# Thermodynamic laws
# in
# isolated systems

Jorn Dunkel

dunkel@mit.edu

Nature Physics 10: 67-72, 2014

SCIENCE VOL 339 4 JANUARY 2013

# 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]*

# Joint work with



Stefan Hilbert

Max Planck Institute for Astrophysics

Garching/Munich

# Outline

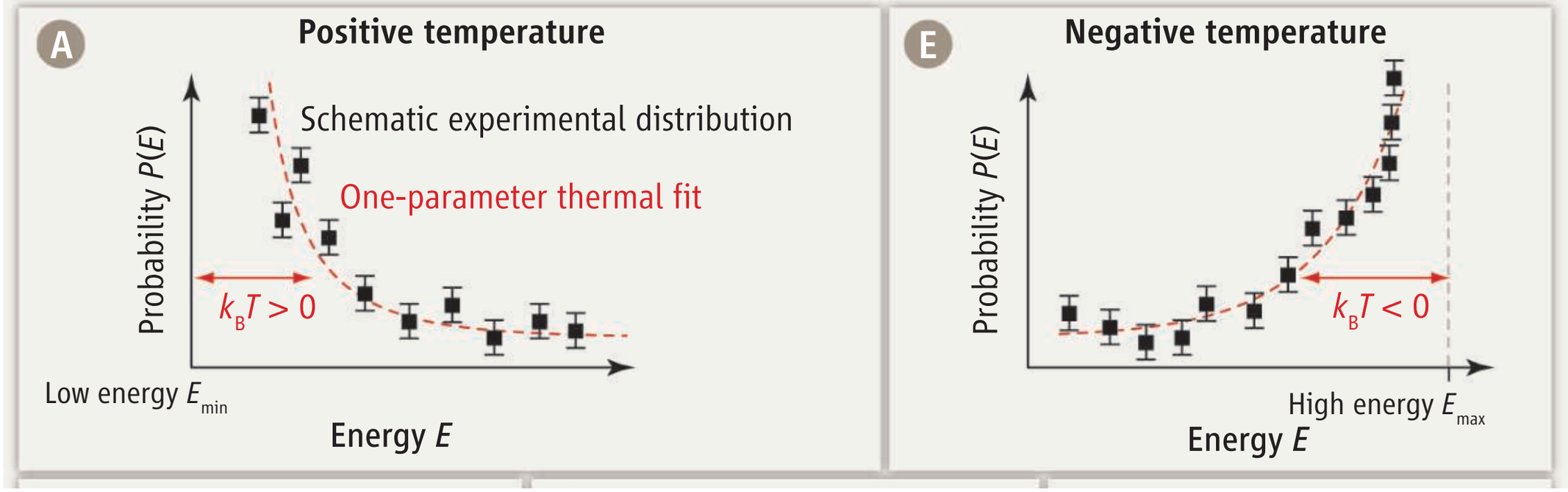
- background & history
- microcanonical thermostatistics revisited
  - Gibbs vs. Boltzmann entropy
  - laws of thermodynamics
  - examples
- Carnot efficiencies >1 ?

PHYSICS

# Negative Temperatures?

**Lincoln D. Carr**

$$P_i \propto e^{-E_i/k_B T}$$




Population inversion of one-particle levels

# Experimental evidence (?)

## A Nuclear Spin System at Negative Temperature

E. M. PURCELL AND R. V. POUND
*Department of Physics, Harvard University, Cambridge, Massachusetts*
November 1, 1950

At field strengths allowing the system to be described by its net magnetic moment and angular momentum, a sufficiently rapid reversal of the direction of the magnetic field should result in a magnetization opposed to the new sense of the field. The reversal must occur in such a way that the time spent below a minimum effective field is so small compared to the period of the Larmor precession that the system cannot follow the change adiabatically. The experiments in zero field reported above[2] showed a zero field resonance at about 50 kc and therefore the following experiment was tried.

nuclear spin
population inversion
in LiF crystal due to
rapid switching of
MF

A system in a negative temperature state is not cold, but very hot, giving up energy to any system at positive temperature put into contact with it. It decays to a normal state through infinite temperature.

E. M. Purcell and R. V. Pound. A nuclear spin system at negative temperature. *Phys. Rev.*, 81(2):279–280, 1951.

EMP
Nobel 1952

PHYSICAL REVIEW VOLUME 103, NUMBER 1 JULY 1, 1956

# Thermodynamics and Statistical Mechanics at Negative Absolute Temperatures

NORMAN F. RAMSEY*
*Harvard University, Cambridge, Massachusetts, and Clarendon Laboratory, Oxford, England*
(Received March 26, 1956)

For this reason and because of the thermodynamic significance of negative temperatures,[4,6] the present paper also contains a more detailed justification for the use of temperature as a description of suitable nuclear spin systems.

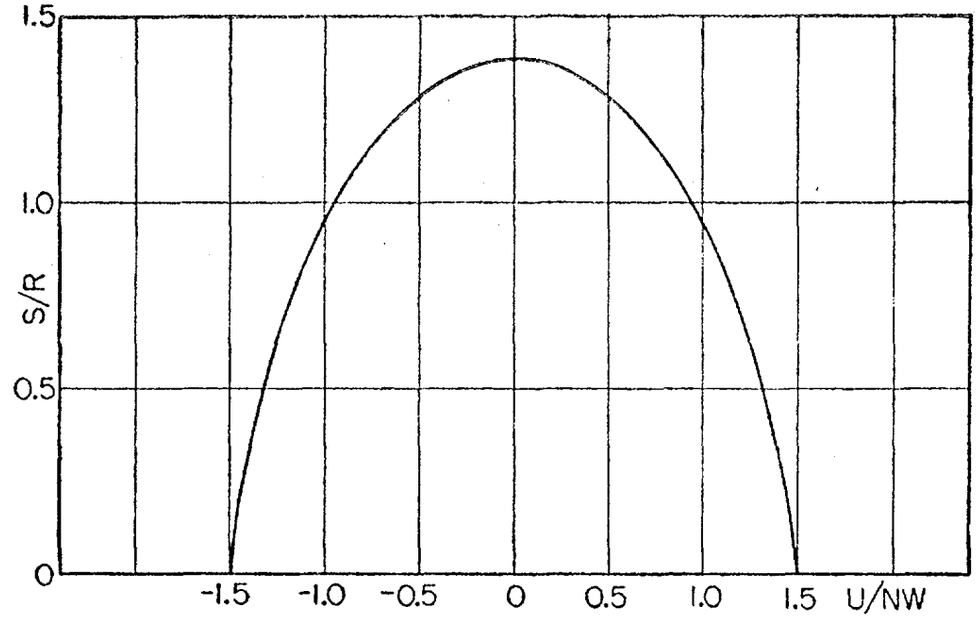



FIG. 1. The entropy is plotted as a function of the internal energy for a system of which each element has four equally spaced energy levels.

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

$$T_{\mathrm{B}}(E,V,A) = \left(\frac{\partial S_{\mathrm{B}}}{\partial E}\right)^{-1} = \frac{1}{k_{\mathrm{B}}}\frac{\omega}{\omega'}$$

Nobel 1989

PHYSICAL REVIEW VOLUME 103, NUMBER 1 JULY 1, 1956

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FIG. 1. The entropy is plotted as a function of the internal energy for a system of which each element has four equally spaced energy levels.

At negative temperatures various cyclic processes, such as magnetic Carnot cycles, can be operated. Just as with positive temperatures, the ratio between two different negative temperatures can be determined absolutely as the ratio of the heats absorbed and rejected by a Carnot cycle operating between the two temperatures.

