On the Use and Abuse of THERMODYNAMIC Entropy in Physics and Elsewhere

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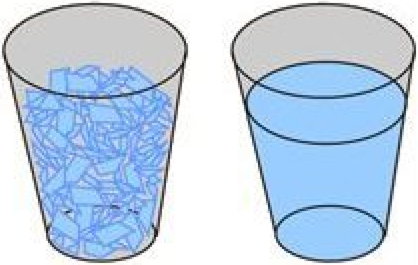
Lit: S. Hilbert, P. Hänggi and J. Dunkel, Phys. Rev. E, Phys. Rev. E **90**, 062116 (2014)
P. Hänggi, S. Hilbert and J. Dunkel, Phil.Trans. Roy. Soc. A **374**, 20150039 (2016)

Which is more disordered? The glass of ice chips or the glass of water?




THE
NEW YORKER

COMMUNICATIONS ON PURE AND APPLIED MATHEMATICS, VOL. XIV, 323-354 (1961)

K. O. Friedrichs anniversary issue

The Many Faces of Entropy*

HAROLD GRAD

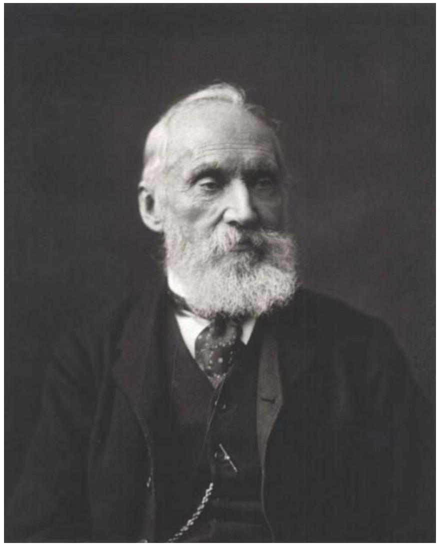
The proper choice will depend on the interests of the individual, the particular phenomena under study, the degree of precision available or arbitrarily decided upon, or the method of description which is employed; and each of these criteria is largely subject to the discretion of the individual.

Second Law

Rudolf Julius Emanuel Clausius
(1822 – 1888)

Heat generally cannot spontaneously flow from a material at lower temperature to a material at higher temperature.

$$\delta Q = T\mathrm{d}S \quad (\text{Zürich, 1865})$$



William Thomson alias Lord Kelvin
(1824 – 1907)

No cyclic process exists whose sole effect is to extract heat from a single heat bath at temperature T and convert it entirely to work.

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)

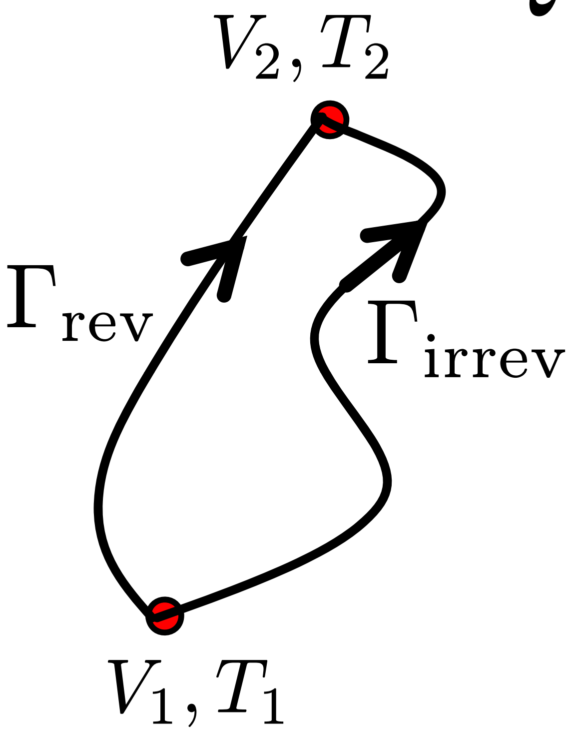
For a non-quasi-static process occurring in a thermally isolated system, the entropy change between two equilibrium states is non-negative.

Second Law (Kelvin)

No work can be extracted from a closed equilibrium system during a cyclic variation of a parameter by an external source.

Entropy S – content of *transformation* „Verwandlungswert“

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



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

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

$$\left.\begin{aligned} S(V_2,T_2) - S(V_1,T_1) &\geq \int_{\Gamma_{\mathrm{irrev}}} \frac{\delta Q}{T} \\ S(V_2,T_2) - S(V_1,T_1) &= \int_{\Gamma_{\mathrm{rev}}} \frac{\delta Q^{\mathrm{rev}}}{T} \end{aligned}\right\} \quad \frac{\partial S}{\partial t} \geq 0$$

NO !

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.

Heat in Thermodynamics

$$\boxed{\Delta U} = \Delta Q^{\mathrm{irrev}} + \Delta W^{\mathrm{noneq}}$$

$$\Rightarrow \Delta Q^{\mathrm{irrev}} = \Delta U - \Delta W^{\mathrm{noneq}}$$

must know must know

ABUSE OF ENTROPY

"The tendency of institutions to become larger, more complex, and more centralized is the same tendency we see with various forms of technology. The reason for this can be found in the operation of the Entropy Law"

"While the Eastern religions have understood the value of minimizing energy flow and lessening the accumulation of disorder, it is the Western religions that have understood the linear nature of history, which is the other important factor in synthesizing a new religious doctrine in line with the requirements of the Entropy Law"

Rifkin and T. Howard, Entropy, A New World View (Granada Publ., London, 1985).

"Yet our personal lives also obey the Entropy Law. We go from birth to death". "The Second Law states unequivocally that the entropy of open [sic] systems must increase. Since we are all open systems, this means that all of us are doomed to die"

J.E. Lovelock, Gaia, A New Look at Life on Earth (OUP, 1987).

"Since biological information resides in biological systems and has a physical interpretation, it must be subject to the consequences of the second law"

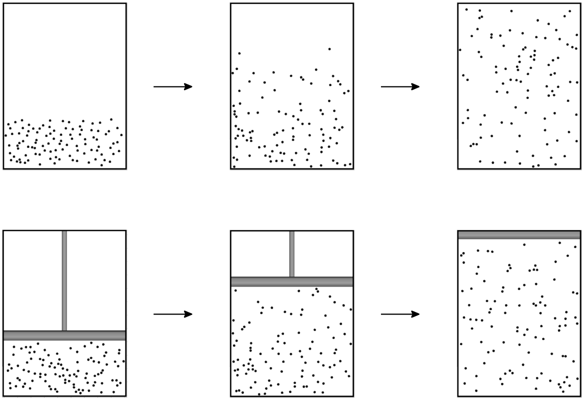
B.H. Weber et al. (Herausg.), Entropy, Information, and Evolution (MIT Press, Cambridge, Mass., 1988), p. 177.

… and finally … from the Vatican

Pope XII: (Pontifical Academy of Sciences, 1952)

….The Second thermodynamic Law by Rudolph Clausius on Entropy increase gives us certainty that spontaneous, *natural processes* are always associated with a certain loss of free exploitable energy, which implies that they cease to exist in a closed materialistic, macroscopic system on the macroscopic level. This deplorable necessity provides a demonstrative testimony to the existence of a higher being [i.e. God]…..

