrm{G}}$$

Example: Single 1-dim Particle

- single particle with energy E
  in one-dimensional box of length L
- $\Omega(E) \propto \sqrt{E}$

$$p_{\mathrm{B}} = -\frac{2E}{L} \neq \left\langle \frac{\partial H}{\partial L} \right\rangle_{\rho}$$

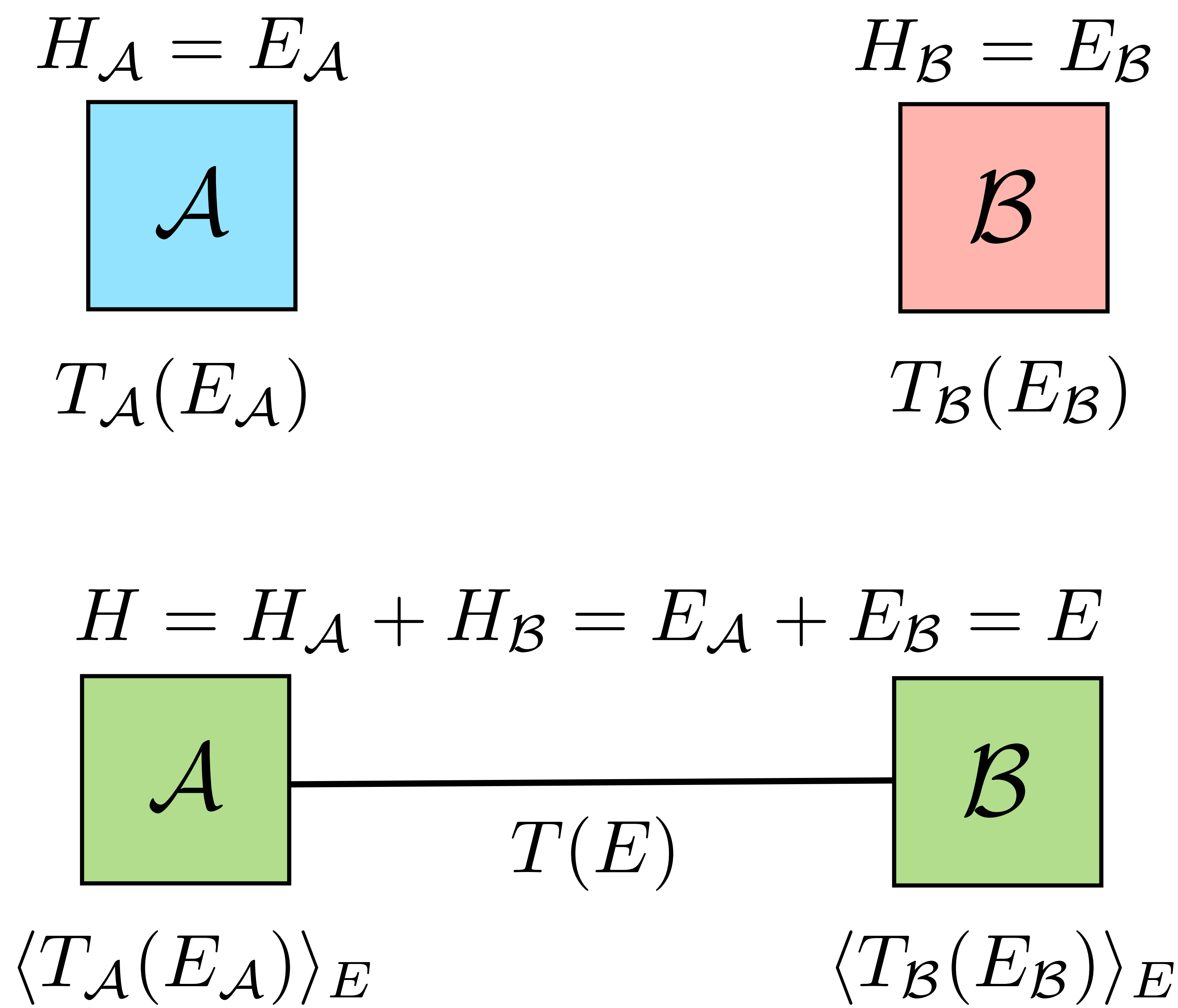
(dark energy?)