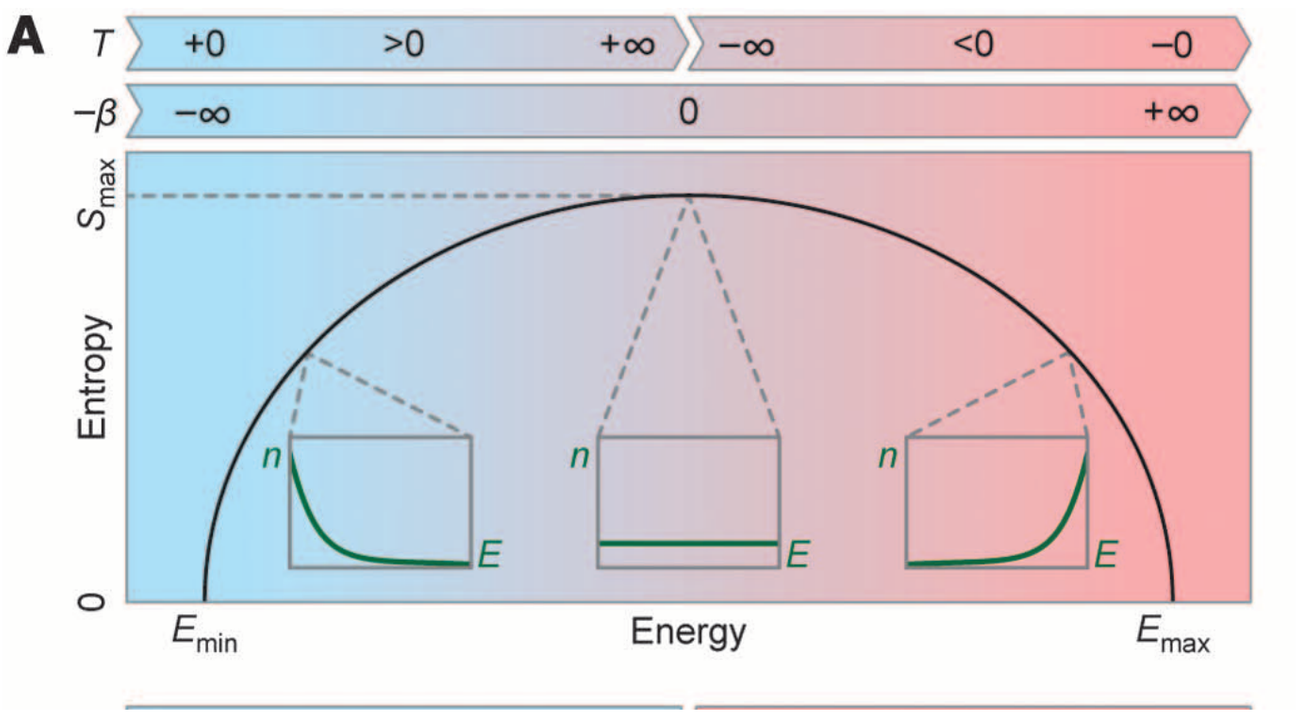
It should be noted, however, that no means has yet been devised by which a Carnot cycle can be operated between positive and negative temperatures. By adi-

$$\eta = 1 - (Q_2/Q_1) = 1 - (T_2/T_1)$$

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Fig 1A

SCIENCE VOL 339 4 JANUARY 2013

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Ultra-cold boson gas in optical lattice $10^5$ $^{39}\mathrm{K}$ atoms

$$H = -J\sum_{\langle i,j\rangle} \hat{b}_i^\dagger \hat{b}_j + \frac{U}{2}\sum_i \hat{n}_i(\hat{n}_i - 1) + V\sum_i \mathrm{r}_i^2 \hat{n}_i$$

via Feshbach resonance

- U>0: repulsive interactions
- U<0: attractive interactions

**Claim:** for U,V<0 spectrum bounded from above, population inversion in momentum space $\Rightarrow T < 0$

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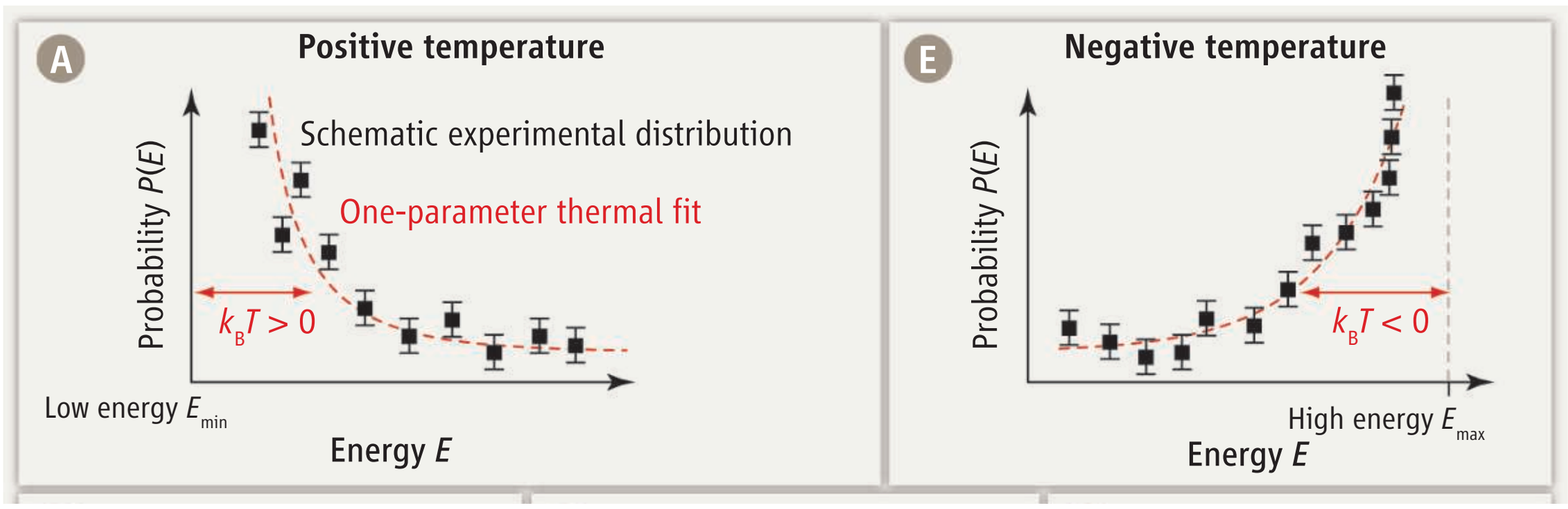
Because negative temperature systems can absorb entropy while releasing energy, they give rise to several counterintuitive effects, such as Carnot engines with an efficiency greater than unity (*4*). Through a stability analysis for thermodynamic equilibrium, we showed that negative temperature states 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

# Key question:

- is the exponential fit parameter the thermodynamic absolute temperature ?
- if not, what happens to the other claims ?




L. D. Carr. Negative temperatures? *Science*, 339:42–43, 2013.

# Microcanonical thermostatistics

Population-inverted system unstable when coupled to an environment (bath)

$\Longrightarrow$ must be kept in isolation & MC description necessary

D-Operator

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

DoS

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

IntDoS

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

Thermodynamic Entropy ?

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

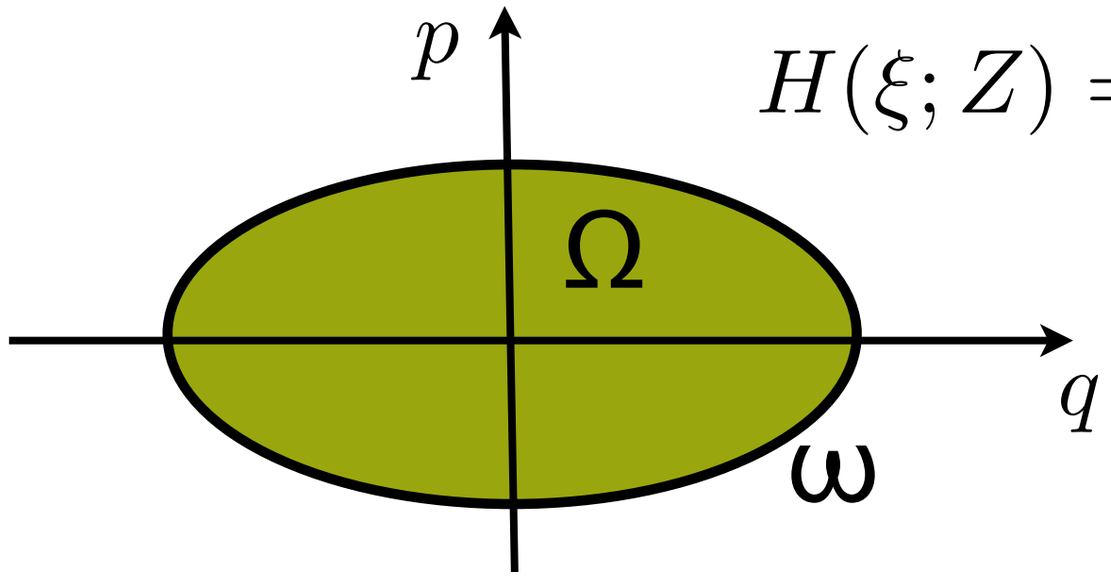
Boltzmann (?)

*vs.*

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

Gibbs (1902), Hertz (1910)

# Microcanonical thermostatistics




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

D-Operator

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

DoS

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

IntDoS

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## Thermodynamic Entropy ?

