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Absolute Zero and Even Colder?

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Abstract

We consider first the absolute zero of temperature and then negative Kelvin temperatures. The unattainability formulation of the Third Law of Thermodynamics is briefly reviewed. It puts limitations on the quest for absolute zero, and in its strongest mode forbids the attainment of absolute zero by any method whatsoever. But typically it is stated principally with respect to thermal-entropy-reduction refrigeration (TSRR). TSRR entails reduction of a refrigerated system's thermal entropy, i.e., its localization in momentum space. The possibility or impossibility of overcoming these limitations via TSRR is considered, with respect to both standard and absorption TSRR. (In standard TSRR, refrigeration is achieved at the expense of work input; in absorption TSRR, at the expense of high-temperature heat input.) We then consider the possibility or impossibility of the attainability of absolute zero temperature via configurational-entropy-reduction refrigeration (CSRR). CSRR entails reduction of a refrigerated system's configurational entropy, i.e., its localization in position space, via positional isolation of entities that happen to be in their ground states. Of course, the Second Law of Thermodynamics requires any decrease in entropy of a refrigerated system to be paid for by a compensating greater (in the limit of perfection, equal) increase in entropy. Or, in other words, the Second Law of Thermodynamics requires any localization in the total momentum-plus-position phase space of a refrigerated system to be paid for by a compensating greater (in the limit of perfection, equal) delocalization in the total momentum-plus-position phase space of the refrigerated system and/or of its surroundings. We also briefly consider energy-reduction refrigeration (ERR), which entails extraction of energy but not entropy from a refrigerated system, and quantum-control refrigeration (QCR). (*S* not *E* denotes entropy in TSRR and CSRR, and *E* denotes energy in ERR, because *S* is the standard symbol for entropy, and *E* for energy.) With respect to both TSRR and CSRR, we consider not only the issue of *attainability* of absolute zero, but also the separate issues, *even if* absolute zero can be *attained*, of *maintaining* it, and of *verifying* that it has been attained. *Purely* dynamic – as opposed to *thermodynamic* – limitations on the quest for absolute zero

under classical versus quantum mechanics are compared and contrasted. Then hot true and cold effective negative Kelvin temperatures are considered. A few fine points concerning the Third Law of Thermodynamics are briefly mentioned in the Appendix.

Keywords: absolute zero, unattainability formulation of the Third Law of Thermodynamics, quantization, energy-time uncertainty principle, negative Kelvin temperatures.

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1. Introduction

We consider first the absolute zero of temperature and then negative Kelvin temperatures.

The unattainability formulation of the Third Law of Thermodynamics is briefly reviewed in Sect. 2.1 It puts limitations of the quest for absolute zero, and in its *strongest mode* forbids the attainment of absolute zero by *any method* whatsoever. But typically it is stated principally with respect to thermal-entropy-reduction refrigeration (TSRR). TSRR entails reduction of a refrigerated system's thermal entropy, i.e., its localization in the momentum part of phase space (in momentum space for short). The possibility or impossibility of overcoming these limitations via TSRR is considered, in Sects. 2.2 and 2.3 with respect to standard TSRR, and in Sect. 2.4 with respect to absorption TSRR. (In standard TSRR, refrigeration is achieved at the expense of work input; in absorption TSRR, at the expense of high-temperature heat input.)

In Sect. 3, we consider the possibility or impossibility of the attainability of absolute zero temperature via configurational-entropy-reduction refrigeration (CSRR). CSRR entails reduction of a refrigerated system's configurational entropy, i.e., its localization in the position part of phase space (in position space for short), via positional isolation of entities that happen to be in their ground states. In TSRR, whether standard or absorption, a refrigerated system's thermal energy, as well as its thermal entropy, is reduced. By contrast, in CSRR only its configurational entropy is reduced: since the entities to be positionally isolated are already in their ground states, their thermal energy *cannot* be reduced. In Sect. 3, we consider CSRR via positional isolation, by means of weighing or Stern-Gerlach apparatus, of entities that happen to be in their ground states, with reference to a specific one of the quantum-control-refrigeration (QCR) methods investigated in Ref. [1], but we will not employ this or any other QCR method per se.

Refrigeration of a system is also possible via extraction only of energy, but not of entropy, from this system. We dub this type of refrigeration as energy-reduction refrigeration (ERR). In order for energy to be extracted from a system without entropy being extracted from it, the energy must be extracted solely as work and not at all as heat. Simple examples include a one-time perfect (isentropic, reversible) adiabatic expansion of a gas, with energy but not entropy extracted from the gas solely via its doing work on its surroundings during expansion, and the one-time expansion of the photon gas comprising the cosmic background

radiation in an ever-expanding Universe (with no steady-state-theory-type “replacement”). In Sect. 2.1 and especially in Sect. 2.5 we will very briefly discuss one-time-expansion ERR, and in Sect. 3 we will very briefly discuss but not employ another type of ERR that is part of a QCR method. (*S* not *E* denotes entropy in TSRR and CSRR, and *E* denotes energy in ERR, because *S* is the standard symbol for entropy, and *E* for energy.)

