Negative temperature

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We consider the system consisting of two states. The energies of the two states are given by $-\varepsilon_0$ (<0) and ε_0 (>0), respectively. These two states are non-degenerate. In the thermal equilibrium. We know that the probability of finding the system in the upper state is

$$P_2 = \frac{1}{Z_1} e^{-\frac{\varepsilon_0}{k_B T}}$$

and that the probability of finding the system in the lower state is

$$P_1 = \frac{1}{Z_1} e^{\frac{\varepsilon_0}{k_B T}} = \frac{1}{Z_1}$$

where Z_1 is the partition function, $$Z_1 = e^{-\frac{\varepsilon_0}{k_B T}} + e^{-\frac{\varepsilon_0}{k_B T}}.$$

When the temperature T is positive (usual case), P_2 is always larger than P_1. When T becomes infinity, P_1 is equal to P_2.

((**Population inversion, negative temperature**))

In statistical mechanics, a **population inversion** occurs while a system (such as a group of atoms or molecules) exists in a state in which more members of the system are in higher, excited states than in lower, unexcited energy states. It is called an "inversion" because in many familiar and commonly encountered physical systems, this is not possible. The concept is of fundamental importance in laser science because the production of a population inversion is a necessary step in the workings of a standard laser. In our notation, the temperature becomes negative since

$$P_2 > P_1$$

Here we discuss the concept of negative temperature using the problem of two energy states (micro-canonical ensemble and canonical ensemble)

1. Micro-canonical ensemble

Reference

R. Kubo, Statistical Mechanics, An Advanced Course with Problems and Solutions (North-Holland, 1965).

There is a system consisting of N independent particles. Each particle can have only one of the two energy levels, $-\varepsilon_0$, and ε_0. Find the thermodynamics weight W_M of a state with the total energy

$$E = M\varepsilon_0 \qquad (M = -N, -N+1, ..., N)$$

and discuss the statistical-thermodynamic properties of the system for the range $E < 0$, deriving especially the relation between temperature T and the energy E as well as the specific heat.

((**Solution**))

If N_- particles are in the state with energy $-\varepsilon_0$ and N_+ particles are in the state with energy ε_0, the energy of the total system is

$$E = -N_-\varepsilon_0 + N_+\varepsilon_0 = M\varepsilon_0, \qquad M = N_+ - N_-$$

Since $N = N_+ + N_-$, one has

$$N_+ = \frac{1}{2}(N+M) = \frac{1}{2}(N+\frac{E}{\varepsilon_0}) = \frac{1}{2}N(1+\frac{E}{N\varepsilon_0})$$

$$N_- = \frac{1}{2}(N-M) = \frac{1}{2}(N-\frac{E}{\varepsilon_0}) = \frac{1}{2}N(1-\frac{E}{N\varepsilon_0})$$

Now we consider the thermodynamic weight which is given by

$$W_M = \frac{N!}{[\frac{1}{2}(N-M)]![\frac{1}{2}(N+M)]!},$$

which is the possible ways of choosing N_- particles out of N to occupy the state with $-\varepsilon_0$, and N_+ particles out of N to occupy the state with ε_0. The entropy of the system is

$$S(E) = k_B \ln W_M$$
$$= k_B \{\ln N! - \ln[\frac{1}{2}(N-M)]! - \ln[\frac{1}{2}(N+M)]!\}$$

Using the Stirling's formula, we get the entropy S as

$$S = k_B\{N \ln N - \frac{1}{2}(N-M)\ln[\frac{1}{2}(N-M)] - \frac{1}{2}(N+M)\ln[\frac{1}{2}(N+M)]$$
$$-N + \frac{1}{2}(N-M) + \frac{1}{2}(N+M)\}$$
$$= k_B\{N \ln N - \frac{1}{2}(N-M)\ln[\frac{1}{2}(N-M)] - \frac{1}{2}(N+M)\ln[\frac{1}{2}(N+M)]$$
$$= k_B\{(N_+ + N_-)\ln N - N_- \ln(N_-) - N_+ \ln(N_+)\}$$
$$= -k_B N\{\frac{N_-}{N}\ln(\frac{N_-}{N}) + \frac{N_+}{N}\ln(\frac{N_+}{N})\}$$
$$= -k_B N[(\frac{1+x}{2})\ln(\frac{1+x}{2}) + (\frac{1-x}{2})\ln(\frac{1-x}{2})]$$

where $x = \frac{U}{N\varepsilon_0}$. We define the temperature T as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{N\varepsilon_0}\frac{\partial S}{\partial x} = \frac{k_B}{2\varepsilon_0}\ln(\frac{1-x}{1+x})$$

