Physics of negative absolute temperatures

BSc Thesis in Physics - University of Trento

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22^{nd} July 2021

Thermodynamic temperature

- Zeroth principle of thermodynamics $\rightarrow$ if systems A,B,C are in equilibrium with each other and D is not, there must exist a function Θ such that

$$\Theta_A(X_A) = \Theta_B(X_B) = \Theta_C(X_C) \neq \Theta_D(X_D)$$

  where X is a set of coordinates that describe systems' equilibrium properties.

- Any function with the above property is a temperature by definition.
- From a statistical mechanics point of view, N systems are in equilibrium with each other when

$$\frac{\partial S_1(E_1)}{\partial E_1} = \frac{\partial S_2(E_2)}{\partial E_2} = \cdots = \frac{\partial S_N(E_N)}{\partial E_N}$$

Thermodynamic temperature

- Then the function $\frac{\partial S}{\partial E}$ can be regarded as a temperature.
- This is what we expect from the first principle of thermodynamics

$$dE(S,V) = TdS - pdV = \frac{\partial E}{\partial S}\,dS + \frac{\partial E}{\partial V}\,dV$$

which tells us that

$$T = \frac{\partial E}{\partial S} \qquad \text{or} \qquad \frac{1}{T} = \frac{\partial S}{\partial E}$$

- Since we derived this temperature by only making use of the zeroth principle of thermodynamics and physical considerations about equilibrium, T is called **absolute temperature**.

Negative absolute temperatures

$$\boxed{\frac{1}{T} = \frac{\partial S}{\partial E}}$$

What are negative absolute temperatures?

- Temperature is a measure of the tendency of the system to increase/decrease its entropy when energy is added
- A negative temperature indicates a decreasing entropy as a function of the energy
- Negative temperatures may be observed in those systems in which the highest energy macrostates correspond to only one or few microstates

Ramsey's criteria

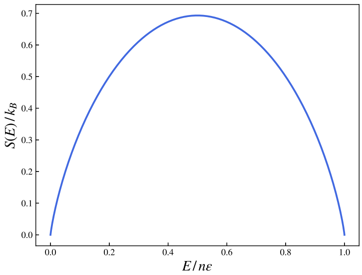
More precisely negative temperatures can be observed in systems that satisfy **Ramsey's criteria** (necessary conditions)

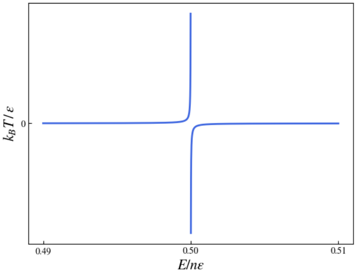
- The various elements of the systems must be in equilibrium with each other
- The energy must be bounded from above, otherwise

  $$p(E) = \frac{e^{-\beta E}}{Z}$$

  is non-negligible only for infinite energies
- Systems that do not respect the above conditions must be thermally isolated from the system under study, or they must act slowly on it

Two levels system



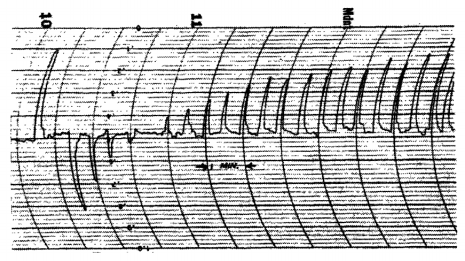


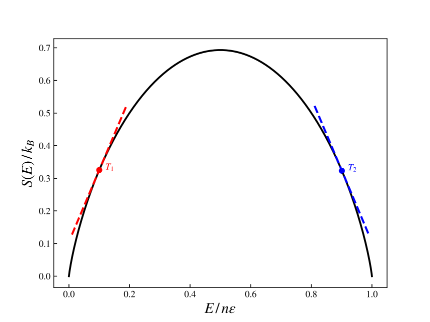
In a two levels system the **highest energy configuration**, as well as the lowest one, **correspond to one single microstate**, while the other states have a higher entropy.

