Meaning of temperature in different thermostatistical ensembles

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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]

SECOND LAW

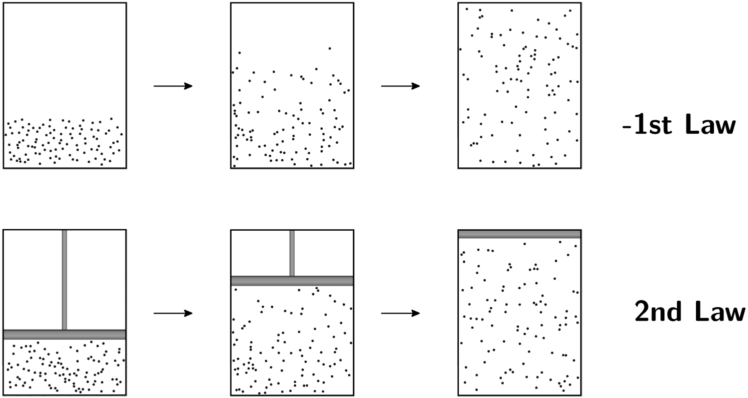
Quote by Sir Arthur Stanley Eddington:

“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.

MINUS FIRST LAW vs. SECOND LAW



Thermodynamic Temperature

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

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

$S(E, ...)$: (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.

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

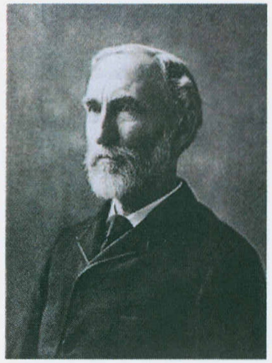
QM: $\Omega_{\mathrm{G}}(E, V, \ldots) = \sum_{0 \le E_i \le E} 1$

classical

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

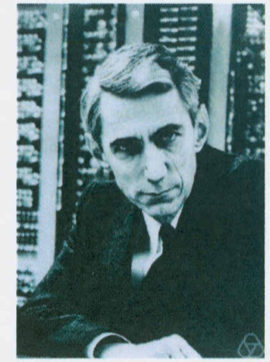
Boltzmann: $\Omega_{\mathrm{B}} = \epsilon_0 \frac{\partial\, \Omega_{\mathrm{G}}}{\partial E} \propto \int \mathrm{d}\Gamma\, \delta\left(E - H(\underline{q}, \underline{p}; V, \ldots)\right)$

density of states



J. W. Gibbs

L. Boltzmann



C. E. Shannon

$$H_G = \int W_N \ln W_N \, d\Gamma_N \qquad H_B = N \int w_1 \ln w_1 \, d\Gamma_1$$

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

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

⊕ 200

Renyi
Relative-
Kullback-Leibler
v. NEUMANN
KOLMOGOROV-SINAI
CONDITIONAL
CLAUSIUS
FISHER
Daroczy-Harvda-Charvat-Tsallis
Hartley-chaitin
WEHRL

ETC.

Entropy in Stat. Mech.

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

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

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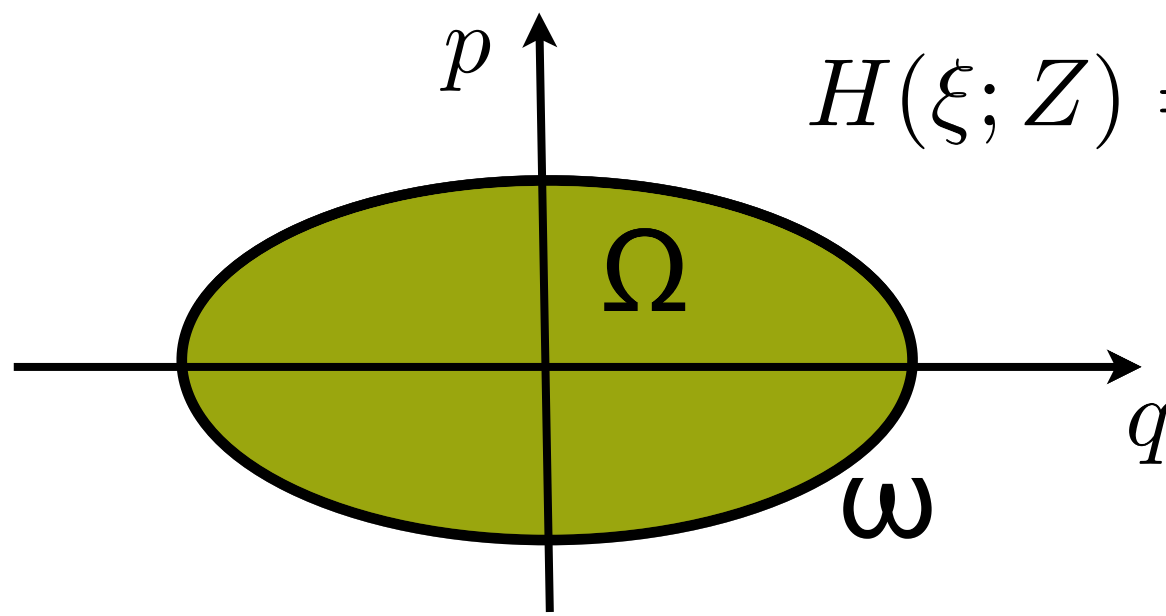
density of states