Figure shows the plot of y vs x.

$$y = \frac{S}{k_B N}$$
$$= -[(\frac{1+x}{2})\ln(\frac{1+x}{2}) + (\frac{1-x}{2})\ln(\frac{1-x}{2})],$$

$$x = \frac{U}{N\varepsilon_0}.$$

where

$$x = \frac{1-e^{1/\overline{T}}}{1+e^{1/\overline{T}}} = -\frac{e^{\beta\varepsilon_0} - e^{-\beta\varepsilon_0}}{e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}}$$

or

$$\overline{T} = \frac{k_B T}{2\varepsilon_0} = \frac{1}{\ln\left(\frac{1-x}{1+x}\right)}$$

with $\beta = \frac{1}{k_B T}$.

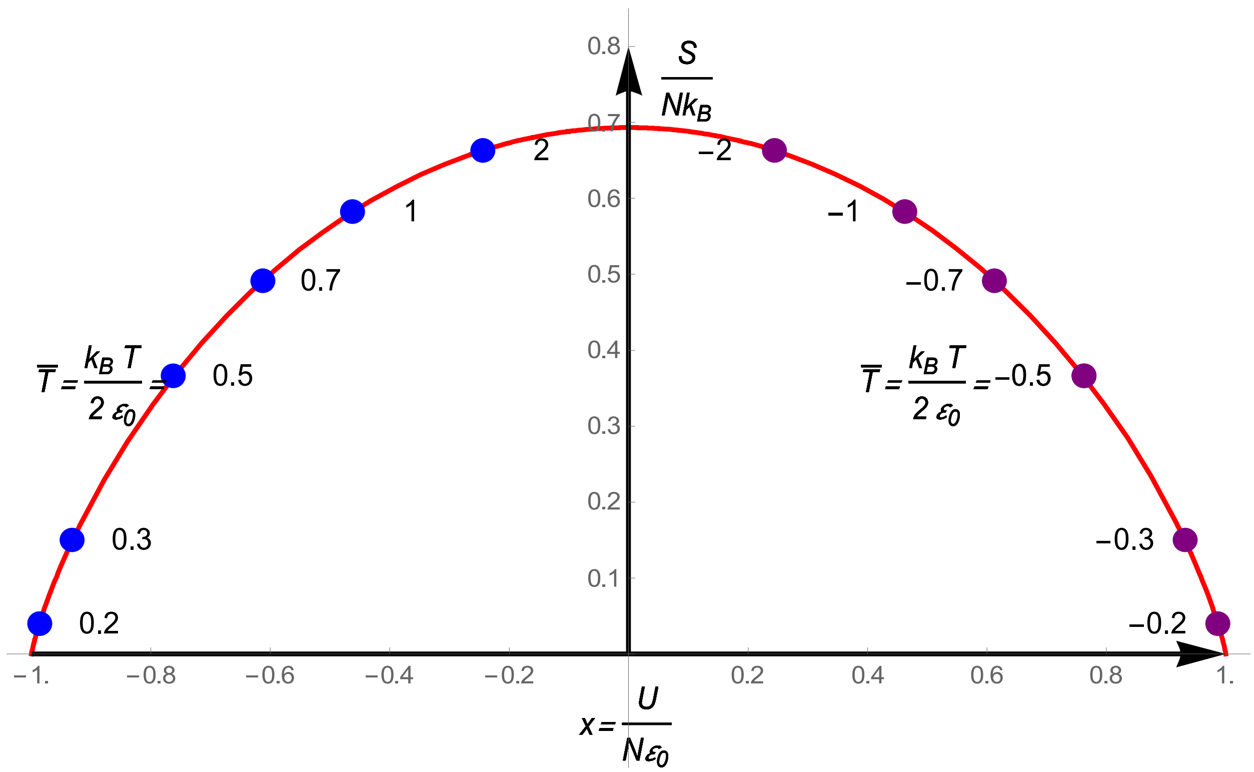


Fig. Plot of $S/(Nk_B)$ vs $U/(N\varepsilon_0)$. The blue points for x<0 correspond to the case of the negative normalized temperature $\overline{T} = \frac{k_B T}{2\varepsilon_0}$ (>0), while the purple points for x>0 correspond to the case of the positive normalized temperature $\overline{T} = \frac{k_B T}{2\varepsilon_0}$ (<0),

