

Theory of thermodynamic ensembles: Do we really understand the old stuff ?



**Peter Hänggi, 826. WE-Heraeus-
Seminar
Bad Honnef, 12.01.2025 -- 17.01.2025**

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.

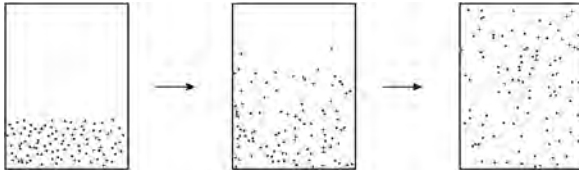
Second Law (Clausius)

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

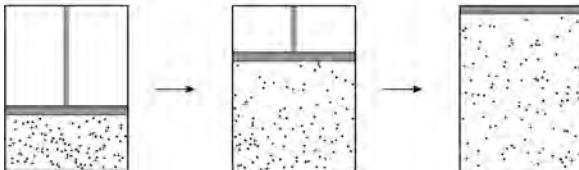
Second Law (Kelvin)

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

MINUS FIRST LAW vs. SECOND LAW



-1st Law



2nd Law

Entropy in Stat. Mech.

$$S = k_B \ln \Omega(E, V, \dots)$$

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

Boltzmann: $\Omega_B = \epsilon_0 \frac{\partial \Omega_G}{\partial E} \propto \int d\Gamma \delta(E - H(\underline{q}, \underline{p}; V, \dots))$

density of states

Thermodynamics of Finite Systems

conventional T.-D.:

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N); \quad \text{etc. } N \gg 1$$

Euler-homogenous functions of order "1"

$$\implies U = TS - pV + \sum_i \mu_i N_i$$

$$\implies G = \sum_i \mu_i N_i$$

$$\text{Gibbs-Duhem: } SdT - Vdp + \sum_i N_i d\mu_i = 0$$

i.g. NO longer valid for N finite

② Specific heat of small grains at low T

$$T < T_{\text{Debye}} :$$

$$C_{\text{Debye}} = \text{const.} \cdot T^3 \quad (\text{Dirichlet b.c.})$$

$$C = C_{\text{Debye}} + \dots \left(\frac{A}{V} \right) T^2 + \dots \left(\frac{L}{V} \right) T$$

OK for $\hbar\omega_1/k_B < T < T_{\text{Debye}}$



compare with $C_{\text{electronic}}$

Montroll, Mazo & Onsager, Kubo,
Baltes & Hilf, etc.

Spectra of Finite Systems

A Review of Weyl's Problem:
The eigenvalue distribution of
the wave equation for finite
domains and its applications on
the physics of small systems.

von
Prof. Dr. Heinrich P. Baltes
Landis & Gyr Zug AG, Zug/Schweiz
Zentrale Forschung und Entwicklung

unter Mitarbeit von
Prof. Dr. Eberhard R. Hilf
Technische Hochschule Darmstadt
Institut für Kernphysik

STATISTICAL MECHANICS

AN ADVANCED COURSE WITH PROBLEMS AND
SOLUTIONS

RYOGO KUBO

University of Tokyo

in cooperation with

*overall -
He (like others)
works with
'surface entropy'*

HIROSHI ICHIMURA

Tokyo Institute of Technology

TSUNEMARU USUI

Kyoto University

NATSUKI HASHITSUME

Ochanomizu University



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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 $p_1, x_1, \dots, p_N, x_N$ 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

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

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

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

$$\phi > 0, \quad \phi' > 0, \quad \phi'' < 0. \quad (1.25)$$

(2) Therefore

$$\Omega = d\Omega_0/dE = \phi' \exp(N\phi) > 0,$$

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

† When some of $(p_1, x_1), (p_2, x_2) \dots (p_N, x_N)$ 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 $h \rightarrow 0$.

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

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):

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

The error involved here is $o(N)$ (or $o(V)$), 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,

$$\frac{\partial S}{\partial E} = \frac{1}{T} \quad (1.28)$$

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

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 $E = O(N)$, one finds:

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

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

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 $\log E/\delta E = O(N) = \alpha N$, 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 $\alpha = O(1)$, 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 $\log E/\delta E = o(N)$ (namely $\alpha = o(1)$).

This distribution is derived in the same way as the canonical or grand canonical distributions.

NOTE: The T - μ distribution and the T - p distribution, like the canonical distribution, can be applied irrespective of the size of the system under consideration.

§ 1.14. PARTITION FUNCTIONS AND THERMODYNAMIC FUNCTIONS

The microcanonical, canonical, T - μ (grand canonical) and T - p distributions are the distributions for given energy ($E = \text{constant}$), given temperature ($T = \text{constant}$), given temperature and chemical potential ($T = \text{constant}, \mu = \text{constant}$) and given temperature and pressure ($T = \text{constant}, p = \text{constant}$), respectively. If the system is macroscopic, then the thermodynamic function (potential) for each of these prescribed conditions is derived from each partition function. This is summarized in the following table:

Distribution	Partition function	Thermodynamic function
Microcanonical	$\Omega(E, V, N)\delta E$ or $\Omega_0(E, V, N)$	$S(E, V, N) = k \log \Omega(E, V, N)\delta E$ or $= k \log \Omega_0(E, V, N)$
Canonical	$Z(T, V, N)$ $= \sum_i e^{-E_i(V, N)/kT}$ $= \int_0^\infty e^{-E/kT} \Omega(E, V, N) dE$	$F(T, V, N) = -kT \log Z(T, V, N)$ $\psi(T, V, N) = k \log Z(T, V, N)$
Grand canonical (T - μ distribution)	$\Xi(T, V, \mu)$ $= \sum_{N=0}^\infty e^{N\mu/kT} Z(T, V, N)$ $= \sum_{N=0}^\infty \lambda^N Z(T, V, N)$	$J(T, V, \mu) \equiv -pV = F - G$ $= -kT \log \Xi(T, V, \mu)$ $q(T, V, \mu) = k \log \Xi(T, V, \mu)$
T - p distribution	$Y(T, p, N)$ $= \int_0^\infty e^{-pV/kT} Z(T, V, N) dV$	$G(T, p, N) = -kT \log Y(T, p, N)$ $\Phi(T, p, N) = k \log Y(T, p, N)$

$\rightarrow \bullet (p/kT)$

In statistical mechanics, the thermodynamic relations between thermodynamic functions are derived as the relations between certain average values obtained from probability laws suitable for the description of the given conditions. Well known transformations (Legendre transformations) for the thermodynamic functions are derived by approximating the partition function Z , Ξ , or Y by taking the maximum term in the sum or the integral.

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Thermodynamic laws in isolated systems

Stefan Hilbert,^{1,*} Peter Hänggi,^{2,3} and Jörn Dunkel⁴

¹*Exzellenzcluster Universe, Boltzmannstr. 2, D-85748 Garching, Germany*

²*Institute of Physics, University of Augsburg, Universitätsstraße 1, D-86135 Augsburg, Germany*

³*Nanosystems Initiative Munich, Schellingstr. 4, D-80799 München, Germany*

⁴*Department of Mathematics, Massachusetts Institute of Technology, 77 Massachusetts Avenue E17-412, Cambridge, Massachusetts 02139-4307, USA*

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**** 23 pages ****

Opinion piece



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One contribution of 16 to a Theo Murphy meeting issue 'Towards implementing the new kelvin'.

Meaning of temperature in different thermostatical ensembles

Peter

Hänggi^{1,2}, Stefan Hilbert³ and Jörn Dunkel⁴

¹Institute of Physics, University of Augsburg, Universitätstrasse 1, 86135 Augsburg, Germany

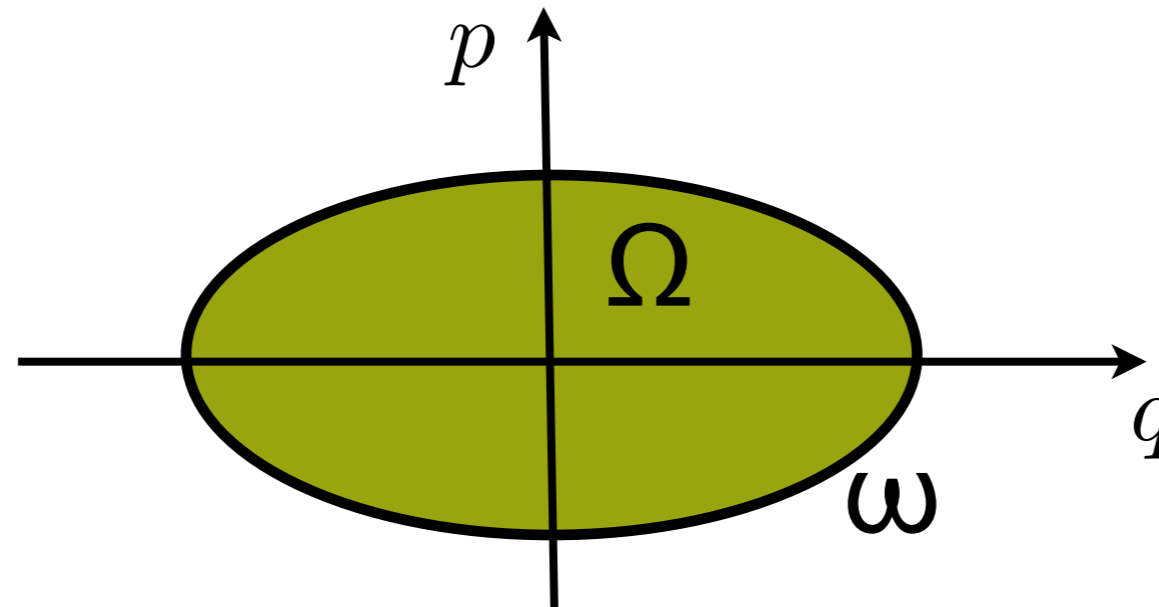
²Nanosystems Initiative Munich, Schellingstrasse 4, 89799 München, Germany

