Positive thinking about negative temperatures
or,
negative absolute temperatures: facts and myths

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Outline

- Some experiments
- Some thermodynamics
- Some statistical mechanics
- Some myths

Does 'Negative absolute temperature' make any sense?

NO

- everybody knows nothing can be colder than absolute zero
- various authorities assert $T > 0$ (as an axiom)
- various formulations of Second Law uncomfortable with $T < 0$
- Ideal gas thermometer $T = pV/Nk$. Gas pressure can't be negative, so neither can T
- The Hamiltonian is normally unbounded above, so that

$$Z = \sum_i \mathrm{e}^{-E_i/kT}$$

normally diverges if $T \leq 0$

YES

- BUT ... suppose energy is bounded above (e.g. Ising model)
- then the sum for Z makes sense even for negative T.
- Example: for a nuclear spin μ in a magnetic field $\mathbf{h}$

$$Z = \mathrm{e}^{\mu\mathbf{h}/kT} + \mathrm{e}^{-\mu\mathbf{h}/kT} = 2\cosh(\mu|\mathbf{h}|/kT)$$

‘Canonical’ probabilities for a single spin-$\frac{1}{2}$ nucleus

- Suppose magnetic moment of nucleus has magnitude μ.
- Directed magnetic moment (plus sign means “parallel to **h**”) is
  either $+\mu$ with energy $-\mu|\mathbf{h}|$ and probability $\propto \mathrm{e}^{\mu|\mathbf{h}|/kT}$
  or $-\mu$ with energy $+\mu|\mathbf{h}|$ and probability $\propto \mathrm{e}^{-\mu|\mathbf{h}|/kT}$
- For positive T the lower-energy state is the more probable; for negative T the higher-energy state is the more probable: negative T is hotter than positive, not colder.
- Expectation magnetic moment of an N-spin system is

$$N\frac{\mu \mathrm{e}^{\mu|\mathbf{h}|/kT} - \mu \mathrm{e}^{-\mu|\mathbf{h}|/kT}}{\mathrm{e}^{\mu|\mathbf{h}|/kT} + \mathrm{e}^{-\mu|\mathbf{h}|/kT}} = N\mu \tanh \frac{\mu|\mathbf{h}|}{kT} \approx \frac{N\mu^2}{kT}|\mathbf{h}|$$

  along direction of **h**; i.e., **M** is parallel to **h** at positive temperatures, but antiparallel at negative temps.
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$$\text{Curie's law } \mathbf{M} \approx \frac{\mathrm{const}}{kT}\mathbf{h}$$

Some experiments

- The Purcell-Pound experiment: first creation of a ‘negative-temperature’ state (1951)
- A nuclear spin system, normally antiferomagnetic, showing ferromagnetic ordering in the ‘negative temperature’ state (1992)
- A lattice system showing Bose-Einstein condensation into the highest single-particle energy level (2013)

Purcell-Pound* experiment on a paramagnetic crystal (LiF)

Think of the crystal as a system of nuclear spins. At sufficiently low temperatures its relaxation time for spin-lattice interactions is of order 10 seconds, but for spin-spin interactions is of order 10 millisec

- **1**: bring to equilibrium with the lattice at a low temperature in a strong magnetic field. Time taken $\gg 10$ sec
- **2**: Remove the strong field (this cools the spin system to an even lower temperature), apply a small oscillating field **h** of period ~ 10 msec. or greater. **M** follows the oscillations and is parallel to **h**
- **3**: reverse the magnetic field in a time ($\ll 10\mu$sec) so short that **M** cannot follow
- **4**: Now, in an oscillating applied field **h** (period ~ 10 msec), **M** follows the oscillations but is anti-parallel to **h**
- Curie's law $\mathbf{M} = \frac{\mathrm{const}}{T}\mathbf{h}$ suggests negative T during step **4**

*E. M. Purcell & R. V. Pound, *A nuclear spin system at negative temperatures* Phys. Rev. **81,** 279 (1951)

A nuclear spin system (Ag) showing both antiferromagnetic and ferromagnetic ordering