MINUS FIRST LAW vs. SECOND LAW



-1st Law

2nd Law

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THE MANY FACETS OF ENTROPY

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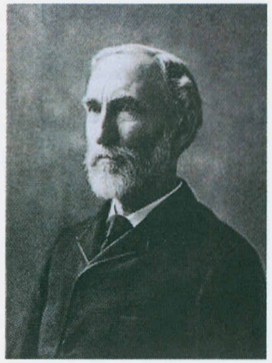
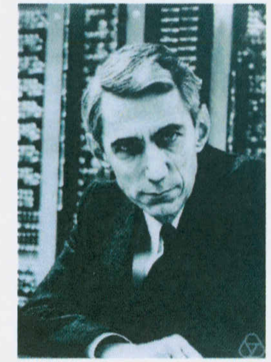
(*Received December 31, 1990*)

Several notions of entropy are discussed: classical entropies (Boltzmann, Gibbs, Shannon, quantum-mechanical entropy, skew entropy, among other notions as well as classical and quantum-mechanical dynamical entropies.



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

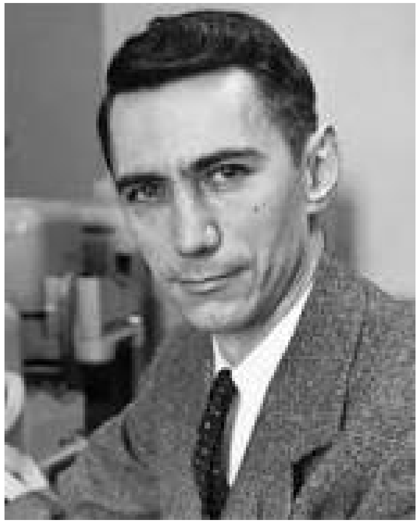
FISHER

Daroczy-Harvda-Charvat-Tsallis

WEHRL

Hartley-chaitin

ETC.



Claude Elwood Shannon

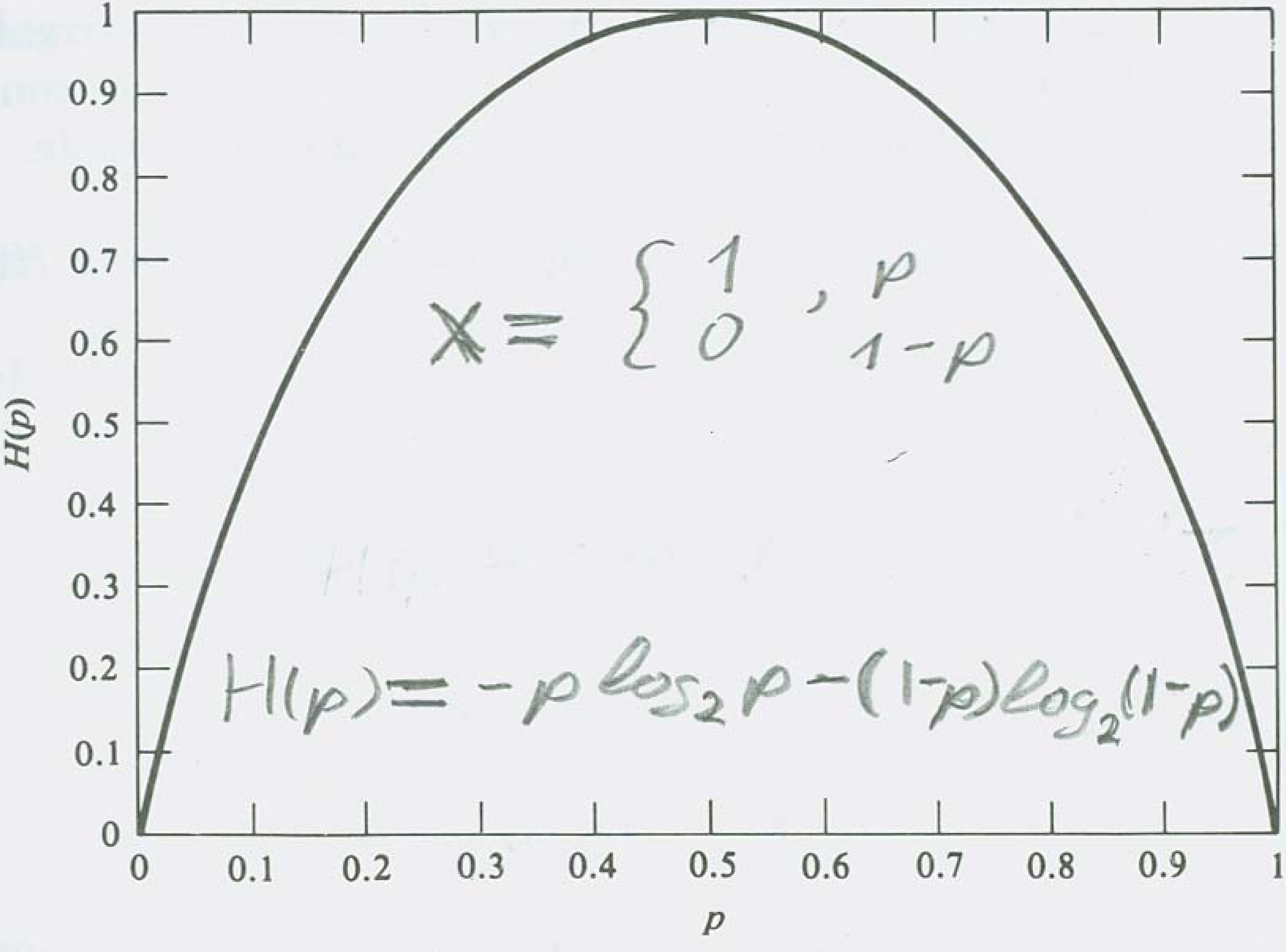
$$H(x) = - \Sigma\, p(x) \log_2 p(x)$$

Shannon entropy is a measure of the average uncertainty in the random variable.

It is the number $\langle n_x \rangle$ of bits on the average required to describe the random variable.

Minimum expected number of binary questions required to determine x is between H(x) and H(x)+1.

$$H(x) \leq n_x < H(x) + 1$$

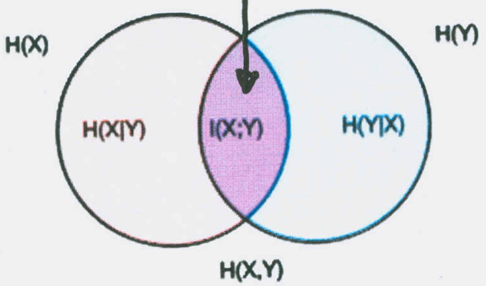


$$X = \begin{cases} 1, & p \\ 0, & 1-p \end{cases}$$

$$H(p) = -p\log_2 p - (1-p)\log_2(1-p)$$

Conditional Entropy

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

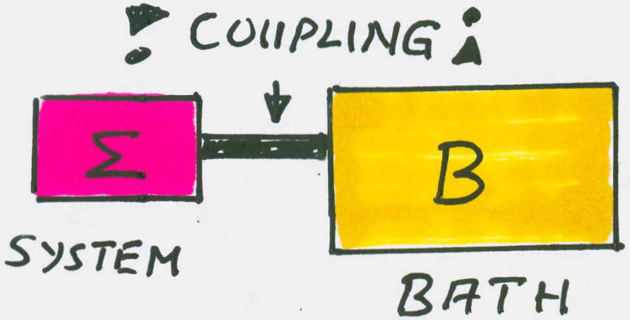


$$H(y|x) = -\sum_{x,y} p(x,y) \ln p(x,y) - \left(-\sum_{x} p(x) \ln p(x)\right)$$

