Beyond Popular Science

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https://www.openbookpublishers.com

ISBN Paperback:	978-1-80511-877-0
ISBN Hardback:	978-1-80511-878-7
ISBN Digital (PDF):	978-1-80511-879-4
ISBN HTML:	978-1-80511-881-7
ISBN Digital ebook (epub):	978-1-80511-880-0
DOI:	10.11647/OBP.0526

Cover image by Enny Silver and David H. Silver
Cover design by Jeevanjot Kaur Nagpal

You’re So Hot, You Cool Me Down

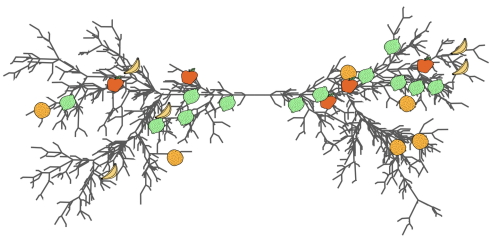
Top (Maximum Entropy – Overcrowded Room): A metaphor for a negative temperature system. The room is so disordered—crammed with objects, decor, and chaos—that any change would make it more ordered. This represents a population-inverted state: energy is at its maximum, and the system is beyond the entropy peak where $\beta = 0$. Thermodynamically, such states must have negative temperature.

Middle (Positive Temperature – Typical Disorder): A moderately cluttered room. It reflects a normal positive temperature system: there's room for more disorder, and adding energy generally increases entropy. This is the typical regime described by classical statistical mechanics.

Bottom (Low Temperature – Ordered State): A clean, sparse room. This is a low-entropy state where most particles (or objects) are in low-energy configurations. Adding energy would increase disorder. The system is clearly in the conventional positive-temperature regime, but near the low end.

You're So Hot, You Cool Me Down

Temperature measures how entropy changes with energy (∂S/∂E), not merely kinetic activity. While unbounded systems such as ideal gases can only reach positive temperatures, quantum systems with finite energy spectra reveal different dynamics. When energy addition increases disorder, temperature is positive; when maximum entropy is reached, temperature becomes infinite; further energy addition creates more ordered states with negative temperatures. These negative temperature states are not colder than absolute zero but as hot as infinity—they transfer energy to any positive-temperature system when brought into contact.



Temperature Definition ∘ Heat Flow Direction ∘ Carnot Universal Scale ∘ Kinetic Theory ∘ Statistical Mechanics ∘ Negative Temperature ∘ Population Inversion ∘ Bounded Energy Systems ∘ Boltzmann vs Gibbs ∘ Dunkel-Hilbert Controversy ∘ Coldness Parameter β

"Give a man a fire and he's warm for a day,
but set fire to him and he's warm for the rest of his life."
— Solid Jackson, Year of the Justifiably Defensive Lobster, 1988 UC

"Winter is coming."
— Eddard Stark, 298 AC

You're So Hot, You Cool Me Down

The concept of temperature originated long before its formal scientific definition. Early thermometry in the 16th and 17th centuries relied on devices such as Galileo's thermoscope, which measured qualitative warmth but lacked a standardised scale. By the early eighteenth century, Daniel Gabriel Fahrenheit introduced a reliable mercury thermometer and a temperature scale, followed by Anders Celsius and William Thomson (Lord Kelvin), whose absolute scale based on thermodynamic principles became the foundation for modern temperature measurement.

The theoretical basis for temperature matured alongside the formulation of classical thermodynamics. The zeroth law of thermodynamics, though articulated last, established the foundational equivalence relation that permits temperature to be meaningfully assigned: if system A is in thermal equilibrium with system B, and system B with system C, then A and C must also be in equilibrium. This abstracted thermal equilibrium from specific substances or instruments, enabling the development of general thermometric devices.

Simultaneously, empirical laws such as those of Boyle (1662), Charles (1787), and Gay-Lussac (1802) revealed regularities in the behaviour of gases, hinting at underlying statistical dynamics. These culminated in the ideal gas law, $PV = nRT$, linking temperature with pressure and volume in a measurable way. However, it was not until the advent of statistical mechanics in the nineteenth century—particularly through the work of Ludwig Boltzmann (1844–1906) and James Clerk Maxwell (1831–1879)—that temperature gained a microscopic interpretation. Boltzmann's definition of entropy and the expression $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$ provided a bridge between macroscopic observations and the probabilistic behaviour of particles.

This statistical framework laid the foundation for interpreting unusual thermodynamic regimes. While classical thermodynamics assumes that entropy increases with energy, leading to strictly positive temperatures, the statistical definition permits a broader spectrum. In systems with bounded energy, entropy can decrease with increasing energy, enabling the possibility of negative absolute temperatures. Such interpretations remained largely theoretical until mid-twentieth century experiments produced states interpreted as having negative temperature.