Negative temperatures are hotter than positive ones and heat is transferred from systems at negative temperatures to systems at positive temperatures

Hotness hierarchy:
$0^+ \rightarrow +\infty \rightarrow -\infty \rightarrow 0^-$

Purcell and Pound's experiment (1951)





Spins of LiF crystal in a uniform magnetic field: first experiment that revealed negative temperatures

The system was cooled down at low temperature $\Rightarrow n_{low} \gg n_{high}$

Then the magnetic field was instantaneously reversed causing an inversion of population (antiparallel spins)

E. M. Purcell and R. V. Pound. Phys. Rev. 81, doi: 10.1103/PhysRev.81.279.

Boltzmann and Gibbs

- Boltzmann and Gibbs provided two different approaches to statistical mechanics
- Boltzmann's approach leads to the definition of microcanonical entropy

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

  where $\omega(E)$ denotes the number of states with energy E.
- Gibbs' approach instead leads to

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

  where $\omega(E) = \Omega'(E)$ and $\Omega(E)$ denotes the number of states with energy less than or equal to E.
- **Gibbs' entropy does not admit negative temperatures**

Boltzmann and Gibbs

- **Boltzmann's entropy** was criticized for **not satisfying the thermostatistical consistency condition**

$$T\left(\frac{\partial S}{\partial A_\mu}\right)_E = -\left(\frac{\partial E}{\partial A_\mu}\right)_S = -\left\langle \frac{\partial H}{\partial A_\mu} \right\rangle$$

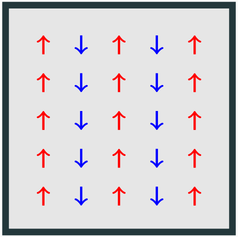
  and for not satisfying the equipartition theorem exactly. For example for an ideal gas one obtains that

$$E = \left(\frac{3N}{2} - 1\right) \; k_B T_B$$

- Later it was shown to satisfy the condition in the limit of large N.
- Gibbs' entropy was criticized for beeing unphysical.
- **Gibbs' entropy fails to meet a basic thermodynamic requirement**, that is predicting equilibrium for systems at the same Gibbs temperature when putting into contact a system that admits negative Boltzmann temperatures and a system that does not.

2D Ising model

2D Ising model: set of spins in a squared lattice



The Hamiltonian of the system is

$$\mathcal{H}(\{\sigma_k\}) = -J\sum_{\langle ij\rangle}\sigma_i\sigma_j = \sum_{\langle ij\rangle}E_{ij} \qquad \text{where } E_{ij} = \pm J$$

If $J > 0$ the interaction is ferromagnetic, if $J < 0$ it is antiferromagnetic.

The system admits negative temperatures.

2D Ising model

At given temperature, the probability of a configuration $\{\sigma_k\}$ is

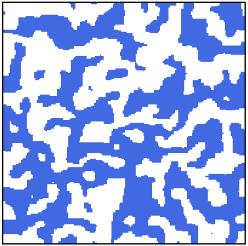
$$p(\{\sigma_k\}) = \frac{e^{-\beta\mathcal{H}(\{\sigma_k\})}}{Z} = \frac{e^{\xi\sum_{\langle ij\rangle}\sigma_i\sigma_j}}{Z}$$

where $\xi \equiv \beta J$.

- The system is initialized in a random configuration, assigning to each spin a value up or down with equal probability
- A value of temperature for the system is estabilished
- The evolution of the system is studied through a Monte Carlo simulation sampling from the probability distribution $p(\{\sigma_k\})$
- After 10^6 cycles the simulation is stopped and the spin configuration is studied

2D Ising model

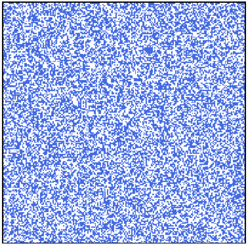
$$\mathcal{H}(\{\sigma_k\}) = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j = \sum_{\langle ij \rangle} E_{ij} \qquad \text{where } E_{ij} = \pm J$$



$T = 0.01\,\mathrm{K}$

$\xi \gg 1$

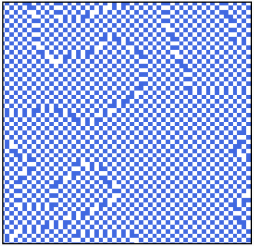
Parallel



$T = 100\,\mathrm{K}$

$0 < \xi \ll 1$

Disordered



$T = -0.01\,\mathrm{K}$

$\xi \ll -1$

Antiparallel

Negative temperatures are hotter than positive ones

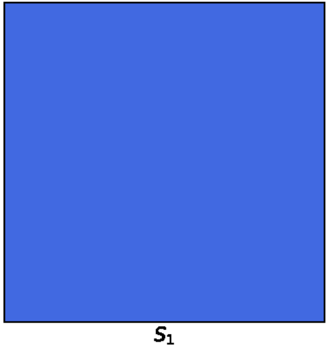
Let us now consider two systems described by the Hamiltonian