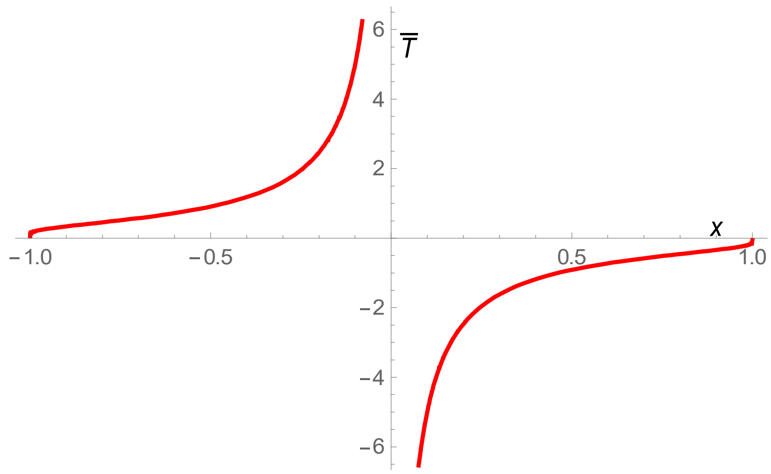


Fig. Temperature $\overline{T}$ vs x. Note that $\overline{T} < 0$ in the region $(0 < x < 1)$.

We note that $\overline{T} < 0$ (negative temperature) for $x = \dfrac{E}{N\varepsilon_0} > 0$. So that this system is not normal in the sense of statistical mechanics. Since, however, it is normal in the range $x = \dfrac{E}{N\varepsilon_0} < 0$. One can discuss the property of this system in this range.

$$\frac{N_+}{N} = \frac{1}{2}(1+x) = \frac{1}{2}\left(1 - \frac{e^{\beta\varepsilon_0} - e^{-\beta\varepsilon_0}}{e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}}\right) = \frac{e^{-\beta\varepsilon_0}}{e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}} \qquad (1a)$$

$$\frac{N_-}{N} = \frac{1}{2}(1-x) = \frac{1}{2}\left(1 + \frac{e^{\beta\varepsilon_0} - e^{-\beta\varepsilon_0}}{e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}}\right) = \frac{e^{\beta\varepsilon_0}}{e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}} \qquad (1b)$$

Thus we have

$$U = \varepsilon_0(N_+ - N_-) = -N\varepsilon_0 \frac{e^{\beta\varepsilon_0} - e^{-\beta\varepsilon_0}}{e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}} = -N\varepsilon_0 \tanh(\beta\varepsilon_0)$$

or

$$\frac{U}{N\varepsilon_0} = -\tanh(\beta\varepsilon_0)$$

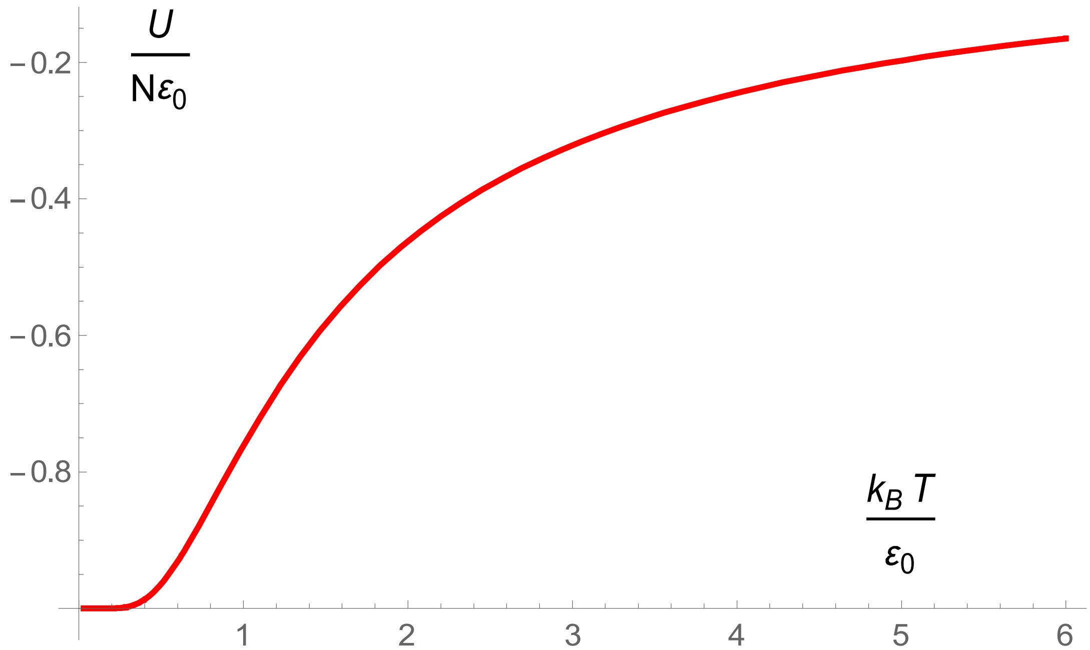


Fig. Plot of the normalized energy $U/(N\varepsilon_0)$ vs the normalized temperature $k_B T/\varepsilon_0$.