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

Quantum Conditional Entropy

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

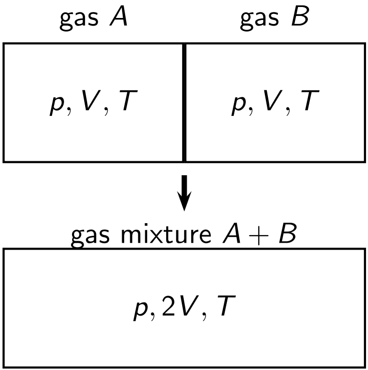


$$S_\Sigma = S_{vN}(\varrho^{can}_{\Sigma\times B}) - S_{vN}(\varrho^{can}_B)$$ can. thermod. entropy

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

$\neq \varrho^{can}_B$

The Gibbs paradox in thermodynamics



Entropy change:

$$\Delta S := S_{A+B} - (S_A + S_B) = 2R \log 2$$

But is A is identical to B then $\Delta S = 0$

	Specific	Generic
Phase space	Γ	$\tilde{\Gamma} = \Gamma / \{\Pi\}$
phase space volume	dx	$d\tilde{x} = dx/N!$
partition function	$Z = \int_\Gamma e^{-\beta H(x)} dx$	$\tilde{Z} = Z/N!$
expectations	$\langle A \rangle_s = \frac{1}{Z} \int_\Gamma A e^{-\beta H} dx$	$\langle A \rangle_g = \frac{1}{\tilde{Z}} \int_\Gamma A e^{-\beta H} d\tilde{x}$
Entropy	$S = \frac{\partial}{\partial T}(kT \log Z)$	$\tilde{S} = \frac{\partial}{\partial T}(kT \log \tilde{Z}$

Only difference between specific and generic view in canonical ensemble is in the entropy

$$\tilde{S} = S - \log N! \approx S - N \log N - N$$

(But since N is constant in the canonical ensemble, this term can be absorbed in in the arbitrary additive constant.)
There are no empirical differences between the specific and generic viewpoints with a fixed N.
But Gibbs prefers generic viewpoint.

for an ideal gas one gets (ignoring terms depending only on T

$$S = \frac{3}{2} kN \log V \quad \text{not extensive}$$

$$\tilde{S} = \frac{3}{2} k \log V/N \quad \text{extensive}$$

For the entropy of mixing in the specific point of view

$$\begin{aligned} \Delta S &= S(2V, 2N) - 2S(V, N) = 3kN \log 2 && \text{same gases} \\ \Delta S &= 3kN \log 2 && \text{different gases} \end{aligned}$$

In generic viewpoint

$$\begin{aligned} \Delta S &= 0 \\ \Delta S &= 3kN \log 2 \end{aligned}$$

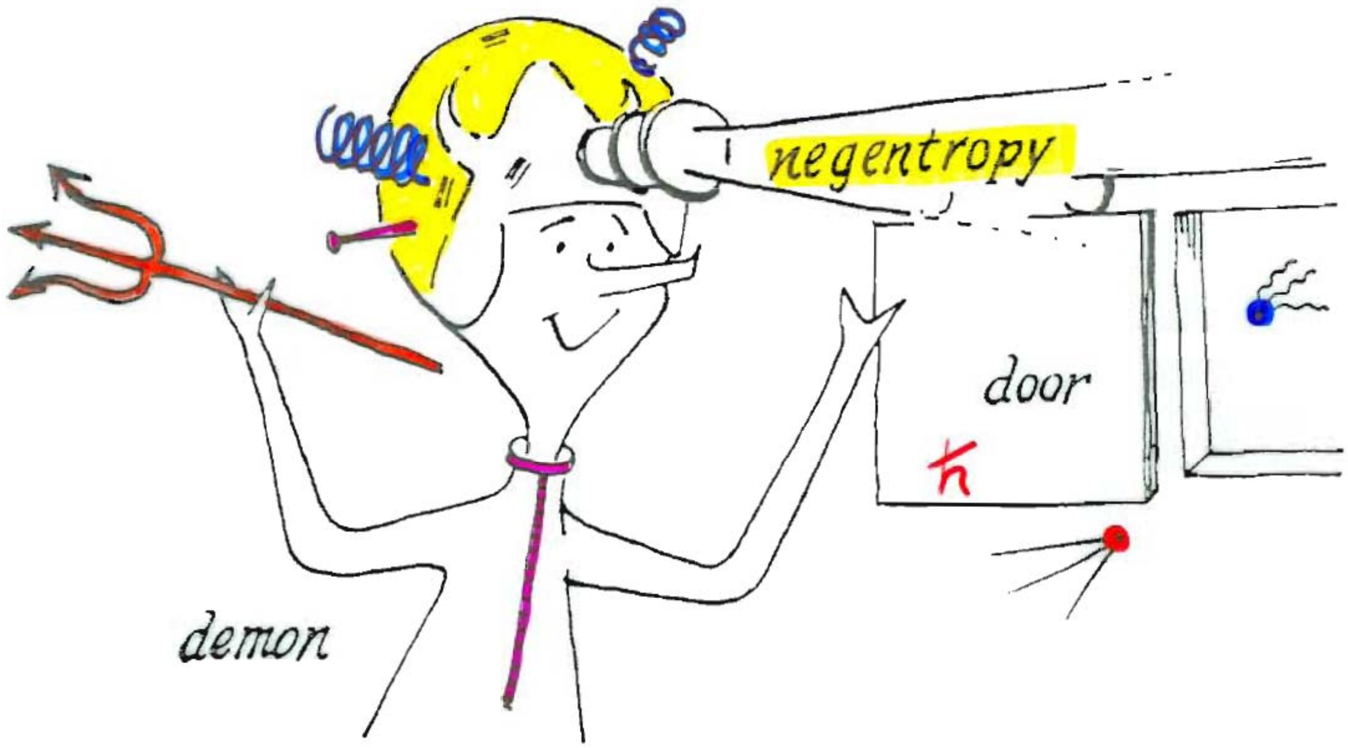
Hence, in the generic viewpoint we reproduce the Gibbs paradox of TD!

Schrödinger (1952, p.61)

> *It was a famous paradox pointed out by W.Gibbs that the same entropy increase must not be taken into account when the molecules are of the same kind, although, according to the naive view, diffusion takes place then too, but unnoticable to us.*
> *The modern view solves this paradox by declaring that the second case is no real diffusion because exchange between like particles is not a real event.*

Quantum Demon ?

A measurement → Increase information → Reduction of entropy



Source: H.S. Leff, *Maxwell's Demon* (Adam Hilger, Bristol, 1990)

Entropy in Stat. Mech.