Microcanonical thermostatistics



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

D-Operator

DoS

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

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

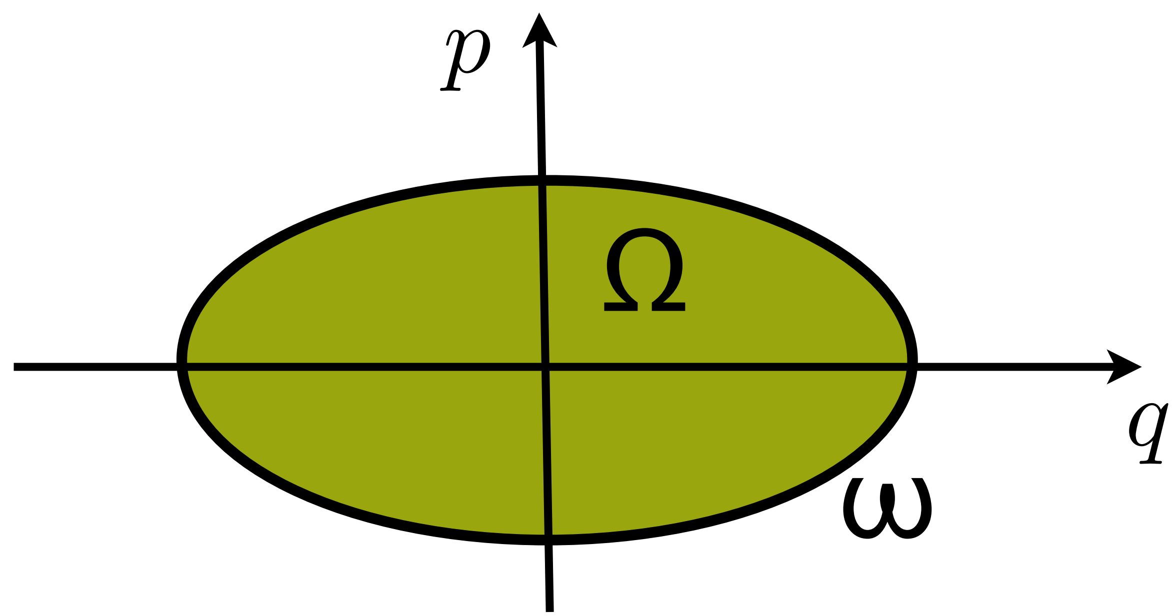
$$\Omega(E,Z) = \mathrm{Tr}[\Theta(E-H)]$$