- Nuclear spins of Ag show antiferromagnetic ordering for $T > 0$ but ferromagnetic for "$T < 0$."
- Magnetic moment is approximately constant for $T_c < T < 0$ with $T_c \approx -2$ nanoKelvin.
- Susceptibility data outside this temperature range fit the Curie-Weiss formula for both signs of T

$$\mathbf{M} \approx \frac{\text{const}}{T - T_c}\mathbf{h} \quad (T < T_c \text{ or } T > 0)$$

- Measuring temperature using $T = \Delta Q/\Delta S$: When $T > 0$, supplying heat increases S and decreases $|\mathbf{M}|$. But when $T < 0$ the system *loses* heat by radiation at the nuclear Larmor frequency, increasing S and decreasing $|\mathbf{M}|$.

P.J. Hakonen, K.K. Nummila, R.T. Vuorinen & O.V. Lounasmaa, *Observation of nuclear ferromagnetic ordering in silver at negative nanokelvin temperatures,* Phys. Rev. Lett. **68**, 365-368 (1992)

B.-E. condensation into *highest* single-particle energy level

- Bosons (^{39}K atoms) in an optical lattice
- Hamiltonian

  $$\mathcal{H} = -J \sum_{\langle ij \rangle} (a_i^\dagger a_j + a_j^\dagger a_i) + U \sum_i a_i^\dagger a_i (a_i^\dagger a_i - 1) + V_0 \sum_i r_i^2 a_i^\dagger a_i,$$

  with U, V_0 positive, is bounded below but not above; hence Z converges only for $T > 0$
- By cunning experimental techniques, they reversed signs of U and V_0, while preserving the B.E.-condensed quantum state
- The new Hamiltonian is bounded above but not below, so new Z converges only for $T < 0$

S. Braun *et al.*, *Negative absolute temperature for motional degrees of freedom*
Science **339**(6115), 5255 (2013)

Time scales of the nuclear spin system

Energy is

$$\begin{aligned} E &= -\mathbf{M}\cdot\mathbf{h} + W_{ss} + W_{sl} \\ &\approx -\mathbf{M}\cdot\mathbf{h} \end{aligned}$$

Hamiltonian is analogous.

Time scales:

- $\tau_L \sim 10\mu\,\mathrm{sec.}$: time scale for changes in **M** (Larmor precession). If $\delta t \ll \tau_L$ then $\delta\mathbf{M} \approx 0$
- $\tau_{ss} \sim 10\,\mathrm{msec.}$: time scale for spin-spin interaction W_{ss} to bring spin system to internal equilibrium. If $\tau_{ss} \ll \delta t$ then process is quasi-static; thermodynamics applies
- $\tau_{sl} \sim 10\,\mathrm{sec}$: time scale for spin-lattice interaction W_{sl} to bring system to eqm with lattice. If $\delta t \ll \tau_{sl}$ then $\mathbf{h}\cdot d\mathbf{M} \approx 0$

The Purcell-Pound process revisited

Summary of time scales

- $\tau_L \sim 10\mu\,\mathrm{sec.}$: if $\delta t \ll \tau_L$ then $\delta \mathbf{M} \approx 0$
- $\tau_{ss} \sim 10\,\mathrm{msec.}$: if $\tau_{ss} \ll \delta t$ then metastable equilibrium
- $\tau_{sl} \sim 10\,\mathrm{sec}$: if $\delta t \ll \tau_{sl}$ then $\int \mathbf{h} \cdot d\mathbf{M} \approx 0$

- The process:
- 1. Cool the specimen to eqm in strong field $\mathbf{h}$, $\delta t \gg \tau_{sl}$. Value of $\mathbf{M}$ depends on $\mathbf{h}$ and temp. of lattice.
- 2. Reduce $\mathbf{h}$, then oscillate it: $\tau_{ss} \ll \delta t \ll \tau_{sl}$. Metastable equilibrium: if material is isotropic, $\mathbf{M}$ will be parallel to $\mathbf{h}$. Since $\mathbf{h} \cdot d\mathbf{M} \approx 0$, magnitude of $\mathbf{M}$ stays the same. $E = -\mathbf{M} \cdot \mathbf{h}$ remains negative
- 3. Reverse $\mathbf{h}$: $\delta t \ll \tau_L$: $\mathbf{M}$ stays the same. E changes sign
- 4. Oscillate $\mathbf{h}$: $\tau_{ss} \ll \delta t \ll \tau_{sl}$. Direction of $\mathbf{M}$ varies as in step 2; E remains positive