Of course, the Second Law of Thermodynamics requires any decrease in entropy of a refrigerated system to be paid for by a compensating greater (in the limit of perfection or reversibility, equal) increase in entropy. Or, in other words, the Second Law of Thermodynamics requires any localization in the total momentum-plus-position phase space of a refrigerated system to be paid for by a compensating greater (in the limit of perfection or reversibility, equal) delocalization in the total momentum-plus-position phase space of the refrigerated system and/or of its surroundings. If *all* of the entropy increase and associated waste heat owing to imperfection or irreversibility can be dumped into the surroundings rather than into a refrigerated system, then the refrigerated system will still be cooled to as low a temperature *as if* refrigeration were perfect (reversible), albeit at higher thermodynamic cost. Although perfect (isentropic, reversible) ERR entails zero *net* entropy change of a refrigerated system, within this zero ERR *does* entail a decrease in this system’s thermal or momentum-space entropy (localization in momentum space) and an increase in its configurational or position-space entropy (delocalization in position space). If ERR is imperfect (irreversible) then the increase exceeds the decrease and hence the net entropy change is positive. But again if *all* of the entropy increase and associated waste heat owing to imperfection or irreversibility can be dumped into the surroundings rather than into a refrigerated system, then the refrigerated system will still be cooled to as low a temperature *as if* ERR were perfect (reversible), albeit at higher thermodynamic cost.

All other things being equal, only if *all* waste heat owing to irreversibility is dumped outside of a system being refrigerated can imperfect (irreversible) refrigeration by *any* method (standard or absorption TSRR, CSRR, ERR, QCR, etc.) attain a temperature as low as that attainable via perfect (reversible) refrigeration, and then only at higher thermodynamic cost than via perfect (reversible) refrigeration. Otherwise, all other things being equal, imperfect (irreversible) refrigeration cannot attain as low a temperature as that attainable via perfect (reversible) refrigeration, not even at higher thermodynamic cost than via perfect (reversible) refrigeration.

The Second Law of Thermodynamics forbids a negative change in total entropy, which would correspond to better-than-perfect refrigeration by *any* method (standard, absorption, or other TSRR), CSRR, ERR, QCR, etc. (In Sect. 3.6, we will give a brief hypothetical consideration of better-than-perfect refrigeration.)

With respect to both TSRR and CSRR, we consider not only the issue of *attainability* of absolute zero, but also the separate issues, *even if* absolute zero can be *attained*, of *maintaining* it, and of *verifying* that it has been attained. The issues of attaining and maintaining absolute zero are considered in both Sects. 2 and 3. The issues of verifiability and *purely* dynamic — as opposed to *thermodynamic* — limitations on the quest for absolute zero are considered in Sect. 3, because they seem to be more transparently understandable with respect to CSRR, but in Sect. 3 we then relate them also with respect to TSRR. *Purely* dynamic — as opposed to *thermodynamic* — limitations on the quest for absolute zero under classical versus quantum

mechanics are compared in Sect. 3 Our considerations in Sects. 2 and 3 are general in nature, rather than of specific technical aspects of any particular refrigeration apparatus.

In Sect. 4, we briefly review hot true negative Kelvin temperatures, and then consider cold effective negative Kelvin temperatures. Brief concluding remarks are provided in Sect. 5 A few fine points concerning the Third Law of Thermodynamics are briefly mentioned in the Appendix.

2. The quest for absolute zero via TSRR

2.1. Limits imposed by the Second Law and by the unattainability formulation of the Third Law on TSRR

According to the unattainability formulation of the Third Law of Thermodynamics, the absolute zero of temperature, 0 K, is unattainable in a finite number of finite operations [2–5].¹ But these operations are usually assumed to be TSRR operations [2–5], and most usually *standard* TSRR operations [2–5]. [It might be argued that a one-time infinite operation, for example a one-time infinite adiabatic expansion of a gas, or of the photon gas comprising the cosmic background radiation in an ever-expanding Universe (with no steady-state-theory-type “replacement”), *can* via ERR attain 0 K. But (except perhaps for an ever-expanding Universe) a one-time infinite operation is as physically impossible and physically unrealizable as an infinite number of finite operations. Hence we will not employ one–time–expansion ERR in this chapter. (In this Sect. 2.1 and especially in Sect. 2.5 we will very briefly discuss one–time–expansion ERR. In Sect. 3 we will very briefly discuss but not employ another type of ERR that does not require infinite volume (and that is part of a QCR method) for cooling to 0 K, but which still encounters another difficulty with respect to cooling to 0 K.)]