$$p_{\mathrm{G}} = +\frac{2E}{L} = \left\langle \frac{\partial H}{\partial L} \right\rangle_{\rho}$$

Thermal equilibrium

before coupling

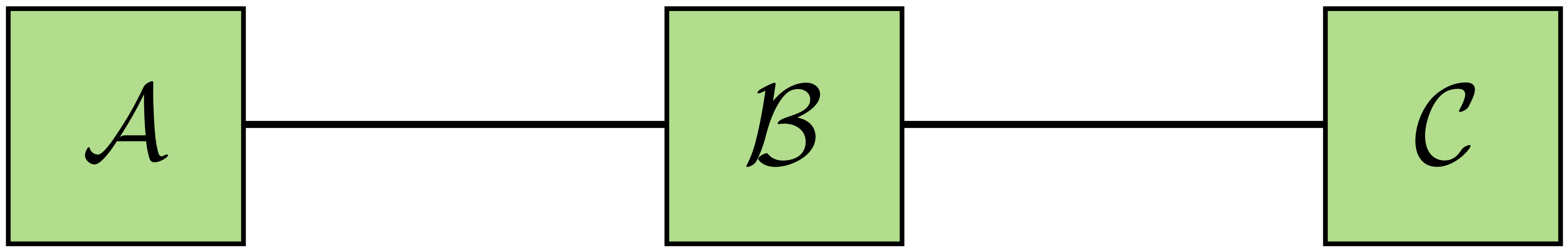
after coupling



$$\langle T_i(E_i)\rangle_E = \int_0^\infty dE_i \; T_i(E_i)\, \pi_i(E_i|E) \qquad \pi_\mathcal{A}(E_\mathcal{A}|E) = \frac{\omega_\mathcal{A}(E_\mathcal{A})\,\omega_\mathcal{B}(E - E_\mathcal{A})}{\omega(E)}.$$

Zeroth law

$T(E)$



$\langle T_{\mathcal{A}}(E_{\mathcal{A}})\rangle_E \qquad \langle T_{\mathcal{B}}(E_{\mathcal{B}})\rangle_E \qquad \langle T_{\mathcal{C}}(E_{\mathcal{C}})\rangle_E$

$$\langle T_i(E_i)\rangle_E \overset{!}{=} T(E)$$

Gibbs

$$\begin{aligned}
\langle T_{\mathrm{G}\mathcal{A}}(E_{\mathcal{A}})\rangle_E &= \int_0^\infty \mathrm{d}E_{\mathcal{A}}\, \frac{\Omega_{\mathcal{A}}(E_{\mathcal{A}})}{\omega_{\mathcal{A}}(E_{\mathcal{A}})}\, \frac{\omega_{\mathcal{A}}(E_{\mathcal{A}})\omega_{\mathcal{B}}(E-E_{\mathcal{A}})}{\omega(E)} \\
&= \frac{1}{\omega(E)} \int_0^E \mathrm{d}E_{\mathcal{A}}\, \Omega_{\mathcal{A}}(E_{\mathcal{A}})\omega_{\mathcal{B}}(E-E_{\mathcal{A}}) \\
&= T_{\mathrm{G}}(E).
\end{aligned}$$

