Comment on "Negative Kelvin temperatures: Some anomalies and a speculation"

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In this note, we prove that for systems that can exhibit negative Kelvin temperature there exist no adiabatic surfaces connecting regions of opposite temperature sign.

The motivation for this proof comes from a note published a few months ago by Tykodi in this Journal,[1] in which he recalled certain properties of systems exhibiting negative Kelvin temperatures and pointed out that it might be necessary to formulate a new law of thermodynamics to forbid the following processes: (a) the running of a Carnot "cycle" between a reservoir of finite temperature and one of infinite temperature since it would permit a *reversible* 100% conversion of heat into work (it is known that at negative temperature the Kelvin–Planck formulation of the second law must be modified to permit *irreversible* 100% conversion of heat into work[2]); (b) the existence of Carnot cycles working between reservoirs of temperatures of opposite signs, since such cycles would perform work and at the same time would "pump" entropy from the colder to the hotter reservoir.

Pippard[3] mentions that "no isentropic surfaces connect positive and negative temperatures." It is clear that no new law would be needed if one could prove such a statement.[4] We shall present such a proof here. It involves nothing more than a plausible hypothesis about systems that can exhibit negative temperature, and it uses very elementary relations of statistical mechanics that can be found in any of the classical texts on the subject.[5]

In the canonical ensemble, the entropy is written[5]

$$S = k\left(\ln Z - \beta \frac{\partial \ln Z}{\partial \beta}\right), \tag{1}$$

where k is Boltzmann's constant and

$$Z(\beta, X_j) = \sum_{i=1}^{N} \exp[-\beta E_i(X_j)] \tag{2}$$

is the partition function. The sum extends over all N possible eigenvalues E_i of the Hamiltonian describing the system. These eigenvalues can depend on a set of external parameters X_j. We will always work with $\beta = (kT)^{-1}$ since it is a parameter that changes continuously between regions of opposite temperature sign.

Following Ramsey[2] we assume that "there is an upper limit to the possible energy of the allowed states of the system." This can imply restrictions on the values of the external parameters. For example, for a spin system the magnetic field must remain finite if the energy is not to diverge. We furthermore assume that N is finite.

We are looking for adiabatic surfaces going from regions where $\beta \neq 0$ to regions where $\beta = 0$ or even crossing completely between regions of opposite temperature sign. In either case β must go through the value $\beta = 0$. All other parameters X_j however are arbitrary. Stated differently, in the space of thermodynamic variables we are looking for the existence of a path going anywhere through the hyperplane $\beta = 0$ and such that the entropy is constant on that path. We shall thus prove that the value of S in the hyperplane $\beta = 0$ can only be different from its value in neighbouring hyperplanes, and then Pippard's statement will be proved. More specifically, we claim the following:

> In the space of thermodynamic variables $(\beta, X_1, X_2, \ldots)$, the entropy S has one and only one value in the hyperplane $\beta = 0$. Furthermore, there exists an ϵ positive such that the entropy is greater in the hyperplane $\beta = 0$ than in any of the hyperplanes $0 < \beta < \epsilon$ and $-\epsilon < \beta < 0$.

Proof: Because $\partial \ln Z / \partial \beta$ does not diverge, as follows from our hypothesis, we have, from (1)

$$S(\beta = 0, X_j) = k \ln N \qquad \textit{for any set of parameters } X_j. \tag{3}$$

This proves the first part of our statement. To prove the second part, we Taylor expand S around $\beta = 0$:

$$S(\beta = \pm\epsilon, X_j) = S(\beta = 0, X_j) + \left.\frac{\partial S}{\partial \beta}\right|_{\beta=0} (\pm\epsilon) + \frac{1}{2!}\left.\frac{\partial^2 S}{\partial \beta^2}\right|_{\beta=0} (\pm\epsilon)^2 + \frac{1}{3!}\left.\frac{\partial^3 S}{\partial \beta^3}\right|_{\beta=\xi} (\pm\epsilon)^3, \tag{4}$$

where the last term is the Lagrange form of the remainder with $0 < \xi < \epsilon$. Using (1), we find, in units $k = 1$,

$$\left.\frac{\partial S}{\partial \beta}\right|_{\beta=0} = 0, \tag{5}$$

$$\left.\frac{\partial^2 S}{\partial \beta^2}\right|_{\beta=0} = -\frac{\partial^2 \ln Z}{\partial \beta^2} = -\langle \tilde{E}^2 \rangle_{\beta=0} < 0, \tag{6}$$

$$\left.\frac{\partial^3 S}{\partial \beta^3}\right|_{\beta=\xi} = -2\frac{\partial^3 \ln Z}{\partial \beta^3} - \xi \frac{\partial^4 \ln Z}{\partial \beta^4} = +2\langle \tilde{E}^3 \rangle_{\beta=\xi} - \xi[\langle \tilde{E}^4 \rangle_{\beta=\xi} - 3\langle \tilde{E}^2 \rangle_{\beta=\xi}^2], \tag{7}$$

where angular brackets refer to averages in the canonical ensemble at the temperature indicated by the subscript. Also,

$$\tilde{E} \equiv E - \langle E \rangle. \tag{8}$$

Recalling that $\xi < \epsilon$, we see that the remainder of the Taylor expansion can be neglected if

$$\epsilon \ll |\langle \tilde{E}^2 \rangle_{\beta=0} / \langle \tilde{E}^3 \rangle_{\beta=\xi}|$$

and

$$\epsilon^2 \ll |\langle \tilde{E}^2 \rangle_{\beta=0} / [\langle \tilde{E}^4 \rangle_{\beta=\xi} - 3\langle \tilde{E}^2 \rangle_{\beta=\xi}^2]|, \tag{9}$$

An ϵ satisfying both inequalities exists because of our assumptions about the allowed energy eigenstates.

With only the first three terms in (4), Eqs. (5) and (6) imply that

$$S(\beta = 0, X_j) > S(\beta = \pm\epsilon, X_j). \tag{10}$$

The same statement is true for any set of parameters X_j'. Equations (3) and (10) together thus imply

$$S(\beta = 0, X_j) > S(\beta = \pm\epsilon, X_j'), \tag{11}$$

where X_j and X_j' are arbitrary, which proves the second part of our statement.

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[1] R. J. Tykodi, Am. J. Phys. **43**, 271 (1975).
[2] N. F. Ramsey, Phys. Rev. **103**, 20 (1956).
[3] A. B. Pippard, *The Elements of Classical Thermodynamics* (Cambridge U.P., Cambridge, England, 1957, reprinted 1964), p. 52.
[4] We do not *a priori* reject the existence of nonquasistatic processes that would permit some kind of "generalized" Carnot cycles.
[5] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), Eqs./6.6.5/6.5.8/.