Entropy, Energy, and Temperature in Small Systems: Impact of a Relative Energy Window on Microcanonical Statistical Mechanics

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Challenges in defining entropy in small systems

Microcanonical (NVE) ensemble in statistical mechanics:[1] less investigated but important

An intense debate in microcanonical statistical mechanics:
What $\boldsymbol{w}$ do we choose in $S = -\sum_i p_i \ln p_i = k_B \ln \boldsymbol{w}$?[2-7]

Gibbs volume entropy
$$S = k_B \ln \Omega$$

Boltzmann surface entropy
$$S = k_B \ln \Big(\underbrace{\frac{\partial \Omega}{\partial E}\epsilon}_{\omega}\Big)$$

Isn't energy fixed to a specified value *E* for an isolated system, and one only looks at degeneracies?

Pathria: "almost every system has some contact with its surroundings, however little it may be; as a result, its energy cannot be defined sharply"

[1]**Govind Rajan**. *J. Chem. Educ.* **2024**, 101, 2448
[2]Gibbs, J. W. Charles Scribner's Sons, NY, **1902** | [3]Hertz, P. *Ann. Phys. (Leipzig)* **1910**, 338, 225 | [4]Pearson et al. *Phys. Rev. A* **1985**, 3030
[5]Dunkel and Hilbert. *Nat. Phys.* **2014**, 10, 67 | [6]Frenkel and Warren. *Am. J. Phys.* **2015**, 83, 163 | [7]Corti et al. *J. Phys. Chem. B* **2023**, 127, 3431

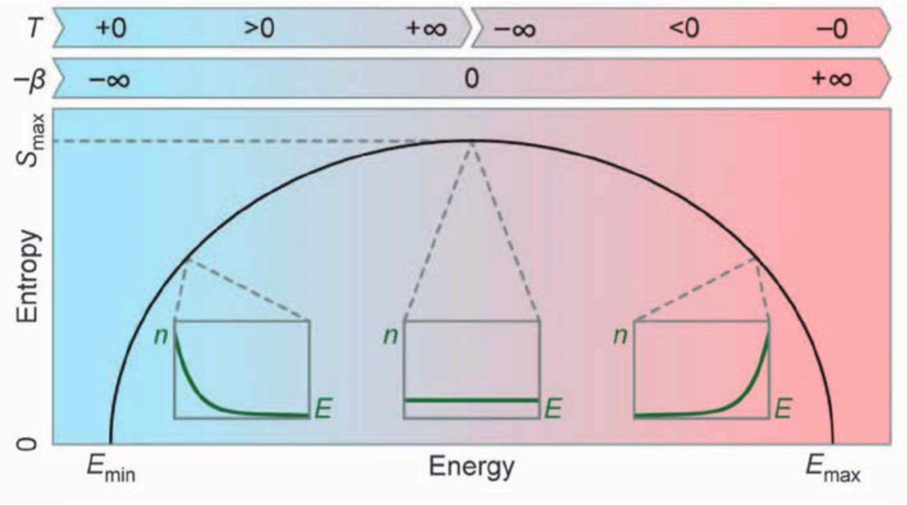
Main point of contention – possibility of negative absolute temperatures

- $T < 0$ K possible in systems with bounded energy as higher energies involve more particles occupying highest-energy level, thus reducing entropy ($\Delta S < 0$) with increase in energy ($\Delta E > 0$)
    - Nuclear spin systems
    - Lasers

  } **Population inversion**

- Previous measurements based, e.g., on
    - $T = \Delta E/\Delta S$ with ΔS calculated from measured loss of nuclear polarization (*Science* **1994**, *265*, 1821)
    - Band imaging of kinetic energy fit to Bose-Einstein distribution (*Science* **2013**, *339*, 52)

- Negative absolute temperatures hotter than positive infinity kelvin – temperature scale is discontinuous, but "hotness" $-\beta = -\frac{1}{k_B T}$ is continuous



Issues plaguing Gibbs and Boltzmann entropy

- Gibbs entropy entirely disallows negative absolute temperatures, in disagreement with experiments [Frenkel and Warren. *Am. J. Phys.* **2015**]

- Boltzmann entropy predicts unphysical negative/infinite absolute temperatures for small systems with unbounded energy spectrum [Dunkel and Hilbert. *Nat. Phys.* **2014**]
  - 1D/2D ideal gas of a single particle
  - Single quantum harmonic oscillator
  - Particle in a 1D box

Relative-energy-constrained Boltzmann surface entropy

$$S = k_B \ln\left(\underbrace{\frac{\partial\Omega}{\partial E}\epsilon_r E}_{\omega_r}\right)$$

Justified by the Heisenberg energy-time uncertainty principle and an eigenstate thermalization time inversely proportional to system energy

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Predictions for an ideal gas and a particle in a box