Summary

- Entropy candidates for isolated systems:

entropy	$S(E)$	0^{th} law	1^{st} law	2^{nd} law	equipart.
...other...					
Boltzmann	$\ln(\epsilon\omega)$	no	no	no	no
Gibbs	$\ln(\Omega)$	yes*	yes	yes	yes

canonical ensemble

$$
\begin{aligned}
\omega(E) &= \mathrm{Tr}\,[\delta(E-H)] \\
&= \mathrm{Tr}_{\mathcal{A}}\,\{\mathrm{Tr}_{\mathcal{B}}\,[\delta(E-H_{\mathcal{A}}-H_{\mathcal{B}})]\} \\
&= \mathrm{Tr}_{\mathcal{A}}\left\{\mathrm{Tr}_{\mathcal{B}}\left[\int_{-\infty}^{\infty} d\,E'_{\mathcal{A}}\,\delta(E'_{\mathcal{A}}-H_{\mathcal{A}})\int_{-\infty}^{\infty} d\,E'_{\mathcal{B}}\,\delta(E'_{\mathcal{B}}-H_{\mathcal{B}})\delta(E-H_{\mathcal{A}}-H_{\mathcal{B}})\right]\right\} \\
&= \mathrm{Tr}_{\mathcal{A}}\left\{\mathrm{Tr}_{\mathcal{B}}\left[\int_{-\infty}^{\infty} d\,E'_{\mathcal{A}}\,\delta(E'_{\mathcal{A}}-H_{\mathcal{A}})\int_{-\infty}^{\infty} d\,E'_{\mathcal{B}}\,\delta(E'_{\mathcal{B}}-H_{\mathcal{B}})\delta(E-E'_{\mathcal{A}}-E'_{\mathcal{B}})\right]\right\} \\
&= \int_{-\infty}^{\infty} d\,E'_{\mathcal{A}}\,\mathrm{Tr}_{\mathcal{A}}[\delta(E'_{\mathcal{A}}-H_{\mathcal{A}})]\int_{-\infty}^{\infty} d\,E'_{\mathcal{B}}\,\mathrm{Tr}_{\mathcal{B}}[\delta(E'_{\mathcal{B}}-H_{\mathcal{B}})]\delta(E-E'_{\mathcal{A}}-E'_{\mathcal{B}}) \\
&= \int_{-\infty}^{\infty} d\,E'_{\mathcal{A}}\,\omega_{\mathcal{A}}(E'_{\mathcal{A}})\int_{-\infty}^{\infty} d\,E'_{\mathcal{B}}\,\omega_{\mathcal{B}}(E'_{\mathcal{B}})\delta(E-E'_{\mathcal{A}}-E'_{\mathcal{B}}) \\
&= \int_{0}^{\infty} d\,E'_{\mathcal{A}}\int_{0}^{\infty} d\,E'_{\mathcal{B}}\,\omega_{\mathcal{A}}(E'_{\mathcal{A}})\omega_{\mathcal{B}}(E'_{\mathcal{B}})\delta(E-E'_{\mathcal{A}}-E'_{\mathcal{B}}) \\
&= \int_{0}^{E} d\,E'_{\mathcal{A}}\,\omega_{\mathcal{A}}(E'_{\mathcal{A}})\omega_{\mathcal{B}}(E-E'_{\mathcal{A}}).
\end{aligned}
$$

$$
\begin{aligned}
\pi_{\mathcal{A}}(E'_{\mathcal{A}}|E) &= \mathrm{Tr}[\rho\,\delta(E'_{\mathcal{A}}-H_{\mathcal{A}})] \\
&= \mathrm{Tr}\left[\frac{\delta(E-H_{\mathcal{A}}-H_{\mathcal{B}})}{\omega(E)}\delta(E'_{\mathcal{A}}-H_{\mathcal{A}})\right] \\
&= \int_{-\infty}^{\infty} d\,E''_{\mathcal{A}}\,\omega_{\mathcal{A}}(E''_{\mathcal{A}})\int_{-\infty}^{\infty} d\,E''_{\mathcal{B}}\,\omega_{\mathcal{B}}(E''_{\mathcal{B}})\frac{\delta(E-E''_{\mathcal{A}}-E''_{\mathcal{B}})}{\omega(E)}\delta(E'_{\mathcal{A}}-E''_{\mathcal{A}}) \\
&= \frac{\omega_{\mathcal{A}}(E'_{\mathcal{A}})\,\omega_{\mathcal{B}}(E-E'_{\mathcal{A}})}{\omega(E)}.
\end{aligned}
$$

canonical ensemble

$$\rho^T = \delta(E^T - H^T(\xi,Z))/\omega^T(E^T,Z) \Rightarrow P(E^S|E^T;Z) = \frac{\omega^S(E^S)\,\omega^B(E^T - E^S)}{\omega_T(E^T)}$$

$$E^T = E^S + E^B$$

$$= \frac{\omega^S(E^S)}{\varepsilon\,\omega^T(E^T)} \exp\left[\frac{S_B^B(\overbrace{E^T - E^S}^{E^B})}{k_B}\right]$$