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

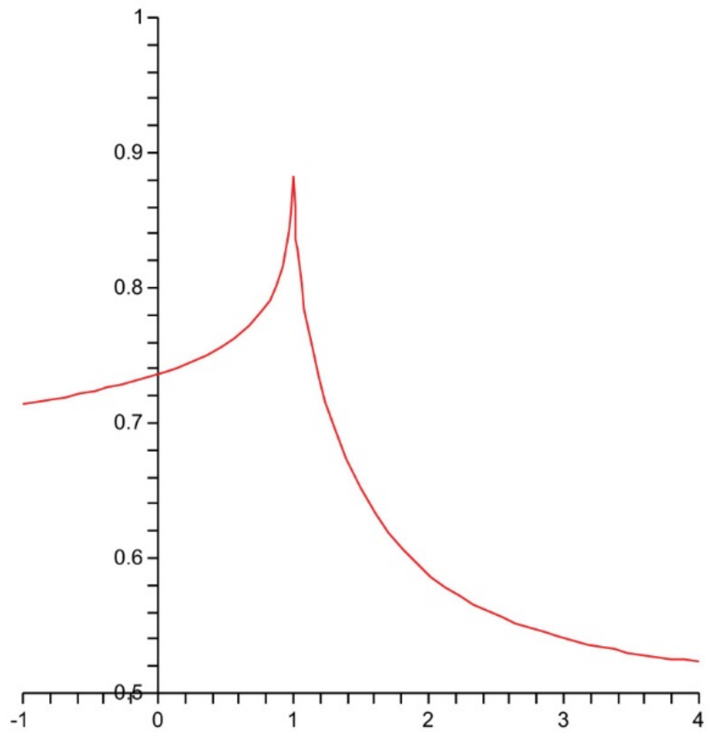


$$S_{\mathrm{B}}(E) = \ln\left(\epsilon\,\omega\right) \qquad\qquad S_{\mathrm{G}}(E) = \ln\Omega$$

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

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

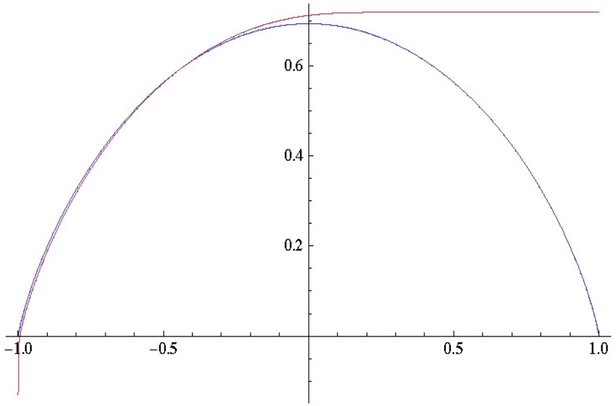
$$\nu(E, Z) = \partial\omega/\partial E,$$



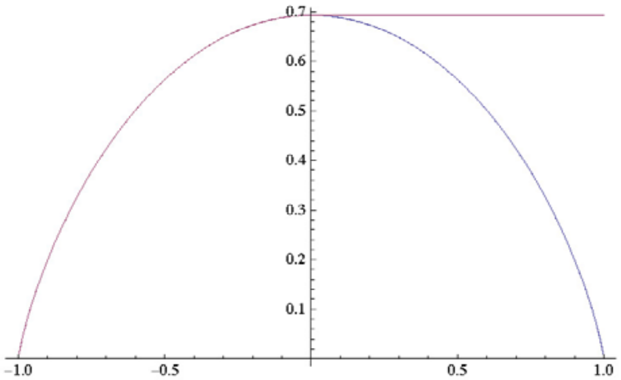
Density of states of the pendulum in reduced units (complete elliptic integrals of the first kind). Fig. 1 in reference: M. Baeten and J. Naudts, Entropy, 13, 1186-1199 (2011).

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

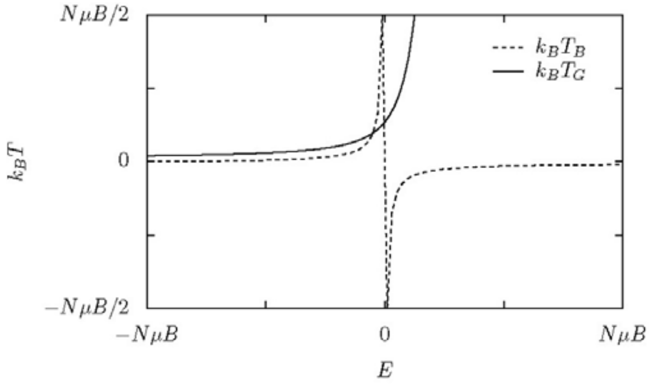
Entropy for N = 100
(magenta: S_G ; blue: S_B

