Book Chapter

Heat Engines, Refrigerators, and Absolute Zero

Jack Denur*

Electric & Gas Technology, Inc., USA

Corresponding Author: Jack Denur, Electric & Gas Technology, Inc., 3305 Main Street, Rowlett, TX 75088-4983, USA

How to cite this book chapter: Jack Denur. Heat Engines, Refrigerators, and Absolute Zero. In: Mohammad Hossein Zhoolideh Haghighi, editor. Entropy: Theory and New Insights: 2nd Edition. Hyderabad, India: Vide Leaf. 2023.

Abstract

It is usually assumed that, *if* a cold reservoir at absolute zero (0K) is available, *then* a (perfect, reversible) Carnot heat engine could operate at 100% efficiency, converting 100% of the heat input from its hot reservoir into work. We show that this is *not* true: *Even if* a cold reservoir at $0\,\mathrm{K}$ is available, even a (perfect, reversible) Carnot heat engine must reject *some* waste heat into this cold reservoir. Thus it *must* operate at *less than* 100% efficiency, converting *less than* 100% of the heat input from its hot reservoir into work. By applying the First and Second Laws of Thermodynamics, we will derive the entropy increase and the waste heat that must be rejected into a cold reservoir at or very near $0\,\mathrm{K}$, and the work output and efficiency of a (perfect, reversible) Carnot heat engine employing such a cold reservoir, *if* such a cold reservoir is available. We then consider the possibility, if only in principle (even if only as thought experiments) rather than in practice, of the existence of cold reservoirs at absolute zero via Carnot, absorption, and stimulated-emission refrigeration. Caveats concerning heat leakage from ambient into cold reservoirs and fluctuations are discussed next, as well as the possibility of a system spontaneously attaining absolute zero via fluctuation. Next, we consider a method that in principle can experimentally determine whether or not a system's temperature is absolute zero with*out* heat leakage into the system. Then, we discuss the nature of hot and cold reservoirs that can and cannot maintain a constant temperature. In the Appendix, we discuss an interesting aspect of the relationship between entropy and heat capacity.

I. INTRODUCTION

It is usually assumed that, *if* a cold reservoir at absolute zero ($T_C = 0\,\mathrm{K}$) is available, *then* a (perfect, reversible) Carnot heat engine could operate at 100% efficiency, converting 100% of the heat input Q_H from its hot reservoir into work W.[1–5] In Section II, we show that this is *not* true: *Even if* a cold reservoir at absolute zero ($T_C = 0\,\mathrm{K}$) is available, if the Second Law of Thermodynamics is not to be violated even a (perfect, reversible) Carnot heat engine must reject *some* waste heat into it. Hence (i) *even if* a cold reservoir at absolute zero ($T_C = 0\,\mathrm{K}$) is available, it could remain at $0\,\mathrm{K}$ *only initially* [i.e., *even if* $T_{C,\mathrm{initial}} = 0\,\mathrm{K}$, $T_C > 0\,\mathrm{K}$ immediately thereafter when even a (perfect, reversible) Carnot heat engine begins operating], and (ii) even a (perfect, reversible) Carnot heat engine employing this cold reservoir *must* operate at *less than* 100% efficiency, converting *less than* 100% of the heat input Q_H from its hot reservoir into work W. (Of course, if there is any imperfection or equivalently any irreversibility, the inequality $T_C > 0\,\mathrm{K}$ immediately thereafter will be stronger than with perfect, reversible operation.) By applying the First and Second Laws of Thermodynamics, we will derive the entropy increase and the waste heat that must be rejected into a cold reservoir *initially* at $T_C = 0\,\mathrm{K}$, and the work output W and efficiency of a (perfect, reversible) Carnot heat engine employing such a cold reservoir, *if* such a cold reservoir is available.

Our results are also valid for non-Carnot-cycle heat engines that equal Carnot-cycle heat engines in efficiency, e.g., Stirling-cycle heat engines with regeneration.[6] [The Stirling cycle with regeneration is more complicated than the Carnot cycle;[6] hence, we focus on the Carnot cycle, which is the archetype, and also probably the simplest conceptually, of maximally thermodynamically efficient heat-engine (and refrigerator and heat-pump) cycles.[1–5] Also, henceforth, when mentioning the Stirling heat-engine cycle (or the reverse Stirling refrigerator/heat-pump cycle),[6] "with regeneration" will be omitted for brevity, but is to be understood.] Moreover, except for the utmost-

low-temperature limit discussed in Section IIC, our results are also valid to within an excellent approximation even if a cold reservoir is initially at $T_{C,\text{initial}} > 0\,\text{K}$ with $0\,\text{K} < T_{C,\text{initial}} \ll T_{C,\text{final}}$.

In Section III, we briefly review the unattainability formulation of the Third Law of Thermodynamics. We then consider some possibilities, if only in principle (even if only as thought experiments[7]) rather than in practice, of the existence of cold reservoirs at absolute zero ($0\,\text{K}$) via Carnot/Stirling, absorption, and stimulated-emission refrigeration. (A thought experiment[7] considers only the *essential* physics and ignores all practical engineering complications. In a paraphrase of a more detailed quote of Einstein,[7] it should be "as simple as possible, but not simpler"[7].) Caveats concerning heat leakage from ambient into cold reservoirs and fluctuations are discussed next, as well as the possibility of a system spontaneously attaining absolute zero via fluctuation. We then consider a method that in principle can experimentally determine whether or not a system's temperature is absolute zero with*out* heat leakage into the system.

In Section IV, we discuss the nature of hot and cold reservoirs that can and cannot maintain a constant temperature. In general, hot and cold reservoirs can be of either type. But we will show that a cold reservoir *initially* at absolute zero ($0\,\text{K}$) or even at a temperature above but arbitrarily close to $0\,\text{K}$ *must* — not merely can — be of the latter type.

Concluding remarks are provided in Section V.

In the Appendix, we discuss an interesting aspect of the relationship between entropy and heat capacity. This relationship per se is true in general, but it is typically manifested only by certain systems at very low temperatures. Our example entails conduction electrons in metals.

II. OPERATION OF A CARNOT/STIRLING HEAT ENGINE *IF* A COLD RESERVOIR AT $T_C = 0\,\text{K}$ IS AVAILABLE

A. Heat engines employing cold reservoirs at absolute zero ($T_C = 0\,\text{K}$)

Consider the operation of a (perfect, reversible) Carnot[1–5] (or Stirling[6]) heat engine employing a hot reservoir at fixed temperature T_H and a cold reservoir at absolute zero ($T_C = 0\,\text{K}$), *if* such a cold reservoir is available. If this heat engine operates at *exactly* 100% efficiency, converting *exactly* 100% of the heat input Q_H from its hot reservoir into work W, by the First Law of Thermodynamics *zero* waste heat would be rejected into its cold reservoir at absolute zero ($T_C = 0\,\text{K}$). Hence the total entropy change would be that of the hot reservoir alone, i.e.,

$$\Delta S_{\text{total}} = \Delta S_H = -\frac{Q_H}{T_H} < 0, \tag{1}$$

as if the cold reservoir at absolute zero ($T_C = 0\,\text{K}$) didn't even exist![8] But this violates the Second Law of Thermodynamics, which requires $\Delta S_{\text{total}} = 0$ even for perfect, reversible operation, and $\Delta S_{\text{total}} > 0$ for less-than-perfect operation. Thus, if the Second Law of Thermodynamics is not to be violated, *some* waste heat must be rejected into the cold reservoir at absolute zero ($T_C = 0\,\text{K}$), even given perfect, reversible operation. Hence, *even if* a cold reservoir at absolute zero ($T_C = 0\,\text{K}$) is available, it could remain at $0\,\text{K}$ *only initially*. If the Second Law of Thermodynamics is not to be violated, it can no longer remain at $0\,\text{K}$ at the instant after even a (perfect, reversible) Carnot[1–5] (or Stirling[6]) heat engine begins operating: hence *even if* $T_{C,\text{initial}} = 0\,\text{K}$, $T_C > 0\,\text{K}$ immediately thereafter. (Of course, if there is any imperfection or equivalently any irreversibility, the inequality $T_C > 0\,\text{K}$ immediately thereafter will be stronger than with perfect, reversible operation.)

Given perfect, reversible operation of a Carnot[1–5] (or Stirling[6]) heat engine employing a hot reservoir at fixed temperature T_H and a cold reservoir *initially* at absolute zero ($T_C = 0\,\text{K}$), the Second Law of Thermodynamics requires:

$$\Delta S_{\text{total}} = \Delta S_C + \Delta S_H = \left(\int_{0\,\text{K}}^{T_{C,\text{final}}} \frac{dQ_C}{T_C} \right) - \frac{Q_H}{T_H} = \left(\int_{0\,\text{K}}^{T_{C,\text{final}}} \frac{C}{T_C} dT_C \right) - \frac{Q_H}{T_H} = 0$$

$$\implies \int_{0\,\text{K}}^{T_{C,\text{final}}} \frac{C}{T_C} dT_C = \frac{Q_H}{T_H}. \tag{2}$$

We employ the symbol C to denote heat capacity, usually of cold reservoirs but sometimes of other systems. It is to be understood that in general heat capacity C is a function of temperature (unless it is specifically mentioned that C is constant in a given particular case). Heat capacity C should not be confused with the subscript $_C$, the latter referring the subscripted quantity to a cold reservoir. (Of course, the subscript $_H$ refers the subscripted quantity to a hot reservoir.) We note that at sufficiently low temperatures it is immaterial to specify whether the heat capacity C is taken to be at constant volume, i.e., C_V, or at constant pressure, i.e., C_P. This is because, in the limit $T_C \to 0\,\text{K}$, not only do $C_V \to 0$ and $C_P \to 0$, but furthermore $(C_P - C_V)/C_V \to 0$.[9–13] {Since in all cases $C_P \geq C_V$ [the equality obtaining only in the rare cases wherein $(\partial V/\partial T)_P = 0$, as for water in the immediate vicinity of $T = 4\,°\text{C}$],[9–13] in the limit $T_C \to 0\,\text{K}$ $(C_P - C_V)/C_P \to 0$ always at least as rapidly and except in said rare cases more rapidly than $(C_P - C_V)/C_V \to 0$.[9–13]}.

Also

$$Q_C = \int_{0\,\text{K}}^{T_{C,\text{final}}} dQ_C = \int_{0\,\text{K}}^{T_{C,\text{final}}} C dT_C. \tag{3}$$

Hence, by the First and Second Laws of Thermodynamics:

$$W = Q_H - Q_C = Q_H - \int_{0\,\text{K}}^{T_{C,\text{final}}} C dT_C$$

$$\implies \epsilon_{\text{Carnot}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{\int_{0\,\text{K}}^{T_{C,\text{final}}} C dT_C}{Q_H}, \tag{4}$$

where ϵ_{Carnot} is the Carnot efficiency. Thus, even assuming perfect, reversible operation of a Carnot[1–5] (or Stirling[6]) heat engine, the Second Law of Thermodynamics requires that even the *tiniest* amount of heat input Q_H from the hot reservoir *must* result in $T_{C,\text{final}} > 0\,\text{K} \implies \epsilon_{\text{Carnot}} < 1$.

Irrespective of the nature of a cold reservoir, its entropy $S_C(T_C)$ at any temperature T_C is nonnegative and finite. For, in general:[14–21]

$$S_C(T_C) = S_C(T_C = 0\,\text{K}) + \int_{0\,\text{K}}^{T_C} \frac{C}{T'_C} dT'_C = k_B \ln g_{C,0} + \int_{0\,\text{K}}^{T_C} \frac{C}{T'_C} dT'_C, \tag{5}$$

where k_B is Boltzmann's constant and $g_{C,0}$ is the degeneracy[14–21] of the ground energy level of the cold reservoir. Heat capacities *always* decrease with decreasing temperature at sufficiently low temperatures as $T_C = 0\,\text{K}$ is approached.[14–21] Hence the integral in Eq. (5) *always* converges — and hence $S_C(T_C)$ is *always* finite.[14–21] [Note: *Even if* C did *not* decrease with decreasing T_C but instead remained constant as $T_C = 0\,\text{K}$ is approached, the integral in Eq. (5) would diverge

only just barely, i.e., only logarithmically, and hence $S_C(T_C)$ would be only just barely, i.e., only logarithmically, infinite.]

B. Heat capacity of a cold reservoir $\propto T_C^n$

In many cases, the heat capacity C of a cold reservoir at very low temperatures is proportional to its temperature raised to a small positive power n,[22–27] i.e.,

$$C = \kappa m T_C^n \ (n > 0),\tag{6}$$

where κ is a constant whose dimensions are $l^2/(t^2 T^{n+1})$ ($l = $ length, $t = $ time, $T = $ temperature) and whose numerical value[22–27] depends on the nature[22–27] of the cold reservoir,[22–27] and where m is the mass of the cold reservoir.

Applying Eq. (6) to Eq. (5), if $C = \kappa m T_C^n \ (n > 0)$

$$
\begin{aligned}
S_C(T_C) &= k_B \ln g_{C,0} + \kappa m \int_{0\,\mathrm{K}}^{T_C} \frac{T_C'^n}{T_C'} dT_C' \\
&= k_B \ln g_{C,0} + \kappa m \int_{0\,\mathrm{K}}^{T_C} T_C'^{n-1} dT_C' \\
&= k_B \ln g_{C,0} + \frac{\kappa m T_C^n}{n} \ (n > 0).
\end{aligned}\tag{7}
$$

[If $n = 0$ the integral in Eq. (7) diverges (albeit only logarithmically), and if $n < 0$ it is negative — both *un*physical results.]

Here are some examples of heat capacities of the form $C = \kappa m T_C^n \ (n > 0)$ given by Eq. (6):[22–27] For a cold reservoir comprised of equilibrium blackbody radiation, or for one comprised of a crystalline solid (Debye model), $n = 3$. For a cold reservoir comprised of conduction electrons in metals, $n = 1$. For a cold reservoir comprised of a Bose-Einstein condensate, $n = 3/2$. (There is an $n = 3$ contribution to C due to lattice vibrations in conductive metals,[28,29] and also higher-order electronic contributions,[28–32] but as $T_C \to 0\,\mathrm{K}$ these contributions become negligible compared to the $n = 1$ electronic contribution.[28–32])

Assuming perfect, reversible operation of a Carnot[1–5] (or Stirling[6]) heat engine, if Eq. (6) applies for our cold reservoir, which is *initially* at $T_C = 0\,\mathrm{K}$, then applying Eq. (6) to the second line of Eq. (2) yields:

$$
\begin{aligned}
&\kappa m \int_{0\,\mathrm{K}}^{T_{C,\mathrm{final}}} \frac{T_C^n}{T_C} dT_C = \kappa m \int_{0\,\mathrm{K}}^{T_{C,\mathrm{final}}} T_C^{n-1} dT_C = \frac{Q_H}{T_H} \\
&\implies \frac{\kappa m T_{C,\mathrm{final}}^n}{n} = \frac{Q_H}{T_H} \\
&\implies T_{C,\mathrm{final}} = \left(\frac{n Q_H}{\kappa m T_H}\right)^{1/n}.
\end{aligned}\tag{8}
$$

Also, applying Eq. (6) to Eq. (3),

$$Q_C = \int_{0\,\mathrm{K}}^{T_{C,\mathrm{final}}} dQ_C = \kappa m \int_{0\,\mathrm{K}}^{T_{C,\mathrm{final}}} T_C^n dT_C = \frac{\kappa m T_{C,\mathrm{final}}^{n+1}}{n+1}.\tag{9}$$

Hence, by the First and Second Laws of Thermodynamics, applying Eq. (9) to Eq. (4):

$$W = Q_H - Q_C = Q_H - \frac{\kappa m T_{C,\text{final}}^{n+1}}{n+1}$$

$$\implies \epsilon_{\text{Carnot}} = \frac{W}{Q_H} = \frac{Q_H - \frac{\kappa m T_{C,\text{final}}^{n+1}}{n+1}}{Q_H} = 1 - \frac{\kappa m T_{C,\text{final}}^{n+1}}{(n+1)\,Q_H}. \tag{10}$$

Upon applying the second line of Eq. (8), Eq. (10) can be put into the alternative form

$$W = Q_H - Q_C = Q_H - T_{C,\text{final}} \left(\frac{\kappa m T_{C,\text{final}}^n}{n+1} \right)$$

$$= Q_H - T_{C,\text{final}} \left[\left(\frac{n}{n+1} \right) \frac{Q_H}{T_H} \right] = Q_H \left[1 - \left(\frac{n}{n+1} \right) \frac{T_{C,\text{final}}}{T_H} \right]$$

$$\implies \epsilon_{\text{Carnot}} = \frac{W}{Q_H} = 1 - \left(\frac{n}{n+1} \right) \frac{T_{C,\text{final}}}{T_H}. \tag{11}$$