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

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

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

$$E = E_{\mathrm{I}} + E_{\mathrm{II}}$$

$$\Omega_{\mathrm{I+II}}(E) = \int dE_{\mathrm{I}}\, \Omega'_{\mathrm{I}}(E_{\mathrm{I}})\, \Omega_{\mathrm{II}}(E - E_{\mathrm{I}})$$

$$\ln \Omega_{\mathrm{I+II}}(E) \neq \ln \Omega_{\mathrm{I}}(E_{\mathrm{I}}) + \ln \Omega_{\mathrm{II}}(E_{\mathrm{II}})$$

$$\omega_{\mathrm{I+II}}(E) = \int dE_{\mathrm{I}}\, \omega_{\mathrm{I}}(E_{\mathrm{I}})\, \omega_{\mathrm{II}}(E - E_{\mathrm{I}})$$

$$\ln \omega_{\mathrm{I+II}}(E) \neq \ln \omega_{\mathrm{I}}(E_{\mathrm{I}}) + \ln \omega_{\mathrm{II}}(E_{\mathrm{II}})$$

Not Additive !

canonical:

$$Z = \int_{E_0}^{\infty} e^{-\beta E} \omega(E) dE$$

$$Z_{\mathrm{I+II}}(T) = Z_{\mathrm{I}}(T) Z_{\mathrm{II}}(T)$$

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

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

The highest temperature you can see

Lightning:

30 000 °C

Typische Temperaturen [°C]

Siedepunkt von Stickstoff	-195.79
Tiefste auf der Erdoberfläche gemessene Temperatur (Vostok, Antarktis – 21. Juli 1983)	-89
Höchste auf der Erdoberfläche gemessene Temperatur (Al' Aziziyah, Libyen – 13. September 1922)	58
Temperatur in der Thermosphäre der Erde (80 - 650 km über der Erdoberfläche)	~ 1500
Schmelzpunkt eines Diamanten	3547
Oberflächentemperatur der Sonne (Photosphäre)	~ 5526
Temperatur im Inneren der Sonne	$\sim 15 \cdot 10^{6}$

Entropy in Stat. Mech.

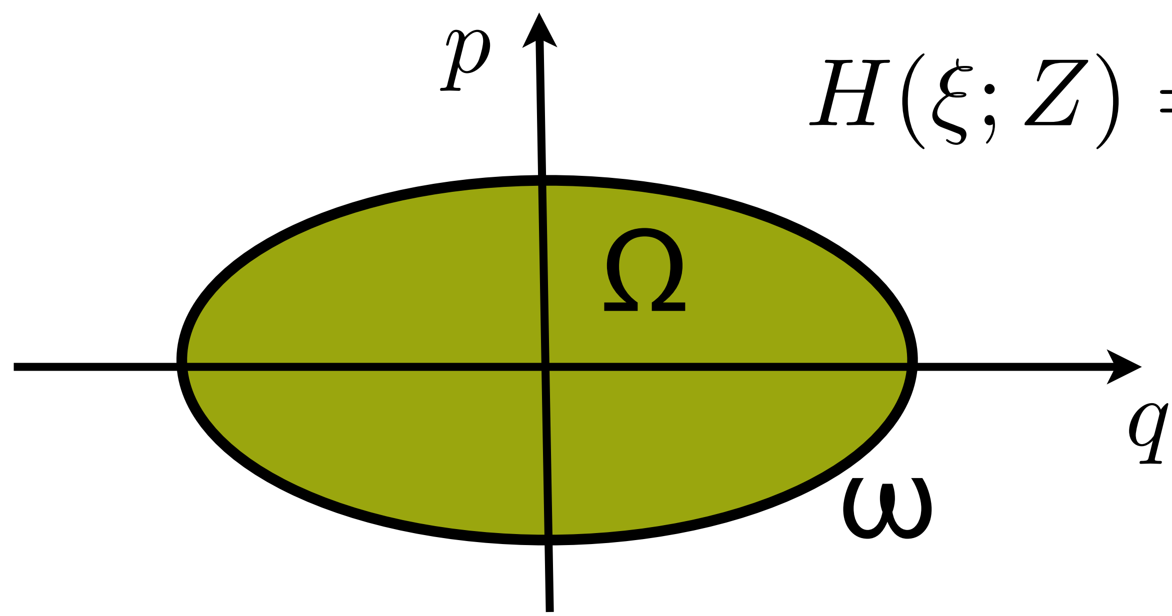
$$S = k_{\mathrm{B}} \ln \Omega(E, V, \ldots)$$

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

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 ?

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

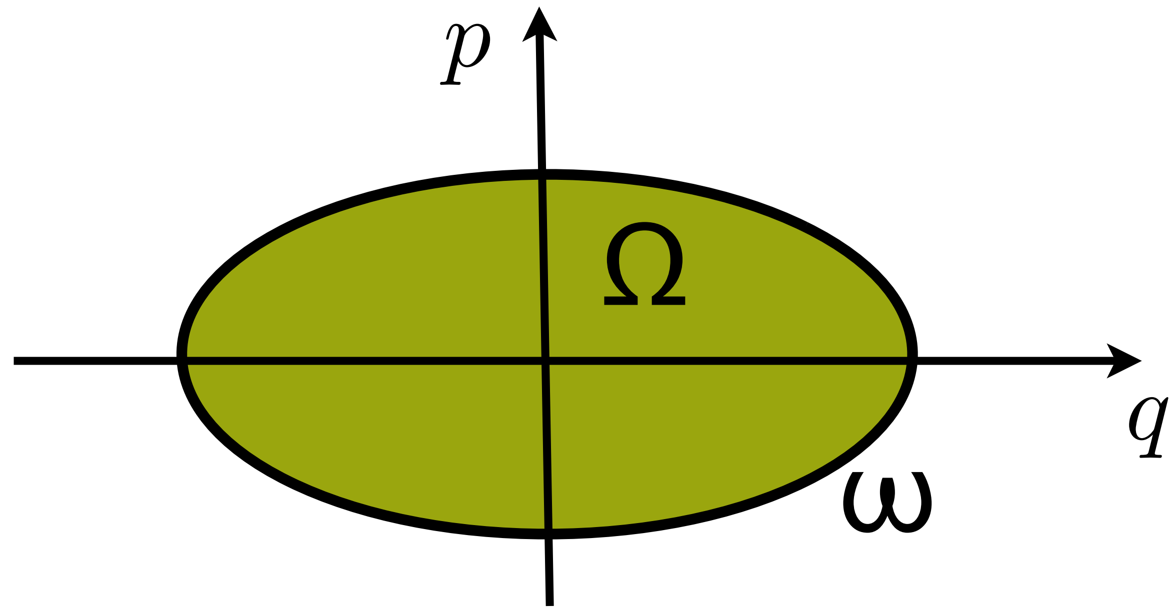
Boltzmann (?)

vs.

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

Gibbs (1902), Hertz (1910)

Boltzmann *vs.* Gibbs



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

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

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

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

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

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

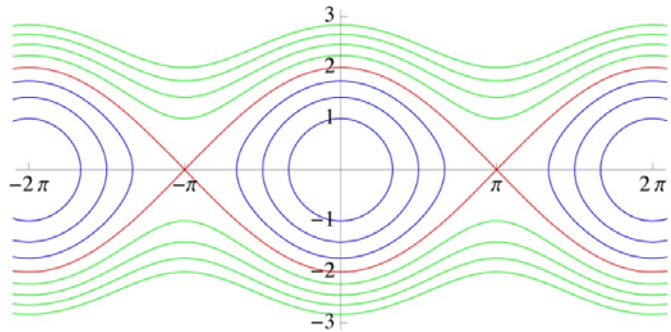


FIG. 1. A pendulum moves in phase space (θ, p) along lines of constant energy, $H(\theta, p) = E$. Blue: finite trajectories (oscillations) for $E < 2$. Green: infinite trajectories (rotation) for $E > 2$. Red: the critical contour, $E = 2$, separating finite and infinite trajectories.