Standard TSRR most typically entails, first, reducing the position-space or configurational entropy of a system to be refrigerated without a compensating increase in its momentum-space or thermal entropy. This first, isothermal, step is *necessary* but *preparatory*, itself *not* yielding a lowering of temperature. An example is isothermal compression of a gas, the heat of compression being expelled to the surroundings, with the surroundings rather than the system to be refrigerated thus suffering the required compensating increase in momentum-space or thermal entropy. The Second Law of Thermodynamics requires that the system’s surroundings must suffer a larger (in the limit of perfection, equal) increase in momentum-space or thermal entropy than the decrease in the refrigerated system’s position-space or configurational entropy owing to compression of the gas to within a smaller volume. In standard TSRR this is accomplished via heat transfer from the system to be refrigerated to its surroundings [2–5]. Thus momentum-space or thermal entropy is dumped from the system into its surroundings [2–5]. Other examples include isothermal condensation

¹ (Re: Entries [2] and [3], Refs. [2] and [3]) Contrary to one minor statement on p. 30 of Ref. [3], internal energy *does* have a uniquely-defined zero, in accordance with $E = mc^2$. Reference [3] does not render Ref. [2] obsolete, because Ref. [2] discusses aspects not discussed in Ref. [3], and vice versa. The cross-reference to Chapter 10 in the second-to-last line of the second-to-last paragraph on p. 30 of Ref. [3] should be to Chapter 11. (Re: Entry [5], Ref. [5]) Reference [5] (see especially Sect. 3.59) seems to be unique in using the phrase “finite number of finite operations” in the unattainability formulation of the Third Law of Thermodynamics, rather than the less complete phrase “finite number of operations”.

or magnetization, with the heat and thermal entropy thereby released similarly dumped into the surroundings [2–5]. In the second, adiabatic, step, the system to be refrigerated is thermally isolated, so that it can receive no heat from its surroundings. Then, via doing work on its surroundings and/or internally within itself, the refrigerated system trades an increase in its position-space or configurational entropy for a decrease in its momentum-space or thermal entropy. Examples include adiabatic expansion of a gas, wherein work is done on the surroundings, and adiabatic evaporation or demagnetization, wherein at least some of the work is done internally against attractive forces within the refrigerated system itself. The refrigerated system thus follows an adiabat towards a decrease in its temperature. Note that lowering of temperature occurs in this second step, the first step being necessary but preparatory. The *net* result of *both* steps is a decrease in our refrigerated system's momentum-space or thermal entropy but no change in its position-space or configurational entropy — localization in position space in the first step is undone by delocalization in position space in the second step. Thus the refrigerated system's *net* localization is in momentum space but not in position space: hence the designation TSRR. The second, adiabatic, step of standard TSRR, being the temperature-lowering step, may seem to be the more important one. But it would be impossible without the first, isothermal, preparatory step. Note that TSRR requires *heat* to be extracted from a refrigerated system at *some* point in the refrigeration process, even if not at the temperature-lowering step. In the examples of standard TSRR given in this paragraph, this required extraction of heat occurs in the first, isothermal, preparatory step.

Standard TSRR is perfect (reversible) if, in the first step, the decrease in the system's position-space or configurational entropy equals the increase in the surroundings' momentum-space or thermal entropy, and if, in the second step, the decrease in the system's momentum-space or thermal entropy equals the increase in the system's position-space or configurational entropy. Thus standard TSRR is perfect (reversible) if the *total* entropy change is zero for each step considered individually and for both steps combined. TSRR is imperfect (irreversible) if the total entropy change is positive. As per the fifth through seventh paragraphs of Sect. 1 applied specifically to TSRR, all other things being equal, only if *all* waste heat is dumped outside of the system being refrigerated can imperfect (irreversible) TSRR attain a temperature as low as that attainable via perfect (reversible) TSRR, and then only at higher thermodynamic cost than via perfect (reversible) TSRR. Otherwise, all other things being equal, imperfect (irreversible) TSRR cannot attain as low a temperature as that attainable via perfect (reversible) TSRR, not even at higher thermodynamic cost.

We will consider two types of TSRR. *Standard* TSRR, which we described briefly in the second and third paragraphs of this Sect. 2.1, and which we will consider more detail in Sects. 2.2 and 2.3, is executed at the expense of *work* input. In standard TSRR, heat is extracted from a refrigerated system at the expense of *work* input. In Sect. 2.4, we will provide a brief comparison with *absorption* TSRR, which is executed at the expense of *heat* input from a high-temperature reservoir. In absorption TSRR, heat is extracted from a refrigerated system at the expense of *heat* input from a high-temperature reservoir.

To re-emphasize, TSRR, whether standard or absorption, always requires energy to be extracted from a refrigerated system via *heat* at *some* point in the refrigeration process, even if not at the temperature-lowering step. In standard TSRR methods described in the second and third paragraphs of this Sect. 2.1 heat must be extracted from a refrigerated system in the first step to maintain the system isothermal despite compression and/or other localization in position space, even though no heat is extracted from it in the second,

adiabatic, temperature-lowering step. Energy may also be extracted from a refrigerated system via work during standard TSRR. As we will see in Sect. 2.4, in absorption TSRR energy is extracted from a refrigerated system continuously via heat, but never via work.