NEXT: $S_B^B(E^T - E^S) = S_B^B(\bar{E}^B) + \frac{1}{T_B^B(\bar{E}_B)}(E^T - E^S - \bar{E}^B) + \dots,$

$$\rightsquigarrow \quad = \frac{\omega^S(E^S)}{\varepsilon\,\omega^T(E^T)} \exp\left[\frac{S_B^B(\bar{E}^B)}{k_B} + \frac{(E^T - \bar{E}^B) - E^S}{k_B T_B^B(\bar{E}^B)} + \dots\right]$$

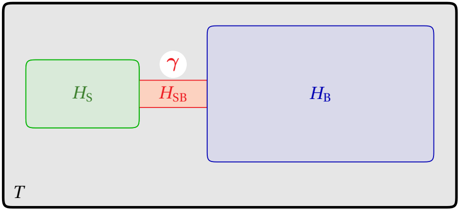
with $+\dots \to 0$! $(\partial^2 S_B^B/\partial^2 E^B) = -1/T_B^2 C_B^B)$

$$\Rightarrow \quad P(E^S|E^T,Z) = \frac{\omega^S(E^S)}{Z_{can}} \exp\left[-\frac{E^S}{k_B T_B^B(\bar{E}^B)}\right]$$

note: $T_B^B(\bar{E}_B) \stackrel{?}{=} T_B^B(E^T)$; IF "normal": $T_B^B = T_G^B = T_G^S = T_G^T$

Finite bath coupling

Universität Augsburg University



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)

Partition function

$$\mathbf{Z_S(t) = \frac{Y(t)}{Z_B}}$$

where $\quad Z_B = \mathrm{Tr}_B\, e^{-\beta H_B}$

An important difference

Route I

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

Route II

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

$$\Rightarrow U = \langle H \rangle - \langle H_B \rangle_B$$

$$= E_S + \left[\langle H_{SB} \rangle + \boxed{\langle H_B \rangle - \langle H_B \rangle_B} \right]$$

For finite coupling E and U differ!

Strong coupling: Example

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

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

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

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

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

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

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

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

Free energy of a system strongly coupled to an environment

Thermodynamic argument:

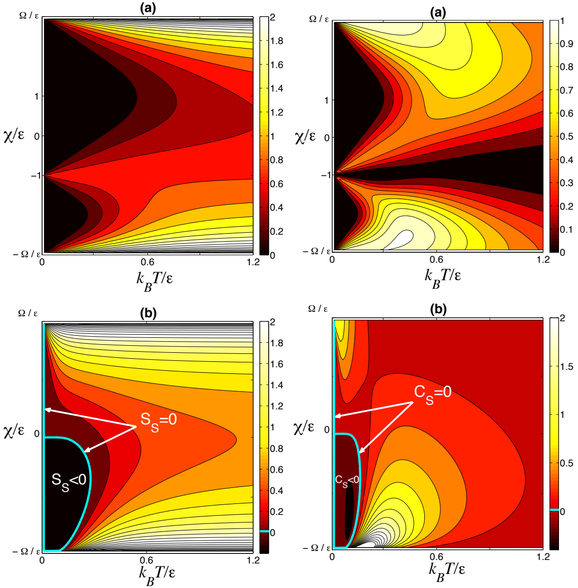
$$F_S = F - F_B^0$$

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**, 0611505 (2009).