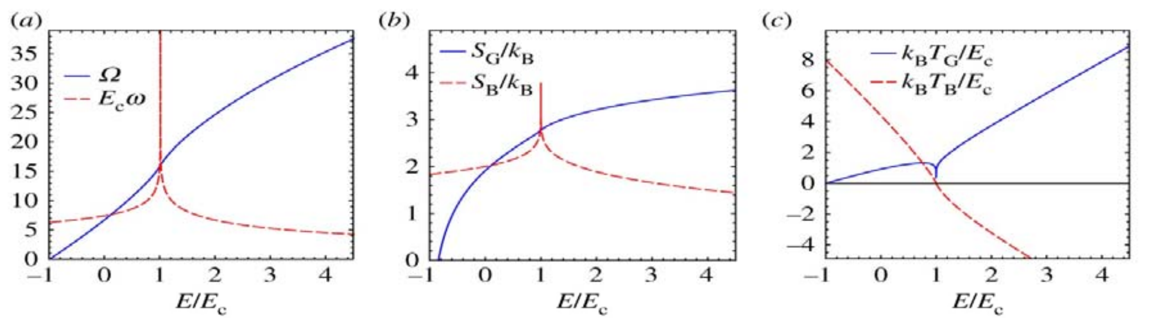


Figure 1. Microcanonical thermostatistics of the pendulum with Hamiltonian (2.10). (*a*) The integrated DoS Ω (blue) grows monotonically while the DoS ω (red dashed) exhibits a singular peak at the critical energy $E_c = mgL$, indicating a change in the phase-space topology. (*b*) The Gibbs entropy S_G (blue) increases monotonically, whereas the Boltzmann entropy S_B (red dashed) becomes singular at E_c and decays for $E > E_c$. (*c*) The Gibbs temperature T_G (blue) approaches asymptotically the caloric equation of state of the ideal one-particle gas, whereas the Boltzmann temperature T_B (red dashed) becomes negative for $E > E_c$.

? Negative Temperature ?

Spin system: $|\vec{S}| = 1/2; \quad \vec{\mu} = \gamma \vec{S}; \quad H = -\sum \vec{\mu}_i \cdot \vec{B}$

$\vec{S} \parallel \vec{B} \Rightarrow$ Two-State-System: $\epsilon_g = -\frac{1}{2}\gamma B < \epsilon_e = +\frac{1}{2}\gamma B = \mu B$

$N = n_g + n_e \;\; \& E = \mu B(n_e - n_g)$, typically $E < 0$

$$\omega = \frac{N!}{n_g! n_e!} \Rightarrow S_B = k_B \ln \omega$$

$$\Rightarrow \frac{1}{T_B} = \frac{\partial S_B}{\partial E}$$

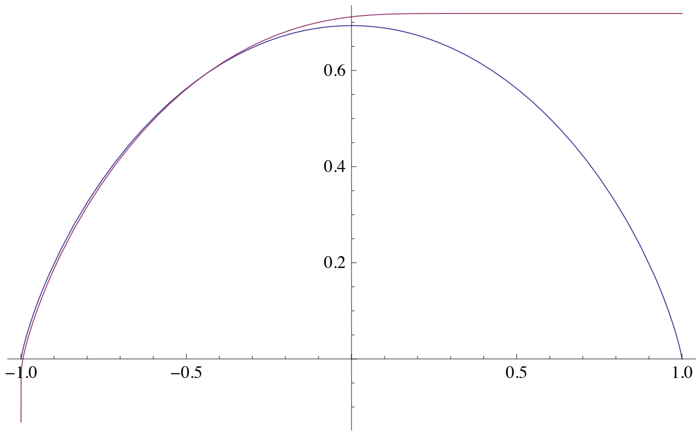
➡ $n_g = \frac{1}{2}\left(N - \frac{E}{\mu B}\right)$

➡ $n_e = \frac{1}{2}\left(N + \frac{E}{\mu B}\right)$

```
In[1]:= SΩ[x_, n_, μ_, B_] :=
         n Log[2] - n / 2 (1 + x / (μ B n)) Log[1 + x / (μ B n)] - n / 2 (1 - x / (μ B n)) Log[1 - x / (μ B n)]
        W[x_, n_, μ_, B_] := Exp[SΩ[x, n, μ, B]]
        Ω[x_, n_, μ_, B_] := Exp[SΩ[x, n, μ, B]] / (2 μ B)
        Ωe[x_, n_, μ_, B_] := Derivative[1, 0, 0, 0][Ω][x, n, μ, B]
        ΩB[x_, n_, μ_, B_] := Derivative[0, 0, 0, B][Ω][x, n, μ, B]
        Φ[x_, n_, μ_, B_] := NIntegrate[Ω[y, n, μ, B], {y, -n μ B, x}]
        ΦB[x_, n_, μ_, B_] := NIntegrate[ΩB[y, n, μ, B], {y, -n μ B, x}]
        S[x_, n_, μ_, B_] := Log[Φ[x, n, μ, B]]
        T[x_, n_, μ_, B_] := Φ[x, n, μ, B] / Ω[x, n, μ, B]
        TΩ[x_, n_, μ_, B_] := Ω[x, n, μ, B] / Ωe[x, n, μ, B]
        MΩ[x_, n_, μ_, B_] := ΩB[x, n, μ, B] / Ωe[x, n, μ, B]
        M[x_, n_, μ_, B_] := -x / B

In[22]:= n = 10^2;
         m = 10^8;
         Plot[{SΩ[e n, n, 1, 1] / n, S[e n, n, 1, 1] / n}, {e, -1, 1}]
         Plot[{SΩ[e m, m, 1, 1] / m, S[e m, m, 1, 1] / m}, {e, -1, 1}]
         Plot[{TΩ[e n, n, 1, 1], T[e n, n, 1, 1]}, {e, -1, 1}, PlotRange → {-100, 100}]
         Plot[{TΩ[e m, m, 1, 1], T[e m, m, 1, 1]}, {e, -1, 1}, PlotRange → {-100, 100}]
         Plot[{MΩ[e n, n, 1, 1] / n, M[e n, n, 1, 1] / n}, {e, -1, 1}]
         Plot[{MΩ[e m, m, 1, 1] / m, M[e m, m, 1, 1] / m}, {e, -1, 1}]
         Clear[n, m]
```

Out[24]=

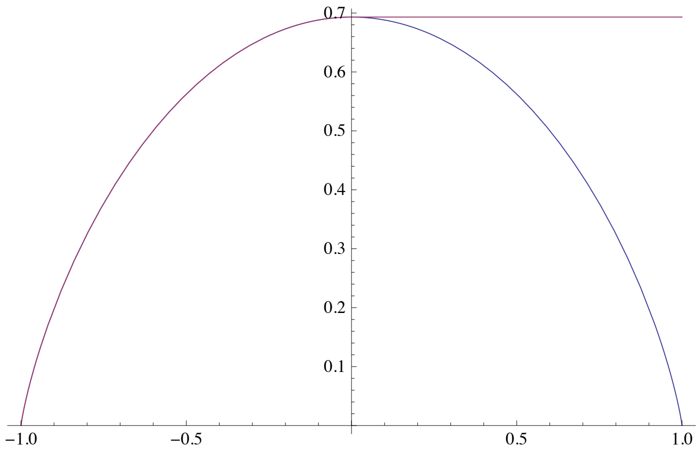


Purple: S_Phi /N
Blue: S_Omega/N

N=100

x-axis in all graphs is E/(2\mu N)