Applying the laws of thermodynamics

Energy is $E = -\mathbf{M} \cdot \mathbf{h} + W \approx -\mathbf{M} \cdot \mathbf{h}$
h is a control variable; **M** is a dynamical variable.

- First Law, neglecting dW

$$\begin{aligned} dE &= \qquad -\mathbf{M} \cdot d\mathbf{h} \qquad\qquad\qquad - \mathbf{h} \cdot d\mathbf{M} \\ &= \text{work done on system} + \text{heat supplied to system} \end{aligned}$$

- analogous to $\qquad -pdV \qquad\qquad + \qquad \delta Q$
- Second Law says $\delta Q = TdS$. Therefore ...

$$\begin{aligned} TdS &= -\mathbf{h} \cdot d\mathbf{M} && (1) \\ &= dE + \mathbf{M} \cdot d\mathbf{h} && (2) \end{aligned}$$

whence

$$\frac{1}{T} = \frac{\partial S(E, \mathbf{h})}{\partial E}$$

Getting more out of the Second Law: the Entropy Principle

Lieb and Yngvason (1998) reformulate the second law of thermodynamics using what they call the Entropy Principle. The relevant part of this principle is:

- $S(X) \leq S(Y)$ *if and only if it is possible to change the [thermodynamic] state from* X *to* Y *by means of an interaction with some device consisting of an auxiliary system and a weight, in such a way that the auxiliary system returns to its original state at the end of the process whereas the weight may have risen or fallen.*

Here, let $X = (\mathbf{M}_0, \mathbf{h}_0)$ and $Y = (\mathbf{M}_0, -\mathbf{h}_0)$. with $\mathbf{h}$ provided by a horseshoe magnet. Reverse $\mathbf{h}$ by rotating the magnet, using pulleys attached to a weight, so fast that $\mathbf{M}$ does not change. Entropy principle says $S(X) \leq S(Y)$. It also says (when applied to the reverse process) $S(Y) \leq S(X)$. It follows that $S(X) = S(Y)$, i.e.

$$S(\mathbf{M}, \mathbf{h}) = S(\mathbf{M}, -\mathbf{h})$$

E H Lieb and J Yngvason *A guide to entropy and the second law of thermodynamics* Notices of the AMS **45** 571-581 (1998)

Entropy principle implies negative temperatures

The entropy principle gave

$$S(\mathbf{M}, \mathbf{h}) = S(\mathbf{M}, -\mathbf{h})$$

Since $E = -\mathbf{h} \cdot \mathbf{M}$ this can be written

$$S(E, \mathbf{h}) = S(-E, -\mathbf{h})$$

Using the definition of temperature, we find

$$\frac{1}{T(E, \mathbf{h})} = \frac{\partial S(E, \mathbf{h})}{\partial E} = -\frac{\partial S(-E, -\mathbf{h})}{\partial E} = -\frac{1}{T(-E, -\mathbf{h})}$$

Thus, a rapid reversal of the applied magnetic field reverses not only the energy but also the temperature.

Statistical mechanics of the nuclear spin system

Hamiltonian is

$$\mathcal{H} = -\mathcal{M} \cdot \mathbf{h} + \mathcal{W} \approx -\mathcal{M} \cdot \mathbf{h}$$