Temperature measures how hot or cold something is. Unlike energy, which emerges from a symmetry principle, temperature seems to be defined only through directionality. Noether's theorem tells us that energy (Noether, 1918) is the conserved quantity associated with time-translation invariance—systems that behave the same way now as they will an hour from now conserve energy. Momentum arises from spatial translation invariance. Angular momentum from rotational invariance. Each conservation law reflects an underlying symmetry in the physical laws.

Temperature is defined operationally. Place two systems in contact, and energy will pass from the one with higher temperature to the one with lower, until a balance is reached.

 https://doi.org/10.11647/OBP.0526.28

Temperature tells us the direction of heat flow without first specifying what temperature is. We cannot derive it from symmetries.

This directional character distinguishes temperature from other conserved quantities. Energy exists in a single isolated system. Temperature exists only through interaction, defined from the balance between energy and entropy when systems exchange heat. A system alone has energy; it acquires temperature only in relation to possible exchanges with other systems.

Early thermometry sought operational definitions through material properties. Galileo's thermoscope (1593) tracked air expansion in a glass bulb—temperature changes moved water levels, but atmospheric pressure variations corrupted readings. Fahrenheit (1724) achieved reproducibility through mercury expansion and three fixed points: a frigorific mixture of ice, water, and ammonium chloride (0°F), water-ice equilibrium (32°F), and human body temperature (96°F; the modern accepted value on his scale is 98.6°F). His mercury-in-glass design minimised pressure effects while his fixed points enabled calibration. Celsius (1742) simplified to two points—water's freezing and boiling at standard pressure—originally inverted with 100° for freezing, 0° for boiling. These scales quantified temperature through material expansion coefficients, each substance yielding slightly different readings. Agreement required careful calibration against shared fixed points.

The concept developed through distinct theoretical frameworks that initially seemed unrelated. Thermometry defined it operationally through thermal expansion—mercury rises in glass tubes, metals expand when heated. Classical thermodynamics formalised it through the Carnot cycle (Carnot, 1824): the efficiency of reversible heat engines operating between two reservoirs depends only on their temperature ratio, providing a universal scale independent of working substance. This universality indicates temperature's nature—not a property of matter but a parameter governing energy distribution.

Carnot's insight preceded atomic theory yet captured a fundamental phenomenon: temperature mediates between mechanical work and heat flow. In his ideal engine, complete conversion of heat to work is impossible not because of friction or engineering limits, but because temperature imposes constraints on energy quality. Hot reservoirs contain high-quality energy; cold reservoirs contain degraded energy. Temperature quantifies this degradation.

Lord Kelvin (1848) recognised that Carnot's efficiency formula $\eta = 1 - T_c/T_h$ contained the seeds of an absolute scale. If engine efficiency depends only on temperature ratios, not working substances, then temperature ratios have universal meaning. Kelvin defined his scale through the work extractable from heat: temperature ratios correspond to ratios of heat exchanged in reversible engines. This freed temperature from material properties—no mercury expansion, no fixed points tied to water. The Kelvin scale's zero represents the temperature at which no work can be extracted from heat, where a Carnot engine's efficiency reaches zero. Temperature became a measure of energy availability, not material response.

The mechanical interpretation of heat predated thermodynamics. Daniel Bernoulli (1738) proposed that gas pressure arises from particle impacts against container walls. His

model—elastic spheres in ceaseless motion—correctly predicted that pressure times volume should be proportional to the kinetic energy of particles. This anticipated the ideal gas law by a century without the concept of temperature as average kinetic energy. Bernoulli wrote of 'increasing the intensity of motion' when heating gases but couldn't quantify the relationship. John Herapath (1820) and John Waterston (1845) independently derived $pV \propto T$ from particle mechanics. Scientific journals ignored or rejected their work. Clausius (1857) finally connected these mechanical models to thermodynamics, showing that Bernoulli's 'intensity of motion' was precisely what thermometers measured.

Kinetic theory offered a microscopic interpretation: temperature measures the average translational kinetic energy of particles, $\langle E_{\text{kin}} \rangle = \frac{3}{2} k_B T$ for ideal gases (where k_B is the Boltzmann constant with units of energy per temperature). However, temperature is not simply motion—a supersonic jet of cold gas has enormous kinetic energy yet low temperature. The random component is what matters, the deviation from collective flow, the microscopic dance beneath the macroscopic averages.

In statistical mechanics, Boltzmann defined entropy as a count of microstates (Boltzmann, 1877), leading to the relationship $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$ that defines temperature as the exchange rate between energy and entropy. When energy is added to a system, the rate at which new configurations become accessible defines temperature. Systems are hot when energy buys little additional disorder, cold when energy opens larger territories of possibility.