Out[25]=

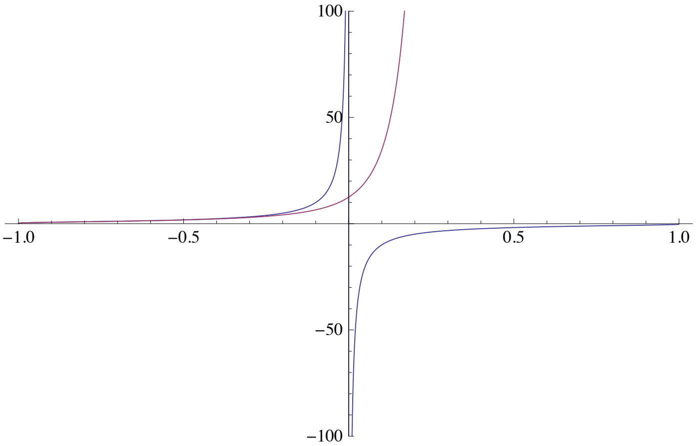


Purple: S_Phi /N
Blue: S_Omega/N

N=10^8

Limit Value = Log 2

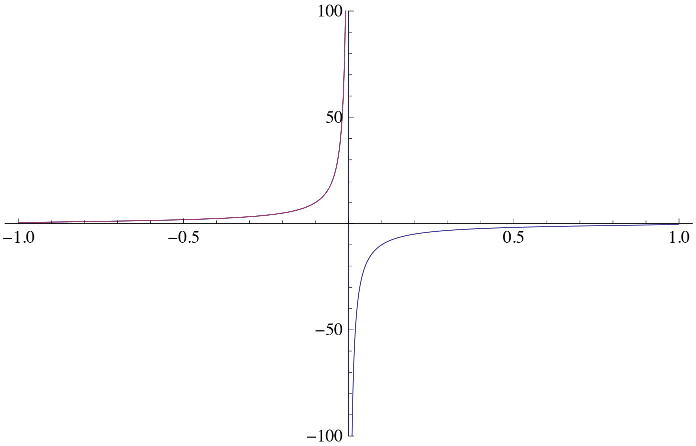
Out[26]=



Purple: T_Phi
Blue: T_Omega

N=100

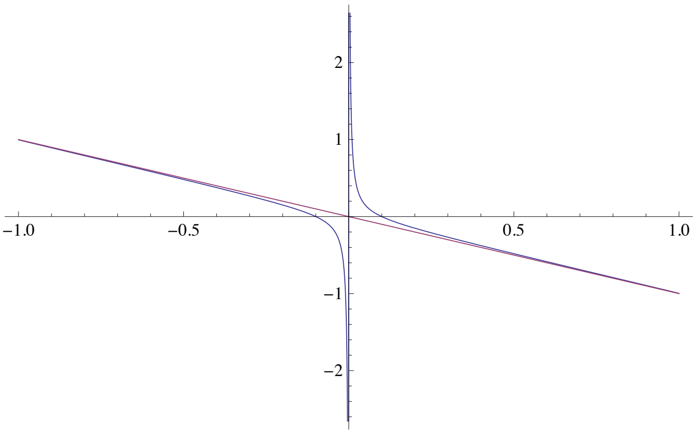
Out[27]=



Purple: T_Phi
Blue: T_Omega

N=10^8

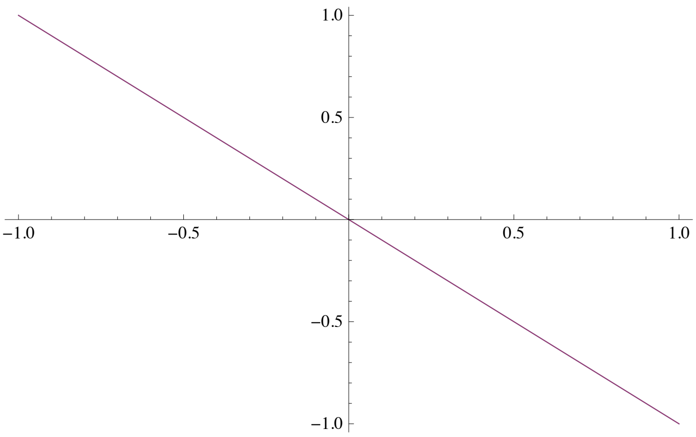
Out[28]=



Purple: M_Phi
Blue: M_Omega

N=100

Out[29]=



Purple: M_Phi
Blue: M_Omega

N=10^8

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Thermodynamic laws in isolated systems