Entropy and specific heat



$\Omega/\epsilon = 3$

$\Omega/\epsilon = 1/3$

Summary

Isolated systems:

- thermodynamic entropy: Gibbs volume entropy
- no negative thermodynamic temperature
- no Carnot efficiencies > 1

Summary

Isolated systems:

- T's before coupling do not predict heat flow during coupling
- bounded spectra $\Rightarrow$ ensembles not equivalent
- thermodynamic entropy not always Shannon-like entropy $S_S = -\mathrm{Tr}\left[\rho \ln \rho\right]$
- incorrect entropy $\Rightarrow$ incorrect temperature, forces, and responses

Summary

Systems coupled to heat bath:

- Boltzmann temperature (of the bath) describes the probability of (energy)-fluctuations
- Boltzmann factor approximate for bath with finite heat capacity
- for certain N-particle isolated systems:
  1-p. $p_i(E_i) \approx \mathrm{c} \exp[-E_i / (k_\mathrm{B}\, T_{\mathrm{B},\, N\text{-}1})]$

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Research

Article submitted to journal

Subject Areas:

Thermodynamic temperature

Keywords:

Thermodynamic ensembles, entropy, isolated systems, weak and strong coupling

Meaning of temperature in different thermostatistical ensembles

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Important UNSOLVED (open) Problems are:

1.) Quantum systems and discrete spectral parts: DoS becomes singular
===> a sum of delta-functions !!!

??? !!! best smoothing procedure ???!!!

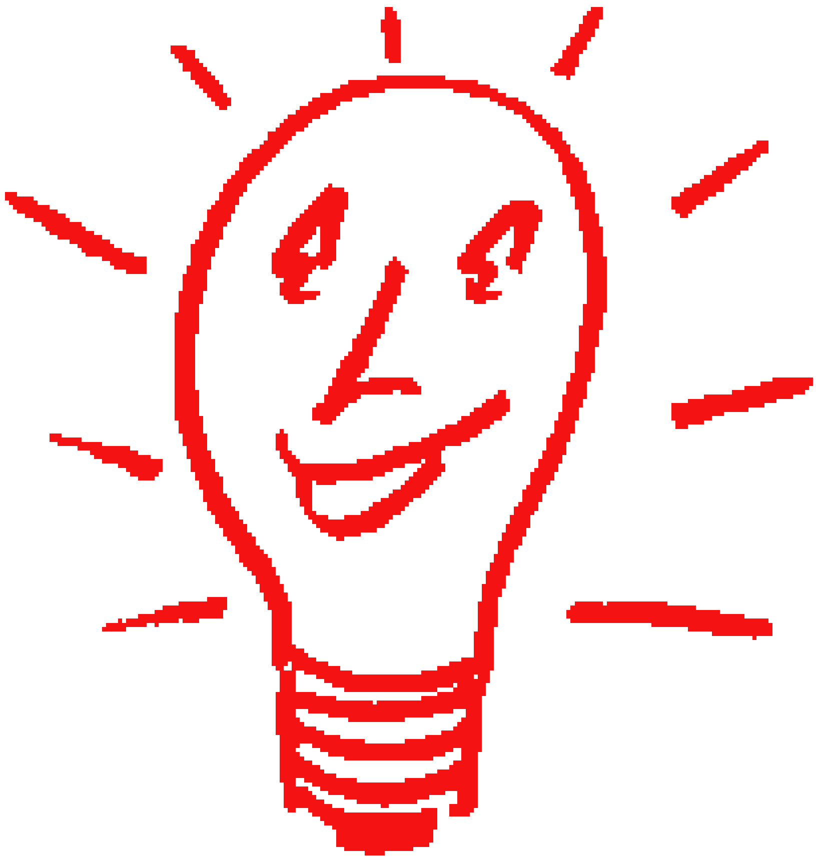
2.) Canonical ensemble: When is the Bolzmanfactor truly OK?

3.) Canonical ensemble and STRONG coupling:

Quantum case: Canonical specific heat can now become negative (!)
despite system being stable

Classical case: Are *negative* canonical specific heat values possible?

A QUESTION ?



