NOTES AND DISCUSSIONS

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

André-Marie Tremblay*
Direction Sciences de base, Institut de recherche de l'Hydro-Québec, Varennes, Québec, Canada
(Received 27 August 1975; revised 18 November 1975)

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)

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

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 $k = 1$,

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

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

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

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

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

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

$$S(\beta = 0, X_j) > S(\beta = \pm\epsilon, X_j). \qquad (10)$$

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

$$S(\beta = 0, X_j) > S(\beta = \pm\epsilon, X_j'), \qquad (11)$$

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

I am grateful to the authorities of the Institut de recherche de l'Hydro-Québec for hospitality during the summer of 1975. I also wish to thank Richard Marchand for very useful correspondence and discussions on the problem, and Dr. V. Fuchs for reading the manuscript.

*Summer student. Home address: 5811, Bois de Coulonges, Ville d'Anjou, Québec H1K 3Z3, Canada.

[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/.

Remarks on Tykodi's note on negative Kelvin temperatures

A. Danielian
Department of Physics, King's College, London WC2R 2LS, England
(Received 12 August 1975; revised 18 November 1976)

In his note on negative Kelvin temperatures,[1] Tykodi expresses doubts as to the extension of the Kelvin temperature scale into the negative temperature region being a simple matter, involving only minor changes in the formulation of the laws of thermodynamics. He considers the Kelvin temperatures $T = \pm 0$ and $T = \pm\infty$ as corresponding to singular states; and from an analysis involving Carnot cycles in various temperature regions, concludes that the state $T = \pm\infty$ may require a new principle of thermodynamics, just as the situation at $T = \pm 0$ is described by the "unattainability" formulation of the third law.

The object of this note is to consider the questions raised in terms of the "absolute interval" scale of temperature τ. This scale is defined by two properties: (a) the usual independence of the properties of any particular substance, and (b) the physical equivalence of equal intervals of temperature (i.e., a degree interval $t \rightarrow t - 1$ should be physically of equal value for all t). It has been shown[2] that such a scale may be obtained from Carnot's theory and consequently

$$\tau_1 - \tau_2 = C \ln T_1/T_2. \qquad (1)$$

It follows that negative Kelvin temperatures ($T \exp i\pi$) are in the complex plane of τ and are represented along the line $\tau + i\pi$ {since in this case, $\tau = C \ln[\exp(i\pi)|T|] = C(i\pi + \ln|T|)$}. This is shown in Fig. 1, in which the real τ axis A-B corresponds to $0 < T < +\infty$, and D-C corresponds to $-0 > T > -\infty$. Thus in the τ plane, Tykodi's singular points $T = \pm 0$ are at $-\infty$, while $T = \pm\infty$ are at $+\infty$.

It has been argued[1] that the τ scale provides the more realistic measure of temperature intervals because of property (b), the absence of which from the present Kelvin scale resulting in the latter's distortion, particularly as $T \rightarrow 0$. It has also been suggested that the so-called "unattainability principle" may be considered superfluous since, from (1), $T = 0$ is separated by an infinite interval from any initial temperature T_0, however low T_0 may be.

Considering the questions raised in terms of the τ plane, the following observations may be made. First, the negative Kelvin temperatures (along D-C, Fig. 1) constitute a distinct "phase" of temperature and are not a simple continuation of the positive scale. Furthermore, the transition from a point $+T_0$ (such as P) to $-T_0(P')$ involves a discontinuous "jump" from the positive temperature "phase" to the negative. These characteristics are in accordance with the fact that only certain special systems can exist in the negative temperature "phase," and the transition to it is a more complex matter than is the case in the usual temperature changes. Second, the special nature of the points $T = \pm 0$ and $T = \pm\infty$ is evident.

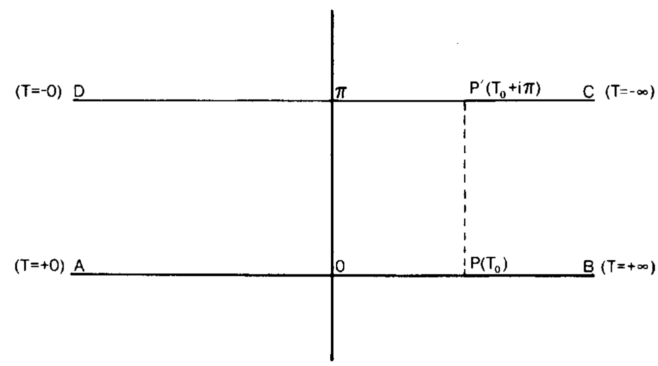

Fig. 1. Complex τ plane. The real axis A-B corresponds to the Kelvin temperature region $+0 < T < +\infty$, while D-C corresponds to $-0 > T > -\infty$.

In conclusion, Tykodi's main points that $T = \pm 0$ and $T = \pm\infty$ correspond to singular states and that negative temperatures are not a simple extension of the positive scale, seem to be more evident in the τ plane. On the other hand, it is not clear that a new principle of thermodynamics concerning $T = \pm\infty$ is needed, any more than the so-called "unattainability principle" is needed at $T = \pm 0$.

[1]R. J. Tykodi, Am. J. Phys. **43**, 271 (1975).
[2]A. Danielian, Phys. Lett. A **51**, 61 (1975).