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

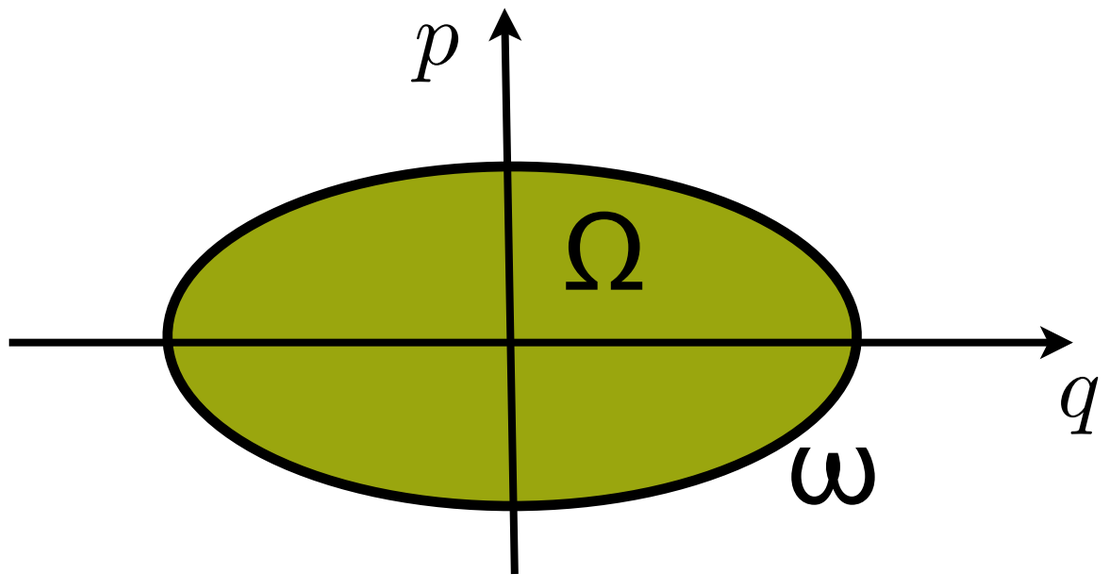
Boltzmann (?)

*vs.*

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

Gibbs (1902), Hertz (1910)

# Boltzmann *vs.* Gibbs




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

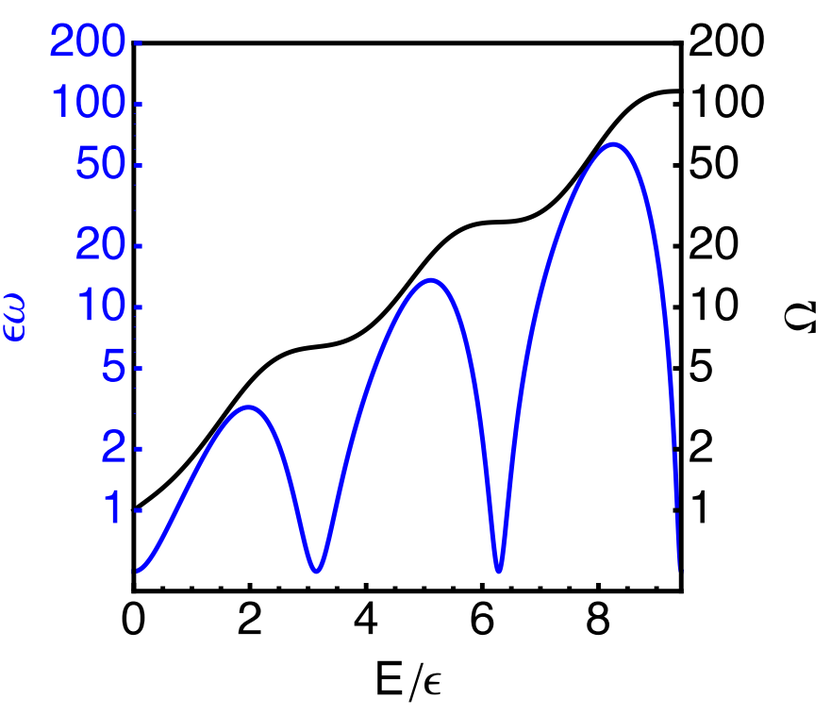
$$T(E,Z) \equiv \left(\frac{\partial S}{\partial E}\right)^{-1}$$

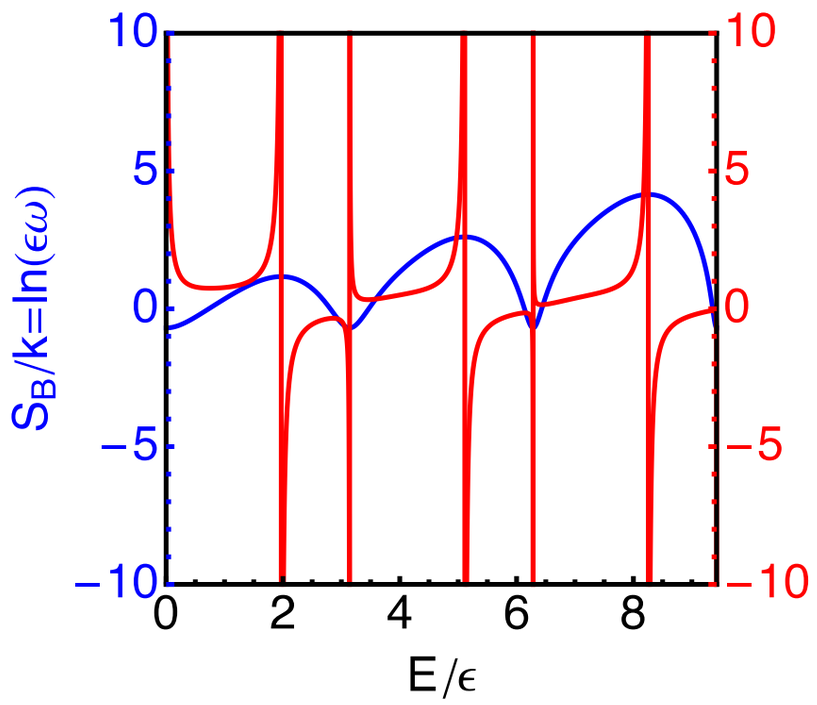
$$T_{\mathrm{B}}(E) = \frac{\omega}{\nu} \gtrless 0 \qquad\qquad T_{\mathrm{G}}(E) = \frac{\Omega}{\omega} \geq 0$$

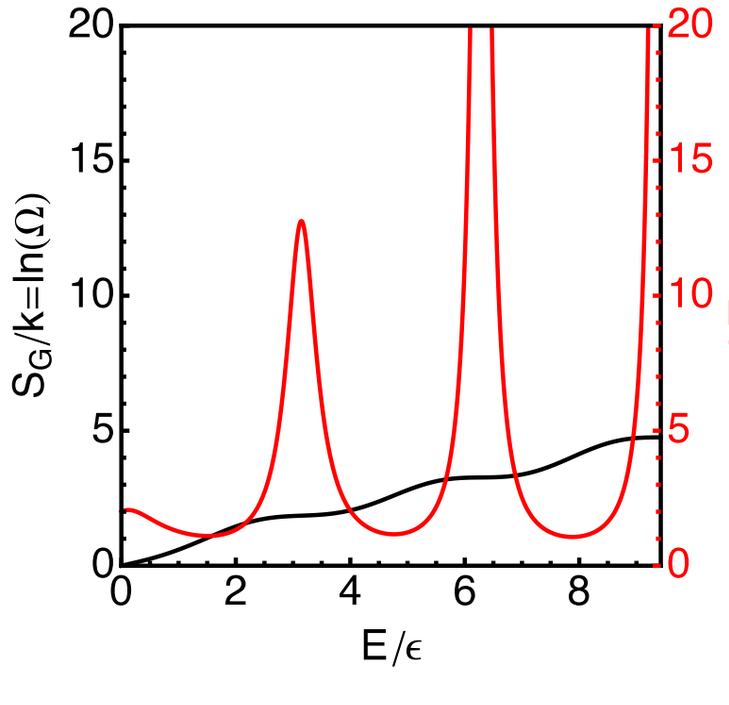
$$\nu(E,Z) = \partial\omega/\partial E,$$