Equations (1a) and (1b) gives the probabilities of finding any one particle in the states $-\varepsilon_0$, and ε_0, respectively, and have the form of a canonical distribution. The specific heat is calculated as

$$C = \frac{dU}{dT} = Nk_B\left(\frac{\varepsilon_0}{k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\varepsilon_0}{k_B T}\right)$$

Wnen $\Delta = 2\varepsilon_0$, one rewrite it as

$$C = \frac{dU}{dT} = \frac{Nk_B}{4}\left(\frac{\Delta}{k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\Delta}{2k_B T}\right)$$

$$= Nk_B\left(\frac{\Delta}{k_B T}\right)^2 \frac{e^{\Delta/(k_B T)}}{(e^{\Delta/(k_B T)}+1)^2}$$

We make a plot of the heat capacity as a function of temperature;

$$y = \frac{C}{Nk_B}, \qquad x = \frac{k_B T}{\Delta}$$

where

$$y = \frac{1}{x^2}\frac{e^{1/x}}{(e^{1/x}+1)^2}$$

$$y' = \frac{e^{1/x}}{(1+e^{1/x})^3 x^4}[1+2x+e^{1/x}(2x-1)]$$

The root of y' = 0 is obtained as $x = 0.416778$.

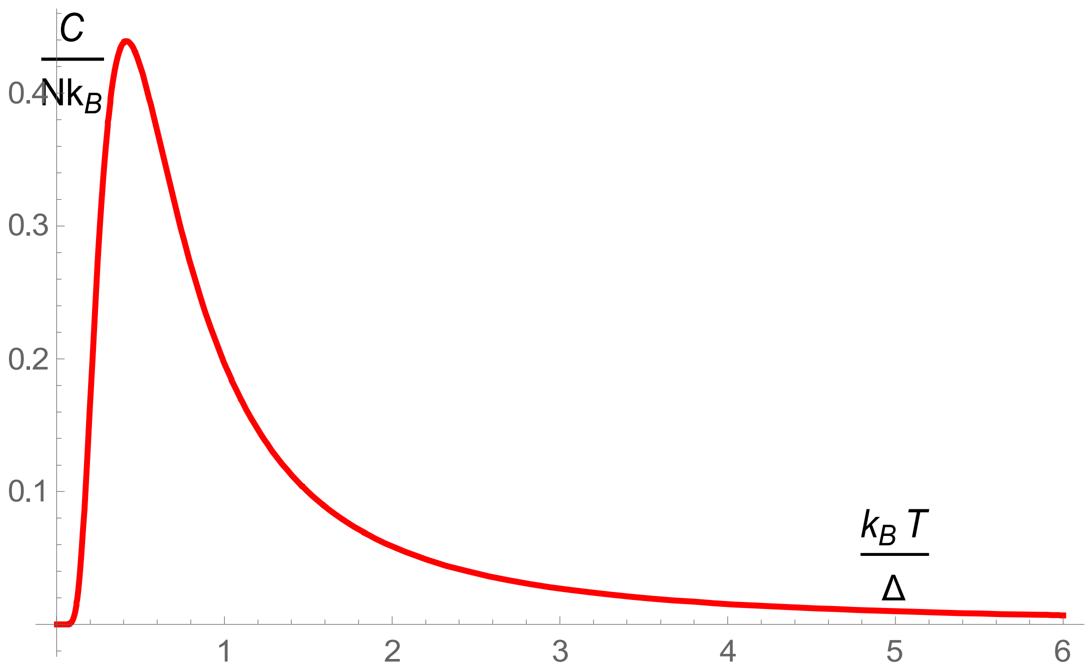


Fig. Plot of the normalized specific heat $C/(Nk_B)$ vs the normalized temperature $x = k_B T/\Delta$. $\Delta = 2\varepsilon_0$. The specific heat show a peak at $x = 0.416778$.