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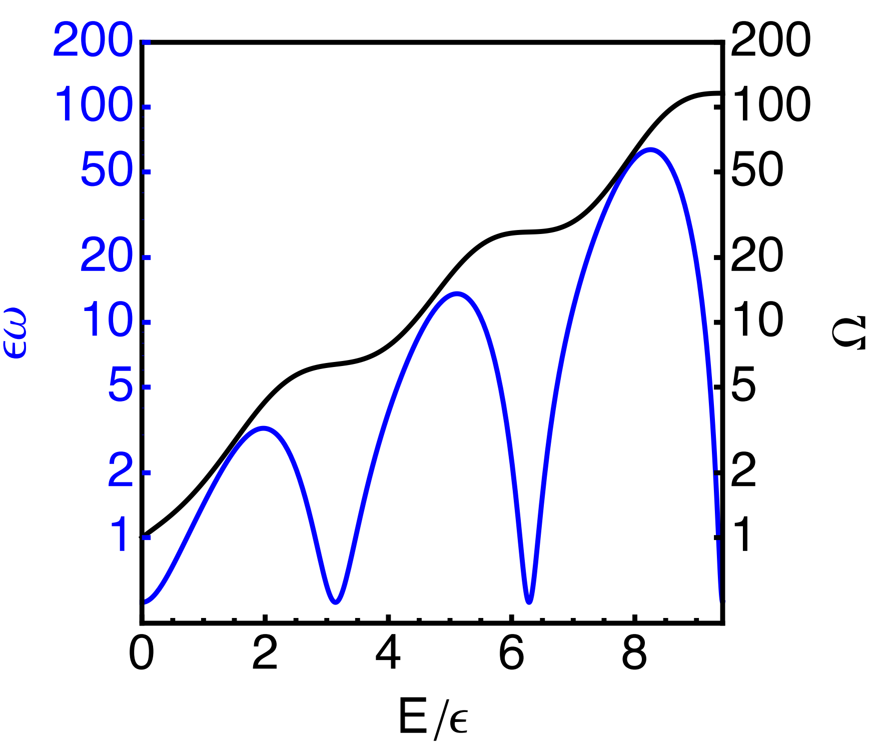
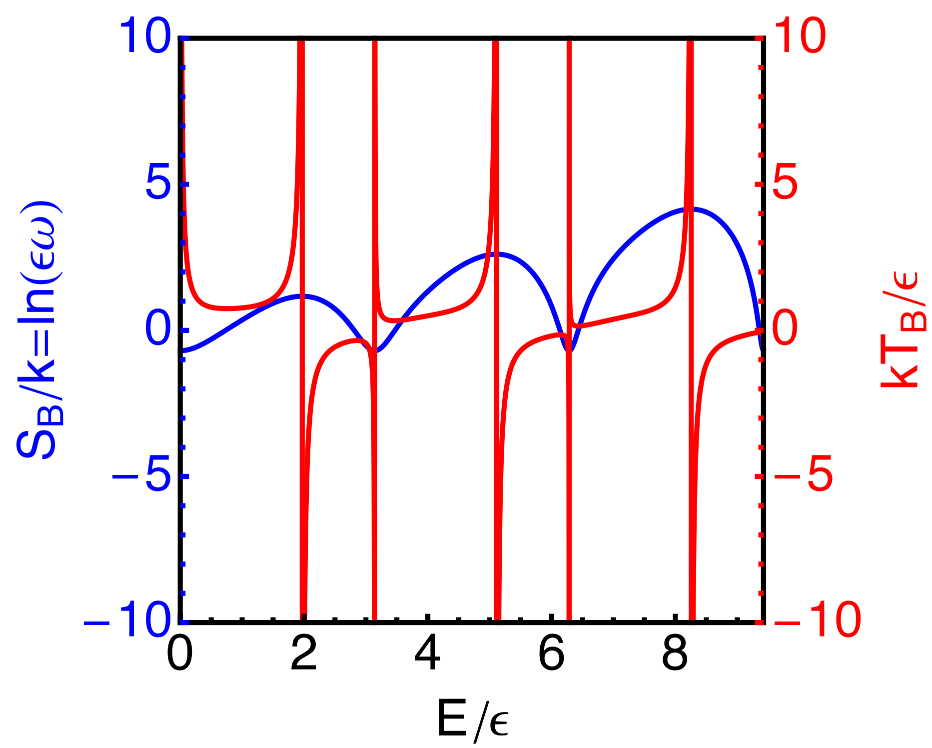
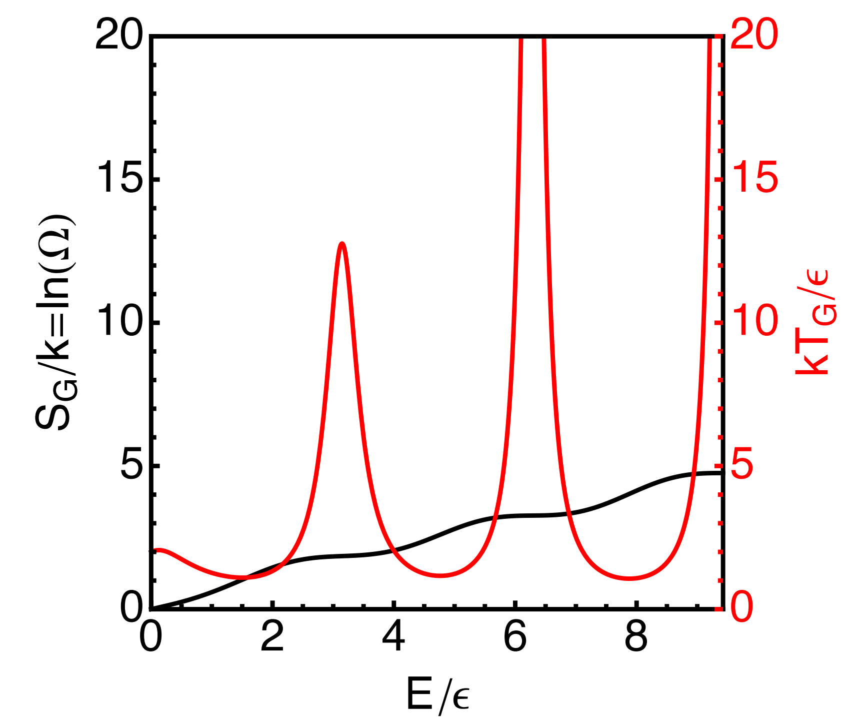
**** 23 pages ****

‘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.

Second law

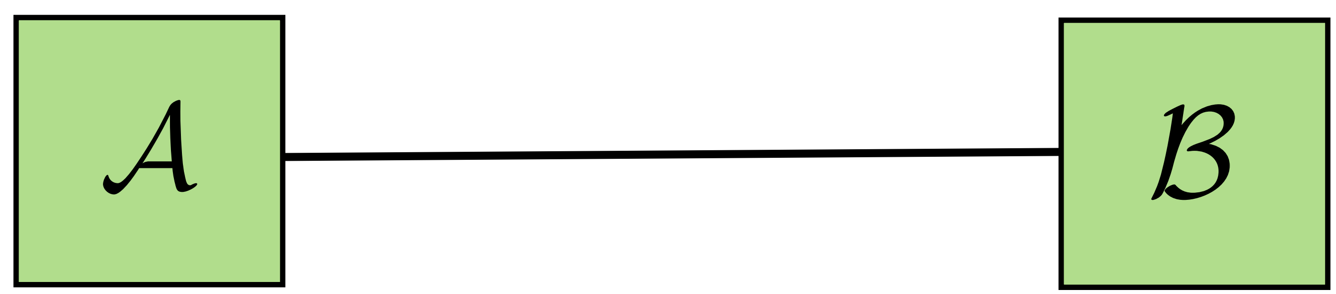
before
coupling

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

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

after
coupling

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



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

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

Second law

Gibbs

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

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

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

Second law

Boltzmann

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

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

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

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	$\ln \Omega + \ln(\Omega_\infty - \Omega) - \ln \Omega_\infty$	yes	yes	no	no
Complementary Gibbs	$\ln[\Omega_\infty - \Omega]$	yes	yes	no	no
Differential Boltzmann	$\ln[\Omega(E+\epsilon) - \Omega(E)]$	yes	no	no	no
Boltzmann	$\ln(\epsilon\omega)$	no	no	no	no

Hilbert, Hänggi & Dunkel, in preparation, 2014

Inconsistent thermostatistics and negative absolute temperatures

Jörn Dunkel and Stefan Hilbert,

nature physics 10: 67-72 (2014)

& ! SUPPL. -MATERIAL !

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 3: 1-dim 1-particle quantum gas

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

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

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

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

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

Dark energy ???

vs.