Because entropy changes become ever smaller as 0 K is approached [2–5], and also because the rate of change of entropy with respect to temperature never becomes infinite [3], the temperature decrease attainable with each successive two-step isothermal-adiabatic standard-TSRR cycle becomes ever smaller [2–5]. Two adiabats can never intercept, and in particular no other adiabat can intercept that corresponding to zero-point entropy and hence to 0 K [2–5]: This is probably the *paramount* reason why, according to the unattainability formulation of the Third Law of Thermodynamics 0 K cannot be reached in a finite number of finite standard-TSRR operations; the reasons cited in the first sentence of this paragraph probably being more of a supplementary nature [2–5]. [It might be argued that a one-time infinite adiabatic expansion of a gas or of the photon gas comprising the cosmic background radiation in an ever-expanding Universe (with no steady-state-theory-type “replacement”), *can* via ERR attain 0 K, and thus via such infinite expansion its adiabat *can* intercept that corresponding to zero-point entropy and hence to 0 K. But (except perhaps for an ever-expanding Universe), a one-time infinite expansion is as physically impossible and physically unrealizable as an infinite number of finite operations.]

Beyond these considerations [2–5] concerning limitations on the quest for 0 K in the classical regime, there is of course a vast literature concerning the quest for 0 K, as well as concerning optimizing refrigerator operation, in the quantum regime. Extensive and thorough discussions, reviews, and bibliographies are provided in Refs. [6] and [7].² We also cite one specific study [8] (of very many). This study [8] investigates optimization of quantum refrigerator operation via maximization of the product of the time rate of heat extraction from a refrigerated system and the thermodynamic efficiency (coefficient of performance) of the refrigerator, maximization of both simultaneously being impossible [8]. The bottom line based on these sources [6–8] seems to be that even in the quantum regime 0 K cannot be attained with finite resources and in finite time [6–8]. Thus, based on these sources [6–8], quantum refrigeration also seems to be under the governance of the unattainability statement of the Third Law, at least in its strongest mode [6–8]. Yet there is an alternative viewpoint [1].

2.2. The Third Law does *not* require *infinite* work to attain $T_C = 0$ K via standard TSRR, but forbids performance of the required *finite* work

The work required to cool any finite sample of matter (and/or of energy such as equilibrium blackbody radiation) maintained within a fixed finite volume V or at constant pressure P from any initial finite fixed relatively hot ambient temperature T_H to what is generally considered to be the ultimate cold temperature $T_C = 0$ K via *standard* TSRR is *finite* — indeed for typical room-temperature T_H and for typical laboratory-size samples typically *small*. Hence the unattainability formulation of the Third Law of Thermodynamics does *not* forbid *attainment* of 0 K via standard TSRR *by requiring infinite work* for the process. Rather, it forbids *attainment* of 0 K via standard TSRR by forbidding the performance of the required *finite*, typically *small*, amount of work.

² (Re: Entry [6], Ref. [6]) The “quest for absolute zero” in the titles of Sects. 2 and 3 of this chapter was borrowed from the titles of Refs. 15 and 36 cited in Ref. [6] of this chapter.

While the coefficient of performance of standard TSRR decreases towards 0 as 0 K is approached, specific heats and heat capacities decrease even more rapidly towards 0 as 0 K is approached. Hence the *finite* — indeed typically *small* — amount of work required to *attain* 0 K via standard TSRR is *not* an issue. Let the cold temperature of a refrigerated system at a given stage of a standard-TSRR process be T_C (T_H assumed fixed). Let dQ_C be the maximum differential increment of heat that the Second Law of Thermodynamics allows to be extracted from this refrigerated system at temperature T_C , with differential increment of heat dQ_H ejected at temperature T_H , at the expense of a given differential increment of work dW . By the First Law of Thermodynamics

$$dQ_H = dQ_C + dW. \quad (1)$$

The best possible standard-TSRR operation and hence the highest possible standard-TSRR coefficient of performance COP_{std} allowed by the Second Law of Thermodynamics is in accordance with [9,10]

$$\begin{aligned} dS_{total} &= dS_C + dS_H = \frac{dQ_C}{T_C} - \frac{dQ_H}{T_H} = \frac{dQ_C}{T_C} - \frac{dQ_C + dW}{T_H} = 0 \\ \implies \frac{dW}{T_H} &= dQ_C \left(\frac{1}{T_C} - \frac{1}{T_H} \right) = dQ_C \frac{T_H - T_C}{T_C T_H} \\ \implies dW &= dQ_C \frac{T_H - T_C}{T_C} \\ \implies COP_{std} &= \frac{dQ_C}{dW} = \frac{T_C}{T_H - T_C} \\ \implies \lim_{T_C \rightarrow 0K} COP_{std} &= \frac{T_C}{T_H}. \end{aligned} \quad (2)$$

In the third step of the first line line of Eq. (2) we applied the First Law of Thermodynamics [Eq. (1)]. In the last two lines of Eq. (2) the coefficient of performance COP_{std} for standard TSRR is given in general and then in the limiting case $T_C \rightarrow 0$ K.