The specific heat of this form is called the Schottky specific heat. When a system has the excitation energy *Δ*, the specific heat anomaly with a peak as shown in the above Figure, is actually observed.

2. Canonical ensemble

The partition function for the canonical ensemble

$$Z_{CN} = (Z_{C1})^N$$

where Z_{C1} is the on-particle partition function,

$$Z_{C1} = e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}$$

The Helmholtz free energy:

$$F = -k_B T \ln Z_{CN} = -Nk_B T \ln Z_{C1}$$

The internal energy:

$$U = -N\frac{\partial}{\partial\beta}\ln Z_{C1} = -N\varepsilon_0 \tanh(\beta\varepsilon_0)$$

or

$$\frac{U}{N\varepsilon_0} = -\tanh(\beta\varepsilon_0)$$

So the result form the approach based on the canonical ensemble is the same as that based on the micro-canonical ensemble.

The heat capacity is

$$\begin{aligned} C &= \frac{dU}{dT} \\ &= \frac{d\beta}{dT}\frac{\partial U}{\partial\beta} \\ &= -k_B\beta^2\frac{\partial U}{\partial\beta} \\ &= Nk_B{\varepsilon_0}^2\beta^2 \operatorname{sech}^2(\beta\varepsilon_0) \end{aligned}$$

or

$$C = Nk_B\left(\frac{\varepsilon_0}{k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\varepsilon_0}{k_B T}\right) \qquad \text{(Schottky-type heat capacity).}$$

The entropy S is calculated as

$$
\begin{aligned}
S &= k_B \int \beta dU \\
&= k_B[\beta U - \int U d\beta] \\
&= Nk_B[-\beta \frac{\partial \ln Z_{C1}}{\partial \beta} + \int \frac{\partial \ln Z_{C1}}{\partial \beta} d\beta] \\
&= Nk_B[\ln Z_{C1} - \beta \frac{\partial \ln Z_{C1}}{\partial \beta}
\end{aligned}
$$

where

$$\ln Z_{C1} = \ln[2\cosh(\beta\varepsilon_0)] \qquad \frac{\partial \ln Z_{C1}}{\partial \beta} = \varepsilon_0 \tanh(\beta\varepsilon_0)$$

Thus we have

$$\frac{S}{Nk_B} = \ln[2\cosh(\beta\varepsilon_0)] - \beta\varepsilon_0 \tanh(\beta\varepsilon_0)]$$

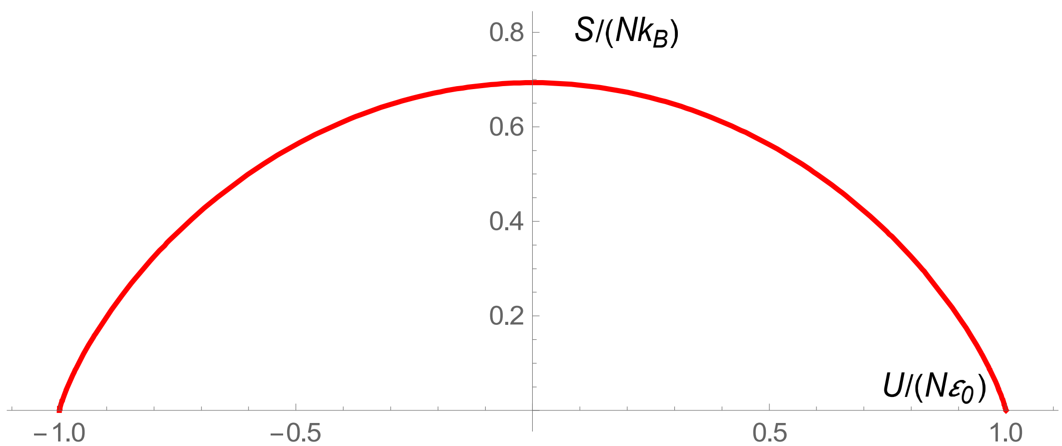
((**Mathematica**)) ParametricPlot

We make a plot (ParametricPlot) of

$$\frac{U}{N\varepsilon_0} = -\tanh(\beta\varepsilon_0), \qquad \text{as } x\text{-axis,}$$

$$\frac{S}{Nk_B} = \ln[2\cosh(\beta\varepsilon_0)] - \beta\varepsilon_0 \tanh(\beta\varepsilon_0)], \qquad \text{as } y\text{-axis}$$

```
Clear["Global`*"];
U1 = -Tanh[x];
S1 = Log[2 Cosh[x]] - x Tanh[x];
h1 = ParametricPlot[{U1, S1}, {x, -20, 20},
  PlotRange → All, AspectRatio → Automatic,
  PlotStyle → {Red, Thick}];
h2 =
 Graphics[
  {Text[Style["U/(Nε0)", Black, Italic, 12],
    {0.85, 0.05}],
   Text[Style["S/(NkB)", Black, Italic, 12],
    {0.2, 0.8}]}];
Show[h1, h2]
```