³Exzellenzcluster Universe, Boltzmannstrasse 2, 85748 Garching, Germany

⁴Department of Mathematics, Massachusetts Institute of Technology, 77 Massachusetts Avenue E17-412, Cambridge, MA 02139-4307, USA

 PH, 0000-0001-6679-2563; JD, 0000-0001-8865-2369

Boltzmann vs. Gibbs



$$S_B(E) = \ln(\epsilon \omega)$$

$$S_G(E) = \ln \Omega$$

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

$$T_B(E) = \frac{\omega}{\nu} \geq 0$$

$$T_G(E) = \frac{\Omega}{\omega} \geq 0$$

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

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

Example I: Classical ideal gas

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

$$S_B(E, V, A) = k_B \ln[\epsilon \omega(E)]$$

$$E = \left(\frac{dN}{2} - 1 \right) k_B T_B$$

vs.

$$S_G(E, V, A) = k_B \ln[\Omega(E)]$$


$$E = \frac{dN}{2} k_B T_G$$

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

$$\begin{aligned}
 T_G \left(\frac{\partial S_G}{\partial Z_j} \right) &= \frac{1}{\omega} \frac{\partial}{\partial Z_j} \text{Tr} \left[\Theta(E - H) \right] = -\frac{1}{\omega} \text{Tr} \left[-\frac{\partial}{\partial Z_j} \Theta(E - H) \right] \\
 &= -\text{Tr} \left[\left(\frac{\partial H}{\partial Z_j} \right) \frac{\delta(E - H)}{\omega} \right] = - \left\langle \frac{\partial H}{\partial Z_j} \right\rangle
 \end{aligned}$$


see also Campisi, Physica A 2007

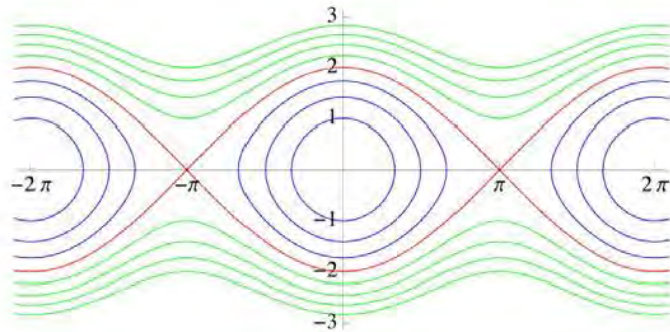


FIG. 1. A pendulum moves in phase space (θ, p) along lines of constant energy, $H(\theta, p) = E$. Blue: finite trajectories (oscillations) for $E < 2$. Green: infinite trajectories (rotation) for $E > 2$. Red: the critical contour, $E = 2$, separating finite and infinite trajectories.

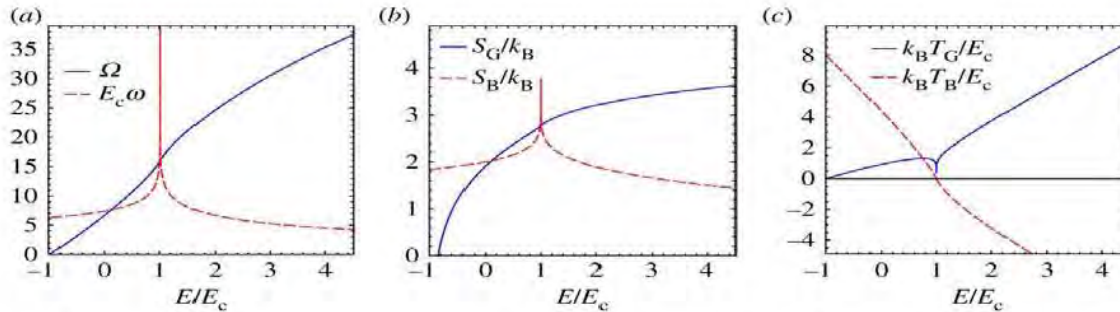


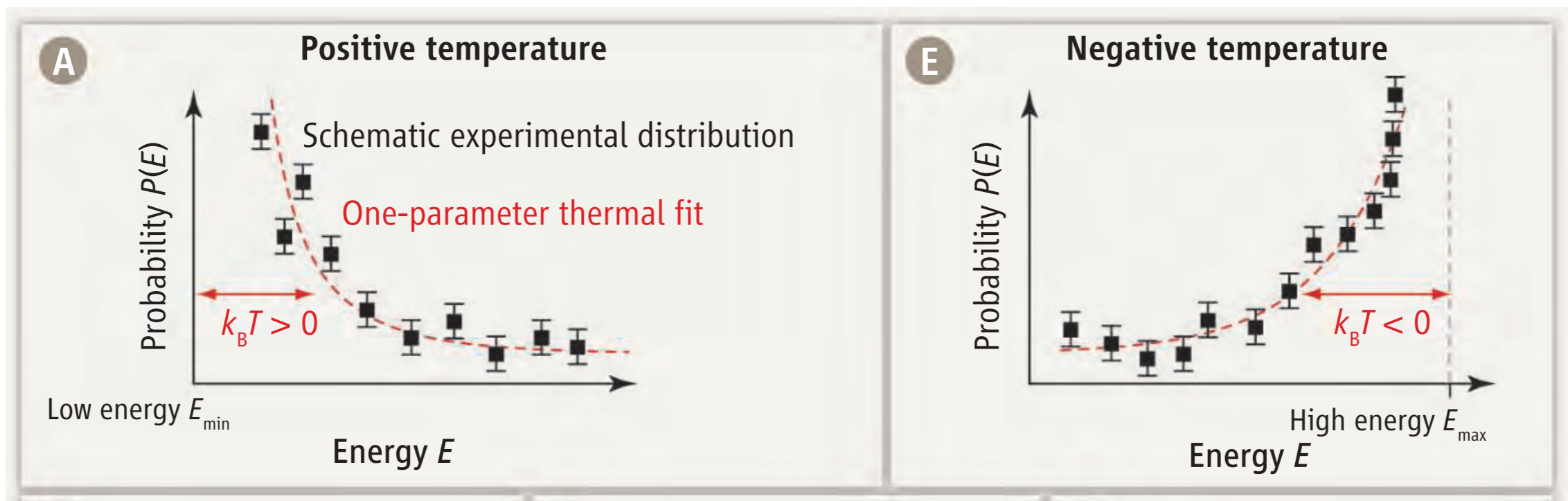
Figure 1. Microcanonical thermostatics of the pendulum with Hamiltonian (2.10). (a) The integrated DoS Ω (blue) grows monotonically while the DoS ω (red dashed) exhibits a singular peak at the critical energy $E_c = mgL$, indicating a change in the phase-space topology. (b) The Gibbs entropy S_G (blue) 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 $E > E_c$.

PHYSICS

Negative Temperatures?

Lincoln D. Carr

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



Population inversion of **one**-particle levels

Troubles with different prescriptions

$$S_B = \ln \frac{\partial \Omega(E, \lambda)}{\partial E} \epsilon$$

✓

e.g. N non-interacting spins

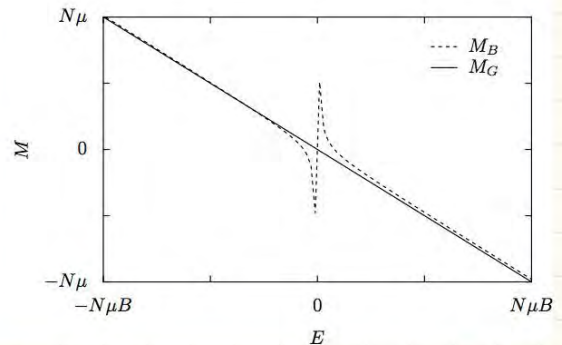
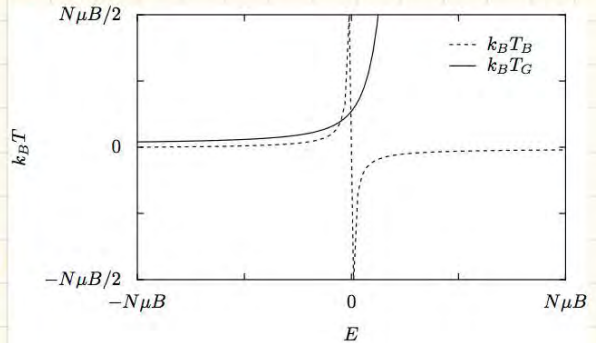
$$H = -B\mu \sum_i \sigma_i$$

$$M = -E/B$$

$$n(E, B) = \frac{N}{2} + \frac{E}{2\mu B}$$

$$\Omega(E, B) = \sum_{k=0}^n \frac{N!}{k! (N-k)!}$$

$$W(E, B) = \frac{\partial \Omega}{\partial E} = \frac{1}{2\mu B} \frac{N!}{n! (N-n)!}$$



$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad M = \frac{\partial S}{\partial B} / \frac{\partial S}{\partial E}$$

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).