Let Q_C be the heat that must be extracted from our refrigerated system to cool it from T_H to 0 K, $C_X(T_C)$ be the heat capacity given condition X ($X = V$ if constant volume, $X = P$ if constant pressure) of this system at temperature T_C as its temperature T_C is lowered from T_H towards 0 K, and W be the minimum work that the Second Law of Thermodynamics requires to cool it from T_H to 0 K via standard TSRR. Then

$$Q_C = \int_{0K}^{T_H} dQ_C = \int_{0K}^{T_H} C_X(T_C) dT_C \quad (3)$$

and

$$\begin{aligned} dW &= \frac{dQ_C}{COP_{std}} = \frac{T_H - T_C}{T_C} dQ_C = \frac{T_H - T_C}{T_C} C_X(T_C) dT_C < \frac{T_H}{T_C} dQ_C = \frac{T_H}{T_C} C_X(T_C) dT_C \\ \implies W &= \int_{0K}^{T_H} dW = \int_{0K}^{T_H} \frac{T_H - T_C}{T_C} C_X(T_C) dT_C < T_H \int_{0K}^{T_H} \frac{C_X(T_C)}{T_C} dT_C. \end{aligned} \quad (4)$$

It has been stated [12,13]: “The coefficient of performance becomes progressively smaller as the temperature T_C decreases relative to T_H . And if the temperature T_C approaches zero, the coefficient of performance also approaches zero (assuming T_H fixed). It therefore requires huge amounts of work to extract even trivially small quantities of heat from a system near $T_C = 0\text{ K}$.” But the quantities of heat that must be extracted from *any* laboratory-size system as $T_C \rightarrow 0\text{ K}$ are *less* than trivially small; hence the required amounts of work are *less* than huge. If $C_X(T_C)$ were constant, independent of T_C , then by Eq. (4) the minimum work W required by the Second Law for cooling *any* finite system to 0 K, i.e., for reducing T_C from T_H to 0 K, would indeed diverge towards ∞ — but even then just barely (logarithmically) — as $T_C \rightarrow 0\text{ K}$. But if $C_X(T_C)$ decreases *at all* — even however slowly — with decreasing T_C , then by Eq. (4) the divergence of W as $T_C \rightarrow 0\text{ K}$ is cured. In fact $C_X(T_C)$ not merely decreases but decreases *rapidly* [14,15] as $T_C \rightarrow 0\text{ K}$; hence the divergence of W as $T_C \rightarrow 0\text{ K}$ is not merely cured but cured by an extremely wide margin. *Any* system constrained within a fixed finite volume, or even within an unfixed but always finite volume for example corresponding to maintenance of constant pressure, *must* obey the two-state model [16] in the limit $T_C \rightarrow 0\text{ K}$ [16], because (as will be discussed in Sect. 3.4) quantum mechanics *requires* discrete energy levels and *forbids* an energy continuum in any system constrained within a fixed finite volume, or even within an unfixed but always finite volume for example corresponding to maintenance of constant pressure.³ And for the two-state model [16] the heat capacity decreases nearly exponentially with decreasing temperature in the limit $T_C \rightarrow 0\text{ K}$ [16]. We note that if T_H is not too high it makes little difference whether we put $C_X(T_C) = C_V(T_C)$ or $C_X(T_C) = C_P(T_C)$ in Eqs. (3) and (4) [14,15], because always $T_C \leq T_H$, with $C_P(T_C) - C_V(T_C) \rightarrow 0$ and $C_P(T_C)/C_V(T_C) \rightarrow 1$ (both from above) as $T_C \rightarrow 0\text{ K}$ [14,15]. Indeed, since solids and liquids are typically only slightly compressible, for solids and liquids $C_P(T_C)$ is typically only marginally larger than $C_V(T_C)$ even at T_C well above 0 K, even as far above 0 K as is consistent with the existence of solids and liquids [17,18].

But as was discussed in Sect. 2.1, in accordance with the unattainability formulation of the Third Law of Thermodynamics [2–5], entropy changes become ever smaller as 0 K is approached, rates of change of entropy with respect to temperature never become infinite [3], and two adiabats can never intercept [2–5]. Hence the temperature decrease attainable with each successive two-step isothermal-adiabatic TSRR cycle becomes ever smaller [2–5]. Especially, two adiabats can never intercept, and in particular no other adiabat can intercept that corresponding to zero-point entropy and hence to 0 K [2–5]. Thus the unattainability formulation of the Third Law forbids the attainment of 0 K via standard TSRR *not* by requiring an *infinite* amount of work to cool a finite sample of matter (and/or of energy) within a finite volume to 0 K, but rather by forbidding the *finite* — typically *small* — required amount of work from being performed via any standard-TSRR process [2–5]. While COP_{std} as per Eq. (2) is the theoretical maximum and the work W as per Eq. (4) is the theoretical minimum allowed by the Second Law of Thermodynamics, for well-designed real-world standard TSRR systems the actual COP_{std} is not more than a few times smaller and the actual required work is not more than a few times larger these theoretical limits, and this small numerical factor in no way contravenes our result.