These definitions converge for ordinary matter but diverge in extreme conditions. The thermodynamic and statistical definitions always agree when both apply. The kinetic interpretation works only for systems with translational degrees of freedom (where energy can be represented as movement); it fails for photon gases, spin systems, or any collection where energy takes non-kinetic forms. The statistical definition remains universal, applying wherever entropy and energy are meaningful—from black holes to quantum fields.

Temperature's statistical nature fails at the boundaries of applicability. A single molecule has no temperature—temperature requires an ensemble where probability distributions make sense. We routinely discuss the temperature of systems containing mere dozens of atoms. The transition to a thermodynamically valid description occurs where statistical averages are not overwhelmed by fluctuations. For nanoscale devices operating at the edge of thermodynamic validity, the transition point where fluctuations overwhelm averages becomes critical.

Different phenomena occur in curved spacetime. The vacuum has no temperature in flat spacetime; accelerating observers perceive it as thermal—the Unruh effect (Unruh, 1976). An observer accelerating at one Earth gravity perceives empty space glowing at 10^{-20} Kelvin. Temperature arises from quantum field correlations across the acceleration horizon, not from matter. Motion through spacetime generates heat from nothing (see Chapter 47).

Black holes embody a temperature paradox. Classically, nothing escapes a black hole, implying zero temperature. Quantum mechanics near the event horizon creates particle pairs, one falling inward, one escaping as Hawking radiation (Hawking, 1974). The hole glows with temperature $T = \hbar c^3/(8\pi G M k_B)$—inversely proportional to mass. Stellar-mass black holes radiate at nanokelvins; microscopic holes would explode in blazing heat.

Temperature results from pure geometry, spacetime curvature creating thermal radiation without matter.

Systems with unbounded energy spectra can reach arbitrarily high temperatures. Ideal gases exemplify this: particle energies face no upper limit beyond total energy input. In systems with a maximum possible energy, the situation changes. Consider a lattice of spins with only two energy states per site. As more energy is added, spins flip to the excited state. When half the spins are excited, entropy is maximised. Adding further energy forces the system into more constrained configurations—more spins aligned against the field—resulting in fewer configurations and thus lower entropy. The derivative $\partial S/\partial E$ becomes negative, yielding negative temperature.

The possibility of negative temperature depends critically on the statistical definition of entropy. Dunkel and Hilbert (2014) challenged sixty years of accepted wisdom about negative temperatures. The controversy centres on two competing entropy definitions: the Boltzmann entropy $S_B = k_B \ln(\Omega_B)$ where $\Omega_B = \epsilon\omega(E)$ counts states in an energy window ϵ around E with density of states $\omega(E)$, and the Gibbs entropy $S_G = k_B \ln(\Omega)$ based on the integrated density of states $\Omega(E) = \int_0^E \omega(E')dE'$. Both yield temperature through $1/T = \partial S/\partial E$, but with different results.

The Boltzmann approach gives $T_B = (k_B\omega'/\omega)^{-1}$. When the density of states peaks and then decreases—as happens in bounded systems where high-energy configurations become constrained—ω' becomes negative, yielding negative temperature. The Gibbs approach gives $T_G = (k_B\omega/\Omega)^{-1}$. Since Ω integrates the density of states, it increases monotonically when ω decreases. The Gibbs temperature remains positive throughout.

Dunkel and Hilbert argued that only the Gibbs entropy satisfies thermodynamic consistency. A Maxwell relation—derived from the equality of mixed partial derivatives of the fundamental relation $dE = TdS - PdV$—requires that pressure computed two different ways must agree: thermodynamically through $P = T(\partial S/\partial V)_E$ and mechanically through $P = -(\partial E/\partial V)_S$. This consistency test fails for Boltzmann entropy. In a quantum particle in a box, Boltzmann predicts negative temperature where Gibbs remains positive, and the two pressure calculations disagree. The Boltzmann entropy also violates equipartition in classical systems and yields incorrect heat capacities for quantum oscillators.

Experiments measuring 'negative temperature' actually measure something different. When Purcell and Pound achieved population inversion in nuclear spins (1951), or when Braun et al. created similar states in ultracold atoms (2013), they extracted temperature by fitting exponential distributions to occupation probabilities. This procedure yields the Boltzmann temperature T_B, not the thermodynamically consistent Gibbs temperature T_G. Near entropy maxima in bounded spectra, the fitted slope can diverge and change sign while other definitions remain finite.

Consider nuclear spins in a magnetic field. A population where most spins occupy the higher energy level represents population inversion. The Boltzmann formalism assigns negative temperature to this state, suggesting it is 'hotter than hot'—energy flows from it to any positive-temperature system. The Gibbs formalism assigns high but positive temperature, recognising that adding energy to an already inverted population decreases

the number of accessible configurations. Both formalisms agree on energy flow direction, but only Gibbs maintains mathematical consistency.