And, upon applying the third line of Eq. (8), Eq. (10) can also be put into the alternative form

$$W = Q_H - Q_C = Q_H - \frac{\kappa m \left[\left(\frac{nQ_H}{\kappa m T_H} \right)^{1/n} \right]^{n+1}}{n+1} = Q_H - \frac{\kappa m \left(\frac{nQ_H}{\kappa m T_H} \right)^{1+\frac{1}{n}}}{n+1}$$

$$= Q_H - \frac{1}{(n+1)\,(\kappa m)^{1/n}} \left(\frac{nQ_H}{T_H} \right)^{1+\frac{1}{n}}$$

$$= Q_H \left\{ 1 - \frac{1}{n+1} \left(\frac{n}{T_H} \right)^{1+\frac{1}{n}} \left(\frac{Q_H}{\kappa m} \right)^{1/n} \right\}$$

$$\implies \epsilon_{\text{Carnot}} = \frac{W}{Q_H} = 1 - \frac{1}{n+1} \left(\frac{n}{T_H} \right)^{1+\frac{1}{n}} \left(\frac{Q_H}{\kappa m} \right)^{1/n}. \tag{12}$$

We can also express W and ϵ_{Carnot} in the form

$$W = Q_H \left(1 - \frac{\langle T_C \rangle}{T_H} \right)$$

$$\implies \epsilon_{\text{Carnot}} = \frac{W}{Q_H} = 1 - \frac{\langle T_C \rangle}{T_H}, \tag{13}$$

where $\langle T_C \rangle$ is the average temperature of the cold reservoir during the operation of the (perfect, reversible) Carnot[1–5] (or Stirling[6]) heat engine as T_C increases from $T_{C,\text{initial}} = 0\,\text{K}$ to $T_{C,\text{final}} > 0\,\text{K}$. (We denote average values via enclosure within angular brackets.) Upon comparing the last two lines of Eq. (11) with Eq. (13), if C is given by Eq. (6) we obtain

$$\langle T_C \rangle = \frac{n}{n+1} T_{C,\text{final}}. \tag{14}$$

C. The extreme low-temperature limit: The Einstein and two-state models

If $T_{C,\text{final}}$ is extremely low, then only the ground state and first excited state of the atoms comprising the cold reservoir need to be considered. Let $\Delta E_{0\to1}$ be the energy gap between the ground state and first excited state of each of these atoms. This low-temperature-limit heat capacity of the Einstein model[33–35] and of the two-state model[36] (which is the same for both models if one sets $h\nu = \Delta E_{0\to1}$ where ν is the vibration frequency of atoms comprising a crystal as per the Einstein model) is then a more physically correct representation than a heat capacity $\propto T_C^n$ ($n > 0$). It is[33–36]

$$C_{\text{E2S},T_C\to0\,\text{K}} = 3Nk_B \left(\frac{\Delta E_{0\to1}}{k_B T_C}\right)^2 e^{-\Delta E_{0\to1}/k_B T_C} = \frac{3N}{k_B}\left(\frac{\Delta E_{0\to1}}{T_C}\right)^2 e^{-\Delta E_{0\to1}/k_B T_C}, \qquad (15)$$

where N is the number of atoms comprising the cold reservoir (the factor of 3 accounting for the 3 translational degrees of freedom per atom owing to space being 3-dimensional). If Eq. (15) applies for our cold reservoir, which is *initially* at $T_{C,\text{initial}} = 0\,\text{K}$, then applying Eq. (15) to the second line of Eq. (2) yields:[37]

$$\frac{3N(\Delta E_{0\to1})^2}{k_B}\int_{0\,\text{K}}^{T_{C,\text{final}}} \frac{e^{-\Delta E_{0\to1}/k_B T_C}}{T_C^3}\,dT_C = \frac{Q_H}{T_H}$$

$$\Longrightarrow \int_{0\,\text{K}}^{T_{C,\text{final}}} \frac{e^{-\Delta E_{0\to1}/k_B T_C}}{T_C^3}\,dT_C = \frac{k_B}{3N(\Delta E_{0\to1})^2}\frac{Q_H}{T_H}$$

$$\Longrightarrow \left.\frac{\left(\frac{\Delta E_{0\to1}}{k_B} + T_C\right)e^{-\Delta E_{0\to1}/k_B T_C}}{\left(\frac{\Delta E_{0\to1}}{k_B}\right)^2 T_C}\right|_{0\,\text{K}}^{T_{C,\text{final}}} = \frac{k_B}{3N(\Delta E_{0\to1})^2}\frac{Q_H}{T_H}$$

$$\Longrightarrow \left.\frac{\left(\frac{\Delta E_{0\to1}}{k_B} + T_C\right)e^{-\Delta E_{0\to1}/k_B T_C}}{T_C}\right|_{0\,\text{K}}^{T_{C,\text{final}}} = \frac{Q_H}{3Nk_B T_H}$$

$$\Longrightarrow \frac{\left(\frac{\Delta E_{0\to1}}{k_B} + T_{C,\text{final}}\right)e^{-\Delta E_{0\to1}/k_B T_{C,\text{final}}}}{T_{C,\text{final}}} = \frac{Q_H}{3Nk_B T_H}$$

$$\Longrightarrow \frac{e^{-\Delta E_{0\to1}/k_B T_{C,\text{final}}}}{T_{C,\text{final}}} = \frac{Q_H}{3NT_H\Delta E_{0\to1}} \quad \text{if } T_{C,\text{final}} \ll \frac{\Delta E_{0\to1}}{k_B}. \qquad (16)$$

The evaluation of the integral in Eq. (16) is courtesy of the Online Integral Calculator at https://www.mathworld.wolfram.com.[37] [The integral in Eq. (16) is finite because, in the limit $T_C \to 0\,\text{K}$, $e^{-\Delta E_{0\to1}/k_B T_C} \to 0$ faster — indeed much faster — than $T_C^3 \to 0\,\text{K}^3$.] Unfortunately, even the simplified result in the last line of Eq. (16) in the limiting case $T_{C,\text{final}} \ll \frac{\Delta E_{0\to1}}{k_B}$, let alone the more general result in the second-to-last line thereof, cannot be solved analytically for $T_{C,\text{final}}$, but must be solved numerically. This is in contrast with Section IIB, wherein $T_{C,\text{final}}$ was derived analytically. Hence, results for Q_C, W, ϵ_{Carnot}, and $\langle T_C\rangle$, which were derived analytically in Section IIB, also would only be obtainable numerically in this Section IIC. Since these numerical calculations can be tedious but would reveal no new concepts, we omit them.

D. The utmost low-temperature limit: Only one quantum of waste heat rejected into the cold reservoir

Now consider the utmost low-temperature limit: only *one quantum* of waste heat being rejected into a cold reservoir, which is *initially* at absolute zero ($T_{C,\text{initial}} = 0\,\text{K}$). In this case we clearly need consider only the ground energy level and the first excited energy level of the *entire* cold reservoir. In this case, $\Delta E_{0\to 1}$, the energy gap between the ground state and first excited state of each of the atoms comprising the cold reservoir, also equals the energy gap between the ground energy level and first excited energy level of the *entire* cold reservoir. Thus

$$Q_C = \Delta E_{0\to 1}. \tag{17}$$

Let the cold reservoir be comprised of N atoms. Then the degeneracy of the first excited energy level of the cold reservoir is $g_{C,1} = N$, because there are N ways to put one quantum of energy among N atoms. (The degeneracy $g_{C,0}$ of the ground energy level, whether it equals or exceeds unity,[14–21] doesn't matter, because it is not changed when one quantum of waste heat is rejected into the cold reservoir.)

Corresponding to one quantum of waste heat $Q_C = \Delta E_{0\to 1}$ being rejected into the cold reservoir

$$\Delta S_C = k_B \ln g_{C,1}. \tag{18}$$

Applying Eq. (18) to the second line of Eq. (2) yields

$$k_B \ln g_{C,1} = \frac{Q_H}{T_H} \implies Q_H = k_B T_H \ln g_{C,1}. \tag{19}$$

Hence, by the First and Second Laws of Thermodynamics, applying Eqs. (17) and (19) to Eq. (4):

$$W = Q_H - Q_C = Q_H - \Delta E_{0\to 1} = k_B T_H \ln g_{C,1} - \Delta E_{0\to 1}$$
$$\implies \epsilon_{\text{Carnot}} = \frac{W}{Q_H} = \frac{k_B T_H \ln g_{C,1} - \Delta E_{0\to 1}}{k_B T_H \ln g_{C,1}} = 1 - \frac{\Delta E_{0\to 1}}{k_B T_H \ln g_{C,1}}. \tag{20}$$

Since after rejection of one quantum of waste heat into it, the cold reservoir has a fixed energy $\Delta E_{0\to 1}$ above the ground energy level rather than a Boltzmann distribution of energies, it doesn't have a well-defined temperature T_C (see Section IIIF2a). (The hot reservoir, of course, still has the well-defined temperature T_H.) If nevertheless we wish to express W and ϵ_{Carnot} in the same form as Eq. (13), we can construe an effective average temperature $\langle T_{C,\text{eff}} \rangle$ (but see Section IIIF2a) during the rejection of one quantum of waste heat into the cold reservoir. Comparing Eq. (20) with Eq. (13), in the utmost-low-temperature limit we obtain

$$\langle T_{C,\text{eff}} \rangle = \frac{\Delta E_{0\to 1}}{k_B \ln g_{C,1}}. \tag{21}$$

It might seem that there should be an extra numerical factor greater than unity in the denominator of Eq. (21), i.e., that the right-hand side of Eq. (21) represents $T_{C,\text{eff,final}}$ rather than $\langle T_{C,\text{eff}} \rangle$. But, again, since after rejection of one quantum of waste heat into it, the cold reservoir has a fixed energy $\Delta E_{0\to 1}$ above the ground energy level rather than a Boltzmann distribution of energies, it doesn't have a well-defined temperature T_C (see Section IIIF2a): the effective average temperature $\langle T_{C,\text{eff}} \rangle$ does *not* connote a well-defined temperature.

III. IS A COLD RESERVOIR AT $T_C = 0\,\mathrm{K}$ POSSIBLE OR IMPOSSIBLE?

A. The unattainability formulation of the Third Law of Thermodynamics

Various formulations of the Third Law of Thermodynamics have been investigated in both the classical and quantum regimes.[8,38–51] (We note that Refs. 38–51 are a limited number of samples from a vast literature. But, hopefully, they are representative samples.) Our main focus is on the unattainability formulation of the Third Law of Thermodynamics.[38,39,41] The unattainability formulation of the Third Law of Thermodynamics states that it is impossible to cool any system to absolute zero ($0\,\mathrm{K}$) via any adiabatic process or via any finite sequence of adiabatic processes, because no adiabat beginning at $T_{C,\mathrm{initial}} > 0\,\mathrm{K}$ can reach $T_{C,\mathrm{final}} = 0\,\mathrm{K}$.[38,39,41] Hence no adiabatic process or finite sequence of adiabatic processes beginning at $T_{C,\mathrm{initial}} > 0\,\mathrm{K}$ can reach $T_{C,\mathrm{final}} = 0\,\mathrm{K}$.[38,39,41]

But it has been conjectured that, *even though* an *infinite sequence* of adiabatic processes would be required to reach absolute zero ($T_C = 0\,\mathrm{K}$), it could still be done in a *finite time*.[44]

Moreover, it should be emphasized that the unattainability formulation of the Third Law of Thermodynamics does *not* go as far as stating that it is impossible to cool a system to absolute zero via *any process whatsoever*.[52,53] It states *only* that this is impossible via *adiabatic* cooling. Indeed, a quantum-mechanical refrigeration method of attaining absolute zero *experimentally* has been investigated.[50]

In this Section III, we will investigate the possibility of attaining absolute zero *in principle* (even if only in thought experiments[7]), rather than in practice, via Carnot/Stirling refrigeration, absorption refrigeration, and stimulated-emission refrigeration. Our investigations of Carnot/Stirling and absorption refrigeration will be strictly within the classical regime, with no quantum-mechanical considerations (except for brief remarks in the last paragraph of Section IIIF1). Of course, stimulated emission is a quantum-mechanical process. (Quantum refrigeration is investigated — in depth — in Refs. 47–50.) We will then consider caveats, including heat leakage from ambient, energy/temperature fluctuations, and the possibility of a system spontaneously attaining absolute zero ($0\,\mathrm{K}$) via fluctuation.

B. Carnot/Stirling refrigeration

We should note that it is impossible to cool any (finite) system to absolute zero via any adiabatic process or finite sequence of adiabatic processes *not* because an infinite (or even an extraordinarily large finite) amount of work would be required to do so. It is indeed true that "it requires huge amounts of work to extract even trivially small amounts of heat from a system near $T_C = 0\,\mathrm{K}$"[54,55]. But owing to the rapid decrease with decreasing temperature T_C of the heat capacity C of any system as $T_C = 0\,\mathrm{K}$ is approached, *less than* — most typically *much less than* — trivially small amounts of heat would need to be extracted to cool any system to $T_C = 0\,\mathrm{K}$. Hence *less than* — most typically *much less than* — huge amounts of work would be required. If there is available a reservoir at temperature $T_{C,\mathrm{initial}}$ for this specific purpose, the work required from a (perfect, reversible) Carnot[1–5,56–58] refrigerator to cool a system from an initial temperature $T_{C,\mathrm{initial}} > 0\,\mathrm{K}$

to $T_C = 0\,\mathrm{K}$ is[1-5,56-58]

$$dW = \frac{T_{C,\text{initial}} - T_C}{T_C} dQ_C = \left(\frac{T_{C,\text{initial}}}{T_C} - 1\right) dQ_C = C\left(\frac{T_{C,\text{initial}}}{T_C} - 1\right) dT_C$$

$$\implies W = \int_{0\,\mathrm{K}}^{T_{C,\text{initial}}} C\left(\frac{T_{C,\text{initial}}}{T_C} - 1\right) dT_C$$

$$= T_{C,\text{initial}} \int_{0\,\mathrm{K}}^{T_{C,\text{initial}}} \frac{C}{T_C} dT_C - \int_{0\,\mathrm{K}}^{T_{C,\text{initial}}} C\, dT_C$$

$$= T_{C,\text{initial}} \int_{0\,\mathrm{K}}^{T_{C,\text{initial}}} \frac{C}{T_C} dT_C - Q_C. \tag{22}$$

This reservoir at $T_{C,\text{initial}}$ is *not* to be confused with the hot reservoir at temperature T_H for a Carnot heat engine as discussed in Section II: ideally, $T_{C,\text{initial}} \ll T_H$. [The result of Eq. (22) is matched by refrigeration via a reversed Stirling cycle.[6]]

Because C *always* decreases with decreasing temperature at sufficiently low temperatures as $T_C = 0\,\mathrm{K}$ is approached, the first integral in the third line of Eq. (22) (which is repeated in the fourth line thereof), like the integral in Eq. (5), *always* converges — and hence W is *always* finite. Furthermore the second integral in the third line of Eq. (22) is *subtracted* from the first integral therein, thereby *decreasing* the already finite contribution to W from the first integral. The second integral in the third line of Eq. (22) is by the fourth line thereof is simply Q_C, the total heat extracted from the cold reservoir. It is in all cases not only finite, but smaller than the first integral in the third line of Eq. (22), because $T_C < T_{C,\text{initial}}$ throughout the range of integration of the first integral except at the upper limit. [Note that *even if* C did *not* decrease with decreasing T_C but instead remained constant as $T_C = 0\,\mathrm{K}$ is approached, the first integral in the third line of Eq. (22) (which is repeated in the fourth line thereof) would diverge only just barely, i.e., only logarithmically, and hence W would be only just barely, i.e., only logarithmically, infinite.]

The coefficient of performance of this Carnot refrigeration[1-5,56-58] (which is matched by refrigeration via a reversed Stirling cycle[6]),

$$\mathrm{COP}_{\text{Carnot}} = \frac{dQ_C}{dW} = \frac{C\, dT_C}{dW} = \frac{T_C}{T_{C,\text{initial}} - T_C}$$

$$\rightarrow \frac{T_C}{T_{C,\text{initial}}} \text{ in the limit } T_C \rightarrow 0\,\mathrm{K}, \tag{23}$$

decreases with decreasing T_C. But the heat capacity C of a cold reservoir decreases *faster*, typically *much faster*, with decreasing T_C. Hence the total integrated work W required for cooling a cold reservoir from $T_{C,\text{initial}} > 0\,\mathrm{K}$ to $T_C = 0\,\mathrm{K}$ as per Eq. (22) is *finite*, and typically of *small* amount.

Perhaps at this point it is worthwhile to re-emphasize that $T_{C,\text{initial}}$ for Carnot[1-5,56-58]/Stirling[6] refrigeration should *not* be confused with T_H for Carnot[1-5]/Stirling[6] heat-engine operation: ϵ_{Carnot} for Carnot[1-5,]/Stirling[6] heat-engine operation is maximized if T_H is *maximized*, but $\mathrm{COP}_{\text{Carnot}}$ for Carnot[1-5,56-58]/Stirling[6] refrigeration is maximized if $T_{C,\text{initial}}$ is *minimized*.