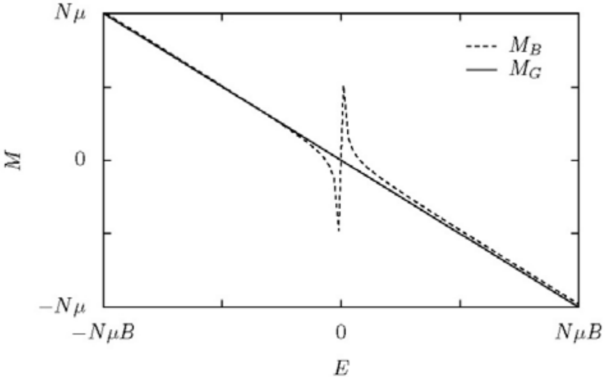


N = 10^8



N = 100





$\Delta = M_B - M = - k_BT_B/B$

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Negative Absolute Temperature for Motional Degrees of Freedom

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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

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Thermodynamic laws in isolated systems

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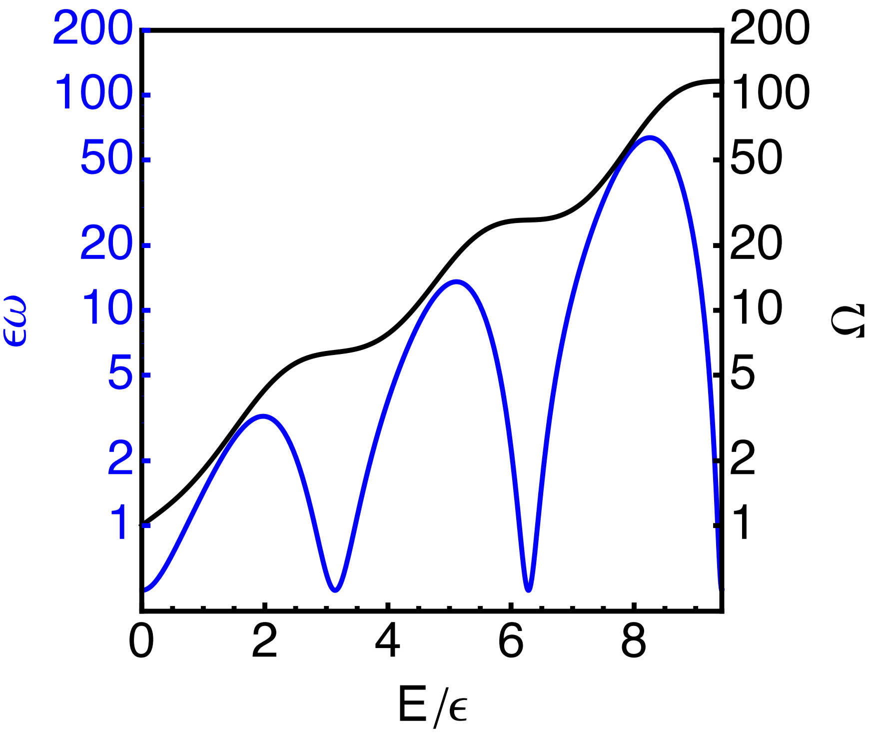
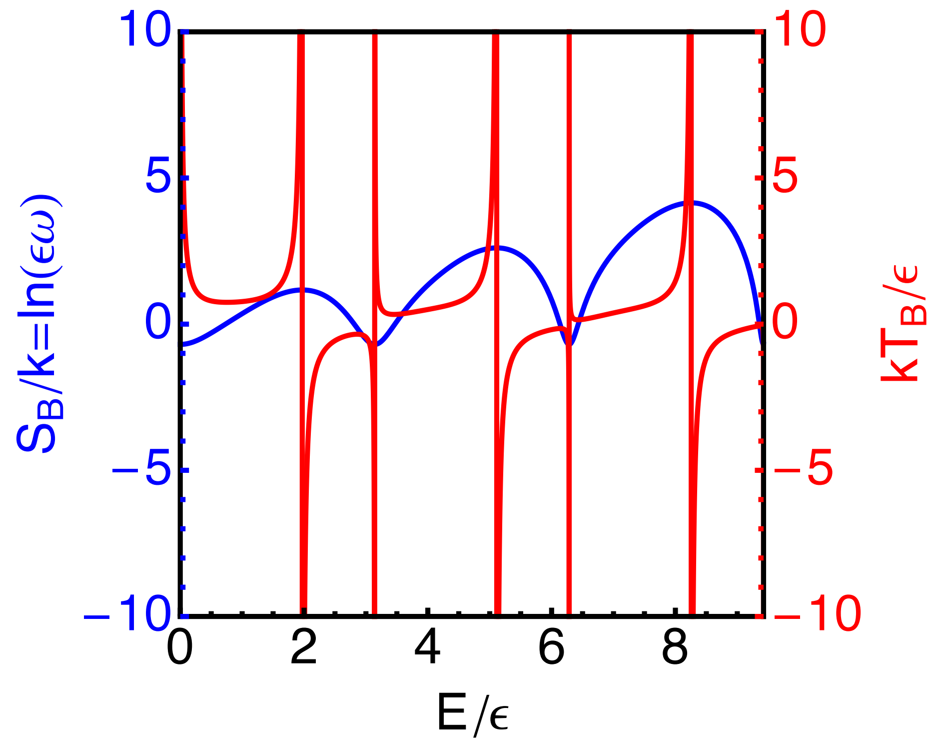
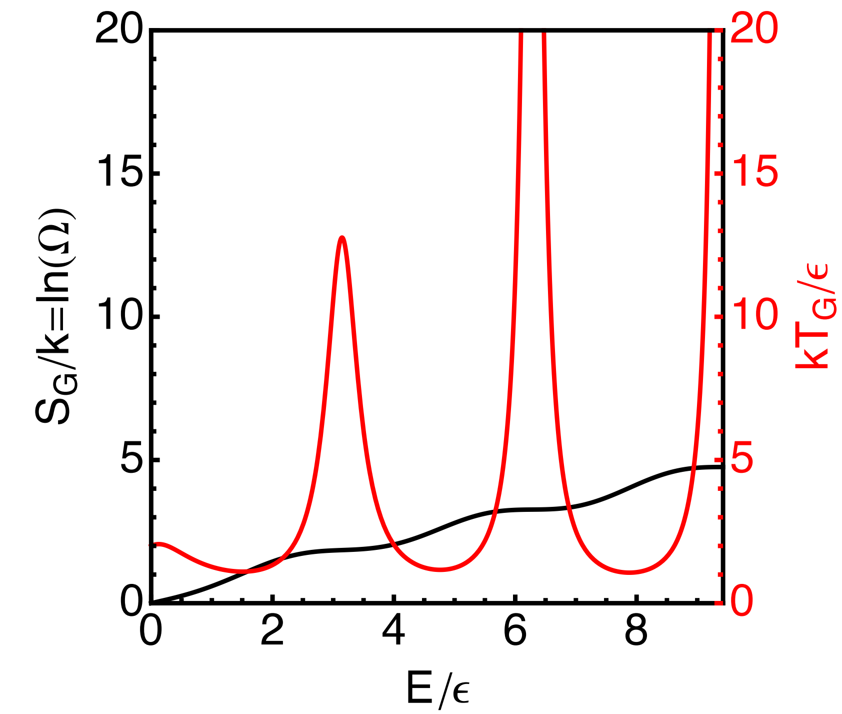
**** 23 pages ****

'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

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

Second law

Gibbs

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