# ‘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.

# Thermal equilibrium

before coupling

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

$\mathcal{A}$

$T_{\mathcal{A}}(E_{\mathcal{A}})$

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

$\mathcal{B}$

$T_{\mathcal{B}}(E_{\mathcal{B}})$

after coupling

$H = H_{\mathcal{A}} + H_{\mathcal{B}} = E_{\mathcal{A}} + E_{\mathcal{B}} = E$

$\mathcal{A}$ — $T(E)$ — $\mathcal{B}$

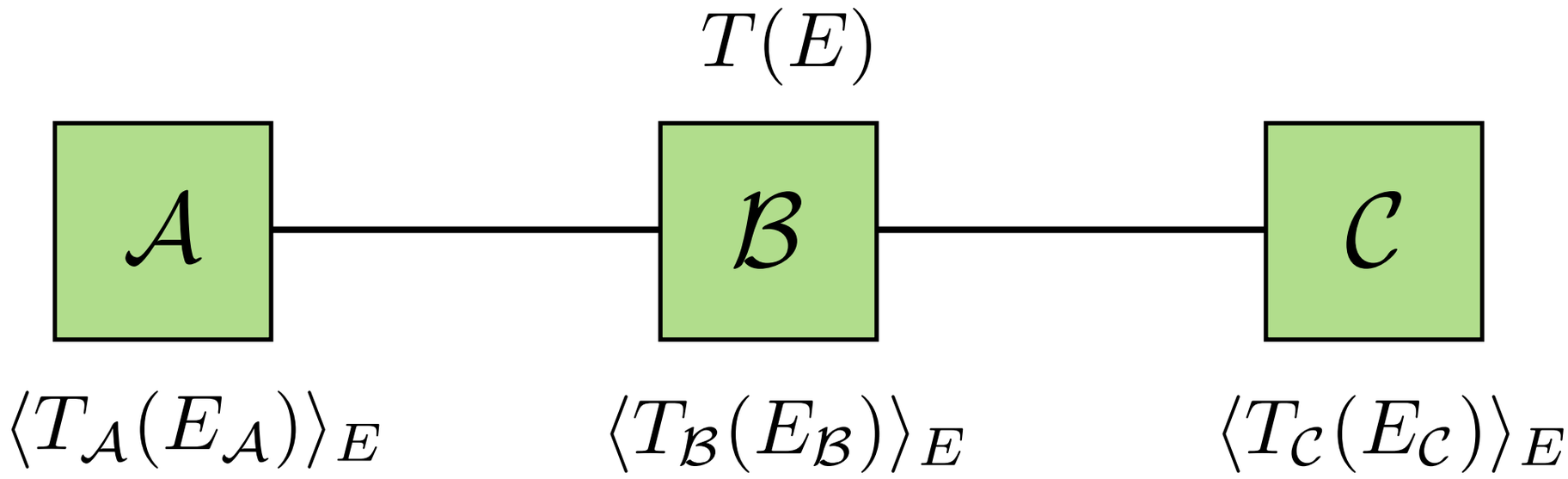
$\langle T_{\mathcal{A}}(E_{\mathcal{A}}) \rangle_E$

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

$$\langle T_i(E_i) \rangle_E = \int_0^\infty dE_i \; T_i(E_i)\, \pi_i(E_i|E)$$

$$\pi_{\mathcal{A}}(E_{\mathcal{A}}|E) = \frac{\omega_{\mathcal{A}}(E_{\mathcal{A}})\, \omega_{\mathcal{B}}(E - E_{\mathcal{A}})}{\omega(E)}$$

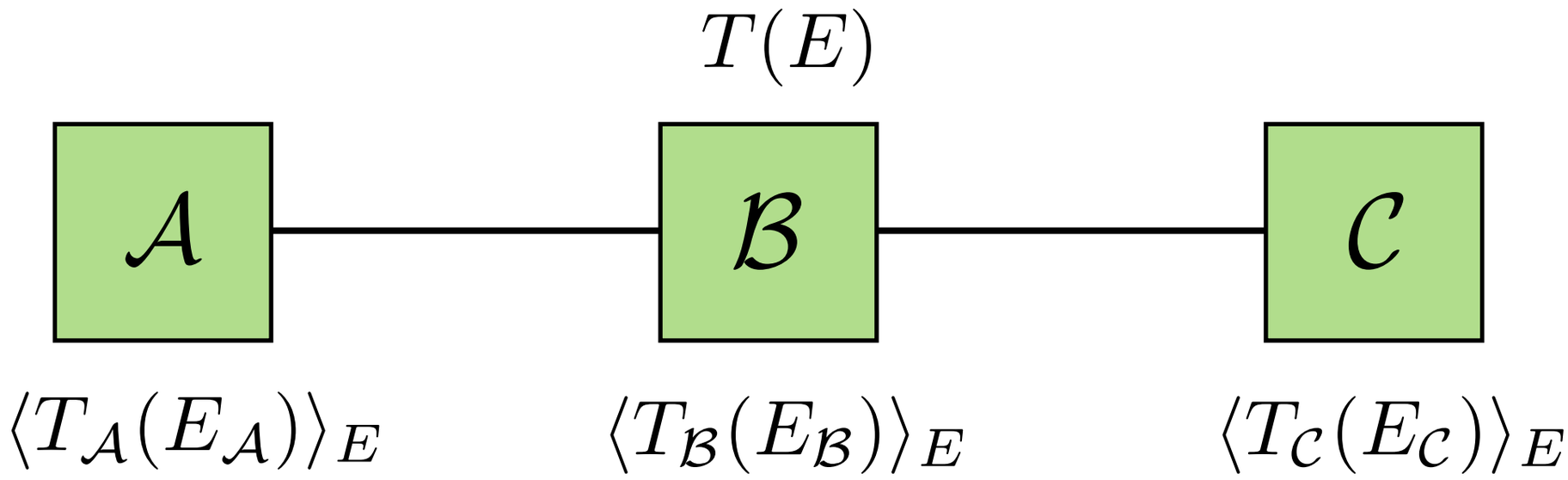
# Zeroth law




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

holds if $\langle T_i(E_i)\rangle_E \stackrel{!}{=} T(E)$

# Zeroth law



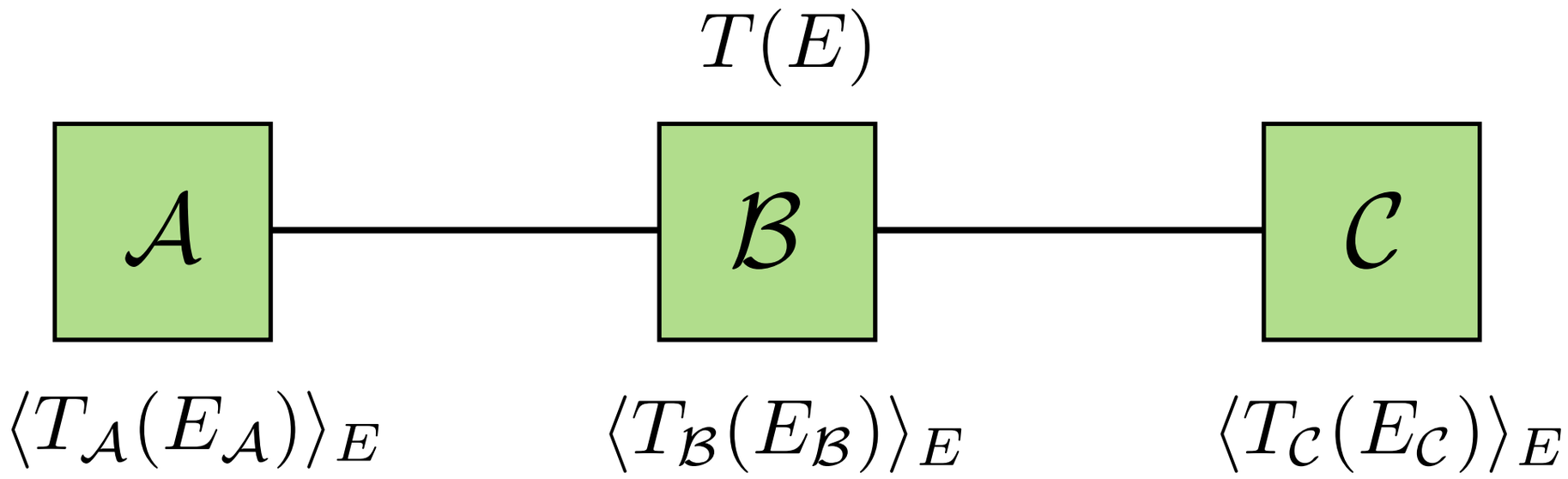

$$\langle T_i(E_i)\rangle_E \stackrel{!}{=} T(E)$$

## Gibbs

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



# Zeroth law




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

## Boltzmann

$$\langle T_{\mathrm{B}\mathcal{A}}(E_{\mathcal{A}})\rangle_E \;=\; \int_0^E \mathrm{d}E_{\mathcal{A}}\, \frac{\omega_{\mathcal{A}}(E_{\mathcal{A}})\omega_{\mathcal{B}}(E-E_{\mathcal{A}})}{\omega(E)}\, \frac{\omega_{\mathcal{A}}(E_{\mathcal{A}})}{\nu_{\mathcal{A}}(E_{\mathcal{A}})} \quad \neq \; T_{\mathrm{B}}(E)$$

satisfies instead $\left\langle \frac{1}{T_{\mathrm{B}\mathcal{A}}} \right\rangle_E = \left\langle \frac{1}{T_{\mathrm{B}\mathcal{B}}} \right\rangle_E = \frac{1}{T_{\mathrm{B}}(E)}$