Suppose that

$$x = \frac{U}{N\varepsilon_0} = -\tanh(\beta\varepsilon_0) = -\frac{e^{\beta\varepsilon_0} - e^{-\beta\varepsilon_0}}{e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}} = -\frac{e^{2\beta\varepsilon_0} - 1}{e^{2\beta\varepsilon_0} + 1}$$

or

$$e^{2\beta\varepsilon_0} = \frac{1-x}{1+x}$$

For $|x| \leq 1$,

$$e^{\beta\varepsilon_0} = \sqrt{\frac{1-x}{1+x}} \qquad \text{or} \qquad \beta\varepsilon_0 = \ln\sqrt{\frac{1-x}{1+x}} = \frac{1}{2}\ln\left(\frac{1-x}{1+x}\right)$$

$$\begin{aligned}
\frac{S}{Nk_B} &= \ln[e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}] - \beta\varepsilon_0 \tanh(\beta\varepsilon_0)] \\
&= \ln[e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}] + \beta\varepsilon_0 x \\
&= \ln[\sqrt{\frac{1-x}{1+x}} + \sqrt{\frac{1+x}{1-x}}] + \frac{x}{2}\ln\left(\frac{1-x}{1+x}\right) \\
&= \ln 2 - \frac{1}{2}\ln[(1+x)(1-x)] + \frac{x}{2}\ln\left(\frac{1-x}{1+x}\right) \\
&= \ln 2 - \frac{1}{2}\ln(1+x) - \frac{1}{2}\ln(1-x) + \frac{x}{2}[\ln(1-x) - \ln(1+x)]
\end{aligned}$$

or

$$\frac{S}{Nk_B} = -\left(\frac{1+x}{2}\right)\ln\left(\frac{1+x}{2}\right) - \left(\frac{1-x}{2}\right)\ln\left(\frac{1-x}{2}\right)$$

with

$$x = \frac{U}{N\varepsilon_0}$$

$$\frac{1}{Nk_B}\frac{\partial S}{\partial x} = -\frac{1}{2}\ln\left(\frac{1+x}{2}\right) + \frac{1}{2}\ln\left(\frac{1-x}{2}\right) = \frac{1}{2}\ln\left(\frac{1-x}{1+x}\right)$$

Using the relation

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right) = \frac{\partial x}{\partial U}\frac{\partial S}{\partial x} = \frac{1}{N\varepsilon_0}\frac{\partial S}{\partial x} = \frac{k_B}{2\varepsilon_0}\ln\left(\frac{1-x}{1+x}\right)$$

The normalized temperature is

$$\overline{T} = \frac{k_B T}{2\varepsilon_0} = \frac{1}{2\beta\varepsilon_0} = \frac{1}{\ln\left(\frac{1-x}{1+x}\right)}$$