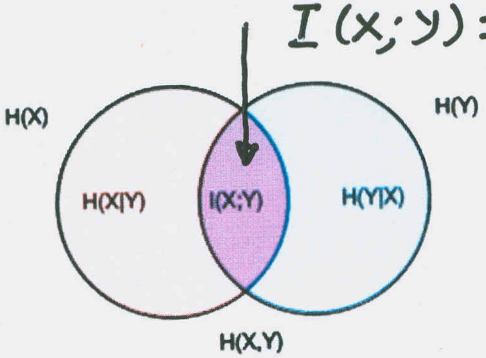
Erunt multi qui, postquam mea scripta legerint, non ad contemplandum utrum vera sint quae dixerim, mentem convertent, sed solum ad disquirendum quomodo, vel iure vel iniuria, rationes meas labefactare possent.

G. Galilei, *Opere* (Ed. Naz., vol. I, p. 412)

There will be many who, when they will have read my paper, will apply their mind, not to examining whether what I have said is true, but only to seeking how, by hook or by crook, they could demolish my arguments.

Conditional Entropy

$$I(x;y) = H(x,y) - H(x|y) - H(y|x)$$

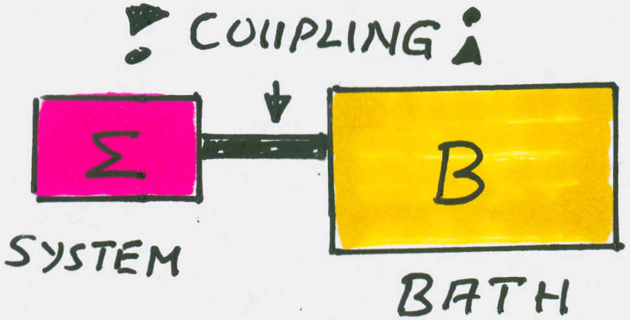


$$H(y|x) = -\sum_{x,y} p(x,y) \ln p(x,y) - \left(-\sum_{x} p(x) \ln p(x)\right)$$

$$= -\sum_{x,y} p(x,y) \ln p(y|x) \geq 0$$

Quantum Conditional Entropy

von NEUMANN: $S_{vN}(\varrho_\Sigma) = -\mathrm{Tr}\, \varrho_\Sigma \ln \varrho_\Sigma$



$$S_\Sigma = S_{vN}\left(\varrho^{can}_{\Sigma \times B}\right) - S_{vN}\left(\varrho^{can}_{B}\right)$$ can. thermod. entropy

quantum cond. entropy $$\overset{?!}{=} S_{vN}\left(\varrho^{can}_{\Sigma \times B}\right) - S_{vN}\left(\varrho_B = \mathrm{Tr}_\Sigma\, \varrho^{can}_{\Sigma \times B}\right)$$

$\uparrow \neq \varrho^{can}_B$

$$\boxed{T_{\mathrm{B}} = \frac{T_{\mathrm{G}}}{1 - k_{\mathrm{B}}/C}}$$

Proof:

$$k_{\mathrm{B}} T_{\mathrm{G}} = \frac{\Omega}{\Omega'} = \frac{\Omega}{\omega} \; , \qquad\qquad k_{\mathrm{B}} T_{\mathrm{B}} = \frac{\omega}{\omega'} = \frac{\Omega'}{\Omega''}$$

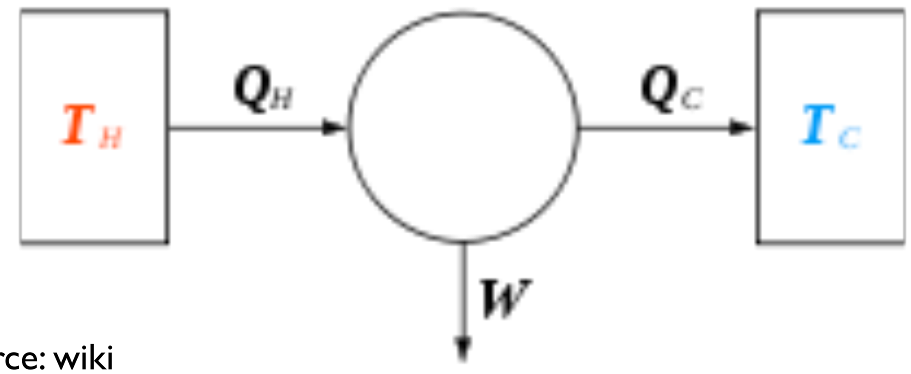
$$\frac{1}{C} \equiv \left(\frac{\partial T_{\mathrm{G}}}{\partial E}\right) = \frac{1}{k_{\mathrm{B}}} \left(\frac{\Omega}{\Omega'}\right)' = \frac{1}{k_{\mathrm{B}}} \frac{\Omega'\Omega' - \Omega\Omega''}{(\Omega')^2}$$