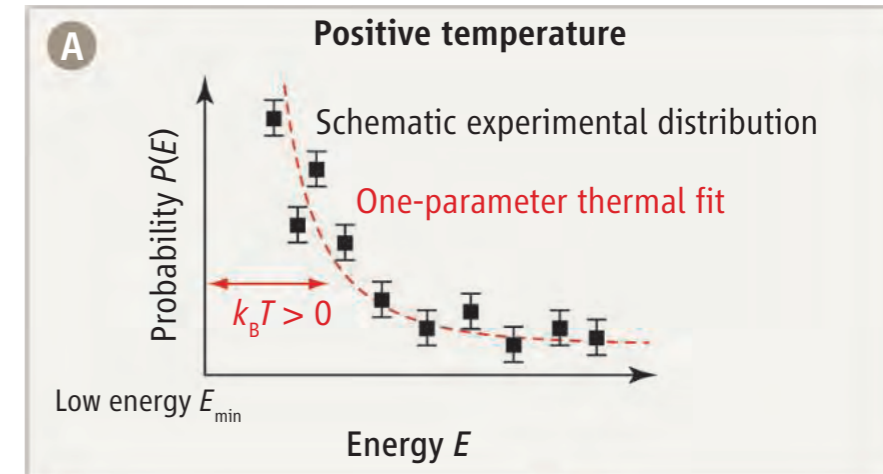
✓ Carnot efficiencies > 1

✓ Dark Energy

Measuring T_B vs. T_G

One-particle distribution

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



Steepest-descent approximation

$$\rho_1 = \exp[\ln \rho_1] \Rightarrow p_\ell \simeq \frac{e^{-E_\ell/(k_B T_B)}}{Z}, \quad Z = \sum_\ell e^{-E_\ell/(k_B T_B)}$$

see e.g. Huang's textbook

features T_B and **not** T_G

\Rightarrow one-particle thermal fit does **not** give absolute $T = T_G$

Generally

$$T_B = \frac{T_G}{1 - k_B/C}$$

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

Consistent thermostatics forbids negative absolute temperatures

Jörn Dunkel^{1*} and Stefan Hilbert²

Over the past 60 years, a considerable number of theories and experiments have claimed the existence of negative absolute temperature in spin systems and ultracold quantum gases. This has led to speculation that ultracold gases may be dark-energy analogues and also suggests the feasibility of heat engines with efficiencies larger than one. Here, we prove that all previous negative temperature claims and their implications are invalid as they arise from the use of an entropy definition that is inconsistent both mathematically and thermodynamically. We show that the underlying conceptual deficiencies can be overcome if one adopts a microcanonical entropy functional originally derived by Gibbs. The resulting thermodynamic framework is self-consistent and implies that absolute temperature remains positive even for systems with a bounded spectrum. In addition, we propose a minimal quantum thermometer that can be implemented with available experimental techniques.

Positivity of absolute temperature T , a key postulate of thermodynamics¹, has repeatedly been challenged both theoretically^{2–4} and experimentally^{5–7}. If indeed realizable, negative temperature systems promise profound practical and conceptual consequences. They might not only facilitate the creation of hyper-efficient heat engines^{2–4} but could also help⁷ to resolve the cosmological dark-energy puzzle^{8,9}. Measurements of negative absolute temperature were first reported in 1951 by Purcell and Pound⁵ in seminal work on the population inversion in nuclear spin systems. Five years later, Ramsay's comprehensive theoretical study² clarified hypothetical ramifications of negative temperature states, most notably the possibility to achieve Carnot efficiencies $\eta > 1$ (refs 3,4). Recently, the first experimental realization of an ultracold bosonic quantum gas⁷ with a bounded spectrum has attracted considerable attention¹⁰ as another apparent example system with $T < 0$, encouraging speculation that cold-atom gases could serve as laboratory dark-energy analogues.

Here, we show that claims of negative absolute temperature in spin systems and quantum gases are generally invalid, as they arise from the use of a popular yet inconsistent microcanonical entropy definition attributed to Boltzmann¹¹. By means of rigorous derivations¹² and exactly solvable examples, we will demonstrate that the Boltzmann entropy, despite being advocated in most modern textbooks¹³, is incompatible with the differential structure of thermostatics, fails to give sensible predictions for analytically tractable quantum and classical systems, and violates equipartition in the classical limit. The general mathematical incompatibility implies that it is logically inconsistent to insert negative Boltzmann 'temperatures' into standard thermodynamic relations, thus explaining paradoxical (wrong) results for Carnot efficiencies and other observables. The deficiencies of the Boltzmann entropy can be overcome by adopting a self-consistent entropy concept that was derived by Gibbs more than 100 years ago¹⁴, but has been mostly forgotten ever since. Unlike the Boltzmann entropy, Gibbs' entropy fulfils the fundamental thermostatical relations and produces sensible predictions for heat capacities and other thermodynamic observables in all exactly computable test cases. The

Gibbs formalism yields strictly non-negative absolute temperatures even for quantum systems with a bounded spectrum, thereby invalidating all previous negative temperature claims.

Negative absolute temperatures?

The seemingly plausible standard argument in favour of negative absolute temperatures goes as follows¹⁰: assume a suitably designed many-particle quantum system with a bounded spectrum^{5,7} can be driven to a stable state of population inversion, so that most particles occupy high-energy one-particle levels. In this case, the one-particle energy distribution will be an increasing function of the one-particle energy ϵ . To fit^{7,10} such a distribution with a Boltzmann factor $\propto \exp(-\beta\epsilon)$, β must be negative, implying a negative Boltzmann 'temperature' $T_B = (k_B\beta)^{-1} < 0$. Although this reasoning may indeed seem straightforward, the arguments below clarify that T_B is, in general, not the absolute thermodynamic temperature T , unless one is willing to abandon the mathematical consistency of thermostatics. We shall prove that the parameter $T_B = (k_B\beta)^{-1}$, as determined by Purcell and Pound⁵ and more recently also in ref. 7 is, in fact, a function of both temperature T and heat capacity C . This function $T_B(T, C)$ can indeed become negative, whereas the actual thermodynamic temperature T always remains positive.

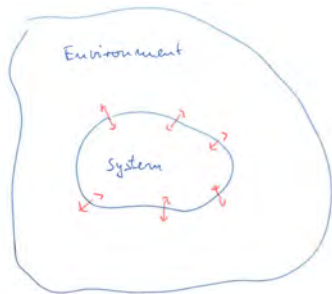
Entropies of closed systems

When interpreting thermodynamic data of new many-body states⁷, one of the first questions to be addressed is the choice of the appropriate thermostatical ensemble^{15,16}. Equivalence of the microcanonical and other statistical ensembles cannot—in fact, must not—be taken for granted for systems that are characterized by a non-monotonic^{2,4,7} density of states (DOS) or that can undergo phase-transitions due to attractive interactions¹⁷—gravity being a prominent example¹⁸. Population-inverted systems are generally thermodynamically unstable when coupled to a (non-population-inverted) heat bath and, hence, must be prepared in isolation^{5–7}. In ultracold quantum gases⁷ that have been isolated from the environment to suppress decoherence, both particle number and energy are in good approximation conserved. Therefore,

¹Department of Mathematics, Massachusetts Institute of Technology, 77 Massachusetts Avenue E17-412, Cambridge, Massachusetts 02139-4307, USA,

²Max Planck Institute for Astrophysics, Karl-Schwarzschild-Straße 1, Garching 85748, Germany. *e-mail: dunkel@math.mit.edu

Weakly coupled systems



$$E_{\text{interaction}} \ll E_{\text{system}}$$

System \oplus Environment in thermal equilibrium at total energy E_{tot}

$$p_{\beta}(\mathbf{x}) = Z^{-1} e^{-\beta H_S(\mathbf{x})}$$

$$Z = \int d\Gamma_S e^{-\beta H_S(\mathbf{x})}$$

$\mathbf{x} \in \Gamma_S$: phase space of system

$$d\Gamma_S = \frac{d^{3N} \mathbf{q} d^{3N} \mathbf{p}}{h^{3N}} : \text{volume element}$$

$$\beta = k_B^{-1} \frac{\partial S_{\text{tot}}}{\partial E_{\text{tot}}} : \text{inverse temperature}$$

Standard form of canonical equilibrium of a subsystem holds for large systems with short-range interactions:

$$E_{\text{interaction}} \propto V_S^{2/3}, \quad E_{\text{system}} \propto V_S$$

canonical ensemble

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

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

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

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

$$\Rightarrow \frac{\omega^S(E^S)}{\mathcal{Z} \omega^T(E^T)} \exp \left[\frac{S_B^B(\bar{E}^B)}{k_B} + \frac{(E^T - \bar{E}^B) - E^S}{k_B T_B^B(\bar{E}^B)} + \dots \right]$$

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



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

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

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.