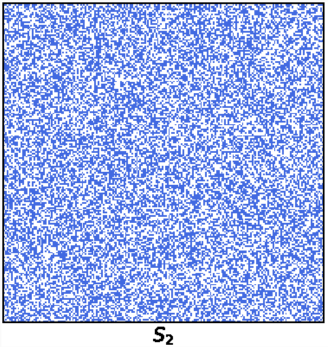
$$\mathcal{H}(\{\sigma_k\}) = -B \sum_i \sigma_i$$

- Both systems are initialized in a random configuration, assigning to each spin a value up or down with equal probability
- System $\mathcal{S}_1$ is prepared at temperature $T_1 < 0$, while system $\mathcal{S}_2$ is prepared at temperature $T_2 > 0$ through a **canonical Monte Carlo** simulation
- The systems are then brought into contact forming a new system
- The evolution of the new system is simulated through a **demon Monte Carlo** method.

The purpose is to show that system $\mathcal{S}_1$ gives energy to system $\mathcal{S}_2$

States before contact



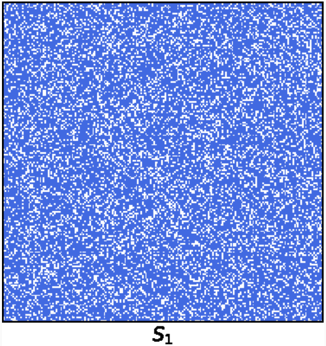


$T_1 = -10^{-6}$ K

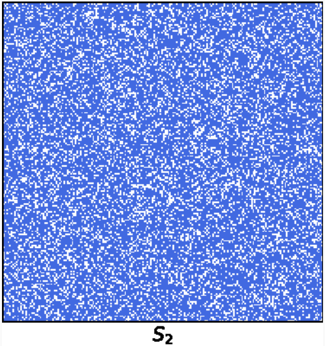
$T_2 = 10^{6}$ K

The system $\mathcal{S}_1$ lies in the highest energy configuration state (all the spins antiparallel with respect to the field), while system $\mathcal{S}_2$ lies in the highest entropy configuration

States after contact



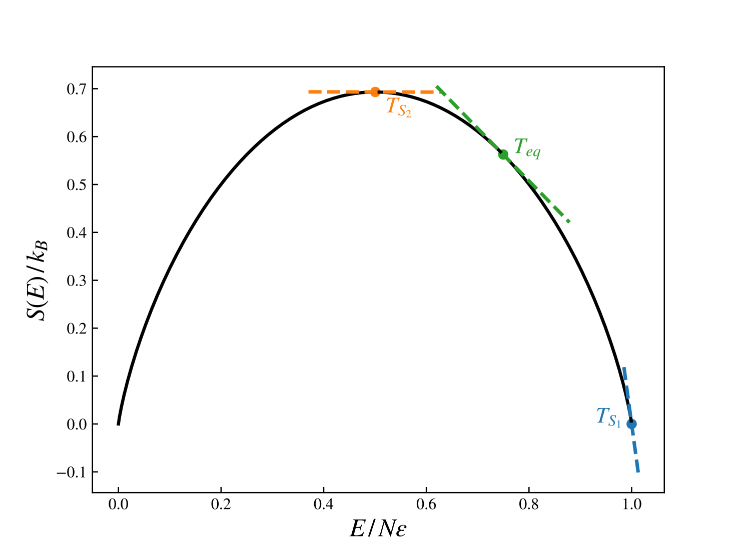
$T_2 = -0.9$ K



$T_2 = -0.9$ K

After being put into contact and reaching thermalization, both systems have energy $E = \frac{E_1+E_2}{2}$ and they have the same temperature, with a majority of spins in the high energy state (energy is conserved)

Negative temperatures are hotter than positive ones



Conclusions

- Temperature is a quantity that identifies systems at equilibrium and indicates the tendency of a system to increase/decrease its entropy when energy is added.
- A negative temperature simply indicates that entropy is a decreasing function of the energy and they can be observed in systems with energy spectra bounded from above.
- Gibbs' entropy is not appropriate to discuss systems capable of negative absolute temperatures.
- The physics of negative temperatures exhibits counterintuitive phenomena. For example heat is transferred from systems at negative temperatures to systems at positive temperatures (i.e. negative temperatures are hotter than positive ones).
- Negative temperatures find applications too. For example they are particularly useful in cosmology since they are related to negative pressures.