For example, if C is given by Eq. (6), i.e., if $C = \kappa m T_C^n$ $(n > 0)$ then, assuming perfect

(reversible) operation and applying Eq. (22), we obtain this *finite* result for W:

$$W = \kappa m \left(T_{C,\text{initial}} \int_{0\,\text{K}}^{T_{C,\text{initial}}} \frac{T_C^n}{T_C} dT_C - \int_{0\,\text{K}}^{T_{C,\text{initial}}} T_C^n dT_C \right)$$

$$= \kappa m \left(T_{C,\text{initial}} \int_{0\,\text{K}}^{T_{C,\text{initial}}} T_C^{n-1} dT_C - \int_{0\,\text{K}}^{T_{C,\text{initial}}} T_C^n dT_C \right)$$

$$= \kappa m \left(T_{C,\text{initial}} \frac{T_{C,\text{initial}}^n}{n} - \frac{T_{C,\text{initial}}^{n+1}}{n+1} \right)$$

$$= \kappa m T_{C,\text{initial}}^{n+1} \left(\frac{1}{n} - \frac{1}{n+1} \right)$$

$$= \frac{\kappa m T_{C,\text{initial}}^{n+1}}{n(n+1)} \ (n > 0). \tag{24}$$

[Note that *even if* C did *not* decrease with decreasing T_C but instead remained constant as $T_C = 0\,\text{K}$ is approached, e.g., if $n = 0$ in Eq. (24), the first integrals in the first two lines of Eq. (24), being a special case of the first integral in the third line of Eq. (22), would diverge only just barely, i.e., only logarithmically, and hence W would be only just barely, i.e., only logarithmically, infinite.]

Thus the unattainability formulation of the Third Law of Thermodynamics does *not* forbid the attainment of absolute zero ($T_C = 0\,\text{K}$) via Carnot[1–5,56–58]/Stirling[6] refrigeration because it would cost an infinite (or even an extraordinarily large finite) amount of work W to do so, but because the inability of any adiabat beginning at $T_{C,\text{initial}} > 0\,\text{K}$ to reach $T_{C,\text{final}} = 0\,\text{K}$ precludes the performance of the required *finite* (typically *small*) amount of work.

Hence, if the Third Law of Thermodynamics — specifically, the unattainability formulation thereof — forbids cooling to absolute zero via Carnot[1–5,56–58]/Stirling[6] refrigeration, it can*not* be because this would cost an infinite (or even an extraordinarily large finite) amount of work W: It must be for *other* reason(s).

But we considered *only* the work W required for extracting heat Q_C from a cold reservoir. This is the ideal or perfect case, assuming perfect insulation, i.e., with no leakage of heat whatsoever from ambient into the cold reservoir. We did not consider leakage of heat from ambient into the cold reservoir. Also, we did not consider the effects of fluctuations on the possibility or impossibility of attaining absolute zero. These issues will be discussed in Sections IIIE, IIIF, and IIIG, with our reasoning explained in Sections IIIF and IIIG.

C. Absorption refrigeration

Absorption refrigeration[59] is powered by heat rather than by work.[59] Heat input Q_H from a heat source or from a hot reservoir at fixed temperature T_H drives heat extraction Q_C from a cold reservoir at temperature T_C, with both Q_C and Q_H, summing to Q_I, being expelled at a fixed intermediate temperature T_I.[59] Of course, T_C is not fixed but decreases as refrigeration proceeds, until T_C is reduced to its lowest possible value. But can this lowest possible value be absolute zero ($T_C = 0\,\text{K}$), even in principle?

By the First Law of Thermodynamics

$$Q_I = Q_C + Q_H. \tag{25}$$

By the Second Law of Thermodynamics, assuming perfect (reversible) operation:

$$\Delta S_{\text{total}} = \Delta S_I + \Delta S_C + \Delta S_H = \frac{Q_I}{T_I} - \frac{Q_C}{T_C} - \frac{Q_H}{T_H} = 0$$

$$\implies \frac{Q_I}{T_I} = \frac{Q_C}{T_C} + \frac{Q_H}{T_H}$$

$$\implies Q_I = T_I \left(\frac{Q_C}{T_C} + \frac{Q_H}{T_H} \right) = \frac{T_I}{T_C} Q_C + \frac{T_I}{T_H} Q_H. \tag{26}$$

The right-hand terms of Eq. (25) and of the last line of Eq. (26) are both equal to Q_I and hence are also equal to each other. Thus, assuming perfect (reversible) operation:

$$Q_C + Q_H = \frac{T_I}{T_C} Q_C + \frac{T_I}{T_H} Q_H$$

$$\implies Q_H \left(1 - \frac{T_I}{T_H} \right) = Q_C \left(\frac{T_I}{T_C} - 1 \right)$$

$$\implies Q_H = Q_C \frac{\frac{T_I}{T_C} - 1}{1 - \frac{T_I}{T_H}} = Q_C \frac{\frac{T_I - T_C}{T_C}}{\frac{T_H - T_I}{T_H}} = Q_C \frac{T_H (T_I - T_C)}{T_C (T_H - T_I)}$$

$$= Q_C \frac{T_H T_I}{T_C (T_H - T_I)} - Q_C \frac{T_H}{T_H - T_I}$$

$$= Q_C \frac{T_H}{T_H - T_I} \left(\frac{T_I}{T_C} - 1 \right). \tag{27}$$

Hence, assuming perfect (reversible) operation, the heat input from a heat source or from a hot reservoir at fixed temperature T_H required to cool the cold reservoir from an initial temperature $T_{C,\text{initial}} > 0\,\text{K}$ to absolute zero ($T_C = 0\,\text{K}$) is

$$dQ_H = \frac{T_H}{T_H - T_I} \left(\frac{T_I}{T_C} - 1 \right) dQ_C$$

$$\implies Q_H = \frac{T_H}{T_H - T_I} \int_{0\,\text{K}}^{T_{C,\text{initial}}} \left(\frac{T_I}{T_C} - 1 \right) dQ_C$$

$$= \frac{T_H}{T_H - T_I} \int_{0\,\text{K}}^{T_{C,\text{initial}}} \left(\frac{T_I}{T_C} - 1 \right) C dT_C$$

$$= \frac{T_H}{T_H - T_I} \left(T_I \int_{0\,\text{K}}^{T_{C,\text{initial}}} \frac{C}{T_C} dT_C - \int_{0\,\text{K}}^{T_{C,\text{initial}}} C dT_C \right)$$

$$= \frac{T_H}{T_H - T_I} \left[\left(T_I \int_{0\,\text{K}}^{T_{C,\text{initial}}} \frac{C}{T_C} dT_C \right) - Q_C \right]. \tag{28}$$

Note that, with the substitutions $W \to Q_H$ and $T_{C,\text{initial}} \to T_I$, the form of Eq. (28) is, except for the prefactor $\frac{T_H}{T_H - T_I}$, identical to that of Eq. (22). Hence exactly the same reasoning applies: Because C *always* decreases with decreasing temperature at sufficiently low temperatures as $T_C = 0\,\text{K}$ is approached, the first integral in the fourth line of Eq. (28) (which is repeated in the fifth line thereof) *always* converges — and hence Q_H is *always* finite. Furthermore the second integral in the fourth line of Eq. (28) is *subtracted* from the first integral therein, thereby *decreasing* the

already finite contribution to Q_H from the first integral. The second integral in the fourth line of Eq. (28) is by the fifth line thereof is simply Q_C, the total heat extracted from the cold reservoir. It is in all cases not only finite, but smaller than the first integral in the fourth line of Eq. (28) because (i) $T_C < T_{C,\text{initial}}$ throughout the range of integration of the first integral except at the upper limit and (ii) the first integral is multiplied by the prefactor $T_I > T_{C,\text{initial}}$ (for absorption refrigeration to operate $T_I > T_C$ must *always* obtain in general, and, in particular, $T_I > T_{C,\text{initial}}$ must obtain). [Note that *even if* C did *not* decrease with decreasing T_C but instead remained constant as $T_C = 0\,\text{K}$ is approached, the first integral in the fourth line of Eq. (28) (which is repeated in the fifth line thereof) would diverge only just barely, i.e., only logarithmically, and hence Q_H would be only just barely, i.e., only logarithmically, infinite.]

Comparing Eq. (28) with Eq. (22):

$$\frac{Q_H}{W} = \frac{T_H}{T_H - T_I} \frac{T_I \int_{0\,\text{K}}^{T_{C,\text{initial}}} \frac{C}{T_C} dT_C - \int_{0\,\text{K}}^{T_{C,\text{initial}}} C dT_C}{T_{C,\text{initial}} \int_{0\,\text{K}}^{T_{C,\text{initial}}} \frac{C}{T_C} dT_C - \int_{0\,\text{K}}^{T_{C,\text{initial}}} C dT_C}$$

$$> 1. \tag{29}$$

The inequality in the second line of Eq. (29) obtains because (i) for absorption refrigeration to operate $T_I > T_C$ must *always* obtain (in particular, $T_I > T_{C,\text{initial}}$ must obtain) and (ii) $\frac{T_H}{T_H - T_I} > 1$. Thus we conclude that more energy as heat Q_H is required to attain $T_C = 0\,\text{K}$ via absorption refrigeration[59] than as work W via Carnot[1-5,56-58]/Stirling[6] refrigeration. But, still, the total integrated heat Q_H from a heat source or from a hot reservoir required for cooling the cold reservoir from $T_{C,\text{initial}} > 0\,\text{K}$ to $T_{C,\text{final}} = 0\,\text{K}$ as per Eq. (28) is *finite*, and typically of *small* amount [larger, but only *finitely* larger, in amount than W as per Eq. (22)]. Moreover, energy to be supplied as heat is of lower quality, and therefore thermodynamically cheaper per unit quantity, than energy to be supplied as work.

Applying Eq. (27), for given T_C and given T_H, the coefficient of performance for absorption refrigeration is[59]

$$\text{COP}_{\text{abs}} = \frac{dQ_C}{dQ_H} = \frac{C dT_C}{dQ_H} = \frac{\frac{T_H - T_I}{T_H}}{\frac{T_I}{T_C} - 1}$$

$$= \frac{\frac{T_H - T_I}{T_H}}{\frac{T_I - T_C}{T_C}} = \frac{T_C}{T_I - T_C} \frac{T_H - T_I}{T_H}$$

$$= \frac{T_C}{T_I - T_C} \left(1 - \frac{T_I}{T_H}\right)$$

$$\to \frac{T_C}{T_I} \left(1 - \frac{T_I}{T_H}\right) \text{ in the limit } T_C \to 0\,\text{K}. \tag{30}$$

Comparing Eq. (30) with Eq. (23):

$$\frac{\text{COP}_{\text{abs}}}{\text{COP}_{\text{Carnot}}} = \frac{\frac{T_C}{T_I - T_C} \left(1 - \frac{T_I}{T_H}\right)}{\frac{T_C}{T_{C,\text{initial}} - T_C}} = \frac{T_{C,\text{initial}} - T_C}{T_I - T_C} \left(1 - \frac{T_I}{T_H}\right)$$

$$= \frac{T_{C,\text{initial}}}{T_I} \left(1 - \frac{T_I}{T_H}\right) \text{ in the limit } T_C \to 0\,\text{K}$$

$$< 1. \tag{31}$$

The inequality in the third line of Eq. (31) obtains because for absorption refrigeration to operate $T_C < T_I < T_H$ must *always* obtain (in particular, $T_{C,\text{initial}} < T_I < T_H$ must obtain). This further confirms our conclusion that more — but only *finitely* more — lower-quality energy as heat Q_H is required to attain $T_C = 0\,\text{K}$ via absorption refrigeration[59] than higher-quality energy as work W via Carnot[1-5,56-58]/Stirling[6] refrigeration.

In this regard, recall (as per the first four paragraphs, especially the third and fourth paragraphs, of Section IIIB) that $\text{COP}_{\text{Carnot}}$ for Carnot[1-5,56-58]/Stirling[6] refrigeration is maximized by minimizing $T_{C,\text{initial}}$. But, by contrast, COP_{abs} is *in*dependent of $T_{C,\text{initial}}$ and hence can*not* be maximized by minimizing $T_{C,\text{initial}}$.

For example, if C is given by Eq. (6), i.e., if $C = \kappa m T_C^n$ ($n > 0$), then, assuming perfect (reversible) operation and applying Eq. (28), we obtain this *finite* result for Q_H:

$$
\begin{aligned}
Q_H &= \kappa m \frac{T_H}{T_H - T_I} \left(T_I \int_{0\,\text{K}}^{T_{C,\text{initial}}} \frac{T_C^n}{T_C} dT_C - \int_{0\,\text{K}}^{T_{C,\text{initial}}} T_C^n dT_C \right) \\
&= \kappa m \frac{T_H}{T_H - T_I} \left(T_I \int_{0\,\text{K}}^{T_{C,\text{initial}}} T_C^{n-1} dT_C - \int_{0\,\text{K}}^{T_{C,\text{initial}}} T_C^n dT_C \right) \\
&= \kappa m \frac{T_H}{T_H - T_I} \left(T_I \frac{T_{C,\text{initial}}^n}{n} - \frac{T_{C,\text{initial}}^{n+1}}{n+1} \right) \\
&= \kappa m \frac{T_H T_{C,\text{initial}}^n}{T_H - T_I} \left(\frac{T_I}{n} - \frac{T_{C,\text{initial}}}{n+1} \right) \quad (n > 0).
\end{aligned}
\tag{32}
$$

[Note that Q_H as per Eq. (32) is always positive, because $T_H > T_I > T_{C,\text{initial}}$ and $n < n + 1$.] Comparing Eq. (32) with Eq. (24):

$$
\begin{aligned}
\frac{Q_H}{W} &= \frac{\kappa m \frac{T_H T_{C,\text{initial}}^n}{T_H - T_I} \left(\frac{T_I}{n} - \frac{T_{C,\text{initial}}}{n+1} \right)}{\frac{\kappa m T_{C,\text{initial}}^{n+1}}{n(n+1)}} \\
&= \frac{n(n+1) T_H}{T_{C,\text{initial}} (T_H - T_I)} \left(\frac{T_I}{n} - \frac{T_{C,\text{initial}}}{n+1} \right) \\
&= \frac{n(n+1) T_H}{T_{C,\text{initial}} (T_H - T_I)} \frac{(n+1) T_I - n T_{C,\text{initial}}}{n(n+1)} \\
&= \frac{T_H [(n+1) T_I - n T_{C,\text{initial}}]}{T_{C,\text{initial}} (T_H - T_I)} \\
&= \frac{T_H}{T_H - T_I} \frac{(n+1) T_I - n T_{C,\text{initial}}}{T_{C,\text{initial}}} \\
&= \frac{T_H}{T_H - T_I} \left[(n+1) \frac{T_I}{T_{C,\text{initial}}} - n \right] \\
&> 1.
\end{aligned}
\tag{33}
$$

The inequality in the last line of Eq. (33) obtains because: (i) $\frac{T_H}{T_H - T_I} > 1$, (ii) for absorption refrigeration to operate $T_I > T_C$ must *always* obtain (in particular, $T_I > T_{C,\text{initial}}$ must obtain), and (iii) $n + 1 > n$.

Hence, our results as per Eqs. (32) and (33) of the special case wherein C is given by Eq. (6), i.e., wherein $C = \kappa m T_C^n$ ($n > 0$), confirm our general results as per Eqs. (25)–(31) that more — but only *finitely* more — lower-quality energy as heat Q_H is required to attain $T_C = 0\,\mathrm{K}$ via absorption refrigeration[59] than higher-quality energy as work W via Carnot[1–5,56–58]/Stirling[6] refrigeration.

The inequalities in Eqs. (29), (31), and (33) are unfavorable for absorption refrigeration insofar as more energy as heat Q_H being required to attain $T_C = 0\,\mathrm{K}$ via absorption refrigeration[59] than as work W via Carnot[1–5,56–58]/Stirling[6] refrigeration. Yet we re-emphasize that: (i) as per Eqs. (28) and (32) the heat Q_H required to attain $T_C = 0\,\mathrm{K}$ via absorption refrigeration[59] is nonetheless *finite*, and typically of *small* amount [larger, but only *finitely* larger, than W as per Eqs. (22) and (24), respectively] and (ii) energy to be supplied as heat is of lower quality, and therefore thermodynamically cheaper per unit quantity, than energy to be supplied as work.

Also, we should mention this important *qualitative* — as opposed to merely quantitative — difference between Carnot[1–5,56–58]/Stirling[6] refrigeration and absorption refrigeration:[59] Carnot[1–5,56–58]/Stirling[6] refrigeration relies on *adiabatic* processes, but absorption refrigeration[59] does *not*. Adiabatic processes entail energy transfer *via work only* — but in absorption refrigeration all energy transfers are *via heat only*.[59] Thus at least *prima facie*, might the unattainability formulation of the Third Law of Thermodynamics, which forbids cooling any system to absolute zero via *adiabatic* processes[38,39,41] — but not necessarily via *any process whatsoever*[52,53] — be circumvented *in principle* via absorption refrigeration, despite the unfavorable inequalities in Eqs. (29), (31), and (33)? The immediately preceding question emphasizes *in principle* (even if only as a thought experiment[7]), rather than in practice.