6. Negative temperature

C. Kittel Elementary Statistical Physics (John Wiley & Sons, 1958) p.114.

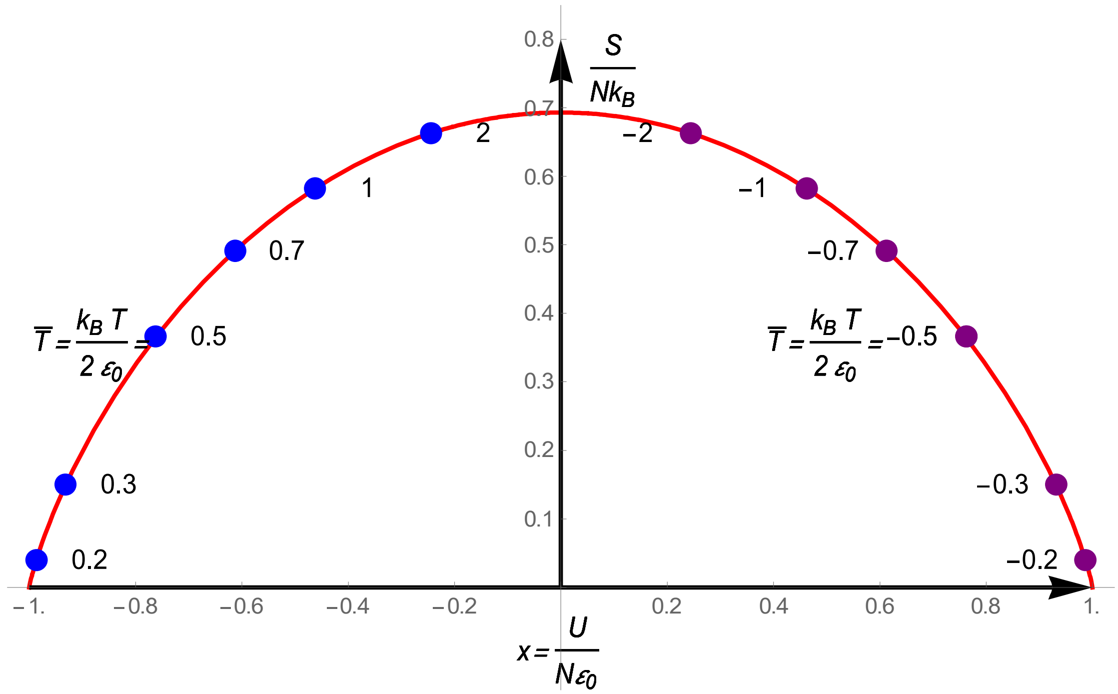


Fig. Entropy as a function of energy for a two-levels system; the sign of the temperature is given by the sign of the slope $\frac{\partial S}{\partial U} = \frac{1}{T}$. $x = \frac{U}{N\varepsilon_0}$

In the above figure, we sketch the dependence of the entropy S on U. Because the slope $\frac{\partial S}{\partial U}$ is positive on the left side of the figure, the temperature there is positive (T>0). On the right side of the figure, on the other side, the slope is negative and the temperature is negative (T<0).

It is instructive to recall that entropy is the logarithm of the number of accessible states. It is then immediately apparent that the entropy will be zero at $x = \frac{U}{N\varepsilon_0} = \pm 1$, because here all the particles are in one state. At intermediate energies the entropy is positive, and we can see that the entropy is symmetric about the zero of energy.

We note that negative temperatures correspond to higher energies than positive temperatures. When a positive- and a negative-temperature system are brought into thermal contact, heat will flow from the negative temperatures to the positive temperatures. Thus we say that negative temperatures are hotter than positive temperatures. The temperature scale from cold to hot runs

T = +0 K, …, +300 K, …, $\pm\infty$ K , .., -300 K, …, (-0) K.

Note particularly that, when a body at -300 K is brought into contact with an identical body at 300 K, the final temperature is not 0 K, but is $\pm\infty$ K , the two signs corresponding actually to the same temperature. In many respects $-1/T$ is a more instructive measure of temperature than is T. Increasing values of -1/T correspond to the body's becoming hotter and hotter.

$$-\frac{1}{T} = -\infty \text{ (cold)},\ldots,\ -\frac{1}{300},\ldots,\ 0,\ldots,\ \ +\frac{1}{300},\ \ ,\ \infty \text{ (hot)}$$

When the temperature is negative, the population in the upper energy state is larger than the population in the ground state.