$$= \frac{1}{k_{\mathrm{B}}} \left[1 - \frac{\Omega\Omega''}{(\Omega')^2}\right] = \frac{1}{k_{\mathrm{B}}} \left(1 - \frac{T_{\mathrm{G}}}{T_{\mathrm{B}}}\right)$$

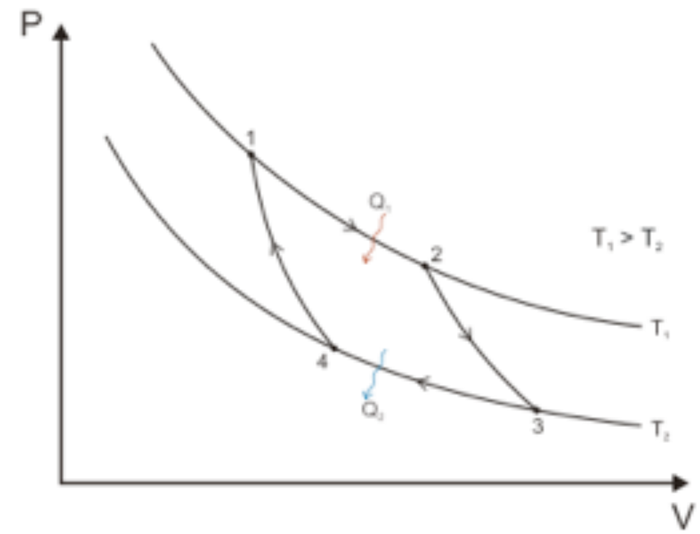
$\square$

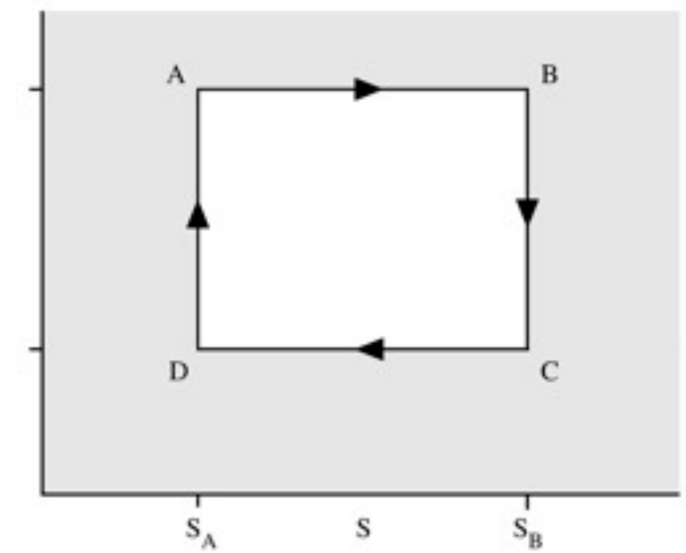
Carnot efficiencies > 1?

$$\eta = 1 - \frac{T^{\mathrm{C}}}{T^{\mathrm{H}}}$$



source: wiki





- Carnot cycle assumes adiabatic switching
- Carnot formula assumes that TD relations are fulfilled ... only for $T_{\mathrm{G}} > 0$ the case

$\Rightarrow$ no Carnot efficiencies > 1 when treated consistently