# 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

$$T_{\mathrm{G}}\left(\frac{\partial S_{\mathrm{G}}}{\partial Z_j}\right) = \frac{1}{\omega}\frac{\partial}{\partial Z_j}\mathrm{Tr}\Big[\Theta(E-H)\Big] = -\frac{1}{\omega}\mathrm{Tr}\left[-\frac{\partial}{\partial Z_j}\Theta(E-H)\right]$$

$$= -\mathrm{Tr}\left[\left(\frac{\partial H}{\partial Z_j}\right)\frac{\delta(E-H)}{\omega}\right] = -\left\langle \frac{\partial H}{\partial Z_j} \right\rangle$$



see also Campisi, Physica A 2007

# First law

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

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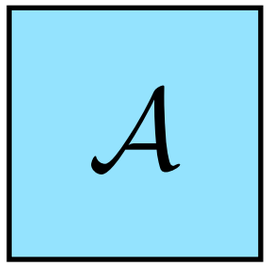
Gibbs ✓ $\Rightarrow$ Boltzmann ✗

see also Campisi, Physica A 2007

# Second law

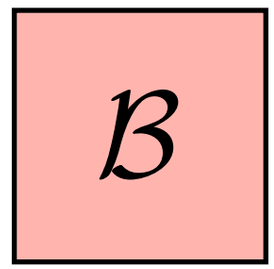
before coupling

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




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

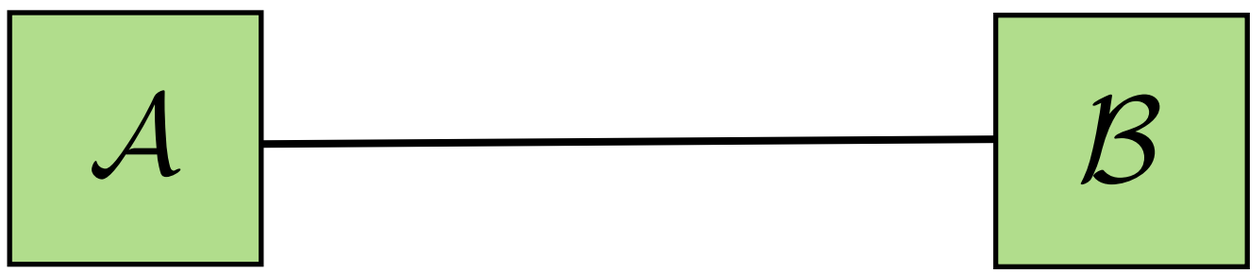
$H_{\mathcal{B}} = E_{\mathcal{B}}$




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

after coupling

$H = H_{\mathcal{A}} + H_{\mathcal{B}} = E_{\mathcal{A}} + E_{\mathcal{B}} = E$




$S_{\mathcal{AB}}(E)$

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

# Second law

Gibbs

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

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

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



# Second law

Boltzmann

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

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

$$\not\geq \quad \epsilon^2 \omega_{\mathcal{A}}(E_{\mathcal{A}})\omega_{\mathcal{B}}(E_{\mathcal{B}})$$

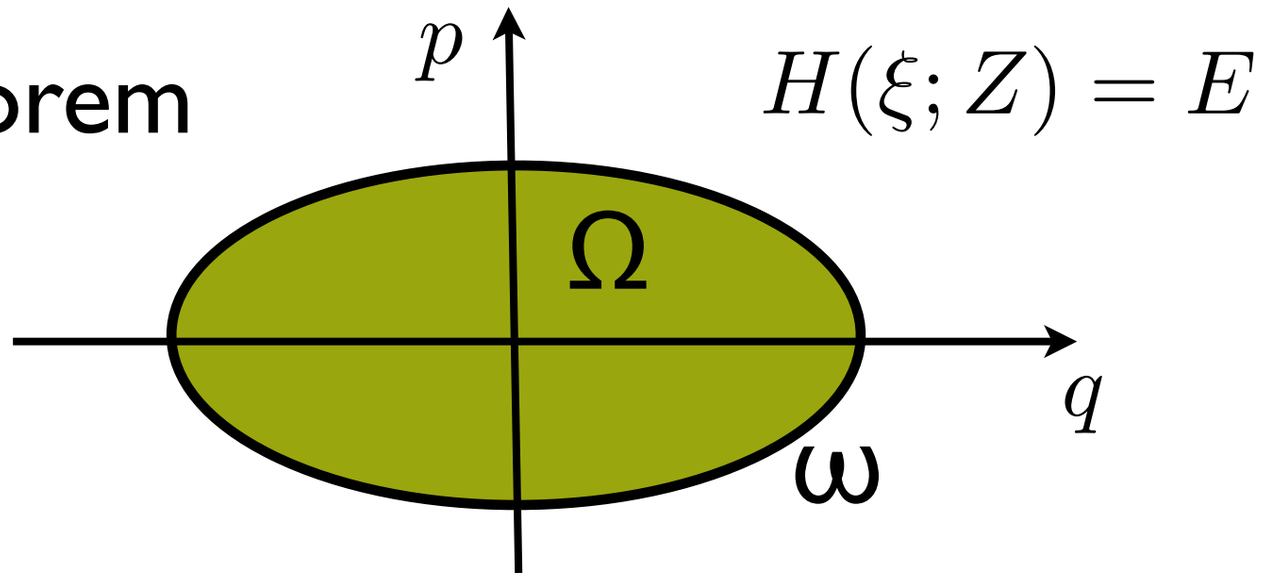


# For Gibbs temperature & classical Hamiltonian systems even more ...

for all canonical coordinates $\xi = (\xi_1, \ldots)$ equipartition

$$\left\langle \xi_i \frac{\partial H}{\partial \xi_j} \right\rangle \equiv \mathrm{Tr}\left[ \left( \xi_i \frac{\partial H}{\partial \xi_j} \right) \rho \right] = k_\mathrm{B} T_\mathrm{G}\, \delta_{ij}$$

... essentially Stokes theorem




A. I. Khinchin. *Mathematical Foundations of Statistical Mechanics*. Dover, New York, 1949.

| Entropy | $S(E)$ | second law Eq. (38) | first law Eq. (37) | zeroth law Eq. (20) | equip artition equipartition |
|---|---|---|---|---|---|
| Gibbs | $\ln \Omega$ | yes | yes | yes | yes |
| Penrose | $\ln \Omega + \ln\big(\Omega_\infty - \Omega\big) - \ln \Omega_\infty$ | yes | yes | no | no |
| Complementary Gibbs | $\ln\big[\Omega_\infty - \Omega\big]$ | yes | yes | no | no |
| Differential Boltzmann | $\ln\big[\Omega(E+\epsilon) - \Omega(E)\big]$ | yes | no | no | no |
| Boltzmann | $\ln\big(\epsilon\omega\big)$ | no | no | no | no |

Hilbert, Hänggi & Dunkel, in preparation, 2014

New results?

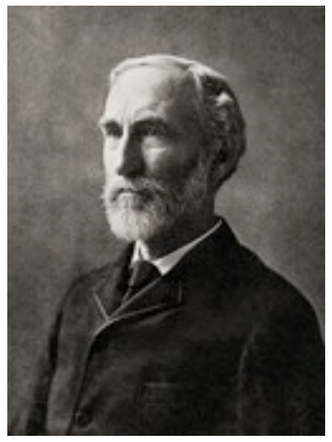
no ... just ignored in many recent papers & textbooks

GIBBS, JOSIAH WILLARD.

# *Elementary principles in statistical mechanics*

Scribner's sons

*New York* 1902



## CHAPTER VIII.

### ON CERTAIN IMPORTANT FUNCTIONS OF THE ENERGIES OF A SYSTEM.

In order to consider more particularly the distribution of a canonical ensemble in energy, and for other purposes, it will be convenient to use the following definitions and notations.

Let us denote by $V$ the extension-in-phase below a certain limit of energy which we shall call $\epsilon$. That is, let

$$V = \int \ldots \int dp_1 \ldots dq_n, \tag{265}$$

the integration being extended (with constant values of the external coördinates) over all phases for which the energy is less than the limit $\epsilon$. We shall suppose that the value of this integral is not infinite, except for an infinite value of the limiting energy. This will not exclude any kind of system to

## CHAPTER XIV.

### DISCUSSION OF THERMODYNAMIC ANALOGIES.

If we wish to find in rational mechanics an *a priori* foundation for the principles of thermodynamics, we must seek mechanical definitions of temperature and entropy. The quantities thus defined must satisfy (under conditions and with limitations which again must be specified in the language of mechanics) the differential equation

$$d\epsilon = T\,d\eta - A_1\,da_1 - A_2\,da_2 - \text{etc.}, \tag{482}$$

where $\epsilon$, $T$, and $\eta$ denote the energy, temperature, and entropy of the system considered, and $A_1\,da_1$, etc., the mechanical work (in the narrower sense in which the term is used in thermodynamics, *i. e.*, with exclusion of thermal action) done upon external bodies.