Conclusions

Markov Chain Monte Carlo

- We need to perform ensemble averages at equilibrium.
- Suppose that equilibrium is described by a normalized probability distribution $p(x)$.
- The expectation value is

$$\langle A \rangle = \sum_i A(x_i)\, p(x_i)$$

- One can let the system make a random walk in the configuration space and store the values of A at each step.
- $\langle A \rangle$ can be calculated as an average of those values if each state is visited with frequency $p(x)$ and all the states are visited.

$\Longrightarrow$ Metropolis-Hastings algorithm let us sample from $p(x)$

- A new configuration of the system x^* is proposed sampling from a proposal distribution $J(x^*|x_i)$.
- Then the ratio w must be calculated

$$w = \frac{J(x_i|x^*)p(x^*)}{J(x^*|x_i)p(x_i)}$$

- if $w \geq 1$ the proposal change is accepted and $x_{i+1} = x^*$.
- otherwise a number r is extracted from a uniform distribution in $[0, 1]$.
- If $w > r$ the proposal change is still accepted and $x_{i+1} = x^*$.
- Otherwise the proposal moved is refused and $x_{i+1} = x_i$.

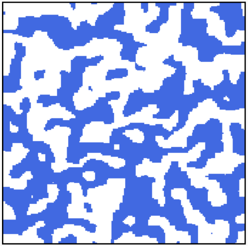
Demon Monte Carlo

The Demon Monte Carlo algorithm can be resumed in the following steps

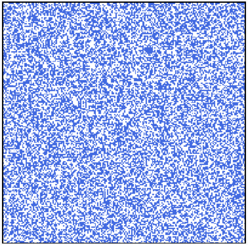
- Propose the new state for the system.
- Calculate the energy difference between the two states.
- If $\Delta E < 0$ the proposal is accepted and the demon takes the energy excess.
- If $\Delta E > 0$ but it is smaller than the demon's energy, the demon releases his energy and the move is accepted.
- Otherwise the move is rejected.
- Repeat from point 1.

If the number of degrees of freedom is high, the demon contribution is negligible but allows the system to move to different states keeping energy (almost) constant.

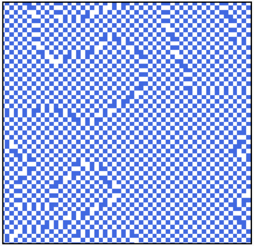
Ferromagnetic-Antiferromagnetic symmetry



$T = 0.01\,\mathrm{K}$



$T = 100\,\mathrm{K}$



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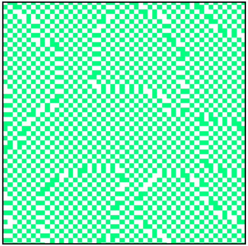

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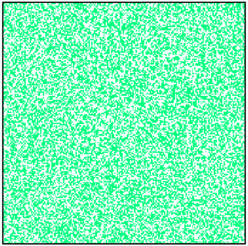
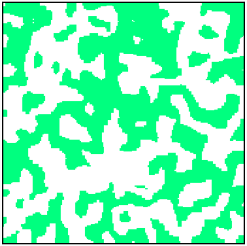


$T = 100\,\mathrm{K}$



$T = -0.01\,\mathrm{K}$

Ferromagnetic-Antiferromagnetic symmetry

The behavior of a ferromagnetic system for positve (negative) temperatures is analogous to the one of an antiferromagnetic system at negative (positive) temperatures.

The probability of a state depends only on $\xi = \beta J$ and not separately on β and J

$$p(\{\sigma_k\}) = \frac{e^{-\beta \mathcal{H}(\{\sigma_k\})}}{Z} = \frac{e^{\xi \sum_{\langle ij \rangle} \sigma_i \sigma_j}}{Z}$$

and

$$\xi = \beta J = (-\beta)(-J) = \beta' J'$$