Hence, if the Third Law of Thermodynamics forbids cooling to absolute zero via absorption refrigeration, it can*not* be because (i) an adiabat beginning at $T_{C,\mathrm{initial}} > 0\,\mathrm{K}$ cannot reach $T_C = 0\,\mathrm{K}$ or (ii) it would cost an infinite (or even an extraordinarily large finite) amount of heat Q_H from a heat source or from a hot reservoir: It must be for *other* reason(s).

But we considered *only* the heat Q_H from a heat source or from a hot reservoir required for extracting heat Q_C from a cold reservoir. This is the ideal or perfect case, assuming perfect insulation, i.e., with no leakage of heat whatsoever from ambient into the cold reservoir. We did not consider leakage of heat from ambient into the cold reservoir. Also, we did not consider the effects of fluctuations on the possibility or impossibility of attaining absolute zero. These issues will be discussed in Sections IIIE, IIIF, and IIIG, with our reasoning explained in Sections IIIF and IIIG.

D. Stimulated-emission refrigeration

Consider the following process, even if it is feasible only in principle (even if only as a thought experiment,[7]), rather than in practice. Let a system be comprised of N identical atoms. Let each of the N atoms comprising this system be pumped into a given excited state x of energy $\Delta E_{0 \to x}$ above its ground state energy E_0. This costs energy $N\Delta E_{0 \to x}/\mathcal{E}$, where $\mathcal{E}$ is the energy efficiency of the pumping. (Given perfection, i.e., $\mathcal{E} = 1$, the energy cost is $N\Delta E_{0 \to x}$.) Let these N atoms be put into their ground states with 100% probability by stimulated emission[60] via employing very strongly *non*equilibrium electromagnetic radiation, e.g., as in a laser. Some stimulated emission[60] from this given excited state x to the ground state will also be effected by the background equilibrium blackbody radiation corresponding to the ambient temperature, $T_{\mathrm{ambient}} > 0\,\mathrm{K}$. (Of course, preferably T_{ambient} should be as low as possible. We note that the cosmic background radiation of outer space is an ambient thermal environment at $T_{\mathrm{ambient}} = 2.7\,\mathrm{K}$.) The probability that this

*non*equilibrium electromagnetic radiation, and for all practical purposes if $\Delta E_{0\to x} \gg kT_{\text{ambient}}$ also the background equilibrium blackbody radiation, will stimulate absorption rather than emission

from this given excited state x to a higher excited state y is 0% if there is no higher excited state y of energy $\Delta E_{x\to y} \le \Delta E_{0\to x}$ above this given excited state x. Let $\Delta E_{0\to 1}$ be the energy gap between an atom's ground state and its *first* excited state. If say, $\Delta E_{0\to 1} \gtrsim 1000 k_B T_{\text{ambient}}$, then the probability that the background equilibrium blackbody radiation corresponding to $T_{\text{ambient}} > 0\,\text{K}$ will stimulate absorption from the ground state to even the *first* excited state during the brief time interval required for stimulated emission is for all practical purposes 0%. For then the probability that any one given atom can be boosted from its ground state to even its *first* excited state by the background equilibrium blackbody radiation corresponding to $T_{\text{ambient}} > 0\,\text{K}$ is $\lesssim e^{-1000}$, i.e., $\lesssim 10^{-430}$. Hence the probability that *any* of the N atoms comprising our system can be boosted from its ground state to even its *first* excited state by the background equilibrium blackbody radiation corresponding to $T_{\text{ambient}} > 0\,\text{K}$ is $\lesssim N e^{-1000}$, i.e., $\lesssim N \times 10^{-430}$. But typical laboratory systems contain only $\approx 10^{22}$ to $\approx 10^{28}$ atoms. Indeed, there are only $\approx 10^{79}$ atoms in the entire observable Universe[61–63] (not counting the unobservable rest of the Multiverse beyond)![61–63] Thus, at least initially upon their preparation, for all practical purposes we can be 100% sure that 100% of the N atoms comprising our system will be in their ground states with 100% probability, and hence that this system of atoms will be at absolute zero with 100% probability.

Since stimulated emission is an essentially instantaneous process, there is essentially no time *during* stimulated emission that puts the atoms comprising our system into their ground states for heat leakage from ambient, as there is during Carnot[1–5,56–58]/Stirling[6] and absorption[59] refrigeration. Of course, if our system is in an ambient environment at temperature at $T_{\text{ambient}} > 0\,\text{K}$, *after* being put into their ground states by stimulated emission the atoms comprising it will thermalize. And after they thermalize, the probability that they are all in their ground states will be less than 100%, and hence this system of atoms will no longer be at absolute zero. But what about *before* these atoms have time to thermalize? *Immediately* upon these atoms being put into their ground states with 100% probability by stimulated emission, at least *prima facie* it seems that such a system of atoms would indeed be in its ground state, and hence at absolute zero, even if only for an instant (and hence, via repetition of the process, for any arbitrary number of instants). (This also seems to be true concerning the method of refrigeration investigated in Ref. 50.)

Note that, like absorption refrigeration discussed in Section IIIC, stimulated-emission refrigeration is *not* an adiabatic process. Thus at least *prima facie*, might the unattainability formulation of the Third Law of Thermodynamics, which forbids cooling any system to absolute zero ($0\,\text{K}$) via *adiabatic* processes[38,39,41] — but not necessarily via *any process whatsoever*[52,53] — be circumvented *in principle* via stimulated-emission refrigeration (and via the method of refrigeration investigated in Ref. 50)? Even if stimulated-emission refrigeration may not be feasible *in practice*, the immediately preceding question emphasizes *in principle* (even if only as a thought experiment[7]). $\Delta E_{0\to 1} \gtrsim 1000 k_B T_{\text{ambient}}$ likely implies an unfeasibly low T_{ambient} on Earth, but as we have noted there is the cold ambient temperature $T_{\text{ambient}} = 2.7\,\text{K}$ of outer space. Moreover, our considerations are in principle (even if only as a thought experiment,[7]), i.e., even if not feasible in practice: Can stimulated-emission refrigeration at least *attain* cooling to $0\,\text{K}$ from *any* T_{ambient} finitely greater, by however little, than $0\,\text{K}$, even in principle, and even if only for an instant (and hence, via repetition of the process, for any arbitrary number of instants)? The issue of *maintaining* $0\,\text{K}$ will be considered in Section IIIF*1*.

Hence, if the Third Law of Thermodynamics forbids cooling to absolute zero via stimulated-

emission refrigeration, it can*not* be because (i) an adiabat beginning at $T_{C,\text{initial}} > 0\,\text{K}$ cannot reach $T_C = 0\,\text{K}$ or (ii) it would cost an infinite (or even an extraordinarily large finite) amount of energy [as we have noted, the required energy is $N\Delta E_{0\to x}/\mathcal{E}$ (given perfection, i.e., $\mathcal{E} = 1$, it is $N\Delta E_{0\to x}$)]: It must be for *other* reason(s).

These issues will be further discussed in Sections IIIE, IIIF, and IIIG, with our reasoning explained in Sections IIIF and IIIG.

E. Insulation with respect to *heat* is *never* perfect

Superinsulation with respect to electricity is the flip side of the coin of superconductivity with respect to electricity. In superconductivity with respect to electricity, resistance to *electric-current* flow becomes zero; in superinsulation with respect to electricity, it becomes infinite. But neither superconductivity nor superinsulation with respect to *heat* flow exist. Superconductors with respect to electricity are *not* also superconductors with respect to heat.[64–66] And superinsulators with respect to electricity are *not* also superinsulators with respect to heat.[67–71] Moreover, in general, i.e., not limited to considerations of superconductors and superinsulators with respect to electricity, insulation with respect to *heat* can be good — but *never* perfect.[72,73] Superinsulation, i.e., perfect insulation, with respect to *heat* does *not* exist.

As a brief aside, we should also mention the related phenomenon of superfluidity, wherein viscosity, i.e., resistance to *fluid* flow, becomes very nearly zero. Superfluidity is *not* accompanied by superconductivity with respect to heat, i.e., by resistance to *heat* flow becoming zero.[74–76] The thermal conductivity of helium (the isotope ^4He) becomes large — but nowhere nearly infinite — at $1.92\,\text{K}$, and decreases both with decreasing temperature below $1.92\,\text{K}$ and with increasing temperature above $1.92\,\text{K}$.[74–76]

As another brief aside, we note that in general, apart from considerations of superinsulation, superconductivity, and superfluidity, significant differences exist between electrical conductivity and heat conductivity. For example, consider purely solid materials (excluding, say, aerogels, which are part solid and part gas) at room temperature, $\approx 300\,\text{K}$. Even though at $\approx 300\,\text{K}$ both electrical conductivity and heat conductivity in metals obtains via conduction electrons, at $\approx 300\,\text{K}$ the best electrical conductors are $\approx 10^{25}$ times as good as the worst ones, but the best heat conductors are only $\approx 10^5$ times as good as the worst ones.

The analyses in Sections IIIB, IIIC, and IIID represent the ideal or perfect case, wherein the *only* burden on a refrigerator is the extraction of heat from a cold reservoir, with no leakage of heat whatsoever from ambient into the cold reservoir in the meantime. But, because perfect insulation with respect to *heat* does *not* exist, heat leakage from ambient into *any* cold reservoir *must* be taken into account.

In Section IIIF*1*, we will show that, if heat leakage from ambient into a cold reservoir is finitely greater than zero, however slightly finitely greater than zero, *maintaining* absolute zero for any finite time, however short, is impossible via Carnot[1–5,56–58]/Stirling[6] or absorption[59] refrigeration. But merely *attaining* absolute zero for an instant (and hence, via repetition of the process, for any arbitrary number of instants) via Carnot[1–5,56–58]/Stirling[6] or absorption[59] refrigeration seems not to be ruled out, at least in principle. In Sections IIIF*2* and IIIG, we will explore the possibility that, since fluctuations can *spontaneously* transfer heat *from* a system being refrigerated *against* the temperature gradient, absolute zero can not only be *attained* via fluctuation, but also *maintained* for the time finitely greater than zero that a fluctuation lasts.

F. Caveats

1. Heat leakage from ambient into a cold reservoir: Increasing the difficulty of attaining — and especially of maintaining — absolute zero

In deriving the energy required for cooling to absolute zero in Sections IIIB, IIIC, and IIID, we considered *only* the energy required for extracting heat from a cold reservoir. This is the ideal or perfect case, assuming perfect insulation, i.e., with no leakage of heat whatsoever from ambient into the cold reservoir. But, as noted in Section IIIE, perfect insulation with respect to *heat* does *not* exist.

Thus we *must* take into account that insulation is *never* perfect and hence that there will *always* be *some* leakage of heat from ambient into a cold reservoir.

Let dQ_C^*/dt be the rate of heat leakage from ambient into a cold reservoir. (We employ star superscripts as required to denote heat leakage from ambient into a cold reservoir and quantities associated therewith. This is distinguished from extracting heat from a cold reservoir in the ideal or perfect case, assuming perfect insulation, i.e., with no leakage of heat whatsoever into the cold reservoir, as discussed in Sections IIIB, IIIC, and IIID.)

Applying the first line of Eq. (22), in the case of Carnot[1-5,56-58]/Stirling[6] refrigeration with $T_{C,\text{initial}} \to T_{\text{ambient}}$, the power $\mathbb{P}^*$ required to offset dQ_C^*/dt is

$$\mathbb{P}^* = \frac{dW^*}{dt} = \left(\frac{T_{\text{ambient}}}{T_C} - 1 \right) \frac{dQ_C^*}{dt}. \tag{34}$$

(Note: We denote power by $\mathbb{P}$; not to be confused with pressure, which we denote by P.) As Carnot[1-5,56-58]/Stirling[6] refrigeration proceeds, T_C decreases. Let t be the *time remaining* until T_C is reduced to absolute zero ($0\,\text{K}$), if attaining $0\,\text{K}$ is possible. Hence the work W^* required to offset Q_C^* for given T_{ambient} while attaining $T_C = 0\,\text{K}$ from a given $T_{C,\text{initial}} > 0\,\text{K}$ is

$$\begin{aligned}
W^* &= - \int_{t_{\text{initial}}}^{0} \mathbb{P}^* dt = \int_0^{t_{\text{initial}}} \mathbb{P}^* dt = \int_0^{t_{\text{initial}}} \left(\frac{T_{\text{ambient}}}{T_C} - 1 \right) \frac{dQ_C^*}{dt} dt \\
&= T_{\text{ambient}} \int_0^{t_{\text{initial}}} \frac{\frac{dQ_C^*}{dt}}{T_C} dt - \int_0^{t_{\text{initial}}} \frac{dQ_C^*}{dt} dt \\
&= T_{\text{ambient}} \int_0^{t_{\text{initial}}} \frac{\frac{dQ_C^*}{dt}}{T_C} dt - \int_0^{t_{\text{initial}}} dQ_C^* \\
&= \left(T_{\text{ambient}} \int_0^{t_{\text{initial}}} \frac{\frac{dQ_C^*}{dt}}{T_C} dt \right) - Q_C^*.
\end{aligned} \tag{35}$$

By Eq. (34), $\mathbb{P}^* \to \infty$ as $T_C = 0\,\text{K}$ unless dQ_C^*/dt decreases with decreasing T_C at least proportionately to T_C itself. But dQ_C^*/dt increases monotonically with increasing $T_{\text{ambient}} - T_C$ unless there is a more than compensating decrease in the thermal conductivity of insulating material surrounding the cold reservoir. This requires that the thermal conductivity vanishes as $T_C \to 0\,\text{K}$. But, as per Section IIIE, superinsulation with respect to heat does *not* exist. Hence this is *impossible*. But even if $\mathbb{P}^* = \infty$ at $T_C = 0\,\text{K}$, this singularity occurs *only* at the point value $T_C = 0\,\text{K}$, and hence the integrated W^* of Eq. (35) can still be finite. If $(dQ_C^*/dt)/T_C \propto t^n$ with $n > -1$, this singularity is sufficiently weak that the integrated W^* of Eq. (35) required to offset Q_C^* in

order to attain $T_C = 0\,\mathrm{K}$ from a given $T_{C,\mathrm{initial}} > 0\,\mathrm{K}$ is finite. Thus even though there must be *some* leakage of heat from ambient into the cold reservoir, by Eqs. (22) and (35) the *total* work $W_{\mathrm{attain}}^{\mathrm{total}} = W + W^*$ required to *attain* $T_C = 0\,\mathrm{K}$ via Carnot[1–5,56–58]/Stirling[6] refrigeration,

$$
\begin{aligned}
W_{\mathrm{attain}}^{\mathrm{total}} = W + W^* &= \left(T_{C,\mathrm{initial}} \int_{0\,\mathrm{K}}^{T_{C,\mathrm{initial}}} \frac{C}{T_C} dT_C \right) - Q_C \\
&+ \left(T_{\mathrm{ambient}} \int_0^{t_{\mathrm{initial}}} \frac{\frac{dQ_C^*}{dt}}{T_C} dt \right) - Q_C^* \\
&= \left(T_{C,\mathrm{initial}} \int_{0\,\mathrm{K}}^{T_{C,\mathrm{initial}}} \frac{C}{T_C} dT_C + T_{\mathrm{ambient}} \int_0^{t_{\mathrm{initial}}} \frac{\frac{dQ_C^*}{dt}}{T_C} dt \right) - Q_C - Q_C^*,
\end{aligned} \tag{36}
$$

is then also finite. (To reiterate, Q_C is the heat that must be extracted from the cold reservoir via Carnot[1–5,56–58]/Stirling[6] refrigeration to cool it from $T_{C,\mathrm{initial}}$ to $T_C = 0\,\mathrm{K}$ with*out* any heat leakage from ambient into the cold reservoir, and Q_C^* is the heat leakage from ambient into the cold reservoir that occurs during this cooling process.) But, by contrast, applying Eq. (34), to *maintain* a given T_C against heat leakage from ambient via Carnot[1–5,56–58]/Stirling[6] refrigeration, we require

$$
\begin{aligned}
W_{\mathrm{maintain}}^* &= - \int_{t_{\mathrm{initial}}}^{0} \mathbb{P}^* dt = \int_0^{t_{\mathrm{initial}}} \mathbb{P}^* dt = \int_0^{t_{\mathrm{initial}}} \frac{dW^*}{dt} dt \\
&= \left(\frac{T_{\mathrm{ambient}}}{T_C} - 1 \right) \int_0^{t_{\mathrm{initial}}} \frac{dQ_C^*}{dt} dt \\
&= \left(\frac{T_{\mathrm{ambient}}}{T_C} - 1 \right) \int dQ_C^* = \left(\frac{T_{\mathrm{ambient}}}{T_C} - 1 \right) Q_C^* \\
&= \infty \text{ if } T_C = 0\,\mathrm{K} \text{ and } Q_C^* \text{ is finitely greater than } 0.
\end{aligned} \tag{37}
$$

Thus, by Eq. (37), W_{maintain}^* required to *maintain* $T_C = 0\,\mathrm{K}$ via Carnot[1–5,56–58]/Stirling[6] refrigeration for any finite time, however short, is infinite if Q_C^* is finitely greater than 0, however slightly finitely greater than 0. It seems that this difficulty can be avoided only if superinsulation with respect to heat can render $Q_C^* = 0$. But, as per Section IIIE, superinsulation with respect to heat does *not* exist. Hence this is *impossible*. Hence, while *attaining* absolute zero via Carnot[1–5,56–58]/Stirling[6] refrigeration for an instant (and hence, via repetition of the process, for any arbitrary number of instants) seems not to be ruled out in principle, *maintaining* it for any finite time, however short, does seem to be.