Using a microcanonical ensemble at energy E, the "Gibbs*" (or "Griffiths†"?) entropy can be defined as

$$S_G(E, \mathbf{h}) = k \log \Omega(E, \mathbf{h})$$

where $\Omega(E, \mathbf{h}) = \mathrm{tr}(\mathrm{step}(E + \mathcal{M} \cdot \mathbf{h}))$ is the number of energy levels below E. Taking the differential we get

$$dS_G(E, \mathbf{h}) = (1/T_G)[dE + \langle \mathcal{M} \rangle_{E,\mathbf{h}} \cdot d\mathbf{h}]$$

where $T_G(E, \mathbf{h}) := (\partial S_G / \partial E)^{-1}$ and $\langle \dots \rangle :=$ microcanonical average. Thus S_G (unlike some other entropy definitions) is "thermostatistically consistent*" meaning that it exactly satisfies

$$TdS = dE + \mathbf{M} \cdot d\mathbf{h} \quad \text{with} \quad \mathbf{M} = \langle \mathcal{M} \rangle_{E,\mathbf{h}}$$

*J Dunkel & S Hilbert *Consistent thermostatistics forbids negative absolute temperatures* Nature Physics **10** 67-72 (2014); †R B Griffiths *Microcanonical ensemble in quantum statistical mechanics* J Math Phys **6** 1447 (1965)

The "Gibbs" entropy and negative temperatures

- The "Gibbs" entropy

  $$S_G(E, \mathbf{h}) = k \log \Omega(E, \mathbf{h})$$

  is monotonic non-decreasing in E; therefore the associated temperature $T_G := (\partial S_G(E, \mathbf{h})/\partial E)^{-1}$ cannot be negative. On this basis it has been argued* that negative absolute temperatures should never be used.
- However, one can get around the difficulty by defining the entropy of a nuclear spin system not by $S = S_G$ but by

  $$S(E, \mathbf{h}) \quad := S_G(-|E|, \mathbf{h})$$

  which agrees with the definition $S = S_G$ for negative E but is even in E as required by the entropy principle.

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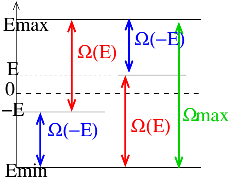
* J Dunkel & S Hilbert *Consistent thermostatistics forbids negative absolute temperatures* Nature Physics **10** 67-72 (2014)

Is the new definition thermostatistically consistent?

The proposed definition is

$$\begin{aligned} S(E,\mathbf{h}) := S_G(-|E|,\mathbf{h}) &= k \log \Omega(E,\mathbf{h}) \quad \text{if} \quad E < 0 \\ \text{but} \quad &= k \log \Omega(-E,\mathbf{h}) \quad \text{if} \quad E > 0 \end{aligned}$$



The energy spectrum is symmetric about $E = 0$, therefore the number of levels below $-E$ equals the number above $+E$ i.e.

$$\Omega(-E,\mathbf{h}) = \Omega_{max} - \Omega(E,\mathbf{h})$$

so that, for $E > 0$,

$$S(E,\mathbf{h}) := S_G(-E,\mathbf{h}) = k \log(\Omega_{max} - \exp(S_G(E,\mathbf{h})/k)) =: f(S_G(E,\mathbf{h}))$$

Yes, the new definition is thermostatistically consistent

To check thermostatistical consistency for $E > 0$:

$$S(E, \mathbf{h}) := S_G(-E, \mathbf{h}) = k \log(\Omega_{max} - \exp(S_G(E, \mathbf{h})/k)) =: f(S_G(E, \mathbf{h}))$$

From this it follows (for $E > 0$) that

$$\begin{aligned} T(E)dS(E) &= \frac{dS(E)}{\partial S(E, \mathbf{h})/\partial E} = \frac{f'(S_G)dS_G(E)}{f'(S_G)\partial S_G(E, \mathbf{h})/\partial E} \\ &= \frac{dS_G(E)}{\partial S_G(E, \mathbf{h})/\partial E} = T_G(E)S_G(E) \end{aligned}$$

Since $S_G(E)$ is already known to be thermostatistically consistent for all E, i.e.