Divertissement/Insertion

INVARIANT

Entropy (phase space) $\stackrel{!}{=} \underset{E}{\text{Entropy (energy space)}}$
 $\Gamma: \{q, p\}$

$$d\Gamma \rightarrow \frac{d\Gamma}{h f.c} \leftarrow \text{symmetry number} \equiv d\tilde{\Gamma}$$

$$Z = \exp(-\beta F) ; Z = \int d\tilde{\Gamma} \exp[-\beta \mathcal{H}(\tilde{\Gamma}, \lambda)] = e^{-\beta F}$$

dimensionless!

$$p_{\tilde{\Gamma}}(\tilde{\Gamma}, \lambda) = \exp(\beta F) \exp(-\beta \mathcal{H}(\tilde{\Gamma}, \lambda))$$

$$p_E(E, \lambda) = \exp(\beta F) \int \frac{d\Gamma}{h f.c} \delta(\mathcal{H}(\Gamma, \lambda) - E) \exp(-\beta \mathcal{H}(\Gamma, \lambda))$$

$$= \exp(\beta F) \int \frac{d\Gamma}{h f.c} \delta(\mathcal{H}(\Gamma, \lambda) - E) \exp(-\beta \mathcal{H}(\Gamma, \lambda))$$

$\omega(E, \lambda) \leftarrow \text{a density} \geq 0$
 not a pdf

$$= \omega(E, \lambda) \exp(-\beta E) / Z$$

$\omega(E, \lambda) \delta E = 1$

$$S_{\tilde{\Gamma}} = -k_B \langle \ln p_{\tilde{\Gamma}}(\tilde{\Gamma}, \lambda) \rangle \stackrel{!}{=} S_E = -k_B \int dE p(E, \lambda) \ln \left\{ \frac{\omega(E, \lambda) e^{-\beta E}}{Z} \right\}$$

dimensionless

Eight physical systems of thermodynamics, statistical mechanics, and computer simulations

By H. W. GRABEN and JOHN R. RAY

Kinard Laboratory of Physics and Astronomy

Clemson University, Clemson, South Carolina 29634-1911, USA

N : # particles
 V : Volume
 E : int. Energy
 T : abs. Temp
 p : pressure
 μ : chem. Potential
 S : entropy

8

$$dE = TdS - pdV + \mu dN$$

$$E = E(S, V, N)$$

$$H = E + pV = H(S, p, N)$$

$$L = E - \mu N = L(S, V, \mu)$$

$$R = E + pV - \mu N = R(S, p, \mu)$$

$$F = E - TS = F(T, V, N)$$

$$G = E - TS + pV = G(T, p, N)$$

$$J = E - TS - \mu N = J(T, V, \mu)$$

$$Z = E - TS + pV - \mu N = Z(T, p, \mu)$$

microcan, ensemble

H-p-N-ensemble (Brown, 1958)

Hill-ensemble (1956)

Ray-ensemble (1990)

Helmholtz

Gibbs

Grand-canonical

"Null"-potential

if $E = TS - pV + \mu N$

$\rightarrow Z = 0$ if Euler of order 1 holds

(Gibbs-Duhem relation)

$$-SdT + Vdp - Nd\mu = 0$$

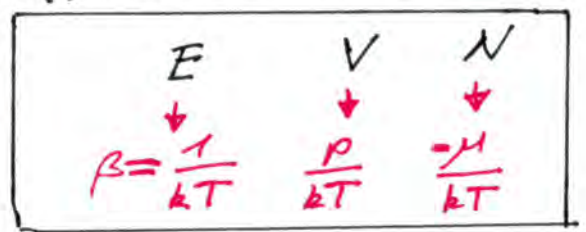
Partition Functions

Weak Coupling Following R. F. Sack, Molecular Physics 2, 8-22 (1958)

$\{X_i\}$: extensive; $\{\rho_i\}$: conjugate intensive

$$dE = TdS - pdV + \mu dN$$

$$k^{-1}dS = \beta dE + \beta p dV - \beta \mu dN$$



R # extensive therm. Variables X_i
 K # conj. intensive variables ρ_i
 replacing those ~~int~~ extensive ones

$$\max S = -\langle \ln S \rangle ; S \rho d\tau_K = 1 \quad \& \quad \int X_i \rho d\tau_K = \langle X_i \rangle$$

λ_1 replacing $X_1 = E$
 $= \beta$
 λ_2 replacing $X_2 = V$

$$\Rightarrow S = Q \exp(-\sum \lambda_i X_i - \eta_K)$$

partition function $Q_K(\dots \lambda_K \dots)$

z.B. $Q_1(\lambda_1, V, N) = Z_{can}(T, V, N)$

$$Q_2(\lambda_1, \lambda_2, N) = Y(T, p, N)$$

\uparrow \uparrow
 β βp

microcanonical ensemble

$$S = k \ln \Omega_c, \text{ where } \Omega_c = C_N \int_0^{\infty} \Theta(E - \mathcal{H}(\dots)) d\Gamma_N; C_N = \frac{1}{h^{3N} N!}$$

$$= k \ln \Omega_c(E, V, N, \dots); X_i: i = E, V, N, \dots, X_R$$

↑ stands for "cumulative"

Then (following R. A. Sack)

$$Q_K(\lambda_1, \lambda_2, \dots, \lambda_K; X_{K+1}, \dots, X_R)$$

$$= \int_{X_K=-\infty}^{+\infty} \exp(-\lambda_K X_K) d[Q_{K-1}(\dots, X_K, \dots)]$$

with $\frac{\partial \ln Q_{K-1}}{\partial X_K} \bullet Q_{K-1} = \left(\frac{\partial Q_{K-1}}{\partial X_K} \right)$ & part. integration of Stieltjes Integral

Q_{K-1} must be monotonically non-decreasing in X_K

$$Q_K = \lambda_K \int \exp(-\lambda_K X_K) Q_{K-1}(\dots, X_K, \dots) dX_K \quad ; \text{ if b.c. vanish}$$

① canonical ensemble: $\lambda_1 = \beta = \frac{1}{kT}$

$$Z(T, V, N) = \int_0^\infty \exp(-\beta E) \rho_E \Omega_c(E, V, N) \quad \swarrow \text{DOS}$$

$$= \frac{d\Omega_c}{dE} dE = \omega_c(E, V, N) dE$$

~~∫~~ partial integration

$$\stackrel{!}{=} \underbrace{\exp(-\beta E) \Omega_c(E, V, N)}_0 \Big|_{E=0}^{E=\infty} + \beta \int_0^\infty \Omega_c \exp(-\beta E) dE$$

Note $\omega_c(E) \& \Omega_c(E) \propto \exp\{-N \phi(E/N)\}$ or $\propto \exp\{V \psi(E/V)\}$

$\Omega_c(E) \& \omega_c(E)$ NOT $\propto \exp\{[c > 0] \cdot E\}$

i.e. $\text{Tr} [\exp(-\beta H)] = \infty$ then diverges $\& \frac{\text{Tr} H \exp(-\beta H)}{\text{Tr} e^{-\beta H}} = \infty$
 $T \rightarrow T_H$ Hagedorn $\equiv T_H$

at T_H : Phase Transition occurs! \rightarrow to quark-gluon plasma (deconfinement)

$$\frac{T_{\text{Planck}}}{T_H \text{ (Hagedorn} \rightarrow \text{quarks)}} \approx 10^{20}; \quad \frac{T_{\text{Planck}}}{T_H \text{ (Hagedorn-strings)}} \approx 100$$

quark-gluon \rightarrow string plasma
deconfinement

The four dimensionless partition functions are given by

$$C_N = \frac{1}{N! h^{3N}}$$

$$Q(E, V, N) = C_N \int dq \int dp \Theta(E - \mathcal{H}), \quad (25)$$

$$Q(H, P, N) = C_N \int dV \int dq \int dp \delta(H - PV - \mathcal{H}), \quad (26)$$

P. Ströcker & K. Meier
PRE (2022)

$$Q(L, V, \mu) = \sum_{N=0}^{\infty} C_N \int dq \int dp \Theta(L + \mu N - \mathcal{H}), \quad (27)$$

$$Q(R, P, \mu) = \sum_{N=0}^{\infty} C_N P \int dV \int dq \int dp \delta(R - PV + \mu N - \mathcal{H}). \quad (28)$$

It is well known that the isothermal partition functions can be generated by a sequence of proper Laplace transformations taken upon $Q(E, V, N)$. These are the following

canonical ens. $Q(T, V, N) = \beta \int_0^{\infty} \exp(-\beta E) Q(E, V, N) dE, \quad (29)$

T-p ens. $Q(T, P, N) = \beta P \int_0^{\infty} \exp(-\beta PV) Q(T, V, N) dV, \quad (30)$

grand can. ens. $Q(T, V, \mu) = \sum_{N=0}^{\infty} \exp(\beta \mu N) Q(T, V, N), \quad (31)$

NULL-ensemble $Q(T, P, \mu) = \beta P \int_0^{\infty} \exp(-\beta PV) Q(T, V, \mu) dV. \quad (32)$

If equation (25) is inserted into equations (29)–(32), familiar, standard forms of the isothermal partition functions will emerge. Note that a ‘discrete’ Laplace transform is taken in equation (31). These Laplace transforms appear in explicit form. In operator form equation (29) may be written as $Q(T, V, N) = \mathcal{L}(\beta E) Q(E, V, N)$ and its inverse as $Q(E, V, N) = \mathcal{L}^{-1}(\beta E) Q(T, V, N)$. Using this notation, we can rewrite equations (29)–(32) as

$$Q(T, V, N) = \mathcal{L}(\beta E) Q(E, V, N), \quad (33)$$

$$Q(T, P, N) = \mathcal{L}(\beta PV) \mathcal{L}(\beta E) Q(E, V, N), \quad (34)$$

$$Q(T, V, \mu) = \mathcal{L}(-\beta \mu N) \mathcal{L}(\beta E) Q(E, V, N), \quad (35)$$

$$Q(T, P, \mu) = \mathcal{L}(-\beta \mu N) \mathcal{L}(\beta PV) \mathcal{L}(\beta E) Q(E, V, N). \quad (36)$$

These four equations are the Laplace transform companions to the four Legendre transforms shown in equations (14)–(17).