In systems with bounded spectra, entropy $S(E)$ rises from the ground state, peaks at some energy E^*, then falls as energy approaches its maximum. The derivative $(\partial S/\partial E)_{N,V}$ changes sign at E^*, causing $T = 1/[k_B(\partial S/\partial E)]$ to jump discontinuously from $+\infty$ to $-\infty$. The inverse temperature $\beta \equiv 1/(k_B T) = (\partial S/\partial E)_{N,V}$ avoids this discontinuity, varying smoothly from $+\infty \to 0 \to -\infty$ as energy increases. The canonical probability $p \propto e^{-\beta\epsilon}$ works uniformly: $\beta > 0$ favours low energies, $\beta = 0$ gives uniform distribution, $\beta < 0$ favours high energies. Physical observables emerge as derivatives with respect to β, not T, making β the natural variable.

Everyday macroscopic systems have unbounded spectra, so β remains positive. Finite-state quantum systems—spin ensembles in strong fields, nuclear spins in crystals—explore the full range. What textbooks call 'negative temperature' is better understood as negative β: a regime where adding energy decreases entropy as the system approaches its highest-energy bound.

Proponents of negative temperature argue these states enable Carnot engines with efficiency exceeding unity—extracting more work than the heat absorbed. Insert negative Boltzmann temperature into the Carnot efficiency $\eta = 1 - T_c/T_h$ and efficiencies above 100% seem possible. Such calculations violate thermodynamic consistency. The Gibbs temperature, always positive, forbids perpetual motion of the second kind. Moreover, creating and destroying population inversion requires non-adiabatic work that standard efficiency formulas do not account for.

Temperature functions as a label for thermal equilibrium, a slope in entropy space, and the control parameter for probability distributions over states. These roles converge in ordinary matter but diverge in engineered quantum systems. The Boltzmann entropy, despite its prevalence in textbooks, fails consistency tests. The Gibbs entropy respects thermodynamic principles at the cost of forbidding negative absolute temperature. Whether we accept systems 'hotter than infinity' or reject such phrasing depends on which of temperature's definitions we prefer. The universe, indifferent to our debates, continues to maximise entropy by whatever name we call it.

Statistical Mechanics of Negative Absolute Temperature

The Entropy-Temperature Connection

Statistical mechanics defines temperature through the relationship between entropy S and energy E: $1/T = \partial S/\partial E$. One common choice is the Gibbs entropy $S_G = k_B \ln \Omega(E)$ with $\Omega(E)$ the integrated density of states. In unbounded systems, Ω always increases with E, yielding $T > 0$. In systems with maximum energy E_{max}, the density of states can decrease near E_{max}. Under a Boltzmann definition that uses the local density of states $\omega(E)$, $\partial S/\partial E$ can become negative, corresponding to negative T in that convention.

Two-Level System: A Clear Example

Consider N spins, each with energy 0 (down) or ϵ (up). With n spins up, the total energy is $E = n\epsilon$ and the number of configurations is $\Omega(n) = \binom{N}{n}$. The entropy $S = k_B \ln \Omega$ peaks at $n = N/2$ (half spins up). For $n < N/2$, adding energy increases entropy; for $n > N/2$, adding energy decreases entropy. In a two-level model one can define an effective inverse temperature via the slope:

$$\beta \equiv \frac{1}{k_B T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}.$$

At $n = N/2$: $\beta = 0$. Population inversion ($n > N/2$) corresponds to $\beta < 0$ under the Boltzmann convention.

Energy Flow and 'Hotter Than Hot'

When two systems exchange energy, entropy maximisation determines the flow direction. For energy δQ flowing from A to B:

$$\Delta S_{\text{tot}} = \delta Q \left(\frac{1}{T_B} - \frac{1}{T_A}\right).$$

For spontaneous flow ($\Delta S_{\text{tot}} > 0$), we need $1/T_B > 1/T_A$. In the β parameterisation, the ordering is continuous:

$$0^+ < \ldots < +\infty \equiv -\infty < \ldots < 0^-.$$

Thus negative temperatures are 'hotter' than all positive temperatures—energy flows from any negative-T system to any positive-T system.

The Gibbs vs Boltzmann Debate

Dunkel and Hilbert (2014) highlighted a controversy about negative temperature by distinguishing two entropy definitions:

- Boltzmann: $S_B = k_B \ln[\omega(E)]$ using density of states $\omega = d\Omega/dE$.
- Gibbs: $S_G = k_B \ln[\Omega(E)]$ using integrated density of states.

For bounded systems where ω peaks and decreases, Boltzmann can give $T_B < 0$ while Gibbs gives $T_G > 0$ always. They argue only Gibbs entropy satisfies certain thermodynamic consistency conditions such as pressure relations. The precise mapping between experimentally inferred parameters and T_G depends on ensemble and constraints, and remains debated.

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