³ (Re: Entry [16], Ref. [3]) In the version of the two-state model presented in Sects. 15-3 and 16-2 of Ref. [3], there is no degeneracy. But the nearly exponential decrease of heat capacity with decreasing temperature as $T \rightarrow 0\text{ K}$ still obtains irrespective of any (finite) degeneracy of one or both energy levels. Degeneracy of the ground level does not affect the heat capacity at all; G -fold degeneracy of the excited level multiplies G -fold the heat capacity as compared to that given a nondegenerate excited level as per Sect. 15-3 of Ref. [3].

2.3. Can the difficulty of infinite power required to maintain $T_C = 0\text{ K}$ be overcome?

The work W required to attain $T_C = 0\text{ K}$ as derived in Sect. 2.2 is that required *only* to extract all of the *internal* thermal energy *out of* a system to be refrigerated via standard TSRR, thus cooling it to $T_C = 0\text{ K}$. But this *unrealistically* assumes that *strictly zero external* thermal energy flows *into* this system in the meantime. Thus we must consider *not only* the work W required to extract all of the *internal* thermal energy *out of* a system to be refrigerated, thus cooling it to $T_C = 0\text{ K}$, i.e., to attain $T_C = 0\text{ K}$. We must *also* consider the power $P = dW'/dt$ and work $W' = \int P dt$ required to overcome the flow of *external* thermal energy, i.e., heat flow dQ_C/dt , into our refrigerated system, requisite to *maintain* it at $T_C = 0\text{ K}$. (Note: Time t should not be confused with temperature T .) Heat transfer into our refrigerated system, indeed heat transfer in general, occurs via three processes: conduction, radiation, and convection [19–21]. Heat transfer dQ_C/dt into our refrigerated system via conduction is proportional to $T_H - T_C$ and via radiation to $T_H^4 - T_C^4$ [19–21]. While convection is a complex phenomenon, which may be either natural or forced, for simplicity and for argument's sake let us accept the most usual result [21], according to which heat transfer via natural convection is proportional to $(T_H - T_C)^{5/4}$ [21]. If we must have convection, we prefer natural convection to forced convection, because the former transfers heat less efficiently. Thus heat transfer dQ_C/dt via conduction is $a(T_H - T_C)$, via radiation $b(T_H^4 - T_C^4)$, and via natural convection $c(T_H - T_C)^{5/4}$ [19–21]; the prefactors a , b , and c corresponding to conductive, radiative, and natural-convective heat transfer, respectively [19–21]. These three prefactors for a given system to be refrigerated are determined by its geometry (size, shape, surface area, etc.), by the type of insulation, usually at least to some extent by T_H and/or T_C , and by any other relevant properties [19–21]. Thus, applying the result for COP_{std} from Eq. (2),

$$\begin{aligned} \frac{dQ_C}{dt} &= a(T_H - T_C) + b(T_H^4 - T_C^4) + c(T_H - T_C)^{5/4} \\ \implies P &= \frac{dW'}{dt} = \frac{dQ_C/dt}{COP_{\text{std}}} = \frac{T_H - T_C}{T_C} \frac{dQ_C}{dt} = \frac{T_H - T_C}{T_C} \left[a(T_H - T_C) + b(T_H^4 - T_C^4) + c(T_H - T_C)^{5/4} \right] \\ \implies \lim_{T_C \rightarrow 0\text{ K}} \frac{dQ_C}{dt} &= aT_H + bT_H^4 + cT_H^{5/4} \\ \implies \lim_{T_C \rightarrow 0\text{ K}} P &= \lim_{T_C \rightarrow 0\text{ K}} \frac{dW'}{dt} = \lim_{T_C \rightarrow 0\text{ K}} \frac{dQ_C/dt}{COP_{\text{std}}} = \lim_{T_C \rightarrow 0\text{ K}} \frac{T_H - T_C}{T_C} \frac{dQ_C}{dt} \\ &= \lim_{T_C \rightarrow 0\text{ K}} \frac{T_H}{T_C} \left(aT_H + bT_H^4 + cT_H^{5/4} \right) = \lim_{T_C \rightarrow 0\text{ K}} \frac{aT_H^2 + bT_H^5 + cT_H^{9/4}}{T_C}. \end{aligned} \tag{5}$$

This expression diverges towards ∞ as $T_C \rightarrow 0\text{ K}$ unless a , b , and c decrease with decreasing T_C at least as rapidly as T_C itself, with $a = b = c = 0$ at least at $T_C = 0\text{ K}$. But given that

a , b , and c in general depend on T_H as well as on T_C and that T_H is fixed, such a functional dependency of a , b , and c on T_C seems unlikely. But perhaps we should not *a priori* rule it out as impossible.