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

$$k_{\mathrm{B}}T_{\mathrm{G}} = 2E, \qquad p_G \equiv T_{\mathrm{G}}\left(\frac{\partial S_{\mathrm{G}}}{\partial L}\right) = \frac{2E}{L}$$

$$p \equiv -\frac{\partial E}{\partial L} = \frac{2E}{L} = p_{\mathrm{G}}$$

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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]*

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

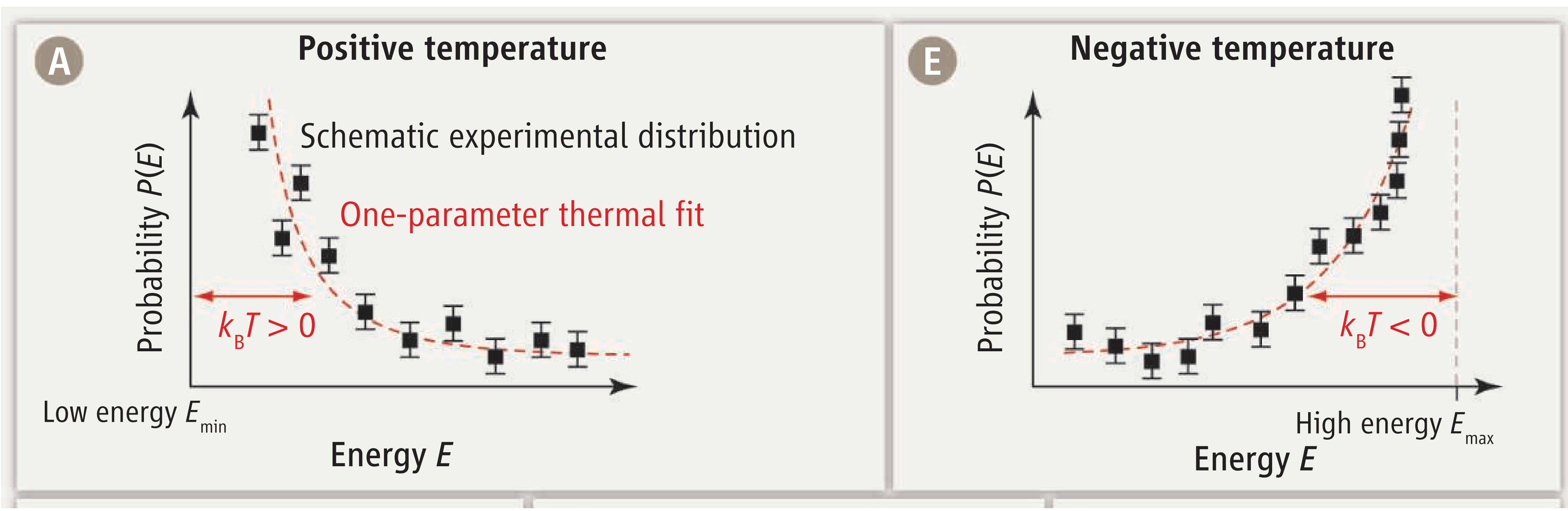
PERSPECTIVES 4 JANUARY 2013 VOL 339 SCIENCE

PHYSICS

Negative Temperatures?

Lincoln D. Carr

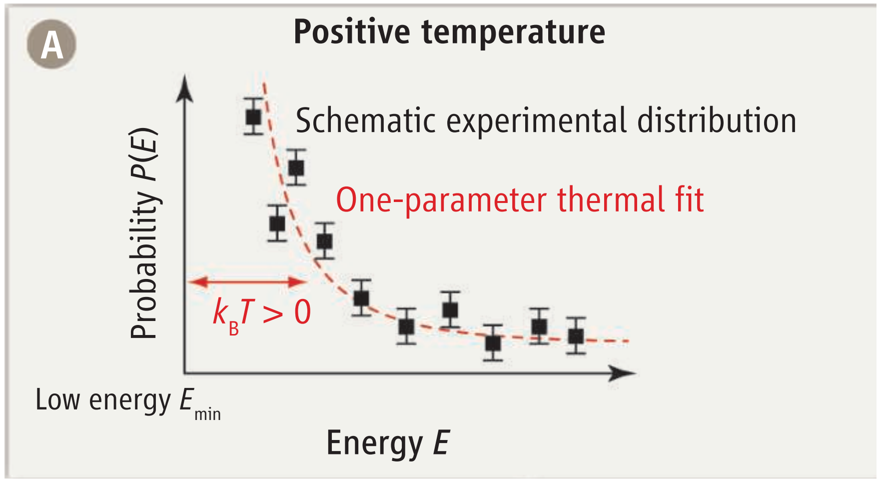
$$P_i \propto e^{-E_i/k_B T}$$



Population inversion of one-particle levels arxiv: 1304.2066

Measuring T_{B} *vs.* T_{G}

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

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

see e.g. Huang's textbook

features T_{B} and not T_{G}

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

Generally

$$\boxed{T_{\mathrm{B}} = \frac{T_{\mathrm{G}}}{1 - k_{\mathrm{B}}/C}} \qquad C = \left(\frac{\partial T_{\mathrm{G}}}{\partial E}\right)^{-1}$$

OPEN SYSTEMS

$$H(\lambda(t)) \longrightarrow H_{SYSTEM}(\lambda(t)) + H_{BATH} + H_{S\text{-}B}$$

canonical ensemble

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

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

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

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

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

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

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

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

Quantum Hamiltonian of Mean Force

$$Z_S(t) := \frac{Y(t)}{Z_B} = \mathrm{Tr}_S\, e^{-\beta H^*(t)}$$

where

$$H^*(t) := -\frac{1}{\beta} \ln \frac{\mathrm{Tr}_B\, e^{-\beta(H_S(t)+H_{SB}+H_B)}}{\mathrm{Tr}_B\, e^{-\beta H_B}}$$

also

$$\frac{e^{-\beta H^*(t)}}{Z_S(t)} = \frac{\mathrm{Tr}_B\, e^{-\beta H(t)}}{Y(t)}$$

M. Campisi, P. Talkner, P. Hänggi, Phys. Rev. Lett. **102**, 210401 (2009).

Strong coupling: Example

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

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

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

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

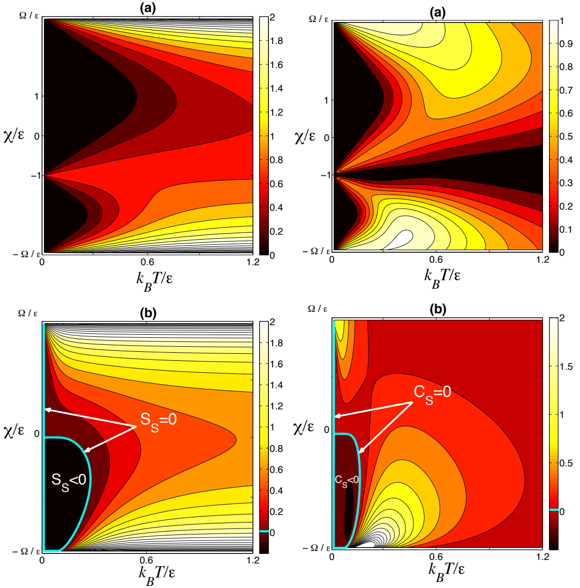
$$\gamma = \frac{1}{2\beta}\ln\left(\frac{1 - 2e^{-\beta\Omega}\cosh(\beta\chi) + e^{-2\beta\Omega}}{(1 - e^{-\beta\Omega})^2}\right)$$

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

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

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

Entropy and specific heat



$\Omega/\epsilon = 3$

$\Omega/\epsilon = 1/3$

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.

Conclusions

- population inversion $\Longrightarrow$ microcanonical
- bounded spectrum $\Longrightarrow$ ensembles not equivalent
- consistent thermostatistics $\Longrightarrow$ Gibbs entropy
- temperature always positive ('by construction')
- no Carnot efficiencies > 1
- please correct textbooks & lecture notes

[redacted]

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

A QUESTION ?

PHYSICAL REVIEW E **90**, 062116 (2014)

Thermodynamic laws in isolated systems

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