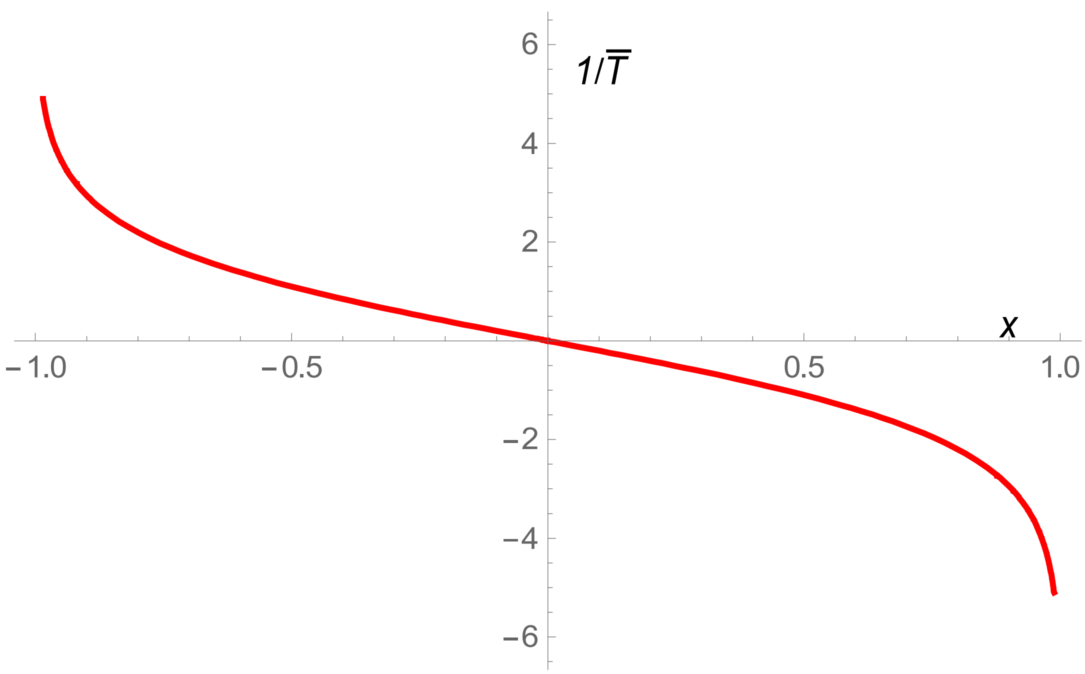


Fig. Inverse temperature $1/\overline{T}$ vs x. $x = \dfrac{U}{N\varepsilon_0}$. $\dfrac{1}{\overline{T}} = \dfrac{2\varepsilon_0}{k_B T}$.

7. Probability

The probability for the low-energy level state

$$P_{\text{low-level}} = \frac{e^{\beta\varepsilon_0}}{e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}} = \frac{e^{2\beta\varepsilon_0}}{e^{2\beta\varepsilon_0} + 1} = \frac{1-x}{2}$$

The probability for the high-energy level state

$$P_{\text{high-level}} = \frac{e^{-\beta\varepsilon_0}}{e^{\beta\varepsilon_0} + e^{-\beta\varepsilon_0}} = \frac{1}{e^{2\beta\varepsilon_0} + 1} = \frac{1+x}{2}$$

Note that

$$P_{\text{low-level}} + P_{\text{high-level}} = 1$$

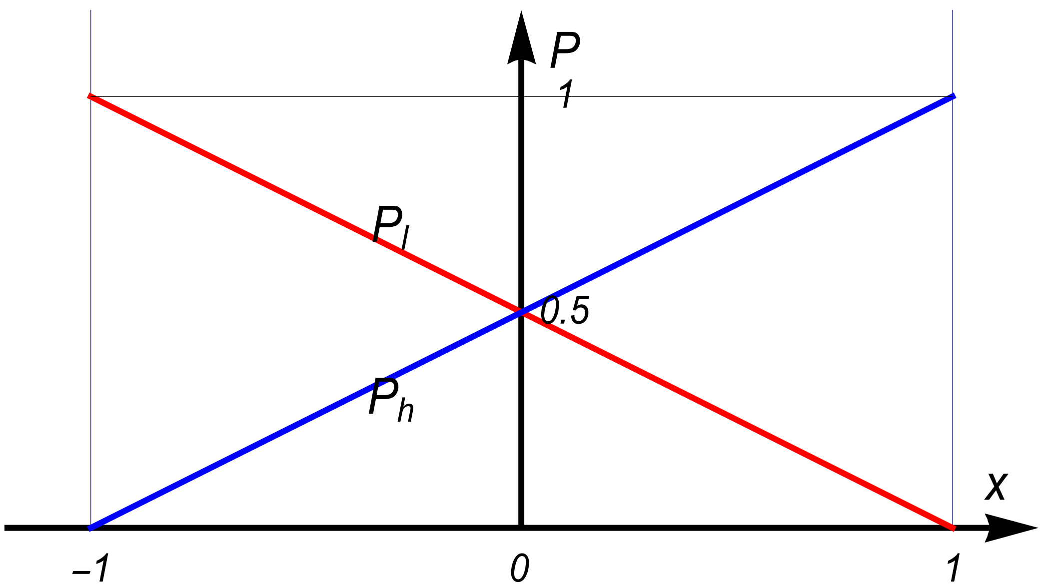


Fig. Probability $P_l = P_{\text{low-level}}$ and probability $P_h = P_{\text{high-level}}$ as a function of x. $x = \dfrac{U}{N\varepsilon_0}$

For $x < 0$, $P_{\text{low-level}} > P_{\text{high-level}}$.

For $x > 0$, $P_{\text{low-level}} < P_{\text{high-level}}$. (population inversion)