The decrease, indeed the typically *rapid* decrease, of $C_X(T_C)$ as $T_C \rightarrow 0$ K [14,15] allows *all* of a finite refrigerated system's *internal* thermal energy to be pumped *out* of it thus cooling it to $T_C = 0$ K via standard TSRR with the expenditure of a finite (typically small) amount of work. The vanishing of $C_X(T_C)$ as $T_C \rightarrow 0$ K within a refrigerated system more than compensates for the vanishing of COP_{std} in Eq. (4) as $T_C \rightarrow 0$ K. But the vanishing of $C_X(T_C)$ as $T_C \rightarrow 0$ K within a refrigerated system does *not* help insofar as overcoming the flow of *external* thermal energy, i.e., heat flow, from surroundings at ambient temperature T_H *into* a refrigerated system, is concerned. Thus in Eq. (5) the vanishing of COP_{std} as $T_C \rightarrow 0$ K is *not* compensated for. Hence *even if* $T_C = 0$ K is *attained* infinite power is required to *maintain* it — *unless* a , b , and c decrease with decreasing T_C at least as rapidly as T_C itself, with $a = b = c = 0$ at least at $T_C = 0$ K. Can this “*unless*” — implying that insulation must become *perfect* [23] as $T_C \rightarrow 0$ K — be realized? Again, given that a , b , and c in general depend on T_H as well as on T_C and that T_H is fixed, such a functional dependency of a , b , and c on T_C seems unlikely, but perhaps we should not *a priori* rule it out as impossible. But *even if* it is impossible, $T_C = 0$ K may be not merely *attainable*, but also *maintainable*, but only for an instant, or at most for a finite number of instants.

Note that $COP_{\text{std}} = 0$ obtains *only* at *exactly* the *point* value $T_C = 0$ K [9,10]. This leaves open the possibility that even if a , b , and c do *not* decrease with decreasing T_C at least as rapidly as T_C itself and remain finite and positive at $T_C = 0$ K, i.e., even if insulation does *not* become perfect as $T_C \rightarrow 0$ K, $T_C = 0$ K could be *attained* and then *maintained for an instant*, because P need be infinite for only an infinitesimally short time so $W' = \int P dt$ could still be finite. But if even given *imperfect* insulation $T_C = 0$ K could thus be *attained even for an instant*, then it could be likewise re-attained for any arbitrarily large (but finite) number \mathfrak{N} instants, since $\mathfrak{N} \int P dt$ would then still be finite. Any finite number of infinitesimally short time intervals still sum to an infinitesimally short time interval. Let the refrigeration process begin at time t_0 and be completed at time t_1 . Let T_H be fixed, and for simplicity and for argument's sake let

$$T_C(t) = T_H \left(1 - \frac{t - t_0}{t_1 - t_0} \right)^\gamma, \quad (6)$$

where γ is a fixed positive real number. Then, for simplicity and for argument's sake, let us consider only the part of the refrigeration process at $T_C \ll T_H$. Within this part of the refrigeration process, T_C has little room to decrease towards $T_C = 0$ K, so since T_H is fixed letting a , b , and c be constants independent of T_C may be a good approximation. Thus we have, applying the last two lines of Eq. (5),

$$\begin{aligned}
 W' &= \int_{t_0}^{t_1} P dt = \left(aT_H^2 + bT_H^5 + cT_H^{9/4} \right) \int_{t_0}^{t_1} \frac{dt}{T_C(t)} \\
 &= \left(aT_H^2 + bT_H^5 + cT_H^{9/4} \right) \int_{t_0}^{t_1} \frac{dt}{T_H \left(1 - \frac{t-t_0}{t_1-t_0} \right)^\gamma} = \left(aT_H + bT_H^4 + cT_H^{5/4} \right) \int_{t_0}^{t_1} \frac{dt}{\left(1 - \frac{t-t_0}{t_1-t_0} \right)^\gamma} \\
 &= \left(aT_H + bT_H^4 + cT_H^{5/4} \right) \int_{t_0}^{t_1} \frac{dt}{\left[\frac{t_1-t_0-(t-t_0)}{t_1-t_0} \right]^\gamma} = \left(aT_H + bT_H^4 + cT_H^{5/4} \right) (t_1 - t_0)^\gamma \int_{t_0}^{t_1} \frac{dt}{(t_1 - t)^\gamma} \\
 &\implies \text{if } 0 < \gamma < 1 \text{ then } W' = \left(aT_H + bT_H^4 + cT_H^{5/4} \right) (t_1 - t_0)^\gamma \frac{(t_1 - t_0)^{1-\gamma}}{1-\gamma} \\
 &= \left(aT_H + bT_H^4 + cT_H^{5/4} \right) \frac{t_1 - t_0}{1-\gamma} \\
 &\implies W' \text{ is finite if } 0 < \gamma < 1 \\
 &\implies W_{\text{total}} = W + W' \text{ is finite if } 0 < \gamma < 1. \tag{7}
 \end{aligned}$$

In the last step of Eq. (7) we applied the finiteness of our result for W as per Eq. (4) and the associated discussions. Thus it seems that the difficulty of infinite power and infinite work required to *maintain* $T_C = 0$ K can, at least to this very limited extent, be overcome.