The quantity in the equation which corresponds to entropy is log $V$, the quantity $V$ being defined as the extension-in-phase within which the energy is less than a certain limiting value ($\epsilon$).

1910. № 12.

# ANNALEN DER PHYSIK.

VIERTE FOLGE. BAND 33.

## 1. *Über die mechanischen Grundlagen der Thermodynamik;* *von Paul Hertz.*

(17) $$\int_{\varepsilon<\varepsilon^*}\int dx_1 \ldots dx_m = V(\varepsilon^*),$$

so ist nach (14)

(18) $$\omega = \frac{dV}{d\varepsilon^*}.$$

(37) $$\overline{\varepsilon_p} = \frac{n}{2}\,\mathrm{t},$$

wo

(38) $$\mathrm{t} = \frac{V}{\omega}$$

gesetzt ist. Nach (18) kann man (38) auch schreiben

(39) $$\frac{1}{\mathrm{t}} = \frac{d\ln V}{d\varepsilon^*}.$$

## 4. *Über die mechanischen Grundlagen der Thermodynamik;* *von Paul Hertz.*

(Fortsetzung von p. 225.)

Inhalt: II. Teil. Thermisch-mechanische Vorgänge. (Der Satz von der Entropievermehrung) p. 537. § 10. Äußere Koordinaten (Zustandsgleichung) p. 537. § 11. Adiabatische Vorgänge p. 544. § 12. Reversible Vorgänge p. 549. § 13. Irreversible Vorgänge p. 550.

„ein eindimensionales Gas“ (Fig. 4a)

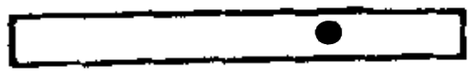


Fig. 4a.

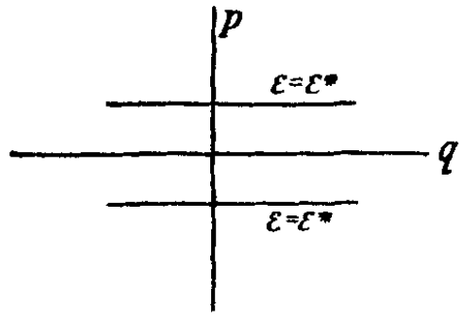



Fig. 4b.

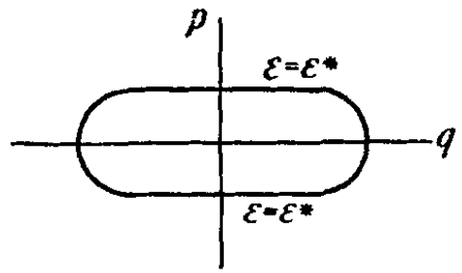



Fig. 4c.

P Hertz, Ann d Phys 33: 225 (1910)
P Hertz, Ann d Phys 33: 537 (1910)

Ann. Phys. (Berlin) **17**, No. 5, 273 – 301 (2008) / **DOI** 10.1002/andp.200810294

**Historical Review**

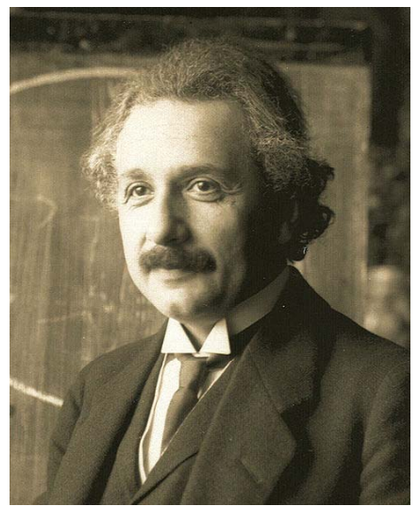
# "… you can't say to anyone to their face: your paper is rubbish."

# Max Planck as Editor of the *Annalen der Physik*

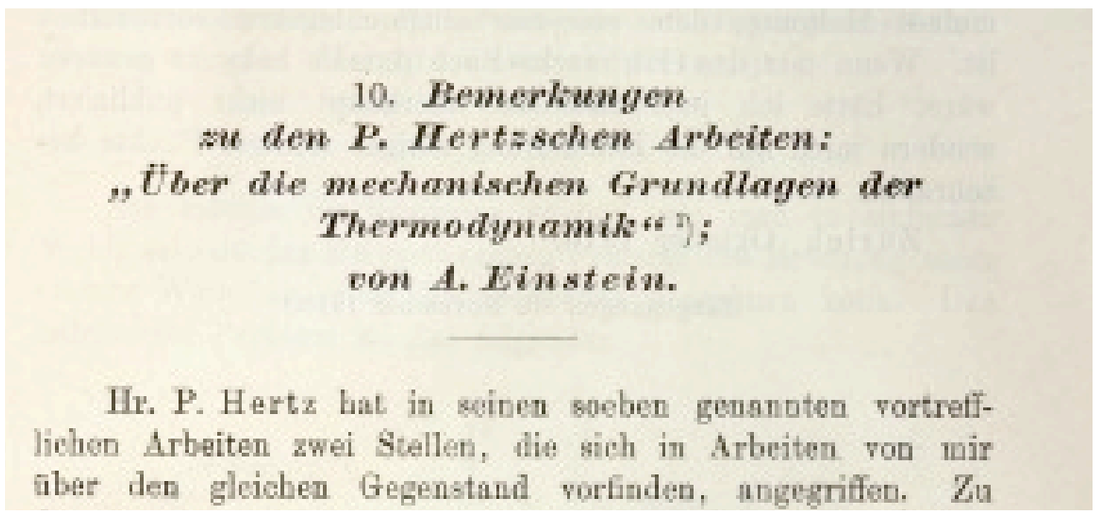
**Dieter Hoffmann***

Max Planck Institute for the History of Science, Boltzmannstr. 22, 14195 Berlin, Germany



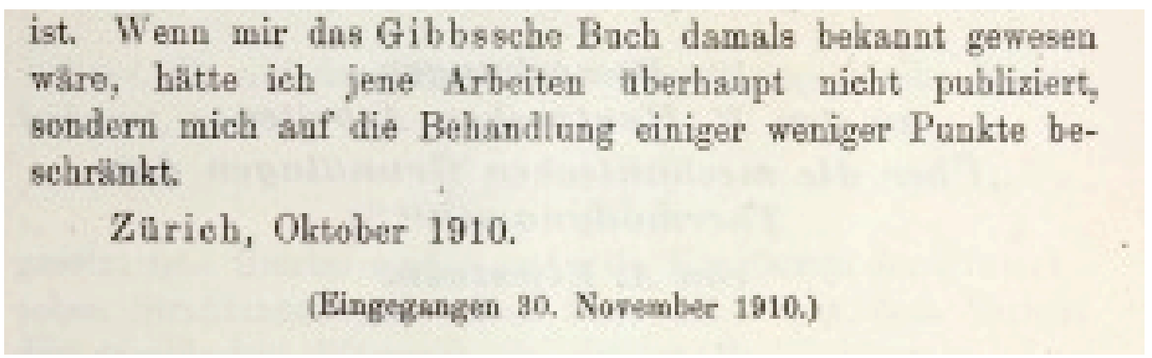


he was concerned to define an editorial policy that would exclude all too mathematical papers. However he was willing to make exceptions, for instance regarding a very mathematical paper on the mechanical foundations of thermodynamics by the Heidelberg physicist (and also later philosopher) Paul Hertz. But this investigation was dealing with such an important and difficult aspect for understanding statistical mechanics, that in this case "the comprehensiveness is a necessity for clarity" [119] and the author was even allowed to publish his work in two parts [120]; of course the problem discussed was also very close to Planck's own thermodynamical work.



10. *Bemerkungen*
*zu den P. Hertzschen Arbeiten:*
*„Über die mechanischen Grundlagen der Thermodynamik"* [1];
*von A. Einstein.*

Hr. P. Hertz hat in seinen soeben genannten vortrefflichen Arbeiten zwei Stellen, die sich in Arbeiten von mir über den gleichen Gegenstand vorfinden, angegriffen. Zu



ist. Wenn mir das Gibbssche Buch damals bekannt gewesen wäre, hätte ich jene Arbeiten überhaupt nicht publiziert, sondern mich auf die Behandlung einiger weniger Punkte beschränkt.

Zürich, Oktober 1910.

(Eingegangen 30. November 1910.)

# 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.

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

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

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# Example 2: 1-dim quantum oscillator

$$E_n = \hbar\nu\left(n + \frac{1}{2}\right), \qquad n = 0, 1, \ldots, \infty$$

$$\Omega = 1 + n = 1/2 + E/(\hbar\nu)$$

$$\omega = (\hbar\nu)^{-1}$$

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

$$T_{\mathrm{B}} = \infty$$

*heat capacity ?*

VS.