Applying the first line of Eq. (28), in the case of absorption refrigeration,[59] the time rate of heat flow dQ_H^*/dt from a heat source or from a hot reservoir required to offset dQ_C^*/dt is

$$
\frac{dQ_H^*}{dt} = \frac{T_H}{T_H - T_I} \left(\frac{T_I}{T_C} - 1 \right) \frac{dQ_C^*}{dt}. \tag{38}
$$

Hence the heat Q_H^* from a heat source or from a hot reservoir required to offset Q_C^* for given

T_{ambient} while attaining $T_C = 0\,\text{K}$ from a given $T_{C,\text{initial}} > 0\,\text{K}$ is

$$
\begin{aligned}
Q_H^* &= -\int_{t_{\text{initial}}}^0 \frac{dQ_H^*}{dt}dt = \int_0^{t_{\text{initial}}} \frac{dQ_H^*}{dt}dt \\
&= \frac{T_H}{T_H - T_I}\int_0^{t_{\text{initial}}} \left(\frac{T_I}{T_C} - 1\right)\frac{dQ_C^*}{dt}dt \\
&= \frac{T_H}{T_H - T_I}\left(T_I\int_0^{t_{\text{initial}}} \frac{\frac{dQ_C^*}{dt}}{T_C}dt - \int_0^{t_{\text{initial}}} \frac{dQ_C^*}{dt}dt\right) \\
&= \frac{T_H}{T_H - T_I}\left(T_I\int_0^{t_{\text{initial}}} \frac{\frac{dQ_C^*}{dt}}{T_C}dt - \int_0^{t_{\text{initial}}} dQ_C^*\right) \\
&= \frac{T_H}{T_H - T_I}\left(T_I\int_0^{t_{\text{initial}}} \frac{\frac{dQ_C^*}{dt}}{T_C}dt - Q_C^*\right).
\end{aligned}
\tag{39}
$$

By Eq. (38), $dQ_H^*/dt \to \infty$ as $T_C = 0\,\text{K}$ unless dQ_C^*/dt decreases with decreasing T_C at least proportionately to T_C itself. But dQ_H^*/dt increases monotonically with increasing $T_{\text{ambient}} - T_C$ unless there is a more than compensating decrease in the thermal conductivity of insulating material surrounding the cold reservoir. This requires that the thermal conductivity vanishes as $T_C \to 0\,\text{K}$. But, as per Section IIIE, superinsulation with respect to heat does *not* exist. Hence this is *impossible*. But even if $dQ_H^*/dt = \infty$ at $T_C = 0\,\text{K}$, this singularity occurs *only* at the point value $T_C = 0\,\text{K}$, and hence the integrated Q_H^* of Eq. (39) could still be finite. If $(dQ_C^*/dt)/T_C \propto t^n$ with $n > -1$, this singularity is sufficiently weak that the integrated Q_H^* of Eq. (39) required to offset Q_C^* in order to attain $T_C = 0\,\text{K}$ from a given $T_{C,\text{initial}} > 0\,\text{K}$ is finite. Thus even though there must be *some* leakage of heat from ambient into the cold reservoir, by Eqs. (28) and (39) the *total* heat $Q_{H,\text{attain}}^{\text{total}} = Q_H + Q_H^*$ required to *attain* $T_C = 0\,\text{K}$ via absorption refrigeration,[59]

$$
\begin{aligned}
Q_{H,\text{attain}}^{\text{total}} = Q_H + Q_H^* &= \frac{T_H}{T_H - T_I}\left[\left(T_I\int_{0\,\text{K}}^{T_{C,\text{initial}}} \frac{C}{T_C}dT_C\right) - Q_C\right] \\
&+ \frac{T_H}{T_H - T_I}\left(T_I\int_0^{t_{\text{initial}}} \frac{\frac{dQ_C^*}{dt}}{T_C}dt - Q_C^*\right) \\
&= \frac{T_H}{T_H - T_I}\left[T_I\left(\int_{0\,\text{K}}^{T_{C,\text{initial}}} \frac{C}{T_C}dT_C + \int_0^{t_{\text{initial}}} \frac{\frac{dQ_C^*}{dt}}{T_C}dt\right) - Q_C - Q_C^*\right],
\end{aligned}
\tag{40}
$$

is then also finite. (To reiterate, Q_C is the heat that must be extracted from the cold reservoir via absorption refrigeration[59] to cool it from $T_{C,\text{initial}}$ to $T_C = 0\,\text{K}$ with*out* any heat leakage from ambient into the cold reservoir, and Q_C^* is the heat leakage from ambient into the cold reservoir that occurs during this cooling process.) But, by contrast, applying Eq. (38), to *maintain* a given

T_C against heat leakage from ambient via absorption refrigeration,[59] we require

$$
\begin{aligned}
Q^*_{H,\text{maintain}} &= -\int_{t_{\text{initial}}}^{0} \frac{dQ^*_H}{dt} dt = \int_{0}^{t_{\text{initial}}} \frac{dQ^*_H}{dt} dt \\
&= \frac{T_H}{T_H - T_I} \left(\frac{T_I}{T_C} - 1 \right) \int_{0}^{t_{\text{initial}}} \frac{dQ^*_C}{dt} dt \\
&= \frac{T_H}{T_H - T_I} \left(\frac{T_I}{T_C} - 1 \right) \int dQ^*_C = \frac{T_H}{T_H - T_I} \left(\frac{T_I}{T_C} - 1 \right) Q^*_C \\
&= \infty \text{ if } T_C = 0 \, \text{K} \text{ and } Q^*_C \text{ is finitely greater than 0.}
\end{aligned}
\tag{41}
$$

Thus, by Eq. (41), $Q^*_{H,\text{maintain}}$ required to *maintain* $T_C = 0\,\text{K}$ via absorption refrigeration[59] for any finite time, however short, is infinite if Q^*_C is finitely greater than 0, however slightly finitely greater than 0. It seems that this difficulty can be avoided only if superinsulation with respect to heat can render $Q^*_C = 0$. But, as per Section IIIE, superinsulation with respect to heat does *not* exist. Hence this is *impossible*. Hence, while *attaining* absolute zero via absorption refrigeration[59] for an instant (and hence, via repetition of the process, for any arbitrary number of instants) seems not to be ruled out in principle, *maintaining* it for any finite time, however short, does seem to be.

This seems to be true *in general*, with respect to *any* method of refrigeration, including therefore with respect to stimulated-emission refrigeration (recall Section IIID) and with respect to the method of refrigeration investigated in Ref. 50: While *attaining* absolute zero via *any* method of refrigeration for an instant (and hence, via repetition of the process, for any arbitrary number of instants) seems not to be ruled out in principle, *maintaining* it for any finite time, however short, does seem to be.

We note that, with the exception of one modification, the results obtained in this Section IIIF*1* remain valid even if we consider heat leakage from ambient into the cold reservoir as occurring discretely, quantum by quantum, rather than continuously. For even though that would imply changing each and every d in Eqs. $(34) - (41)$ to a Δ, these results would remain unchanged. The one modification: While *attaining* absolute zero via *any* method of refrigeration for less than the time required for leakage of one quantum of heat from ambient into the cold reservoir (and hence, via repetition of the process, for any arbitrary number of such time intervals) seems not to be ruled out in principle, *maintaining* it for any longer does seem to be.

2. Energy fluctuations and temperature fluctuations

2a. Thermal energy fluctuations and temperature fluctuations: An overview

There seems to be two viewpoints concerning energy fluctuations and temperature fluctuations in systems in thermodynamic equilibrium with thermal reservoirs in general,[77] and with thermal reservoirs very near but not at absolute zero in particular.[27,78,79] We consider a system in thermodynamic equilibrium with a thermal reservoir at fixed temperature T_{res} in general[77] (in the cases of interest, T_{res} is low but nonzero[27,78,79]).

One viewpoint ascribes to fluctuations only in energy.[27,77] According to this viewpoint, the temperature of a system in thermodynamic equilibrium with a thermal reservoir at fixed temperature T_{res} (in the cases of interest, low but nonzero fixed temperature T_{res}) is itself also fixed at T_{res}, but the system's energy fluctuates owing to energy exchanges with the thermal reservoir.[27]

The other viewpoint ascribes to fluctuations in both energy and temperature.[77–79] According to this viewpoint, owing to energy exchanges with a thermal reservoir at fixed temperature T_{res}, a

system's temperature as well as its energy fluctuates. When the system fluctuates to higher-than-average energy, it also fluctuates to higher-than-average temperature, i.e., to a temperature higher than T_{res}; when the system fluctuates to lower-than-average energy, it also fluctuates to lower-than-average temperature, i.e., to a temperature lower than T_{res}.[77–79]

But the validity of the concept of temperature requires that the *entire* probability distribution of a system's energy corresponds to thermodynamic equilibrium, i.e., that it is a Boltzmann distribution corresponding to the given temperature. It is *not* sufficient, for example, merely for the peak of a system's energy distribution to move to a higher-than-average value when it fluctuates to higher-than-average energy, and to a lower-than-average value when it fluctuates to lower-than-average energy. Thus the requirement for the validity of the concept of temperature fluctuations is that a system relax to internal thermodynamic equilibrium, i.e., to a Boltzmann distribution, in much less time (say, in $< 1/10$ as much time) than that required for a given energy fluctuation.

Even so, *complete* relaxation to *exactly* a Boltzmann distribution seems to be a stricter requirement than necessary. Relaxation to *close enough* to exactly a Boltzmann distribution seems sufficient for validity *for all practical purposes* of the concept of temperature during an energy fluctuation, and hence for validity *for all practical purposes* of construing this energy fluctuation to also be a temperature fluctuation.

More quantitatively, let a system be in thermodynamic equilibrium with a thermal reservoir at fixed temperature T_{res}, let $\langle E \rangle$ be the system's average energy, and consider a fluctuation ΔE_{fluc} of the system's energy away from this average value $\langle E \rangle$ (ΔE_{fluc} could be positive or negative). Let $\mathrm{Pr}_{j,B}(E)$ be the probability that the system is in quantum state j corresponding to internal thermodynamic equilibrium, i.e., to a Boltzmann distribution, when its energy happens to be $E = \langle E \rangle + \Delta E_{fluc}$, let $\mathrm{Pr}_j(E)$ be the probability that it is actually in this quantum state j when $E = \langle E \rangle + \Delta E_{fluc}$, let $\Delta \mathrm{Pr}_j(E) \equiv \mathrm{Pr}_j(E) - \mathrm{Pr}_{j,B}(E)$, and let $\langle \Delta t \rangle$ be the average time required for an energy fluctuation ΔE_{fluc} away from $\langle E \rangle$. Thus, more quantitatively, the requirement for the validity *for all practical purposes* of construing this energy fluctuation ΔE_{fluc} away from $\langle E \rangle$ to also be a temperature fluctuation ΔT_{fluc} away from T_{res} is: for *all* Pr_js, $|\Delta \mathrm{Pr}_j(E)| \, / \, \mathrm{Pr}_{j,B}(E)$ relaxes to a value $\ll |\Delta E_{fluc}| \, / \, \langle E \rangle$ (say, to a value $< |\Delta E_{fluc}| \, /10 \langle E \rangle$), in a time $\ll \langle \Delta t \rangle$ (say, in a time $< \langle \Delta t \rangle \, /10$).

This requirement for the validity of the concept of temperature fluctuations, as discussed in this Section IIIF*2a*, seems to be assumed to be met, at least implicitly, in Refs. 78 and 79.

Reference 27 considers energy fluctuations, and Refs. 78 and 79 consider both energy and temperature fluctuations, with respect to systems at low but nonzero temperatures. But we again note that this issue has been investigated more generally.[77]

2b. Quantum nonthermal energy fluctuations: an overview

There is still the issue of the energy-time uncertainty principle, which we have not thus far considered. We describe two viewpoints.[80,81] According to the first viewpoint,[80] the energy-time uncertainty principle does not effect fleeting violations of energy conservation (the First Law of Thermodynamics): energy is strictly conserved, but measuring it entails significant uncertainty if a system's state can only be maintained for a very short time, let alone an infinitesimally short time (an instant). According to the second viewpoint,[81] the energy-time uncertainty principle does effect fleeting violations of energy conservation (the First Law of Thermodynamics): a system's energy does not have a well-defined value if the system's state can only be maintained for a very short time, let alone an infinitesimally short time (an instant). According to both viewpoints,[80,81]

the minimum root-mean-square (rms) energy-time uncertainty product,

$$(|\Delta E| \, \Delta t)_{\text{rms,min}} = \hbar/2 \doteq 1.0546 \times 10^{-34} \, \text{J s}, \tag{42}$$

is very small (if expressed in SI units). (The absolute value $|\Delta E|$ is employed because ΔE could be positive or negative as per both viewpoints:[80,81] As per the first viewpoint,[80] a measurement uncertainty could be either positive or negative; as per to the second viewpoint,[81] energy could either be borrowed or discarded.)

The second viewpoint[81] goes beyond Eq. (42), and gives the probability that the energy-time uncertainty product equals or exceeds a given value $|\Delta E| \, \Delta t$ as the exponentially-decreasing function[81]

$$\Pr\left(\geq |\Delta E| \, \Delta t\right) = e^{-(|\Delta E| \Delta t)/(|\Delta E| \Delta t)_{\text{rms,min}}} = e^{-2|\Delta E| \Delta t/\hbar}. \tag{43}$$

[The exponential form of Eq. (43) is reminiscent of the Boltzmann distribution, but like most analogies, this one should not be pressed too far. Quantum probabilities arise from probability amplitudes, i.e., from pre-probabilities,[82] and hence entail interference effects,[82] which are absent in thermal-fluctuation probabilities as per the Boltzmann distribution.[82]] As per the second viewpoint,[81] $\Pr\left(\geq |\Delta E| \, \Delta t\right)$ is the probability that, owing to quantum energy fluctuations effected via the energy-time uncertainty principle, there can obtain nonconservation (borrowing or discarding) of energy of magnitude $|\Delta E|$ or more for a time Δt, or, alternatively, of magnitude $|\Delta E|$ for a time Δt or longer. If a system's first excited state is, say, $10\,\text{eV} \doteq 1.602 \times 10^{-18}\,\text{J}$ (a typical value) above its ground state, even according to the second viewpoint[81] there is negligible probability that quantum energy fluctuations effected via the energy-time uncertainty principle can boost the system from its ground state to its first excited state even for a time interval $\Delta t \approx 10^{-15}\,\text{s}$. Perhaps a time interval $\Delta t \approx 10^{-15}\,\text{s}$, even though not infinitesimally short, is nonetheless short enough to qualify as an instant.

But even this seems to miss the main point. Even according to the second viewpoint:[81] (i) It is unclear whether quantum energy fluctuations effected via the energy-time uncertainty principle that borrow energy temporarily boost a system out of its ground state, or instead temporarily increase its energy within the ground state itself. Certainly those that *discard* energy temporarily decrease its energy within the ground state itself. (ii) Most importantly: Unlike (classical or quantum) *thermal* energy fluctuations effected via heat flow to a system from its thermal reservoir or vice versa, quantum energy fluctuations effected via the energy-time uncertainty principle as per the second viewpoint[81] do *not* entail heat flow to or from a system and hence do *not* temporarily raise or lower its temperature. Thermal energy fluctuations are *thermo*dynamic, i.e., heatlike. By contrast, energy fluctuations effected via the energy-time uncertainty principle as per the second viewpoint[81] are *purely* dynamic, i.e. worklike. If a thermal fluctuation in accordance with the Boltzmann distribution accelerates (decelerates) a Brownian particle, there is (keeping in mind the caveats discussed in Section IIIF*2a*) accompanying cooling (warming) of the Brownian particle and its thermal surroundings such that energy conservation (the First Law of Thermodynamics) is strictly obeyed. By contrast, if a quantum energy fluctuation effected via the energy-time uncertainty principle accelerates (decelerates) a Brownian particle as per the second viewpoint,[81] it does so by dint of fleeting violation of energy conservation, and hence *no* accompanying cooling (warming) of the Brownian particle and its thermal surroundings. This is perhaps most convincingly construed by considering energy fluctuations effected via the energy-time uncertainty principle in a system in its *ground* state and hence at absolute zero ($0\,\text{K}$) that *discard* rather than borrow energy. Such

fluctuations — indeed no fluctuation whatsoever — can lower the temperature of a system in its ground state to below $0\,\mathrm{K}$!

Hence, we need take into account only *thermal* energy/temperature fluctuations in considering the increase or decrease in difficulty effected by fluctuations in attaining and maintaining absolute zero. In considering temperature fluctuations, we keep in mind the caveats discussed in Section IIIF*2a*.