Expressions leading to identical results to those produced in equations (30)–(32)

(2) p - T ensemble $\lambda_1 = \beta$; $\lambda_2 = \beta p$

$$Q(\lambda_1, \lambda_2, N) = \mathcal{Y}(T, p, N)$$

$$= \int_0^\infty \exp(-pV/kT) \underbrace{\partial_V [Z(T, V, N)]}_{(*)} \quad (*)$$

$$\left(\frac{\partial Z}{\partial V}\right) dV = Z \underbrace{\left(\frac{\partial \ln Z}{\partial V}\right)}_{= \beta p''(T, V)} dV$$

$$= \int_0^\infty \exp(-\beta pV) Z \cdot (\beta p''(T, V)) dV$$

\Rightarrow partial integration of (*)

$$= \exp(-\beta pV) Z(T, V, N) \Big|_0^\infty + (\beta p) \int_0^\infty Z(T, V, N) \exp(-\beta pV) dV$$

dimensionless!

$$F_S = -\beta^{-1} \ln Z : \quad \text{free energy}$$

$$U_S = -\frac{\partial}{\partial \beta} \ln Z = \langle H_S \rangle_S : \quad \text{internal energy}$$

$$S_S = k_B \ln Z_S - k_B \beta \frac{\partial}{\partial \beta} \ln Z_S = -k_B \langle \ln p_\beta \rangle_S : \quad \text{entropy}$$

yielding

$$F_S = U_S - TS_S \quad (1)$$

$$U_S = \frac{\partial}{\partial \beta} (\beta F_S) \quad (2)$$

$$S_S = k_B \beta^2 \frac{\partial}{\partial \beta} F_S \quad (3)$$

Any pair of the three equations (1 – 3) implies the third one.

Potentials F_S , U_S and S_S satisfying (1 –3) are

THERMODYNAMICALLY CONSISTENT.

COMMENTS

Comment on “Length Scale for the Constant Pressure Ensemble: Application to Small Systems and Relation to Einstein Fluctuation Theory”

David S. Corti

Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095

Received: May 30, 1997

In an article published in this journal early last year, Koper and Reiss¹ introduced a volume scale that allows the partition function within the isothermal–isobaric ensemble (pressure, temperature, and particle number are held fixed) to be represented by a dimensionless integral. The need to introduce a volume or length scale arises because the relevant partition function involves a sum over a set of unspecified system volumes. Replacing the sum by an integral to include *all volumes* results in a partition function that is not dimensionless but has the dimensions of volume. In the thermodynamic limit, the sum over discrete unspecified volumes yields a completely negligible error,² in essence because only the maximum term in the sum was important. However, as emphasis has turned to the theory of small systems (e.g., clusters³ and microemulsions⁴), there is an obvious need to include all the terms and obtain the correct partition function as an integral over volume.

For a system composed of N particles, maintained at a temperature T , and subject to a constant external pressure p , Koper and Reiss showed that the partition function Δ , if evaluated over a continuous set of system volumes, is

$$\Delta = \int_V \frac{p''}{kT} Q(N, V, T) e^{-p''V/kT} dV \quad (1)$$

where

$$\frac{p''}{kT} = \left(\frac{\partial \ln Q}{\partial V} \right)_{N, T} \quad (2)$$

provides the appropriate length scale of inverse volume such that Δ is dimensionless. Note that p'' is the pressure of the system at volume V . (Koper and Reiss correctly state that the meaning of p'' in eq 2 is not necessarily that of a *pressure* since for a small system there are usually additional independent thermodynamic variables (e.g., surface area, curvature, etc.) that need to be considered. However, it is convenient to refer to p'' as a pressure even though it denotes a specific volume derivative of Q .) In the above equations, $Q(N, V, T)$ is the canonical ensemble partition function for a system containing N particles in a volume V at the given temperature T , while k is Boltzmann's constant. Equation 1 was derived by eliminating all redundant microstates that had the same volume. Koper and Reiss found that (eq 4.20 in their paper)

~~$$G = -kT \ln \Delta - kT \ln \Delta \quad (3)$$~~

thermodynamic limit. However, this result is inconsistent with their eq 4.9 in which

$$\Omega_i = \Delta \exp \left[\frac{\bar{U} + p\bar{V} + TS_0(\bar{U}_0, \bar{V}_0, N_0)}{kT} \right] \quad (4)$$

Ω_i is the total hypervolume available to an isolated system composed of N_i particles at a fixed volume V_i and energy U_i . The system is divided into two parts: the subsystem of interest (not necessarily macroscopic) and a bath of macroscopic size. The external bath imposes a constant temperature T and pressure p on the subsystem. The subsystem is described by U , V , and N while the bath is described by U_0 , V_0 and N_0 . An overbar above a variable denotes the average (equilibrium) value. If we take the logarithm of both sides of eq 4, we find that

$$\ln \Omega_i = \frac{S_i}{k} = \ln \Delta + \frac{\bar{U}}{kT} + \frac{p\bar{V}}{kT} + \frac{S_0}{k} = \ln \Delta + \frac{\hat{H}}{kT} + \frac{S_0}{k} \quad (5)$$

where we define⁵

$$\hat{H} \equiv \bar{U} + p\bar{V} \quad (6)$$

Since the entropy is additive, we note that the total entropy of the isolated system must be equal to the sum of the individual entropies of the bath and subsystem ($S_i = S + S_0$). Therefore, if we let

$$\hat{G} \equiv \bar{U} + p\bar{V} - TS = \hat{H} - TS \quad (7)$$

we find that⁵

$$\hat{G} = -kT \ln \Delta(N, p, T) \quad (8)$$

Note that \hat{G} is not equivalent to the Gibbs energy of the subsystem, as Koper and Reiss suggest in eq 3, but can be thought of as a modified Gibbs energy due to the appearance of p (and not the internal pressure) in eq 7. Koper and Reiss obtained eq 3 by ignoring the temperature dependence of p'' in their eq 4.13.⁶ Equation 8 is applicable to a system of any size and is consistent with previous formulations² for systems in the thermodynamic limit. Koper and Reiss showed that $p'' = p$ for a macroscopic system (eq 6.5 in their paper) and, in this limit only, does \hat{G} necessarily equal the Gibbs energy G of the subsystem.

We can now determine what thermodynamic variables are related to the derivatives of \hat{G} . For a system in which a constant external pressure p is imposed, we note that the differential change in the internal energy \bar{U} is equal to⁵

$$d\bar{U} = T dS - p d\bar{V} + \mu dN \quad (9)$$

where $-p d\bar{V}$ is the work performed by the system against the fixed external pressure p and μ is the chemical potential. Using eqs 7 and 9, one can show that

$$\left(\frac{\partial \hat{G}}{\partial S} \right) = -S \quad (10)$$

Length Scale for the Constant Pressure Ensemble: Application to Small Systems and Relation to Einstein Fluctuation Theory

Ger J. M. Koper and Howard Reiss*

Department of Physical and Macromolecular Chemistry, Leiden University, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Deriving the isothermal–isobaric ensemble: The requirement of a “shell” molecule and applicability to small systems

David S. Corti, and Gerardo Soto-Campos

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View online: <https://doi.org/10.1063/1.476236>

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Articles you may be interested in

On the isothermal-isobaric ensemble partition function

Molecular dynamics in the isothermal-isobaric ensemble: The requirement of a “shell” molecule. I. Theory and phase-space analysis

Mark J. Uline, and David S. Corti

Citation: The Journal of Chemical Physics **123**, 164101 (2005); doi: 10.1063/1.2064512

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LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 2001 issue.

