On the use and abuse of thermodynamic entropy

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Let us elaborate on the notion of *thermodynamic* entropy S (Clausius 1865) and its consequences. Gibbs put forward two notions entropy that I commonly will refer to as the volume entropy (involving the integrated density of states) and as the surface entropy, being proportional to the density of states, commonly also known (incorrectly) as the Boltzmann entropy. The absolute temperature, i.e. $T^{-1} = \partial S/\partial E$, is then related to the thermodynamic entropy; – but which "S" to use? – The consistency for thermodynamics, i.e. dS = an exact differential, singles out the volume entropy [1, 2].

I shall address shortcomings that relate to the thermodynamics of small systems when sticking to the (Boltzmann)-surface entropy [2, 3]. Most of all, the uncritical use of Boltzmann entropy for microcanonical systems may formally yield *negative* values of absolute temperatures. This is not only physically incorrect for the concept of an absolute temperature [1], but also would violate thermodynamic stability if the system is brought into (weak) contact with an omnipresent sort of environment of radiation source or otherwise. Particularly, this criticism applies to the concept of absolute negative (spin) temperatures and, as well, to the negative absolute temperature interpretation of most recent (otherwise correct) experiments with ultra-cold atomic gases [4].

Next, we address canonical entropy when describing quantum systems that interact *strongly* with an environment. Then, the canonical specific heat can in fact assume negative (!) values away from absolute zero temperature [5, 6, 7]. Likewise, the thermodynamic entropy for a strongly coupled system, assuming a form which mimics a conditional entropy (but not quite) can be negative away from absolute $T = 0$ [6, 7].

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