2c. Energy/temperature fluctuations: Increasing the difficulty of attaining, let alone maintaining, absolute zero

It has been stated that energy fluctuations[27] and temperature fluctuations[78,79] render even the attaining, let alone the maintaining, of absolute zero ($0\,\mathrm{K}$) at least more difficult and perhaps impossible, because they could render it impossible at least in practice and possibly even in principle for the temperature to attain $0\,\mathrm{K}$, let alone to be maintained at $0\,\mathrm{K}$. Moreover, *even if* absolute zero could be attained and even maintained, it has furthermore been stated that energy fluctuations[27] and temperature fluctuations[78,79] render *confirmation* that $0\,\mathrm{K}$ has actually been reached at least more difficult and perhaps impossible, at least in practice and possibly even in principle.[27,78,79]

2d. Energy/temperature fluctuations: Decreasing the difficulty of attaining, and even maintaining, absolute zero: Absolute zero via fluctuation?

But fluctuations can work both ways,[27] i.e., either hindering or helping in attempting to attain absolute zero.[27] (See especially the last paragraph of Ref. 27.) Let E_0 be the ground-state energy of a system in thermodynamic equilibrium with a thermal reservoir at fixed temperature T_{res} (in the cases of interest, low but nonzero fixed temperature T_{res}). The help can arise because, owing to fluctuations — specifically, owing to *maximal* fluctuations to lower-than-average energy [$\Delta E_{\mathrm{fluc}} = -(\langle E \rangle - E_0) = E_0 - \langle E \rangle$] — the values of the entropy and also of all other thermodynamic properties of such a system can fluctuate to those corresponding to $0\,\mathrm{K}$. For a *maximal* fluctuation to lower-than-average energy [$\Delta E_{\mathrm{fluc}} = -(\langle E \rangle - E_0) = E_0 - \langle E \rangle$] will leave *all* of the system's atoms in their ground states and thus the *entire* system in its ground state of energy E_0!

Reference 27 ascribes strictly to the energy-fluctuation viewpoint. But while a *maximal* fluctuation to lower-than-average energy lasts, the requirement for the validity of the concept of temperature fluctuations, as discussed in Section IIIF*2a*, is not merely met but *maximally* met: the *only* occupied state is then the ground state, hence $\mathrm{Pr}_j\,(E_0) = \mathrm{Pr}_{j,B}\,(E_0) = 1$ and $\Delta\,\mathrm{Pr}_j\,(E) \equiv \mathrm{Pr}_j\,(E_0) - \mathrm{Pr}_{j,B}\,(E_0) = 1 - 1 = 0$. Thus is then not a *maximal* fluctuation to lower-than-average energy [$\Delta E_{\mathrm{fluc}} = -(\langle E \rangle - E_0) = E_0 - \langle E \rangle$], while it lasts, also a temperature fluctuation to absolute zero?[27,78,79] And since *any* fluctuation lasts for a time finitely greater than zero, is not absolute zero thereby not merely *attained*, but also *maintained* for a time finitely greater than zero — specifically, for the time finitely greater than zero that a *maximal* fluctuation to lower-than-average energy lasts?[27,78,79] Fluctuations can *spontaneously* transfer heat *from* a system being refrigerated *against* the temperature gradient: hence insulation with respect to heat never being perfect (recall Section IIIE) does *not* preclude not only *attaining* absolute zero via fluctuation, but also *maintaining* it during the finite time interval that such a fluctuation lasts. Indeed, *perfect* insulation *precludes* thermal fluctuations!

Of course, in the best-case scenario for attaining absolute zero via fluctuation, preferably T_{res} should be as low as possible. (We note that the cosmic background radiation of outer space is an ambient thermal environment that can serve as a thermal reservoir at $T_{\mathrm{ambient}} = T_{\mathrm{res}} = 2.7\,\mathrm{K}$.) A system such as that described in Section IIID, wherein $\Delta E_{0\to 1} \gtrsim 1000 k_B T_{\mathrm{ambient}}$, will be in its ground state almost all of the time. Maximal fluctuations to lower-than-average energy characterize

by far the most probable state of such a system. Even on those rare occasions when the system fluctuates to above its ground state, the Poincaré recurrence time[83] for its return to its ground state will be extremely short.

But let us also consider the worst-case scenario for attaining absolute zero via fluctuation. Even if T_{res} (or T_{ambient}) is high and even if our system is large, maximal fluctuations to lower-than-average energy are improbable but not impossible: hence, their average time interval between their recurrences, i.e., the Poincaré recurrence time,[83] is finite, not infinite. In this regard, it may be worthwhile to recall this famous quote from Josiah Willard Gibbs with respect to the Second Law of Thermodynamics: "the impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability"[84]. If it turns out that absolute zero can be attained, even in principle, *only* via maximal fluctuations to lower-than-average energy, then a corresponding statement with respect to the unattainability formulation of the Third Law of Thermodynamics would be: Even if T_{res} (or T_{ambient}) is high and even if our system is large, the impossibility of attaining absolute zero seems to be reduced to an improbability. If it turns out that absolute zero can furthermore also be maintained for a time finitely greater than zero (the time that a maximal fluctuation to lower-than-average energy lasts), even in principle, *only* via maximal fluctuations to lower-than-average energy, then a corresponding statement with respect to the unattainability formulation of the Third Law of Thermodynamics would be: Even if T_{res} (or T_{ambient}) is high and even if our system is large, the impossibility of not only *attaining* absolute zero, but then also *maintaining* it for a time finitely greater than zero (the time that a maximal fluctuation to lower-than-average energy lasts), seems to be reduced to an improbability. And, again, this is the worst-case scenario. In the best-case scenario, described in the immediately preceding paragraph, maximal fluctuations to lower-than-average energy characterize by far the most probable state.

G. Experimental confirmation that a system's temperature is absolute zero by weighing

At least in principle, it can be *experimentally confirmed* that a maximal fluctuation to lower-than-average energy has reduced a system's temperature to absolute zero with*out* any heat leakage whatsoever into the system. Simply place the system on an extremely sensitive and extremely accurate scale. (A sufficiently sensitive and sufficiently accurate scale is beyond current technology, but it violates no law of physics; hence it is valid to employ it, at least in a thought experiment.[7]) Let the system's *total* energy when *all* of its atoms are in their ground states and thus the *entire* system is in its ground state — and hence when its temperature is absolute zero — be E_0. Let its *total* energy when one — and only one — of its atoms is in its first excited state and all of its other atoms are in their ground states and thus the *entire* system is in its first excited state be $E_0 + \Delta E_{0 \to 1}$. Hence the corresponding masses are, respectively, E_0/c^2 and $(E_0 + \Delta E_{0 \to 1})/c^2$, and the corresponding weights in a uniform gravitational field g are, respectively, $E_0 g/c^2$ and $(E_0 + \Delta E_{0 \to 1})\,g/c^2$. Hence, considering as a specific example the system discussed in Section IIIF*2d*, it can in principle be *experimentally confirmed* that a maximal fluctuation to lower-than-average energy has reduced the temperature to absolute zero by *weighing* the system. Because (i) weighing a system requires *zero* heat leakage into it, (ii) maximal fluctuations to lower-than-average energy occur *spontaneously* in the face of lack of thermal isolation and *spontaneously* transfer heat *from* a system being refrigerated *against* the temperature gradient, and (iii) for any finite-size system, $\Delta E_{0 \to 1}$ is *finite* — not infinitesimally small: the "profound problems of absolute thermal isolation and infinitely precise temperature measurability"[53] seem, at least *prima facie* and at least in principle, to be circumvented. (Of course, if the *entire* system is in its second or higher excited state, its

energy exceeds that of its ground state by finitely more than $\Delta E_{0 \to 1}$, but the essence of the above line of reasoning is unchanged.) And, again, "infinitely precise temperature measurability"[53] is not required, because $\Delta E_{0 \to 1}$ is *finite* — not infinitesimally small. Concerning (ii) immediately above: Insulation with respect to heat never being perfect (recall Section IIIE) does *not* preclude not only *attaining* absolute zero via fluctuation, but also *maintaining* it during the finite time interval that such a fluctuation lasts. Indeed, *perfect* insulation *precludes* thermal fluctuations!

By contrast, other methods of *experimentally confirming* that absolute zero has been attained entail greater difficulties, even in principle. Three examples: (i) Employing a thermometer entails heat leakage from the thermometer into a system at absolute zero (unless the thermometer itself is also at absolute zero). Thus (unless the thermometer itself is also at absolute zero), after the thermometer has been employed the system will be warmer than absolute zero and the thermometer will be cooler than its initial temperature. Of course, based on the heat capacities of both the system and the thermometer as functions of temperature, this can be accounted for, and it can thereby be ascertained whether or not the system was at absolute zero before the thermometer was employed. But this is an extra complication. (ii) Since $(\partial V / \partial T)_P \to 0$ as $T \to 0\,\mathrm{K}$,[85–88] infinitely precise[53] volume measurements at constant pressure would be required to ascertain whether or not a system maintained at constant pressure is at absolute zero:[85–88] compare the *finiteness* of $\Delta E_{0 \to 1}$. (iii) Since $(\partial P / \partial T)_V \to 0$ as $T \to 0\,\mathrm{K}$,[85–88] infinitely precise[53] pressure measurements at constant volume would be required to ascertain whether or not a system maintained at constant volume is at absolute zero:[85–88] compare the *finiteness* of $\Delta E_{0 \to 1}$.

In general, the weight of a system *alone* can*not* reveal its temperature, without one additional requirement being met. For the weight of a system can*not* distinguish between random, thermal energy, which contributes to temperature, and nonrandom, nonthermal energy, which does not. Consider supplying a given amount of energy to a system (a) thermally,[89] via heat and/or via work frictionally dissipated into heat, thereby raising its temperature, versus (b) supplying the same amount of energy nonthermally, via work sequestered, say, by compressing a spring, hence leaving its temperature unchanged. Both (a) and (b) result in the same increase in weight. And consider extracting a given amount of energy from a system (c) thermally,[89] via heat, thereby lowering its temperature, versus (d) extracting the same amount of energy nonthermally, via work, say, by relaxing a spring, hence leaving its temperature unchanged. Both (c) and (d) result in the same decrease in weight. Thus the one additional requirement *in general* is that all energy transfers to and/or from a system must be only of type (a) and/or type (c), respectively, if the system's temperature is to be determined by its weight *alone*. Or, if there are energy transfers to and/or from a system of type (b) and/or type (d), respectively, this must be accounted for in addition to the system's weight to determine its temperature.

But in the *special* case wherein *all* of a system's atoms are in their ground states and thus the *entire* system is in its ground state, the system's weight *alone* — with*out* the aforementioned additional requirement — *always experimentally confirms* that its temperature is absolute zero, because there is only *one* way that *all* of any system's atoms can be in their ground states.

We discussed *experimental confirmation* that a system's temperature is absolute zero by *weighing* with respect to the specific example of the system discussed in Section IIIF*2d*, wherein absolute zero is attained via a maximal fluctuation to lower-than-average energy. But at least in principle weighing seems to be a method of *experimentally determining* whether or not a system's temperature has been reduced to absolute zero via *any (nonadiabatic) process whatsoever*.[52,53] Nonetheless, at least *prima facie*, it seems that a maximal fluctuation to lower-than-average energy, as

discussed in Section III*F2d*, seems to be the easiest and most likely method of attaining absolute zero ($0\,\mathrm{K}$) — if $0\,\mathrm{K}$ can be attained at all. For fluctuations occur *spontaneously*, and hence require no effort. Thermal fluctuations in general, and maximal ones to lower-than-average energy in particular, can occur *only* if insulation with respect to heat is *im*perfect (compare Section IIIE). And, again, "infinitely precise temperature measurability"[53] is not required, because $\Delta E_{0\rightarrow1}$ is *finite* — not infinitesimally small.

IV. HOT AND COLD RESERVOIRS THAT CAN AND CANNOT MAINTAIN A CONSTANT TEMPERATURE

We now discuss the nature of hot and cold reservoirs that can and cannot maintain a constant temperature. In general, hot and cold reservoirs be of either type. But we will show that a cold reservoir *initially* at absolute zero ($0\,\mathrm{K}$) or even at a temperature above but arbitrarily close to $0\,\mathrm{K}$ *must* — not merely can — be of the latter type.

In order for a hot reservoir to maintain an *exactly*[89] constant temperature T_H,[89] energy must be continually added to it if it is the heat source for a heat engine, and energy must be continually extracted from it if it is the heat sink for a refrigerator or heat pump.[89] (This is most commonly done for heat engines via combustion of fuels, solar thermal energy input, etc.) Likewise, in order for a cold reservoir to maintain an *exactly*[89] constant temperature T_C,[89] energy must be continually extracted from it if it is the heat sink for a heat engine, and energy must be continually added to it if it is the heat source for a refrigerator or heat pump.[89] (This is most commonly done for heat engines, whose cold reservoir is most typically the ambient atmosphere, because the ambient atmosphere is in radiative thermal contact with the even colder $2.7\,\mathrm{K}$ vastness of outer space.)

A hot reservoir that is the heat source for a heat engine or a heat sink for a refrigerator or heat pump can maintain a very nearly but not exactly constant temperature T_H even with*out* compensating additions or extractions of energy (as described in the immediately preceding paragraph) if the heat supplied from it to the heat engine or rejected to it by the refrigerator or heat pump is only a tiny fraction of the hot reservoir's total reserve of thermal energy, $\kappa m \int_{0\,\mathrm{K}}^{T_H} C dT$. Likewise, a cold reservoir that is the heat sink for a heat engine or a heat source for a refrigerator or heat pump can maintain a very nearly but not exactly constant temperature T_C even with*out* compensating additions or extractions of energy (as described in the immediately preceding paragraph) if the heat rejected to it by the heat engine or extracted from it by the refrigerator or heat pump is only a tiny fraction of the cold reservoir's total reserve of thermal energy, $\kappa m \int_{0\,\mathrm{K}}^{T_C} C dT$.

In usual considerations[1–6] of the operation of heat engines, refrigerators, and heat pumps, both the hot and cold reservoirs are assumed to have such huge total reserves of thermal energy that, even with*out* compensating additions or extractions of energy, temperature changes of both reservoirs are a negligible fraction of their initial temperatures.[1–6] And in most cases, such compensating additions or extractions of energy *are* made.[1–6] But there are also well-known examples for which this is *not* the case.

Let us consider two of the simplest of these well-known examples. The first example[90,91] consists of hot and cold reservoirs both of the same mass m and the same constant heat capacity

$C = \kappa m$ at initial temperatures T_H and T_C powering a Carnot,[1–5] Stirling,[6] or any other perfect, reversible heat engine[1–6] until the temperature difference between the two reservoirs has been completely neutralized and hence the maximum possible work W_{max} allowed by the First and Second Laws of Thermodynamics has been extracted.[90,91] In this case the final temperature is the geometric mean of T_C and T_H, i.e., $(T_C T_H)^{1/2}$.[90,91] The initial thermal energy owes to the arithmetic mean of T_H and T_C, i.e., $(T_C + T_H)/2$ and therefore is $E_{\text{thermal,initial}} = 2\kappa m \left[(T_C + T_H)/2 \right] = \kappa m (T_C + T_H)$.[90,91] And the final thermal energy is $E_{\text{thermal,final}} = 2\kappa m (T_C T_H)^{1/2}$. Hence

$$W_{\text{max}} = E_{\text{thermal,initial}} - E_{\text{thermal,final}}$$
$$= \kappa m \left[T_C + T_H - 2 (T_C T_H)^{1/2} \right]. \tag{44}$$

The heat supplied by the hot reservoir is

$$Q_H = \kappa m \frac{T_H - T_C}{2}. \tag{45}$$

The instantaneous Carnot efficiency decreases monotonically from its initial value $1 - (T_C/T_H)$ towards its final value of zero. The overall Carnot efficiency is

$$\epsilon_{\text{Carnot}} = \frac{W_{\text{max}}}{Q_H} = \frac{2 \left[T_C + T_H - 2 (T_C T_H)^{1/2} \right]}{T_H - T_C}. \tag{46}$$

In the second example,[92] the cold reservoir's temperature T_C is fixed but the temperature T_H of a hot reservoir of mass m and constant heat capacity $C = \kappa m$ is to be reduced to T_C via powering a Carnot,[1–5] Stirling,[6] or any other perfect, reversible heat engine[1–6] until the maximum possible work W_{max} allowed by the First and Second Laws of Thermodynamics has been extracted.[92] In this case[92]

$$W_{\text{max}} = \kappa m \left[(T_H - T_C) - T_C \ln \frac{T_H}{T_C} \right]$$
$$= \kappa m \left[T_H - T_C \left(1 + \ln \frac{T_H}{T_C} \right) \right], \tag{47}$$

and the heat supplied by the hot reservoir is

$$Q_H = \kappa m (T_H - T_C). \tag{48}$$

In this case also, the instantaneous Carnot efficiency decreases monotonically from its initial value $1 - (T_C/T_H)$ towards its final value of zero. In this case the overall Carnot efficiency is

$$\epsilon_{\text{Carnot}} = \frac{W_{\text{max}}}{Q_H} = \frac{(T_H - T_C) - T_C \ln \frac{T_H}{T_C}}{T_H - T_C} = 1 - \frac{T_C \ln \frac{T_H}{T_C}}{T_H - T_C}$$
$$= \frac{T_H - T_C \left(1 + \ln \frac{T_H}{T_C} \right)}{T_H - T_C}. \tag{49}$$

There are numerous other examples of cases wherein changes in the temperatures of hot and/or cold reservoirs are not negligible and therefore must be taken into account.[93,94] Thus, even under

ordinary circumstances, i.e., with temperatures of hot and/or cold reservoirs within ordinary ranges, it is not uncommon that changes of temperatures of hot and/or cold reservoirs that are not small compared to their initial temperatures *can* occur.[90–94]

But for a cold reservoir initially at absolute zero $(0\,\mathrm{K})$, changes of temperature that are not small, but an *infinite* number of times greater than its initial temperature of $0\,\mathrm{K}$, *must* — not merely can — occur. Consider a cold reservoir *initially* at absolute zero, assuming that such can exist for a Carnot,[1–5] Stirling,[6] or any other perfect, reversible heat engine. If the Second Law of Thermodynamics is to be obeyed, enough heat must be rejected into this cold reservoir to increase its entropy enough to offset the entropy decrease of the hot reservoir: recall Eqs. (1) and (2). And the rejection of even the tiniest amount of heat into a cold reservoir at absolute zero $(0\,\mathrm{K})$ results in a temperature greater than $0\,\mathrm{K}$, which, however low, is an *infinite* number of times greater than its initial temperature of $0\,\mathrm{K}$. Thus the rise in temperature of such a cold reservoir *must always* be accounted for, we have done in this chapter. Even if only a cold reservoir initially at a temperature above but arbitrarily close to absolute zero is available, the rejection of even a tiny amount of heat into it *must* — not merely can — result in a temperature greater than its initial temperature by a *huge* (albeit not infinite) number of times. Hence the rise in temperature of cold reservoirs initially at $0\,\mathrm{K}$ or even above but arbitrarily close to $0\,\mathrm{K}$ *must always* be accounted for, as we have done in this chapter. (Of course, if there is any imperfection or equivalently any irreversibility, the increase of the temperature of the cold reservoir will be greater than with perfect, reversible operation.)