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

$$k_{\mathrm{B}} T_{\mathrm{G}} = \frac{\hbar\nu}{2} + E$$

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$$E_n = an^2/L^2, \qquad a = \hbar^2\pi^2/(2m), \qquad n = 1, 2, \ldots, \infty$$

$$\Omega = n = L\sqrt{E/a}$$

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

$$k_{\rm B}T_{\rm B} = -2E < 0$$

$$p_{\rm B} \equiv T_{\rm B}\left(\frac{\partial S_{\rm B}}{\partial L}\right) = -\frac{2E}{L} \neq p$$

*Dark energy ???*

**vs.**

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

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# ... what about
# N-particle systems with bounded spectrum ?

## A Nuclear Spin System at Negative Temperature

E. M. PURCELL AND R. V. POUND
*Department of Physics, Harvard University, Cambridge, Massachusetts*
November 1, 1950

SCIENCE VOL 339 4 JANUARY 2013

## Negative Absolute Temperature for Motional Degrees of Freedom

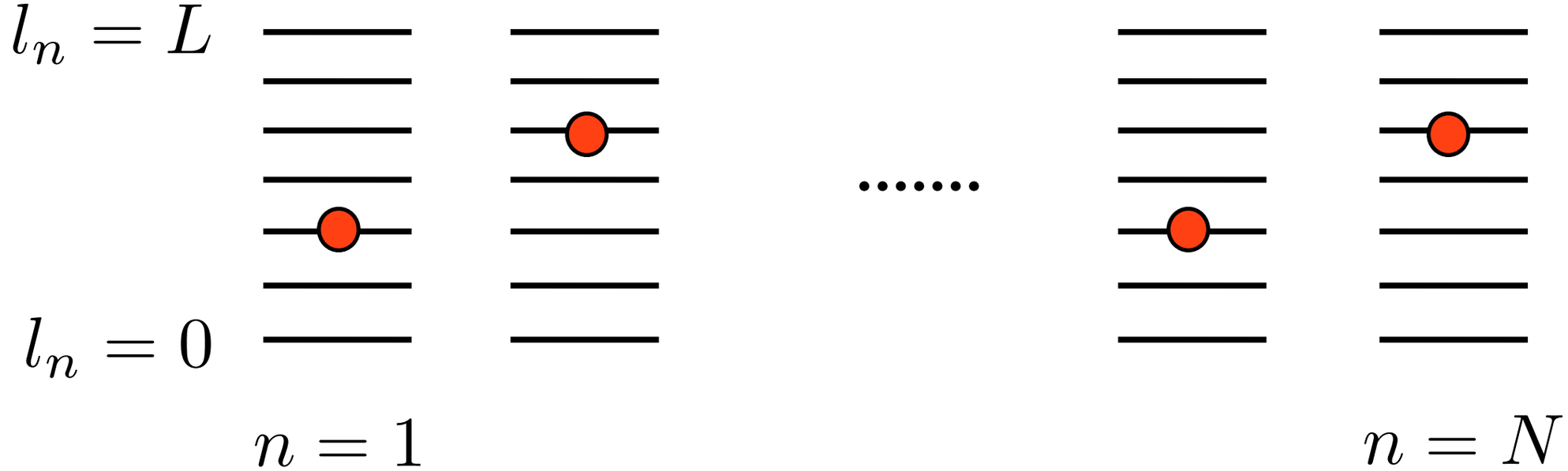
S. Braun,[1,2] J. P. Ronzheimer,[1,2] M. Schreiber,[1,2] S. S. Hodgman,[1,2] T. Rom,[1,2]
I. Bloch,[1,2] U. Schneider[1,2]*

# Generic spin or oscillator model

arxiv: 1304.2066

$$H_N \simeq \sum_{n=1}^{N} h_n, \qquad E_{\ell_n} = \epsilon \ell_n \qquad \ell_n = 0, 1 \ldots, L$$

$$E_\Lambda = \epsilon(\ell_1 + \ldots + \ell_N) \qquad 0 \leq E_\Lambda \leq E_+ = \epsilon L N$$



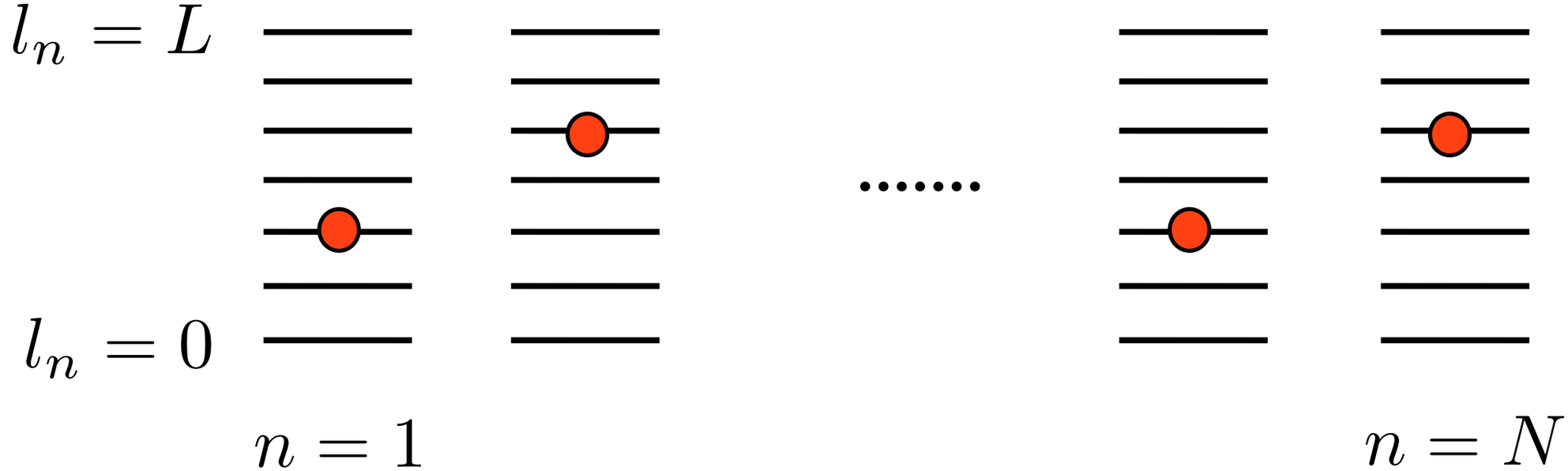
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$$\omega(E) \simeq \omega_* \exp[-(E - E_*)^2/\sigma^2] \qquad \Omega(E) \simeq 1 + \frac{\omega_* \sqrt{\pi}\sigma}{2} \left[ \mathrm{erf}\left( \frac{E - E_*}{\sigma} \right) + \mathrm{erf}\left( \frac{E_*}{\sigma} \right) \right]$$