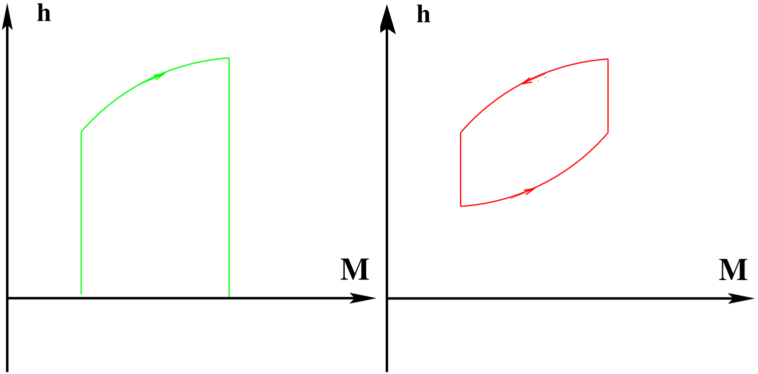
$$T_G dS_G = dE + \langle \mathcal{M} \rangle \cdot d\mathbf{h}$$

it follows that $S(E)$ is also thermostatistically consistent for $E > 0$, and hence for all E

$$TdS = dE + \langle \mathcal{M} \rangle \cdot d\mathbf{h}$$

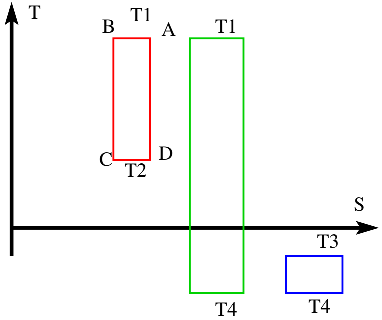
The myth of Carnot efficiencies greater than 100%

Heat input and work output in a cycle



$$\begin{aligned}\text{clockwise cicrcuit: area} &= \int \mathbf{h}\cdot d\mathbf{M} \\ &= -(\text{heat supplied to system}) \\ \text{anticlockwise circuit: area} &= -\oint \mathbf{h}\cdot d\mathbf{M} \\ &= \text{heat input} = \text{work output}\end{aligned}$$

Carnot efficiencies : always ≤ 1



- red cycle: heat in $= T_1 \Delta S$, work done $= (T_1 - T_2)\Delta S$
  efficiency $= \frac{\text{work output}}{\text{heat input}} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} < 1$
- green cycle: heat in $= T_1 \Delta S + |T_4| \Delta S$, work done $= (T_1 - T_4)\Delta S$
  efficiency $= \frac{\text{work output}}{\text{heat input}} = \frac{T_1 - T_4}{T_1 + |T_4|} = 1$
- blue cycle: heat in $= |T_4| \Delta S$, work done $= (T_3 - T_4)\Delta S$
  efficiency $= \frac{\text{work output}}{\text{heat input}} = \frac{T_3 - T_4}{|T_4|} = \frac{|T_4| - |T_3|}{|T_4|} < 1$

Negative temperatures in cosmology?

- “negative temperature states of motional degrees of freedom necessarily possess negative pressure 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”.
- S. Braun *et al.*, *Negative absolute temperature for motional degrees of freedom* Science **339**(6115), 5255 (2013)

Where it all started

- Onsager : "statistical hydrodynamics"* (1949)
  2-D system of vortices in an ideal fluid (C-C Lin)

$$\begin{aligned} k_i dx_i/dt &= \partial H/\partial y_i \\ k_i dy_i/dt &= -\partial H/\partial x_i \\ H &:= -(1/2\pi)\sum k_i k_j \log|x_i - y_j| \end{aligned}$$

$$\Omega(E) := \int_{H<E} \prod dx_i dy_i$$

- "$\Omega'(E)$ must assume its maximum value for some finite E_m". Identifies $\log\Omega'(E)$ with entropy. His prediction: for $E < E_m$ the temperature $T := (dS/dE)^{-1}$ is positive and vortices of opposite sign approach one another; but for $E > E_m$, T is negative and vortices of the *same* sign tend to cluster.
- BUT: in thermodynamic limit, $T \geq 0$
- **Nuov. Cim. Suppl.* **6** 279 (1949), see also Fröhlich & Ruelle, *Commun. Math. Phys.* **87** *1-36 (1982)* and Eyink & Sreenivasan, *Rev. Mod. Phys.* **78** 87-135 (2006)