NOTES

On the isothermal-isobaric ensemble partition function

Kyu-Kwang Han

*Department of Physics and Research Institute of Natural Science, Pai Chai University,
Taejeon 302-735, Korea*

Hyeon S. Son

*Bioinformatics Team, Korea Institute of Science and Technology Information, Yusong,
Taejeon 305-600, Korea*

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We briefly review the isothermal-isobaric ensemble partition function correctly derived by Corti and Soto-Campos [J. Chem. Phys. **108**, 7959 (1998)] from the view point of usual simulations in which the external bath of a system is appropriately approximated. We show that, for the homogeneous system, the partition function can be reduced to the result of Attard [J. Chem. Phys. **103**, 9884 (1995)] which was criticized by Corti and Soto-Campos. **We conclude that the volume scale cannot be defined in general** but in some particular cases and the recently controverted volume scales are those of the cases. We also confirm the validity of Brown's [Mol. Phys. **1**, 68 (1958)] partition function which has never been used in simulations before, by demonstrating that it is equivalent to the one of Corti and Soto-Campos. © 2001 American Institute of Physics.

10.1063/1.1427557

Review

Molecular Dynamics at Constant Pressure: Allowing the System to Control Volume Fluctuations via a “Shell” Particle

Mark J. Uline ^{1,*} and David S. Corti ²

¹ Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA

² School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA;

E-Mail: dscorti@purdue.edu

* Author to whom correspondence should be addressed; E-Mail: uline@cec.sc.edu;

Tel.: +1-803-777-2030; Fax: +1-803-777-8265.

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Abstract: Since most experimental observations are performed at constant temperature and pressure, the isothermal-isobaric (NPT) ensemble has been widely used in molecular simulations. Nevertheless, the NPT ensemble has only recently been placed on a rigorous foundation. The proper formulation of the NPT ensemble requires a “shell” particle to uniquely identify the volume of the system, thereby avoiding the redundant counting of configurations. Here, we review our recent work in incorporating a shell particle into molecular dynamics simulation algorithms to generate the correct NPT ensemble averages. Unlike previous methods, a piston of unknown mass is no longer needed to control the response time of the volume fluctuations. As the volume of the system is attached to the shell particle, the system itself now sets the time scales for volume and pressure fluctuations. Finally, we discuss a number of tests that ensure the equations of motion sample phase space correctly and consider the response time of the system to pressure changes with and without the shell particle. Overall, the shell particle algorithm is an effective simulation method for studying systems exposed to a constant external pressure and may provide an advantage over other existing constant pressure approaches when developing nonequilibrium molecular dynamics methods.

Keywords: isothermal-isobaric ensemble; molecular dynamics

case of ideal gas

Textbook

with volume scale

$$\begin{aligned}
 \underline{\underline{\mathcal{Y}^{TB}(T, p, N)}}} &= \frac{1}{N!} \int_0^\infty dV \int \frac{dT}{h^{3N}} \exp -\beta (\sum_i H_i + pV) \\
 &= \int_0^\infty dV \exp(-\beta pV) [Z(T, V, N)]^N \\
 &= \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{3N/2} \int_0^\infty dV \exp(-\beta pV) V^N \\
 &= \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3N}{2}} \int_0^\infty \underbrace{d(\beta pV)}_{(\beta p)^{N+1}} \underbrace{(\beta pV)^N e^{-(\beta pV)}}_{= N! = \Gamma(N+1) \text{ fct.}} \\
 &= \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3N}{2}} \frac{1}{(\beta p)^{N+1}} \cdot N! \\
 &= \underline{\underline{\left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3N}{2}} \frac{1}{(\beta p)^{N+1}}}}
 \end{aligned}$$

$$\beta p \cdot \mathcal{Y}^{TB}(T, p, N) = \mathcal{Y}(T, p, N)$$

$$\mathcal{Y}(T, p, N) = \frac{1}{(\beta p)^N} \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3N}{2}}$$

$$G(T, p, N) = -\frac{1}{\beta} \ln \mathcal{Y}(T, p, N); \quad dG = -SdT + Vdp + \mu dN$$

$$\begin{aligned}
 V &= \left(\frac{\partial G}{\partial p} \right)_{T, N}; \quad C_p = k \beta^2 \frac{\partial^2 \ln \mathcal{Y}}{\partial \beta^2}; \quad \mu = \left(\frac{\partial G}{\partial N} \right)_{T, p} \\
 &= -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{p, N}
 \end{aligned}$$

results

$$\mathcal{Y}^{TB}(T, p, N)$$

$$V = (N+1) \left(\frac{1}{\beta p} \right) \Rightarrow pV = \underline{(N+1)kT}$$

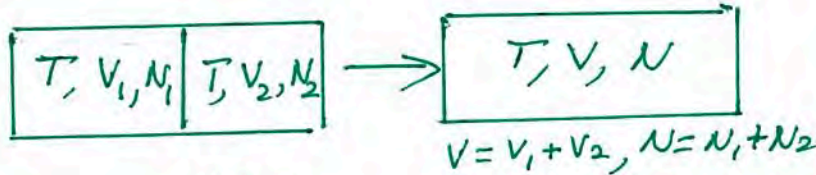
$$C_p = k \left(\frac{5}{2} N + 1 \right)$$

$$\mathcal{Y}(T, p, N)$$

$$V = N / (\beta p) \Rightarrow pV = \underline{NkT} \quad \checkmark$$

$$C_p = k \frac{5}{2} N = kN \left(\frac{3}{2} + 1 \right) \quad \checkmark$$

noteworthy:



canonical $\Delta S^{id} = 0$
 $\Delta S^{nid} \neq 0$

p-T-ensemble $S = - \left(\frac{\partial G}{\partial T} \right)_{p, N}$
 remove wall & $V \rightarrow \infty$

$$\mathcal{Y}_{final} = \mathcal{Y}_{initial} = \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3N}{2}} \frac{1}{(\beta p)^N}$$

$$N_T = N_1 + N_2 = N$$

mixing entropy

vanishes

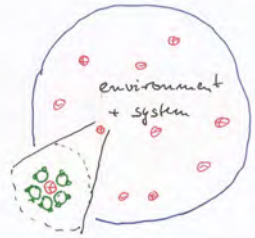
Strongly coupled systems



microscopic system



macroscopic system
with long-range
interactions



solvated system,
e.g. pinch of salt in
a pot of water

$H_{\text{tot}}(\mathbf{x}, \mathbf{y}) = H_S(\mathbf{x}) + H_i(\mathbf{x}, \mathbf{y}) + H_B(\mathbf{y})$: total system's Hamiltonian

$\mathbf{x} \in \Gamma_S$, Γ_S phase space of system

$\mathbf{y} \in \Gamma_B$, Γ_B phase space of environment

Strongly coupled systems

$H_{\text{tot}}(\mathbf{x}, \mathbf{y}) = H_S(\mathbf{x}) + H_i(\mathbf{x}, \mathbf{y}) + H_B(\mathbf{y})$: total system's Hamiltonian

$\mathbf{x} \in \Gamma_S$, Γ_S phase space of system

$\mathbf{y} \in \Gamma_B$, Γ_B phase space of environment

Let the total system stay in a canonical equilibrium state at inverse temperature β :

$$\rho_\beta(\mathbf{x}, \mathbf{y}) = Z_{\text{tot}}^{-1} e^{-\beta H_{\text{tot}}(\mathbf{x}, \mathbf{y})}$$

$$Z_{\text{tot}} = \int d\Gamma_S d\Gamma_B e^{-\beta H_{\text{tot}}(\mathbf{x}, \mathbf{y})}$$

Then the system is in the state

$$\rho_\beta(\mathbf{x}) = \int d\Gamma_B \rho_\beta(\mathbf{x}, \mathbf{y})$$

The reduced state $p_\beta(\mathbf{x})$ in general differs from the Gibbs state $Z_S^{-1} e^{-\beta H(\mathbf{x})}$ of a weakly coupled system. To write $p_\beta(\mathbf{x})$ in the form of a Gibbs state one introduces the **HAMILTONIAN OF MEAN FORCE** $H^*(\mathbf{x})$ defined by

$$\begin{aligned} e^{-\beta H^*(\mathbf{x})} &= \langle e^{-\beta(H_S(\mathbf{x})+H_i(\mathbf{x},\mathbf{y}))} \rangle_B \\ &= Z_B^{-1} \int d\Gamma_B e^{-\beta(H_S(\mathbf{x})+H_i(\mathbf{x},\mathbf{y})+H_B(\mathbf{y}))} \end{aligned}$$

$$Z_B = \int d\Gamma_B e^{-\beta H_B(\mathbf{y})}$$

$$H^*(\mathbf{x}) = H_S(\mathbf{x}) - \beta^{-1} \ln \langle e^{-\beta H_i(\mathbf{x},\mathbf{y})} \rangle_B$$

$$p_\beta(\mathbf{x}) = Z_S^{-1} e^{-\beta H^*(\mathbf{x})}$$

$$Z_S = \int d\Gamma_S e^{-\beta H^*(\mathbf{x})} = Z_{\text{tot}}/Z_B$$

Warning

W1 Note that \hat{H}^* ($H^*(\mathbf{x})$) determines \hat{p}_β ($p_\beta(\mathbf{x})$) but not vice versa:

$$\ln p_\beta = -\beta H^* - \ln Z_S$$

In other words, H_S^* cannot be inferred from the intrinsic point of view of the open system, say in terms of tomography of the open system density matrix. Additional information from the environment in the form of $Z_S = Z_{\text{tot}}/Z_B$ is required.