Of course, in *all* cases, by the First and Second Laws of Thermodynamics:[89–94]

$$W_{\mathrm{max}} = Q_H - Q_C$$

$$\implies \epsilon_{\mathrm{Carnot}} = \frac{W_{\mathrm{max}}}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

subject to the condition

$$\Delta S_{\mathrm{total}} = \Delta S_C + \Delta S_H = \int_{T_{C,\mathrm{initial}}}^{T_{C,\mathrm{final}}} \frac{dQ_C}{T_C} - \int_{T_{H,\mathrm{initial}}}^{T_{H,\mathrm{final}}} \frac{dQ_H}{T_H} = 0$$

$$\Longleftrightarrow \int_{T_{C,\mathrm{initial}}}^{T_{C,\mathrm{final}}} \frac{dQ_C}{T_C} = \int_{T_{H,\mathrm{initial}}}^{T_{H,\mathrm{final}}} \frac{dQ_H}{T_H}. \tag{50}$$

What has been stated in this Section IV with respect to hot and cold reservoirs obviously also applies with respect to intermediate-temperature reservoirs employed in absorption refrigeration.[59]

V. CONCLUSION

It is usually assumed that, *if* a cold reservoir at absolute zero $(T_C = 0\,\mathrm{K})$ is available, *then* a (perfect, reversible) Carnot heat engine can operate at 100% efficiency, converting 100% of the heat input Q_H from its hot reservoir into work W. We discussed (perfect, reversible) Carnot heat engines employing cold reservoirs at $T_C = 0\,\mathrm{K}$ in Section II. We showed that even a (perfect, reversible) Carnot heat engine employing a cold reservoir at $T_C = 0\,\mathrm{K}$ can*not* operate at 100% efficiency: *Even if* a cold reservoir at absolute zero $(T_C = 0\,\mathrm{K})$ is available, if the Second Law of Thermodynamics is not to be violated even a (perfect, reversible) Carnot heat engine must reject *some* waste heat into it. Hence (i) *even if* a cold reservoir at absolute zero $(T_C = 0\,\mathrm{K})$ is available, it could remain at $0\,\mathrm{K}$ *only initially* [i.e., *even if* $T_{C,\mathrm{initial}} = 0\,\mathrm{K}$, $T_C > 0\,\mathrm{K}$ immediately

thereafter when even a (perfect, reversible) Carnot heat engine begins operating], and (ii) even a (perfect, reversible) Carnot heat engine employing a cold reservoir at $T_C = 0\,\text{K}$ *must* operate at *less than* 100% efficiency, converting *less than* 100% of the heat input Q_H from its hot reservoir into work W. (Of course, if there is any imperfection or equivalently any irreversibility, the inequality $T_C > 0\,\text{K}$ immediately thereafter will be stronger than with perfect, reversible operation.) By applying the First and Second Laws of Thermodynamics, we derived the entropy increase and the waste heat that must be rejected into the cold reservoir, and the work output and efficiency of a (perfect, reversible) Carnot heat engine, *if* a cold reservoir *initially* at $T_C = 0\,\text{K}$ is available.

Our results are also valid for non-Carnot-cycle heat engines that equal Carnot-cycle heat engines in efficiency, e.g., Stirling-cycle heat engines.[6] [The Stirling cycle is more complicated than the Carnot cycle;[6] hence, we focused on the Carnot cycle, which is the archetype, and probably also the simplest conceptually, of maximally thermodynamically efficient heat-engine (and refrigerator and heat-pump) cycles.[1–5]] Moreover, except for the utmost-low-temperature limit discussed in Section IIC, our results are also valid to within an excellent approximation even if the cold reservoir is initially at $T_{C,\text{initial}} > 0\,\text{K}$ with $0\,\text{K} < T_{C,\text{initial}} \ll T_{C,\text{final}}$.

While there are challenges[95,96] to the Second Law of Thermodynamics (Refs. 95 and 96 being just two samples, but hopefully two representative samples, from a vast literature concerning such challenges, especially during the past few decades), it has been correctly pointed out that: "If the Second Law should be shown to be violable, it would nonetheless remain valid for the vast majority of natural and technological processes"[97]. Hence, hopefully, *even if* the Second Law should be shown to be violable, our analyses in this chapter would still be helpful within what would still be its vast range of validity.

In Section III, we considered the possibility, if only in principle (even if only as thought experiments[7]) rather than in practice, of the existence of a cold reservoir at absolute zero via Carnot, absorption, and stimulated-emission refrigeration. Caveats concerning heat leakage from ambient into cold reservoirs and energy/temperature fluctuations were discussed next, as well as the possibility of a system spontaneously attaining absolute zero via fluctuation. We then considered *weighing* a system to *experimentally determine* whether or not a system's temperature is absolute zero. We accepted the formulations of the Third Law of Thermodynamics that deny the possibility of attaining absolute zero via adiabatic processes,[38,39,41] and also those concerning the entropy at absolute zero.[14–21] We posed questions concerning only the formulations of the Third Law of Thermodynamics that deny the possibility of attaining absolute zero via *any process whatsoever*.[52,53]

In Section IV, we discussed the nature of hot and cold reservoirs that can and cannot maintain a constant temperature. In general, hot and cold reservoirs can be of either type. But we showed that a cold reservoir *initially* at absolute zero ($0\,\text{K}$) or even at a temperature above but arbitrarily close to $0\,\text{K}$ *must* — not merely can — be of the latter type.

In the Appendix, we will discuss an interesting aspect of the relationship between entropy and heat capacity. This relationship per se is true in general, but it is typically manifested only by certain systems at very low temperatures. Our example entails conduction electrons in metals.

ACKNOWLEDGMENTS

APPENDIX: WHEN ENTROPY AND HEAT CAPACITY HAVE THE SAME NUMERICAL VALUE: QUANTITATIVELY BUT NOT QUALITATIVELY EQUAL

It is of course well-known that both entropy and heat capacity have the same units (energy $\div$ temperature, J / K in SI units). But it is possible for both entropy and heat capacity to *also* have *the same numerical value*.

Consider heat capacities of the form given by Eq. (6), i.e., $C = \kappa m T^n$ ($n > 0$). The entropy of a system with such a heat capacity and with a nondegenerate[14–21] ground state is, at temperature T,

$$S = \int_{0\,\mathrm{K}}^{T} \frac{dQ}{T'} = \int_{0\,\mathrm{K}}^{T} \frac{CdT'}{T'} = \kappa m \int_{0\,\mathrm{K}}^{T} \frac{T'^n dT'}{T'} = \kappa m \int_{0\,\mathrm{K}}^{T} T'^{n-1} dT' = \frac{\kappa m T^n}{n}. \qquad (A1)$$

The second and third terms in Eq. (A1) are general expressions entailing the heat that must be added to such a system to raise its temperature from $0\,\mathrm{K}$ to T, while the last two terms thereof are specific expressions valid if $C = \kappa m T^n$ ($n > 0$). If $n = 1$, i.e., if $C = \kappa m T$, as is the case (to within an excellent approximation[28–32]) for conduction electrons in metals at very low temperatures,[28–32,98] then also $S = \kappa m T$, i.e.,

$$\kappa m T = S \mathbin{\widehat{=}} C \iff \kappa m T = C \mathbin{\widehat{=}} S, \qquad (A2)$$

where the $\widehat{=}$ sign denotes "quantitatively but not qualitatively equal", or, equivalently, "numerically but not conceptually equal".[99]

Thus if heat capacity is directly proportional to temperature, both entropy and heat capacity have not only the same units but *also the same numerical value*. This statement is true in general. But heat capacities directly proportional to temperature are typically actually manifested only by certain systems at very low temperatures, our example being conduction electrons in metals.

Even though in this case both entropy and heat capacity have not only the same units but also the same quantitative, i.e., numerical, value, they are, in this case as in all cases, of course qualitatively, i.e., conceptually, unequal.[99] Entropy is Boltzmann's constant, k_B, times the natural logarithm of the multiplicity Ω, i.e., $S = k_B \ln \Omega$; heat capacity is the energy that must be imparted to a system via heat, or via work frictionally dissipated into heat, to raise its temperature by $1\,\mathrm{K}$.[99]

Even if the ground state *is* degenerate,[14–21] i.e., even if its degeneracy[14–21] is $g_0 > 1$, we would still have, if $C = \kappa m T^n$ ($n > 0$),

$$S(T) - S(0\,\mathrm{K}) = \frac{\kappa m T^n}{n}, \qquad (A3)$$

and hence, if $n = 1$, i.e., if $C = \kappa m T$,

$$\kappa m T = S(T) - S(0\,\mathrm{K}) = S(T) - k_B \ln g_0 \mathbin{\widehat{=}} C$$
$$\iff \kappa m T = C \mathbin{\widehat{=}} S(T) - S(0\,\mathrm{K}) = S(T) - k_B \ln g_0. \qquad (A4)$$

[1] Herbert B. Callen, *Thermodynamics* (John Wiley & Sons, New York, 1960), Chapter 4 (especially Sections 4.4 through 4.8).

[2] Herbert B. Callen, *Thermodynamics and an Introduction to Thermostatistcs*, 2nd edition (John Wiley & Sons, New York, 1985), Chapter 4 (especially Sections 4-5, 4-6, and 4-7). Reference 2 does not render Ref. 1 obsolete, because Ref. 1 includes material omitted from Ref. 2 not because of obsolescence, but to keep the length of Ref. 2 reasonable.

[3] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965; reissued by Wavelend Press, Long Grove, Illinois, 2009, Kindle Edition), Sections 5.11 and 5.12. See also Problems 5.22, 5.23, 5.24, and 5.26.

[4] Ralph Baierlein, *Thermal Physics* (Cambridge University Press, Cambridge, UK, 1999), Chapter 3.

[5] Daniel V. Schroeder, *Thermal Physics* (Addison Wesley Longman, San Francisco, 2000), Chapter 4 (especially Sections 4.1 and 4.2).

[6] Reference 5, Problem 4.21.

[7] The quote "Make Physics as simple as possible, but no simpler" and variants thereof are often attributed to Einstein. This variant is cited at the top of the first page of the Preface in Wolfgang Rindler, *Relativity: Special, General, and Cosmological*, Second Edition (Oxford University Press, Oxford, UK, 2006). It, and variants thereof, are cited as "Possibly or Probably by Einstein" in Alice Colaprice, *The Ultimate Quotable Einstein* (Princeton University Press, Princeton, NJ, 2011, Kindle Edition), pp. 384 and 474–475. A certain, and longer, Einstein quote, which refers to theories rather than to thought experiments and is cited on p. 384 of the latter reference, is: "It can scarcely be denied that the supreme goal of all theory is to make the irreducible basic elements as simple and as few as possible without having to surrender the adequate representation of a single datum of experience." (My synopsis of this longer quote is: The supreme goal of all theory is to get the most from the least!) The shorter quote cited in the former reference, even if only "Possibly or Probably by Einstein", seems more applicable to thought experiments, which focus on the representation of only the *essential* data of experience (but, within this limitation, still getting the most from the least).

[8] Peter T. Landsberg, "Answer to Question #34. What is the third law of thermodynamics trying to tell us?," *Amer. Jour. Phys.* **65** (4), 269–270 (1997).

[9] Reference 1, Section 3.5.

[10] Reference 2, Section 3-9.

[11] Reference 3, Section 5.7, especially pp. 168–170.

[12] Reference 5, Section 3.2 (especially the subsection entitled "Measuring Entropies" on pp. 93–95), and most especially Problem 5.14.

[13] It has been suggested that the heat capacity of equilibrium blackbody radiation at constant pressure (as opposed to at constant volume) might not vanish as the temperature is reduced to absolute zero. See Robert E. Kelly, "Thermodynamics of blackbody radiation," *Amer. Jour. Phys.* **49** (8), 714–719 (1981). But the proof that *all* heat capacities vanish as the temperature is reduced to absolute zero, as stated in Ref. 11, seems to be completely general. See also, for example: Ref. 1, Sections 10.2 and 11.7; Ref. 2, Sections 11-2 and 12-8; and Ref. 5, Problems 5.13, 5.14, 5.15, and 5.16. Moreover, as the temperature is reduced, the longer wavelengths of equilibrium blackbody radiation in a cavity of any given fixed size and given fixed shape are cut off, which would require modifications to the results in Robert E. Kelly's paper cited in this endnote. See, for example, W. W. Duley, "Blackbody Radiation in Small Cavities," *Amer. Jour. Phys.* **40** (9), 1337–1338 (1972) and H. P. Baltes, "Comment on Blackbody Radiation in Small Cavities," *Amer. Jour. Phys.* **42** (6), 505–507 (1974).

[14] Reference 1, Sections 10.1, 10.2, and 11.7.

[15] Reference 2, Chapter 11 and Section 12-8.

[16] Reference 3, Sections 3.10, 3.11, 4.5, 4.6, 5.7, and 6.6. (In Section 5.7, see especially the subsection entitled "Limiting properties near absolute zero" on pp. 169–170.)

[17] Reference 4, Sections 14.4 and 14.5.

[18] Reference 5, Section 3.2.

[19] Terrell Hill, *Introduction to Statistical Thermodynamics* (Addison-Wesley; Reading, MA, 1960, second printing 1962; unabridged, corrected republication of the second printing by Dover, New York, 1986), Sections 2-4 and 9-4.

[20] Terrell Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956; unabridged, unaltered republication of the second printing thereof by Dover, Mineola, New York, 1987). See the subsection entitled "Entropy in Statistical Mechanics" on pp. 75–79, especially pp. 76–78. Unlike Refs. 14–19, Ref. 20 does not provide an explicit expression for entropy as a function of temperature, but instead focuses on the fundamental nature of entropy, especially at absolute zero.

[21] It has been contended that — ultimately — all ground states must be nondegenerate: see Ref. 1, Section 10.1 and Ref. 5, pp. 94–95. But, to the contrary, it has also been contended that we can never be sure that a ground state is nondegenerate: see Ref. 20, pp. 76–78. Intermediate viewpoints are expressed in Refs. 14–19.

[22] Reference 19, Sections 5-2, 5-3, 22-2, 22-3, and 22-4.

[23] Reference 2, Sections 16-7, 16-8, and 18-4.

[24] Reference 3, Sections 9.13 through 10.2.

[25] Reference 4, Chapters 6, 9, and 14. See especially Sections 6.2, 6.3, 6.5, 9.1, and 9.4.

[26] Reference 5, Chapter 7 (especially Sections 7.3, 7.4, and 7.5).

[27] William Band, "Statistical Fluctuations at Very Low Temperatures," *Amer. Jour. Phys.* **23** (1), 46–50 (1955). In the second paragraph of the section entitled "Energy Fluctuations" in the second column on p. 49, it is stated that the heat capacity of liquid helium (the isotope ^{4}He) is $C \propto T^6$ temperatures below, but not too far below, the lambda point. As the temperature is reduced further towards absolute zero the heat capacity of liquid helium (the isotope ^{4}He) goes over towards a $C \propto T^3$ law. In this chapter, we do not consider liquid helium in the range of temperatures below, but not too far below, the lambda point, wherein $C \propto T^6$. [The lambda point of liquid helium (the isotope ^{4}He) is discussed in, for example, Ref. 4, pp. 205–206.]