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

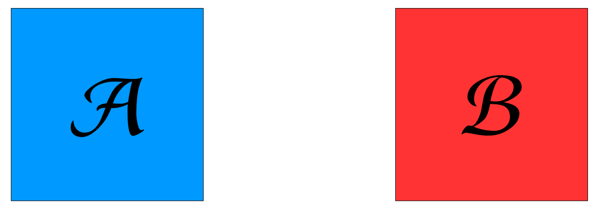
$$\Rightarrow \quad S_{\mathrm{G}\mathcal{A}\mathcal{B}}(E_{\mathcal{A}} + E_{\mathcal{B}}) \geq S_{\mathrm{G}\mathcal{A}}(E_{\mathcal{A}}) + S_{\mathrm{G}\mathcal{B}}(E_{\mathcal{B}})$$

✓

Second Law

before coupling

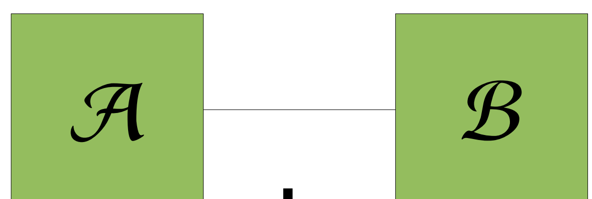
$$H_{\mathcal{A}} = E_{\mathcal{A}} \qquad H_{\mathcal{B}} = E_{\mathcal{B}}$$



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

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

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

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

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

✗

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.