At high temperatures/energies, the energy states form a continuum

$$\omega_r = \frac{\partial \Omega}{\partial E} \epsilon_r E \qquad S_{B_r} = k_B \ln \omega_r \qquad T_{B_r} = \frac{\partial E}{\partial S_{B_r}}$$

At low temperatures/energies, the discreteness of states is apparent

$$\omega_r = \frac{\Delta \Omega}{\Delta E} \epsilon_r E \qquad T_{B_r} = \frac{\Delta E}{\Delta S_{B_r}}$$

Entropy → / System ↓	Degeneracy	Gibbs	Boltzmann	Proposed	Canonical
3D ideal gas (high T)	not defined	$E = \frac{3N}{2} k_B T_G$	$E = \left(\frac{3N}{2} - 1\right) k_B T_B$	$E = \frac{3N}{2} k_B T_{B_r}$	$E = \frac{3N}{2} k_B T_C$
Particle in a 1D box (high T)	$T_D \to \infty$	$E = \frac{k_B T_G}{2}$	$E = -\frac{k_B T_B}{2}$	$E = \frac{k_B T_{B_r}}{2}$	$E = \frac{k_B T_C}{2}$

Boltzmann/degeneracy entropy seem to fail for these two systems

The new definition agrees well with canonical predictions, without being forced to

But Gibbs' definition seems to agree too?

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Examining a quantum harmonic oscillator

Unbounded energy spectrum

$$E_n = h\nu\left(n + \frac{1}{2}\right)$$

Total number of states

$$\Omega = 1 + n = \frac{E}{h\nu} + \frac{1}{2}$$

Gibbs entropy misses zero-point energy

$$\frac{E - E_0}{h\nu} = \frac{3 - \exp\left(\frac{h\nu}{k_B T_G}\right)}{2\exp\left(\frac{h\nu}{k_B T_G}\right) - 2}$$

Relative-energy-constrained
Boltzmann entropy correct $\forall\, T \in [0, \infty)$

$$\frac{E - E_0}{h\nu} = \frac{1}{\exp\left(\frac{h\nu}{k_B T_{B_r}}\right) - 1}$$

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Two-level system with negative temperatures

Bounded energy spectrum

$$E = N_1 E_1; \quad E_{\max} = N E_1$$

Proposed partition function

$$\omega_r = \frac{\Delta\Omega}{\Delta E}\epsilon_r E = \frac{N!}{(N_0 - 1)!\,(N_1 + 1)!}\frac{\epsilon_r E}{E_1}$$

Density of states

$$\Omega = \sum_{N_0'=1}^{N_1} \frac{N!}{N_0'!\,N_1'!}$$

Gibbs entropy misses negative temperatures; Boltzmann entropy close to degeneracy

$$T_B = \frac{\Delta E}{\Delta S_B} = \frac{E_1}{k_B \ln\left(\frac{N_0 - 1}{N_1 + 2}\right)}$$

Proposed entropy again agrees with canonical predictions

$$T_{B_r} = \frac{\Delta E}{\Delta S_{B_r}} = \frac{E_1}{k_B \ln\left(\frac{(N_1 + 1)(N_0 - 1)}{N_1(N_1 + 2)}\right)}$$

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Is there precedent for a relative-energy window?

- **An energy tolerance that makes the microcanonical and canonical (C) ensembles agree:**
  - Proposed by Gurarie (*Am. J. Phys.* **2007**, *75*, 747)
  - Used recently by Burke and Haque (*Phys. Rev. E* **2023**, *107*, 034125)

$$\epsilon = \sqrt{2\pi k_B T_C^2 C_C} \quad \textbf{versus} \quad \epsilon = \epsilon_r E$$

- **Works for an ideal gas, but gives incorrect results for a harmonic oscillator**

$$T = \frac{h\nu}{S(E + h\nu - E_0) - S(E - E_0)} = \frac{h\nu}{k_B \ln\left(\sqrt{\frac{\frac{h\nu}{E + h\nu - E_0} + 1}{\frac{h\nu}{E - E_0} + 1}}\left(\frac{E + h\nu - E_0}{E - E_0}\right)\right)}$$

versus

$$T = \frac{h\nu}{k_B \ln\left(\frac{E - E_0 + h\nu}{E - E_0}\right)}$$

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Conclusions

$$\sigma_E \Delta t \geq \frac{\hbar}{2}$$

$$\Delta t \sim \frac{h}{E}$$

$$\Rightarrow \quad \sigma_E \sim E$$

(1) Entropy definition for isolated systems considering a relative energy window

(2) Motivated by Heisenberg uncertainty principle and a thermalization time inversely proportional to energy

(3) Preserves zero-point energy of a quantum harmonic oscillator and *T* > 0 K for unbounded energy systems

(4) Predicts *T* < 0 K when appropriate; closest to canonical ensemble

Thank you for listening

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