[28] Reference 3, Section 9.16.

[29] Reference 5, Section 7.3.

[30] Reference 2, Section 9.17.

[31] Reference 2, Section 18-4.

[32] Reference 19, Section 22-2.

[33] Reference 2, Section 15-2.

[34] Reference 3, Section 7.7.

[35] Reference 19, Section 5-1.

[36] Reference 2, Section 15-3.

[37] Online Integral Calculator in Wolfram MathWorld at <https://www.mathworld.wolfram.com>; accessed October 21, 2020.

[38] Reference 1, Chapter 10 and Section 11.7.

[39] Reference 2, Chapter 11 and Section 12-8.

[40] Reference 3, pp. 119–121 and 123, Section 4.6, and pp. 169–170 and 216.

[41] Reference 4, Sections 14.4 and 14.5 (especially Section 14.4).

[42]Reference 5, Section 3.2 and Problems 4.35, 4.36, 4.37, 5.13, 5.14, 5.15, and 5.16.

[43]Reference 19, Section 2-4 and pp. 168–170.

[44]Steve Blau and Brad Halfpap, "Question #34. What is the third law of thermodynamics trying to tell us?," *Amer. Jour. Phys.* **64** (1), 13–14 (1996).

[45]Salvador Meté and Juan de la Rubia, "Answer to Question #34. What is the third law of thermodynamics trying to tell us?," *Amer. Jour. Phys.* **66** (4), 277 (1998).

[46]Christopher Rose-Innes, "Answer to Question #34. What is the Third Law of Thermodynamics trying to tell us?," *Amer. Jour. Phys.* **67** (4), 273 (1999).

[47]Amen E. Allahverdyan, Karen Hovhannisyan, and Guenter Mahler, "Optimal refrigerator," *Phys. Rev. E* **81** (5), Article Number 051129, 12 pages (2010).

[48]Ronnie Kosloff and Amikan Levy, "Quantum Refrigerators and the III-Law of Thermodynamics," *Phys. Rev. E* **85** (6), Article Number 061126, 9 pages (2012).

[49]Ronnie Kosloff and Amikan Levy, "Quantum Heat Engines and Refrigerators: Continuous Devices," *Ann. Rev. Phys. Chem.* **65**, 365–393 (2014).

[50]Marlan O. Scully, Yakir Aharonov, Kishore T. Kapale, David J. Tannor, Georg Süssmann, and Herbert Walther. "Sharpening accepted thermodynamic wisdom via quantum control: or cooling to an internal temperature of zero by external control fields without spontaneous emission," *Journal of Modern Optics* **49** (14), 2297–3307 (2002).

[51]Jack Denur, "Absolute Zero and Even Colder?," in *Recent Advances in Thermo and Fluid Dynamics*, edited by Mofid Gorji-Bandfy (IntechOpen, London, UK, 2017), Chapter 9 (pp. 261–302). Some of the material in this chapter was previously discussed in Ref. 51. Where improvements, clarifications, and/or corrections were found, hopefully it is better presented in this chapter.

[52]Reference 1, Section 10.4.

[53]Reference 2, Section 11-3.

[54]Reference 1, p. 75.

[55]Reference 2, p. 116.

[56]Reference 1, Sections 4.7 and 4.8.

[57]Reference 2, Sections 4-6 and 4-7.

[58]Reference 3, Sections 5.11 and 5.12.

[59]Reference 5, Problem 4.15.

[60]Ultimately, *all* emission is *stimulated*: So-called "spontaneous" emission is really emission that is *stimulated* by virtual photons in the quantum-mechanical vacuum. See, for example, David J. Griffiths and Darrell F. Schroeter, *Introduction to Quantum Mechanics*, Third (Kindle) Edition (Cambridge University Press, Cambridge, UK, 2018), Sections 11.2 and 11.3. See especially Subsection 11.2.2. In Section IIID of this chapter, we mean by stimulated emission only "standard" stimulated emission, i.e., only emission that is stimulated by real photons of our very strongly *non*equilibrium electromagnetic radiation (as in a laser) and of the equilibrium blackbody radiation corresponding to ambient temperature $T_{\text{ambient}} > 0\,\text{K}$. [An electron between the plates of a capacitor indeed falls *spontaneously* — with*out* any stimulation — towards lower potential energy (towards the positively-charged plate), but its potential energy decreases *monotonically* from the negative plate towards the positive plate. By contrast, an electron in an excited state of an atom is in a local potential-energy *minimum*, and hence *must* be *stimulated* to escape this local potential-energy minimum and fall to the ground state (the global potential-energy minimum), or to a lower excited state (a lower local potential-energy minimum) if one or more lower excited state(s) exist between its initial excited state and the ground state.]

[61]Kenneth R. Lang, *Essential Astrophysics* (Springer-Verlag, Berlin, 2013), Sections 1.10, 3.3, 5.4.4, 6.1, and 10.1.8, p. 477, 478, 482, and 544, and Appendixes I and II.

[62]Wolfgang Rindler, *Essential Relativity: Special, General, and Cosmological*, 2nd edition (Oxford University Press, Oxford, UK, 2006), Sections 1.11, 11.2C, and 16.1D.

[63]As per Refs. 61 and 62, there are an average of $\approx 10^{57}$ atoms per star (including its planets, comets, etc.) And (see especially Ref. 62), there are an average of $\approx 10^{11}$ stars per galaxy; and there are $\approx 10^{11}$ galaxies, and hence $\approx 10^{22}$ stars, in the observable Universe (not counting the unobservable rest of the Multiverse beyond). Hence there are $\approx 10^{79}$ atoms in the observable Universe (not counting the unobservable rest of the Multiverse beyond).

[64]K. Mendelssohn, "Thermal Conductivity of Superconductors," *Physica* **19**, 775–787 (1953).

[65]K. Mendelssohn, "Thermal Conductivity of Superconductors," *Physica* **24**, Supplement 1, S53–S62 (1958).

[66]Tomas Löfwander and Mikael Fogelström, "Low-Temperature Thermal Conductivity of Superconductors with Gap Nodes," *Phys. Rev. Lett.* **95** (10), Article Number 107006, 4 pages (2005).

[67]Jack Denur, "Are or are not superinsulators with respect to electricity also superinsulators with respect to heat?," <https://www.researchgate.net/post/Are_or_are_not_superinsulators_with_respect_to_electricity_also_superinsulators_with_respect_to_heat>; accessed October 21, 2020.

[68]"Superinsulator," in Wikipedia <https://www.wikipedia.org>; accessed October 21, 2020. See also the references cited therein.

[69]Valerii M. Vinokur, Tatyana I. Baturina, Mikhail V. Fistul, Alexsey Yu. Mironov, Mikhail R. Baklanov, and Christoph Strunk, "Superinsulator and quantum synchronization," *Nature* **452**, 613–616 (2008).

[70]Tatyana I. Baturina and Valerii M. Vinokur, "Superinsulator-Superconductor Duality in Two Dimensions," *Ann. Phys.* **331**, 236–257 (2013).

[71]References 68, 69, and 70 discuss various aspects of superinsulators. Hence they may be helpful, even if they do not specifically discuss thermal conductivity of superinsulators.

[72]Hideyuki Mizuno, Stepheno Mossa, and Jean-Louis Barrat, "Beating the amorphous limit in thermal conductivity by superlattices design," *Scientific Reports* **5**, Article Number 14116, 15 pages, (2015).

[73]Matthew C. Wingert, Jianlin Zheng, Soonshin Kwon, and Renkun Chen, "Thermal transport in amorphous materials: a review," *Semicond. Sci. Technol.* **31**, Article Number 113003, 16 pages, (2016).

[74]Claude Grenier, "Thermal Conductivity of Liquid Helium. I" *Physical Review* **83** (2), 598–603 (1951).

[75]Allen L. King, *Thermophysics* (W. H. Freeman, San Francisco, 1962), Sections 19.1–19.5 (especially Sections 19.3 and 19.5). See also the references cited therein.

[76]P. Leiderer and F. Pobell, "Mutual Friction and the Thermal Conductivity of Superfluid Helium Near T_λ," *Journal of Low Temperature Physics* **3** (6), 577–588 (1970).

[77]The issue of whether energy fluctuations in a system in thermodynamic equilibrium with a thermal reservoir should be construed as being accompanied by temperature fluctuations, and if so, under what circumstances, has been thoroughly debated. Following is a (hopefully representative) sampling of references: Favoring only energy fluctuations: Arnold Munster, *Statistical Thermodynamics*, Volume I (Springer-Verlag, Berlin, 1969), pp. 192–193; C. Kittel, "On the Nonexistence of Temperature Fluctuations in Small Systems," *Amer. Jour. Phys.* **41** (10), 1211–1212 (1973); and Charles Kittel, "Temperature Fluctuation: An Oxymoron," *Physics Today* **41** (5), 93 (1988). Favoring energy fluctuations being accompanied by temperature fluctuations: R. M. Mazo, "Temperature Fluctuations in Thermodynamic Equilibrium," *Physica* **25**, 57–59 (1959); Richard McFee, "On Fluctuations of Temperature in Small Systems," *Amer. Jour. Phys.* **41** (2), 230–234 (1973); Richard McFee, "Comments on Professor C. Kittel's Letter "On the Nonexistence of Temperature Fluctuations in Small Systems," *Amer. Jour. Phys.* **41** (10), 1212 (1973) (see especially Item 3); Herman Feshbach, "Small Systems: When Does Thermodynamics Apply?," *Physics Today* **40** (11),

9–11 (1987); Bernoit B. Mandelbrot, "Temperature Fluctuation: A Well-Defined and Unavoidable Notion," *Physics Today* **42** (1), 9–11 (1989); Jack Denur, "Velocity-Dependent Fluctuations: Breaking the Randomness of Brownian Motion," Phys. Rev. A **40** (9), 5390–5399 (1989) (see especially Appendix A and Endnote 7); and Grey Sh. Boltachev and Jüm W. P. Schmelzer, "On the definition of Temperature and its fluctuations in small systems," *Jour. Chem Phys.* **133** (13), Article Number 134509, 12 pages (2010).

[78]Salvador Maté, Jose A. Manzanares, and Juan de la Rubia, "On the use of the statistical definition of entropy to justify Planck's form of the third law of thermodynamics," *Amer. Jour. Phys.* **68** (10), 932–935 (2000).

[79]X. Wang, Q. H. Liu, and W. Dong, "Dependence on the existence of thermal equilibrium on the number of particles at low temperatures," *Amer. Jour. Phys.* **75** (5), 431–433 (2007).

[80]Reference 60, Section 3.5.3.

[81]Mark J. Hagmann, "Distribution of times for barrier traversal caused by energy fluctuations," *Jour. Appl. Phys.* **74** (12), 7302–7305 (1993).

[82]Richard W. Hamming, *The Art of Probability for Scientists and Engineers*, Kindle Edition (CRC Press, Boca Raton, Fla., 2018), Sections 1.1, 8.12, and 8.13 (especially Section 8.13).

[83]P. C. W. Davies, *The Physics of Time Asymmetry* (First Paperback Edition, University of California Press, 1977), Chapter 3, Sections 5.2, 5.7,and 5.9, and pp. 164, 173, and 193. See also the references cited therein.

[84]"Page:Scientific Papers of Josiah Willard Gibbs.djvu/203," <https://en.wikisource.org/wiki/Page:Scientific_Papers_of_Josiah_Willard_Gibbs.djvu/203>; accessed October 21, 2020.

[85]Reference 1, Section 10.2.

[86]Reference 2, Section 11-2.

[87]Reference 4, Section 14.5.

[88]Reference 5, Problems 1.7 and 5.13.

[89]Any *finite* system has a *finite* heat capacity C. Hence any *finite* transfer of energy *thermally* to or from any *finite* system *always* results in a *finite* change in this system's temperature. For finite systems comprised of N atoms at ordinary temperatures, most typically $C \sim N k_B$. $C_P \geq C_V$, but for solids and liquids the inequality is weak [the equality obtains in the rare cases wherein $(\partial V/\partial T)_P = 0$, as for water in the immediate vicinity of $T = 4\,°\mathrm{C}$], and even for gases the inequality is moderate. Hence at ordinary temperatures, most typically $C \sim N k_B$ obtains for both C_P and C_V. (Recall the third paragraph of Section IIA.) By contrast, as per Refs. 22–36, for finite systems comprised of N atoms, at low temperatures $C \ll N k_B$, with $C \to 0$ as the temperature T approaches absolute zero, i.e., as $T \to 0\,\mathrm{K}$. It is sometimes stated that for finite systems comprised of N atoms at first-order phase transitions, $C_P = \infty$. But this is *incorrect*. In *actuality*, for finite systems comprised of N atoms at first-order phase transitions, $C_P \sim N^2 k_B$. This is $\sim N$ times larger than most typically at ordinary temperatures, i.e., than $C_P \sim N k_B$, but still *finite*. Following is a simple derivation (for more detailed considerations of first-order phase transitions see, for example, Appendix 9 of Ref. 20): Consider a system comprised of N atoms in thermodynamic equilibrium with thermal and pressure reservoirs at temperature T and pressure P, respectively. As per what is sometimes *in*correctly stated, this system *ostensibly* undergoes a first-order phase transition with enthalpy change of magnitude $|\Delta H|$ *only* at *exactly* temperature T — hence *ostensibly* with $C_P = \infty$ — corresponding to a given pressure P. But, in accordance with Section IIIF*2* (especially Section IIIF*2a*, keeping in mind the caveats discussed in Section IIIF*2a*), Endnote 77 and the references cited therein, and Refs. 78 and 79, this system's temperature can *fluctuate* about T and hence need *not* always be *exactly* T. If this system were in *actuality* to undergo this first-order phase transition when its temperature is $T[1 + (\delta T/T)]$ ($|\delta T| << T$; δT could be positive or negative), its entropy would change by $\Delta S_{\text{sys}} = \pm|\Delta H|/(T + \delta T) = \pm|\Delta H|/\{T[1 + (\delta T/T)]\} \doteq (\pm|\Delta H|/T)[1 - (\delta T/T)]$. [The $(+)$ $(-)$ sign in $\pm$ corresponds to this system undergoing the phase

transition in the endothermic (exothermic) direction.] The thermal reservoir's entropy would change by $\Delta S_{\text{res}} = \mp |\Delta H|/T$. [The $(-)$ $(+)$ sign in $\mp$ corresponds to this system undergoing the phase transition in the endothermic (exothermic) direction.] The total entropy change would be $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{res}} \doteq -|\Delta H|\delta T/T^2$. By Boltzmann's relation between entropy and probability, this is at least fairly probable if $|\Delta S_{\text{total}}| \doteq |\Delta H|\delta T/T^2 \lesssim k_B$. Typically, $|\Delta H| \sim \alpha N k_B T$, where α is a numerical factor [typically, at 1 atmosphere pressure, $1 \lesssim \alpha \lesssim 5$ for solid-liquid first-order phase transitions and $\alpha \approx 10$ for liquid-gas first-order phase transitions: see, for example, R. Stephen Berry, Stuart A. Rice, and John Ross, *Physical Chemistry*, Second Edition, (Oxford University Press, New York, 2000), Sections 14.4 and 17.5, and Chapter 24 (especially Sections 14.4 and 17.5)]. Thus it is at least fairly probable for this first-order phase transition to occur over a range of system temperatures $2\delta T \approx 2k_B T^2/|\Delta H| \sim 2k_B T^2/\alpha N k_B T \sim 2T/\alpha N$ centered at T. Hence, in *actuality*, for finite systems comprised of N atoms at first-order phase transitions, $C_P \sim |\Delta H|/2\delta T \sim \alpha N k_B T/(2T/\alpha N) = \alpha^2 N^2 k_B/2 \sim N^2 k_B$. [We note that similar considerations obtain with respect to *ostensibly* infinite heat capacities at critical points as discussed, for example, in Section 24.2B of the immediately aforementioned reference, in Chapter 10 (especially Section 10-3) of Ref. 2, and in Chapter 16 (especially Section 16.2 and pp. 402–409) of Ref. 4.]

[90]Reference 1, Section 4.6.

[91]Reference 2, Problem 4.5-9.

[92]Reference 1, Problems 4.6-3.

[93]Reference 1, Problems 4.6-1 through 4.6-9.

[94]Reference 2, Problems 4.5-5 and 4.5-9 through 4.5-22.

[95]Vladislav Čápek and Daniel P. Sheehan, *Challenges to the Second Law of Thermodynamics: Theory and Experiment* (Springer-Verlag, Dordrecht, The Netherlands, 2005).

[96]Daniel P. Sheehan, Editor, *Limits to the Second Law of Thermodynamics: Experiment and Theory*, Special Issue of *Entropy*, in Volume **19** (2017).

[97]Reference 95, p. 13.

[98]Reference 4, Section 9.1.

[99]Dr. Donald H. Kobe dubbed and employed the concept "numerically but not conceptually equal", as well as the sign $\widehat{=}$ denoting this concept.