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

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

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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vs.

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

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

canonical ensemble

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

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

canonical ensemble

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

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

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

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

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

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": $T_B^B = T_G^B = T_G^S = T_G^T$

gives an approximation to the number of states below E for a system consisting of N identical particles. The indistinguishability of identical particles introduces the denominator $N!$ in the above expression because the $N!$ classical states † arising from a given phase point $p_1, x_1, \ldots p_N, x_N$ must be identified with each other by this principle (see the Note to Chapter 2, problem 33 for a more rigorous discussion).

NOTE: The denominator $N!$ was very difficult to understand before the principle of the indistinguishability of identical particles was introduced into quantum mechanics. In spite of this, the necessity for this denominator term had long been recognized in order to make the entropy defined by (1.18) an extensive quantity as it should be.

§ 1.6. NORMAL SYSTEMS IN STATISTICAL THERMODYNAMICS

Asymptotic forms of the number of states and state density of a macroscopic system: A system consisting of a great number of particles, or of a system with an indefinite number of particles but with a volume of macroscopic extension usually has a number of states $\Omega_0(E)$ which shows the following properties (in which case the system will be called *normal in the statistical-thermodynamic sense*):

(1) When the number N of particles (or the volume V) is large, the number of states $\Omega_0(E)$ approaches asymptotically to

$$\Omega_0 \sim \exp\left\{N\phi\left(\frac{E}{N}\right)\right\} \quad \text{or} \quad \exp\left\{V\psi\left(\frac{E}{V}\right)\right\}, \tag{1.24a}$$

$$\Omega_0 \sim \exp\left\{N\phi\left(\frac{E}{N}, \frac{V}{N}\right)\right\} \quad \text{or} \quad \exp\left\{V\psi\left(\frac{E}{V}, \frac{N}{V}\right)\right\}. \tag{1.24b}$$

If E/N (or E/V) is looked upon as a quantity of the order of $\mathrm{O}(1)$ ††, ϕ is also $\mathrm{O}(1)$ (the same holds for ψ), and

$$\phi > 0, \qquad \phi' > 0, \qquad \phi'' < 0. \tag{1.25}$$

(2) Therefore

$$\Omega = \mathrm{d}\Omega_0/\mathrm{d}E = \phi' \exp(N\phi) > 0,$$

$$\frac{\mathrm{d}\Omega}{\mathrm{d}E} = \left(\phi'^2 + \frac{\phi''}{N}\right)\mathrm{e}^{N\phi} \sim \phi'^2 \mathrm{e}^{N\phi} > 0. \tag{1.26}$$

† When some of (p_1, x_1), (p_2, x_2) ... (p_N, x_N) coincide with each other, the number of classical states produced by the permutation of particle states is less than $N!$. But the chance for such coincidence is negligible in the limit of $h \to 0$.

†† One writes $y = \mathrm{O}(x)$ and $z = \mathrm{o}(x)$ if $\lim_{x\to\infty} y/x = \text{finite} \neq 0$ and $\lim_{x\to\infty} z/x = 0$.

When N (or V) is large, Ω_0 or Ω increases *very rapidly* with energy E. No general proof of these properties will be attempted here. If a system existed which did not have these properties, it would show a rather strange macroscopic behavior, very different from ordinary thermodynamic systems (see example 4, Chapter 1).

Entropy of a normal system: For the statistical entropy defined by (1.18), one finds the following from (1.24)–(1.26):

(1)
$$S = k\log\{\Omega(E)\delta E\} \simeq k\log\Omega_0(E) = kN\phi. \tag{1.27}$$

The error involved here is $\mathrm{o}(N)$ (or $\mathrm{o}(V)$), and so is negligible for a macroscopic system (for which N, V, or E is very large).