# Generic spin or oscillator model

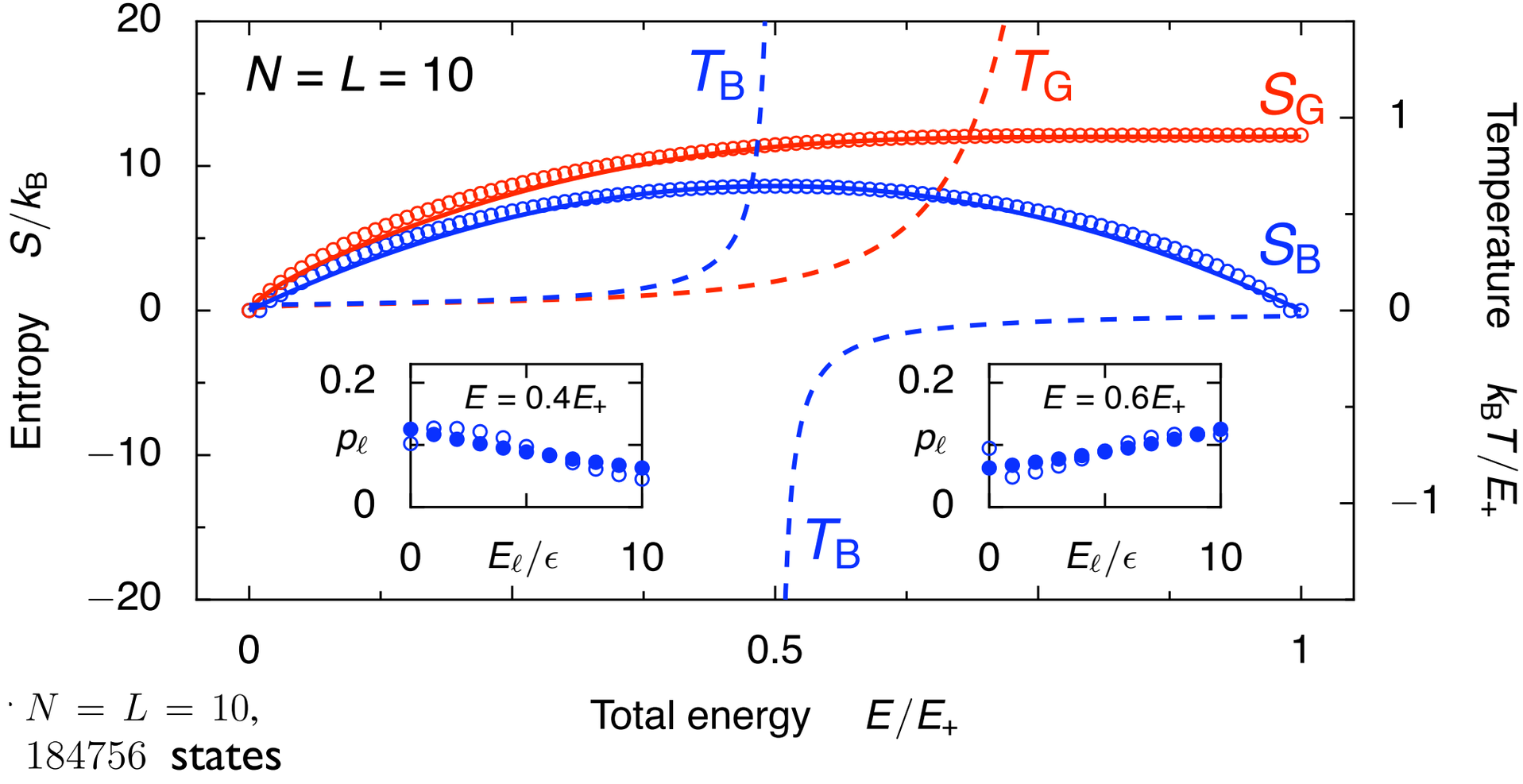
arxiv: 1304.2066

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$$k_{\mathrm{B}} T_{\mathrm{B}} = \frac{\sigma^2}{E_+ - 2E}$$

but

$$T_{\mathrm{G}} > 0$$

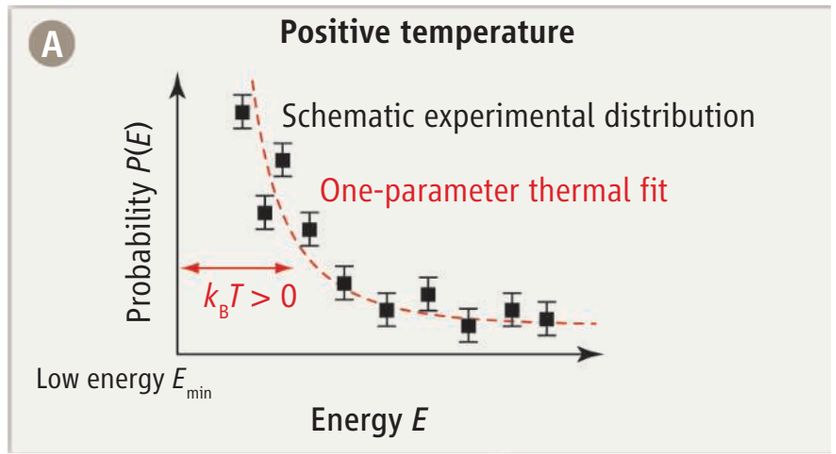
- $N = L = 10$, 184756 states

# Measuring $T_{\rm B}$ *vs.* $T_{\rm G}$

arxiv: 1304.2066

## One-particle distribution

$$\rho_1 = \mathrm{Tr}_{N-1}[\rho_N] = \frac{\mathrm{Tr}_{N-1}[\delta(E - H_N)]}{\omega_N}$$




## Steepest-descent approximation

$$\rho_1 = \exp[\ln \rho_1] \quad \Rightarrow \quad p_\ell \simeq \frac{e^{-E_\ell/(k_{\rm B}T_{\rm B})}}{Z}, \qquad Z = \sum_\ell e^{-E_\ell/(k_{\rm B}T_{\rm B})}.$$

see e.g. Huang's textbook

features $T_{\rm B}$ and not $T_{\rm G}$

$\Rightarrow$ one-particle thermal fit does not give absolute $T = T_{\rm G}$

Generally

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

$$C = \left(\frac{\partial T_{\rm G}}{\partial E}\right)^{-1}$$

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

Proof:

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

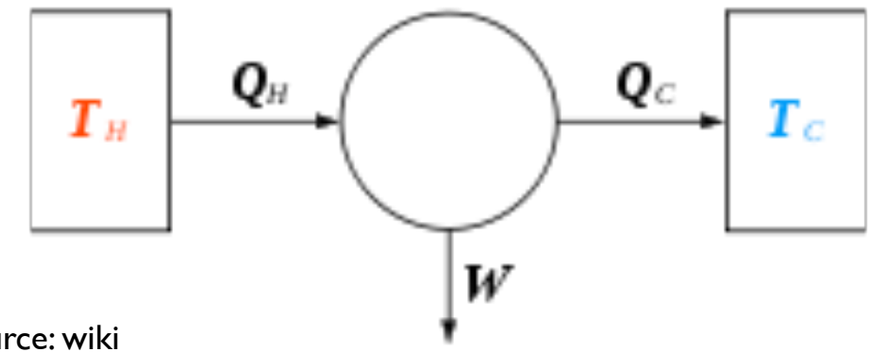
$$\frac{1}{C} \equiv \left( \frac{\partial T_{\mathrm{G}}}{\partial E} \right) = \frac{1}{k_{\mathrm{B}}} \left( \frac{\Omega}{\Omega'} \right)' = \frac{1}{k_{\mathrm{B}}} \frac{\Omega'\Omega' - \Omega\Omega''}{(\Omega')^2}$$

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

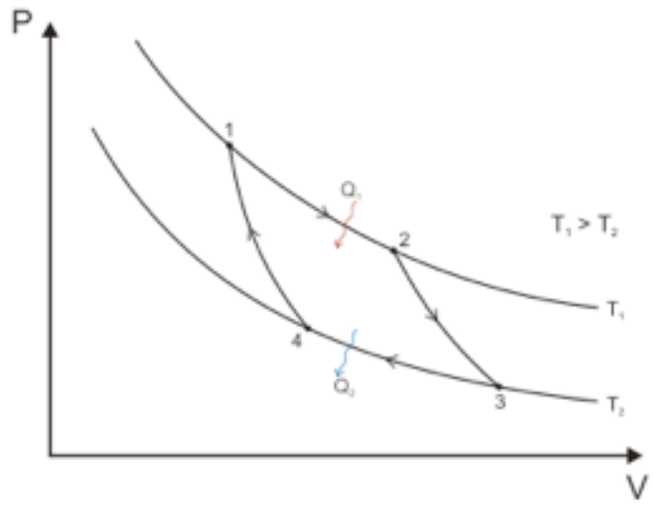
□

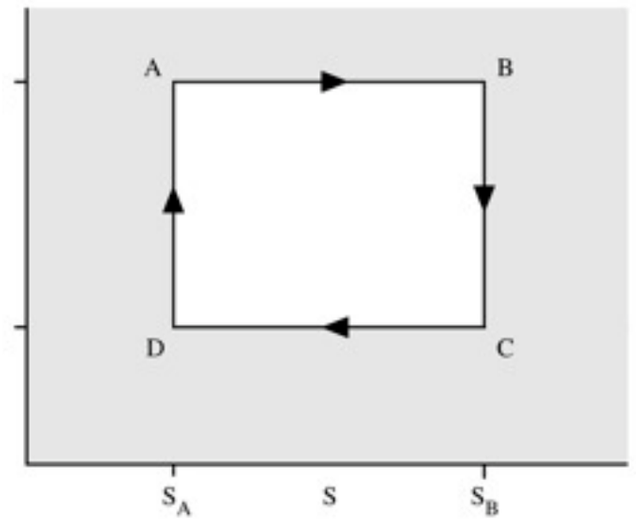
# Carnot efficiencies > 1?

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




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

# Conclusions

- population inversion $\Rightarrow$ microcanonical
- bounded spectrum $\Rightarrow$ ensembles not equivalent
- consistent thermostatistics $\Rightarrow$ Gibbs entropy

- temperature always positive ('by construction')
- no Carnot efficiencies > 1
- please correct textbooks & lecture notes

Nature Physics 10: 67-72, 2014

# “Myths”

- TD entropy = information entropy (which?)
- MC Boltzmann entropy = information entropy
- non-degenerate states must have *S=0*
- if spectrum invariant under $E \rightarrow -E$ , then so should be entropy
- Gibbs entropy violates second law

Joshi & Campisi EPJB (2013) 86: 157