Thermodynamics

$$F_S = -\beta^{-1} \ln Z_S = F_{\text{tot}} - F_B$$

$$U_S = \frac{\partial}{\partial \beta} \beta F_S = U_{\text{tot}} - U_B$$

$$S_S = k_B \beta^2 \frac{\partial}{\partial \beta} F_S = S_{\text{tot}} - S_B$$

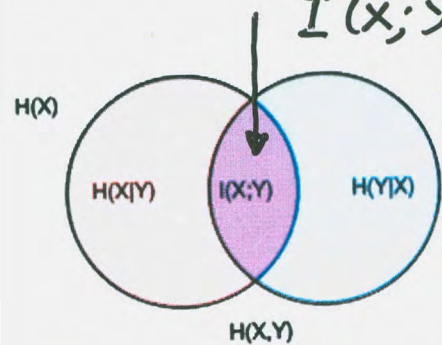
$$C_S = -k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \beta F_S = C_{\text{tot}} - C_B$$

The potentials F_S , U_S and S_S are thermodynamically consistent because they follow from a partition function.

-
- R.P. Feynman, F.L. Vernon, Ann. Phys. (N.Y.) **24**, 118 (1963).
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**, 061105 (2009).

Conditional Entropy

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



$$H(X) = H(X|Y) + I(X; Y)$$

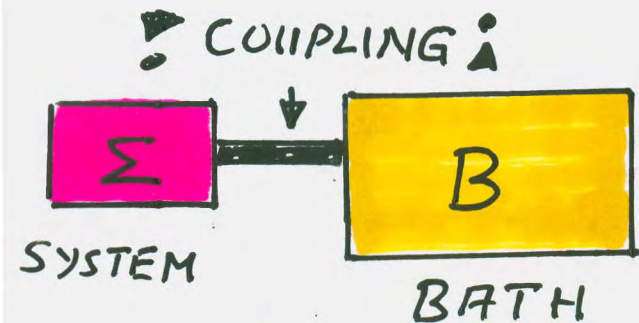
$$H(Y) = H(Y|X) + I(X; Y)$$

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

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

Quantum Conditional Entropy

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



$$S_\Sigma = S_{vN}(\rho_{\Sigma \times B}^{can}) - S_{vN}(\rho_B^{can})$$

can. thermod. entropy

quantum cond. entropy

$$\stackrel{?!}{=} S_{vN}(\rho_{\Sigma \times B}^{can}) - S_{vN}(\rho_B = \text{Tr}_\Sigma \rho_{\Sigma \times B}^{can})$$

$\uparrow \neq \rho_B^{can}$

Further warnings

W2 INTERNAL ENERGY

$$U_S = -\frac{\partial}{\partial \beta} \ln Z_S = \left\langle \frac{\partial}{\partial \beta} \beta H^* \right\rangle_S = \langle H^* \rangle_S + \beta \langle \partial H^* / \partial \beta \rangle_S$$

$$\langle \cdot \rangle_S = Z_S^{-1} \int d\Gamma_S \cdot e^{-\beta H^*}$$

The internal energy in general does not agree with the average of the Hamiltonian of mean force. The temperature dependence of H^* entails an additional contribution.

W3 ENTROPY

$$S_S = -k_B \langle \ln p_\beta \rangle_S + k_B \beta^2 \langle \partial H^* / \partial \beta \rangle_S$$

The entropy in general deviates from the Shannon-Gibbs (von Neumann) entropy due to the temperature dependence of the Hamiltonian of mean force.

strong coupling

$$Z(T, V, N) \rightarrow Z^*(T, V, N) \\ = C_N \int d\Gamma_S \exp(-\beta H^*(\beta, \text{disc.}))$$

$$Y^*(T, p, N) = (\beta p) \int_0^\infty dV \exp(-\beta p V) Z^*(T, V, N)$$

thermal equilibrium: mean values vs. fluctuations

internal energy: $U_S = -\frac{\partial}{\partial \beta} \ln Z_S = \left\langle \frac{\partial}{\partial \beta} \beta H^* \right\rangle_{\rho_B}$

depends on β & γ
 $\rho_B \equiv S_{\text{system}}^{\text{eq}} \equiv "S"$

$$= \langle H_S \rangle_S + [\langle H_{\text{INT}} \rangle + \langle H_B \rangle_{\text{tot}} - \langle H_B \rangle_B]$$

fluctuating internal energy $E(x; \lambda) = \frac{\partial}{\partial \beta} [\beta H^*(x; \lambda)] ; U_S = \langle E(x; \lambda) \rangle_S$

TaPiner & H. PRE 94
 App. B 022143 (2016)

$$= \langle H_{\text{tot}} | x \rangle_{w^{\text{eq}}} - \langle H_B \rangle_B$$

$$w^{\text{eq}}(y|x) = \frac{S_{\text{tot}}^{\text{eq}}(x,y)}{S_{\text{system}}^{\text{eq}}(x)}$$

eq. preparation class
 G.+H.+T. Z. Physik B26
 389 (1979) (epc)

Now $\delta H_{\text{INT}}(x,y) = H_{\text{INT}}(x,y) - \langle H_{\text{INT}}(x,y) | x \rangle_{w^{\text{eq}}}$

$\int dy H_{\text{INT}}(x,y) w^{\text{eq}}(y|x)$

with $S_{\text{epc}}^{\circ} = w^{\text{eq}}(y|x) \rho^{\circ}(x)$
 arbitrary

$$\langle \delta H_{\text{INT}}(x,y) \rangle_{S_{\text{epc}}^{\circ}} \stackrel{!}{=} 0 ; \forall S_{\text{epc}}^{\circ}$$

ambiguity for fluctuating potentials: $E(x; \lambda)$; etc.

$$E(x; \lambda) \Rightarrow e(x, y; \lambda) = E(x; \lambda) + \alpha(x) \delta H_{INT}(x, y) + h_E(x; \lambda)$$

set $\{h(x; \lambda); \int dx h(x; \lambda) \rho^{eq}(x; \lambda) = 0\}$
null-space \rightarrow fix!

T. & H. PRE 94 (2016)

$$\langle e(x, y; \lambda) \rangle_{S_{tot}^{eq}} \stackrel{D}{=} \langle E(x; \lambda) \rangle_{S_S^{eq} = \rho_B} = U_S$$

but $\langle e^n(x, y; \lambda) \rangle_{S_{tot}^{eq}} \neq \langle E^n(x; \lambda) \rangle$; $n > 1$

$$\int dx dy \alpha(x) \left\{ H_{INT} \frac{\rho_{tot}^{eq}(x, y)}{\rho_S^{eq}(x)} \cdot \rho^0(x) - \langle H_{INT}(x, y) | x \rangle \frac{\rho_{tot}^{eq}(x, y)}{\rho_S^{eq}(x)} \rho^0(x) \right\}$$

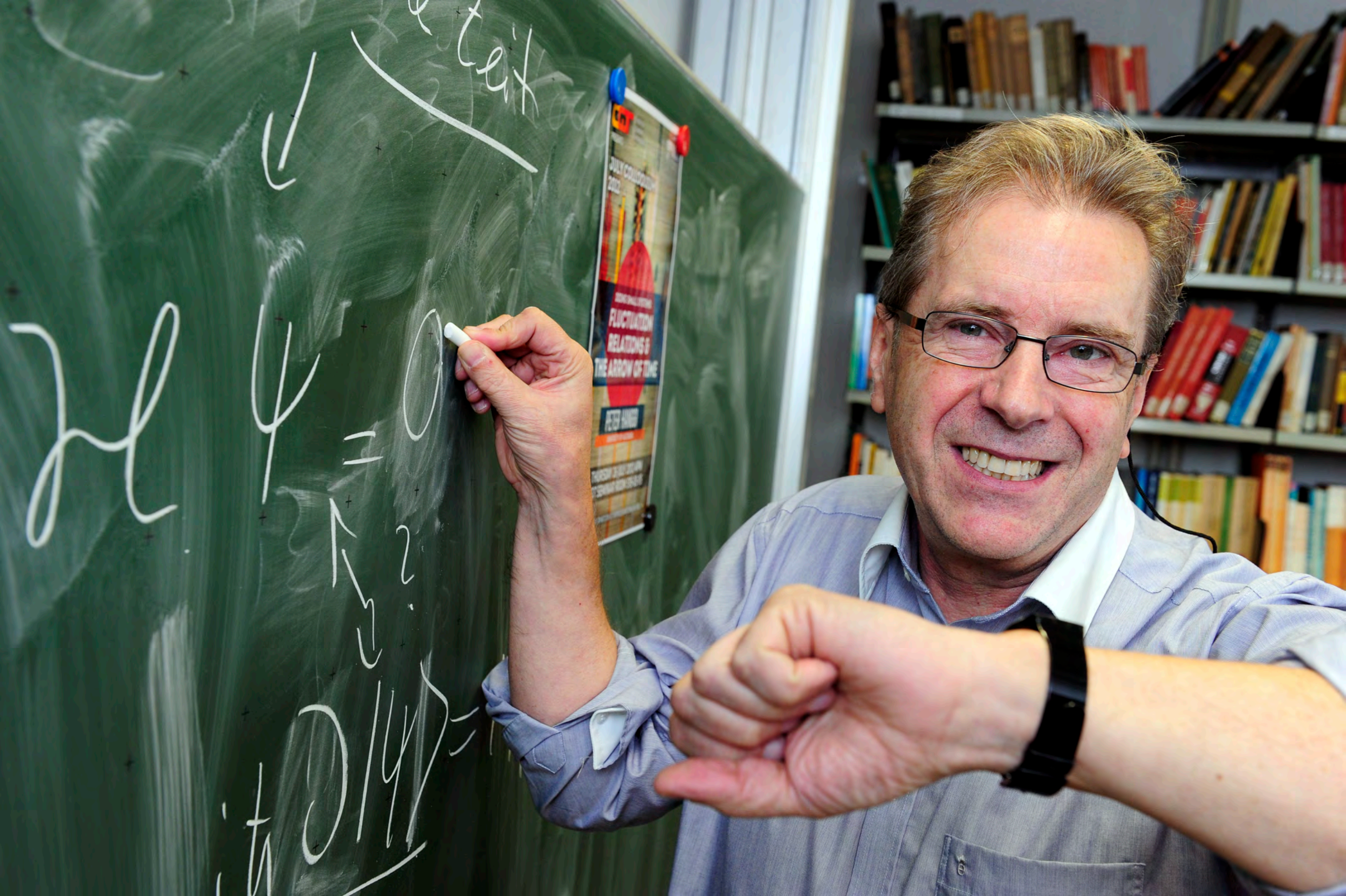
$$= \int dx \alpha(x) \rho^0(x) \left\{ \underbrace{\langle H_{INT}(x, y) | x \rangle - \langle H_{INT}(x, y) | x \rangle \cdot 1}_{0} \right\} = 0$$