(2) The statistical temperature $T(E)$ is introduced by means of the definition,

$$\frac{\partial S}{\partial E} = \frac{1}{T} \tag{1.28}$$

$$T(E) = \frac{1}{k\phi'} > 0. \tag{1.29}$$

By (1.24) and (1.25) it will be shown later that this temperature in fact agrees with the thermodynamic temperature (see § 1.9).

The allowance of the energy and the definition of entropy: By (1.24)–(1.26), the function $\Omega_0(E)$ is positive and increases monotonically with E. Therefore one has

$$\Omega(E)\delta E < \Omega_0(E) < \Omega(E)E,$$

thus
$$S = k\log\Omega(E)\delta E < k\log\Omega_0(E) < k\log\Omega(E)E.$$

Also by (1.24) and (1.25) and using the fact that $E = \mathrm{O}(N)$, one finds:

$$k\{\log\Omega(E)E - \log\Omega_0(E)\} = k\log E\cdot\phi' = \mathrm{O}(\log N) = \mathrm{o}(N) \quad (\text{or} \quad \mathrm{o}(V))$$

and

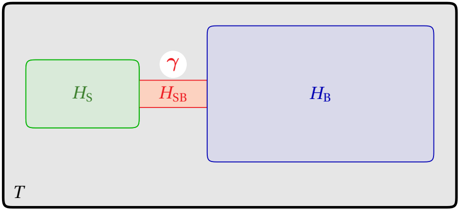
$$k\{\log\Omega(E)E - \log\Omega(E)\delta E\} = k\log E/\delta E = \mathrm{o}(N)\dagger \quad (\text{or} \quad \mathrm{o}(V)).$$

Therefore (1.27) is seen to be valid.

§ 1.7. CONTACT BETWEEN TWO SYSTEMS

There can be various kinds of interactions between two systems in contact.

† If one supposes that $\log E/\delta E = \mathrm{O}(N) = \alpha N$, then $\delta E = E\exp(-\alpha N)$. According to the uncertainty principle (1.16) the time of the observation t is then $t \sim h/\delta E = (h/E)\exp \alpha N$. If $\alpha = \mathrm{O}(1)$, this t is astronomically long for a macroscopic system. Therefore, for a t of ordinary length, δE cannot be so small and thus one must have $\log E/\delta E = \mathrm{o}(N)$ (namely $\alpha = \mathrm{o}(1)$).



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)

An important difference

Route I

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

Route II

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

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

For finite coupling E and U differ!

Strong coupling: Example

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

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

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

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

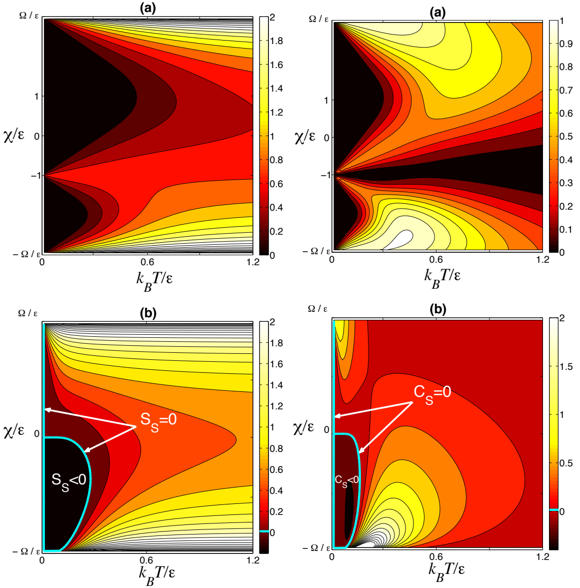
$$\gamma = \frac{1}{2\beta}\ln\left(\frac{1 - 2e^{-\beta\Omega}\cosh(\beta\chi) + e^{-2\beta\Omega}}{(1 - e^{-\beta\Omega})^2}\right)$$

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

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

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

Entropy and specific heat



$\Omega/\epsilon = 3$

$\Omega/\epsilon = 1/3$

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?

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.

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Thermodynamic laws in isolated systems

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A QUESTION ?