PHYSICAL REVIEW A **69**, 052109 (2004)

Is the dynamics of open quantum systems always linear?

Karen M. Fonseca Romero,* Peter Talkner, and Peter Hänggi
Institut für Physik, Universität Augsburg, Universitätsstrasse 1, D 86315 Augsburg, Germany
(Received 1 December 2003; published 17 May 2004)

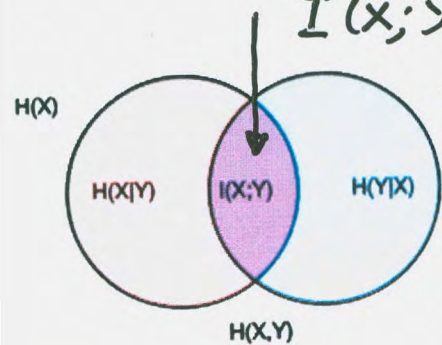
We study the influence of the preparation of an open quantum system on its reduced time evolution. In contrast to the frequently considered case of an initial preparation where the total density matrix factorizes into a product of a system density matrix and a bath density matrix the time evolution generally is no longer governed by a linear map nor is this map affine. Put differently, the evolution is truly nonlinear and cannot be cast into the form of a linear map plus a term that is independent of the initial density matrix of the open quantum system. As a consequence, the inhomogeneity that emerges in formally exact generalized master equations is in fact a nonlinear term that vanishes for a factorizing initial state. The general results are elucidated with the example of two interacting spins prepared at thermal equilibrium with one spin subjected to an external field. The second spin represents the environment. The field allows the preparation of mixed density matrices of the first spin that can be represented as a convex combination of two limiting pure states, i.e., the preparable reduced density matrices make up a convex set. Moreover, the map from these reduced density matrices onto the corresponding density matrices of the total system is affine only for vanishing coupling between the spins. In general, the set of the accessible total density matrices is nonconvex.



JULY COLLECTION 2012
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FLUCTUATION RELATIONS & THE ARROW OF TIME
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Conditional Entropy

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$$H(X) = H(X|Y) + I(X; Y)$$

$$H(Y) = H(Y|X) + I(X; Y)$$

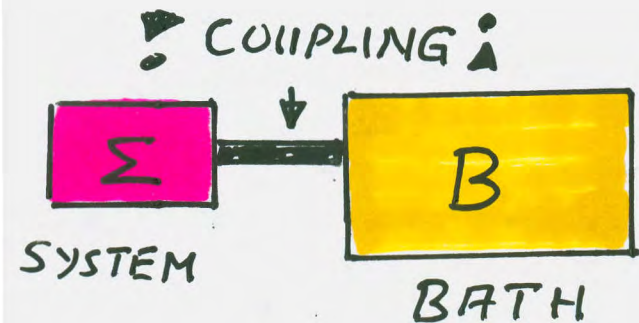
$$H(Y|X) = -\sum_{x,y} p(x,y) \ln p(x,y)$$

$$= -\left(-\sum_x p(x) \ln p(x)\right)$$

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

Quantum Conditional Entropy

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



$$S_\Sigma = S_{vN}(\rho_{\Sigma \times B}^{can}) - S_{vN}(\rho_B^{can})$$

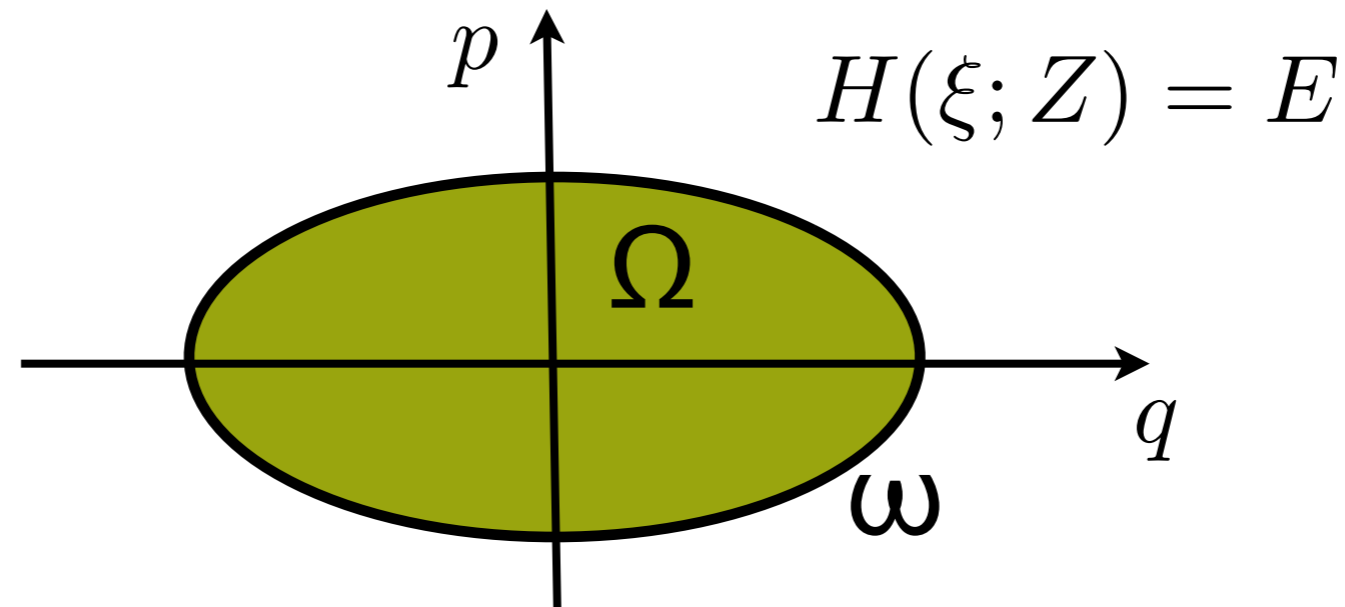
can. thermod. entropy

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$$\stackrel{?!}{=} S_{vN}(\rho_{\Sigma \times B}^{can}) - S_{vN}(\rho_B = \text{Tr}_\Sigma \rho_{\Sigma \times B}^{can})$$

$\uparrow \neq \rho_B^{can}$

Microcanonical thermostatics



D-Operator

DoS

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

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

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

IntDoS

Thermodynamic Entropy ?

$$S_B(E) = \ln(\epsilon \omega)$$

Boltzmann (?)

vs.

$$S_G(E) = \ln \Omega$$

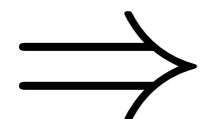
Gibbs (1902), Hertz (1910)

Second law

Gibbs

$$S_G(E) = \ln \Omega$$

$$\begin{aligned}
 & \Omega(E_A + E_B) \\
 &= \int_0^{E_A + E_B} dE' \Omega_A(E') \omega_B(E_A + E_B - E') \\
 &= \int_0^{E_A + E_B} dE' \int_0^{E'} dE'' \omega_A(E'') \omega_B(E_A + E_B - E') \\
 &\geq \int_{E_A}^{E_A + E_B} dE' \int_0^{E_A} dE'' \omega_A(E'') \omega_B(E_A + E_B - E') \\
 &= \int_0^{E_A} dE'' \omega_A(E'') \int_0^{E_B} dE''' \omega_B(E''') \\
 &= \Omega_A(E_A) \Omega_B(E_B).
 \end{aligned}$$



$$S_{G_{AB}}(E_A + E_B) \geq S_{G_A}(E_A) + S_{G_B}(E_B)$$



Second law

Boltzmann

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

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

$$\neq \epsilon^2 \omega_{\mathcal{A}}(E_{\mathcal{A}}) \omega_{\mathcal{B}}(E_{\mathcal{B}})$$