W' and hence $W_{\text{total}} = W + W'$ can remain finite if $T_C = 0$ K is to be maintained for *finitely longer than* an instant or finite number of instants given fixed finite $T_H > 0$ K only if a , b , and c decrease with decreasing T_C at least as rapidly as T_C itself, with $a = b = c = 0$ at least at $T_C = 0$ K. And this in the face of a , b , and c in general depending on T_H as well as on T_C , with T_H being fixed. Thus we require *perfect* [23] — not merely good — insulation at $T_C = 0$ K, yet also with fixed finite $T_H > 0$ K. And perfect insulation — $a = b = c = 0$ — is hard to come by. Hard, but perhaps not impossible. Again, for simplicity and for argument's sake, let us consider only the part of the refrigeration process at $T_C \ll T_H$. By surrounding our refrigerated system including its insulation with a vacuum, and with the insulation being comprised entirely of solids (not fluids: liquids or gases), we can indeed achieve $c = 0$ — solids certainly exist at finite $T_H > 0$ K. Convection (whether natural or forced) occurs only in fluids (gases and liquids), and is nonexistent in solids or in a vacuum. But even though we have thus achieved $c = 0$, we must still achieve $a = 0$ and $b = 0$. Superinsulators — perfect (not merely good) — insulators with respect to electricity have recently been discovered [23], with the superinsulating state existing at temperatures up to $T_{SI,elec,max}$ finitely greater than 0 K [23]. (Reference [23] provides a thorough and excellent review, as well as an extensive bibliography.) So perhaps we should not *a priori* rule out superinsulators with respect to heat, with the superinsulating state existing at $0 \text{ K} \leq T_H \leq T_{SI,heat,max}$ [23]. Even if superinsulation with respect to heat exists, we do not know if $T_{SI,heat,max} = T_{SI,elec,max}$. But all we require is that $0 \text{ K} < T_H < T_{SI,heat,max}$ [23]. If superinsulation with respect to heat exists, then $a = 0$ can obtain at finite $T_H > 0$ K. [Superinsulation should not be confused with the typical exponential improvement of ordinary insulation with decreasing temperature. The latter obtains, for example, if conduction of heat and electricity is via electrons thermally promoted from the valence band to the conduction band with the two bands separated by a fixed finite energy gap ΔE . Then the probability of such promotion per attempt to jump the gap decreases exponentially with decreasing T_H in accordance with the Boltzmann factor $e^{-\Delta E/kT_H}$ (k is Boltzmann's constant) and hence is very small for low T_H . But it does not vanish *perfectly* except at $T_H = 0$ K and hence ordinary insulation remains *imperfect* at any finite $T_H > 0$ K.] If furthermore the vacuum surrounding our refrigerated system with its superinsulating shield with respect to heat is permeated by equilibrium blackbody radiation at fixed finite T_H below the upper temperature limit $T_{SI,heat,max}$ of the superinsulating state

with respect to heat, then this radiation will not destroy the superinsulating state. (Indeed a vacuum *must* be permeated by equilibrium blackbody radiation at any temperature finitely greater than 0 K.) If the superinsulator is opaque to this equilibrium blackbody radiation, with the radiation being thermalized in its outer layer to internal energy at $T_H < T_{SI,heat,max}$, or scattered or reflected away, then $b = 0$. A nonopaque superinsulator can be shielded by an opaque material, with the radiation being thermalized in the outer layer of this opaque material to internal energy at $T_H < T_{SI,max}$, or scattered or reflected away, so that $b = 0$. Of course for $b = 0$ *exactly* the opacity must be not merely good but *perfect*. While this perfection may be impossible to achieve *exactly*, it can be achieved *for all practical purposes*. Typically the fraction of incident radiation not thermalized as internal energy within an opaque material, or not scattered or reflected away, decreases exponentially increasing thickness of an opaque material. An incident photon has a probability of $e^{-\mathcal{N}}$ of penetrating through a thickness of \mathcal{N} or more e -folding lengths without being thermalized as internal energy within an opaque material, or being scattered or reflected away. If, say, $\mathcal{N} \gtrsim 1000$, then for all practical purposes we can rest assured that not even 1 photon will get through during the time required for any refrigeration experiment and hence that, even if not exactly then for all practical purposes, $b = 0$.

Thus at least *prima facie* it seems that there seems to be no difficulty in principle in achieving $c = 0$, and even if not perfectly then for all practical purposes also $b = 0$. The main concern is whether or not $a = 0$ is achievable, namely whether or not superinsulation exists with respect to heat as it does with respect to electricity [23]. Probably the best that we can do at this point is to admit that we do not know; that this is an open question [23].

2.4. A brief comparison with absorption TSRR

The discussions in Sects. 2.2 and 2.3 presuppose *standard* TSRR, which operates as a heat engine in reverse. In heat engine operation heat flows from a hot reservoir via the engine into a cold reservoir; within the limit imposed by the Second Law of Thermodynamics, the engine can convert part of this heat flow into work output. Standard TSRR operates as a heat engine in reverse, with work input driving heat flow from a cold reservoir into a hot one, also within the limit imposed by the Second Law of Thermodynamics.

However, there is one other commonly-employed type of TSRR that we wish to consider — *absorption* TSRR [24]. While absorption TSRR is not employed in practice to reach cryogenic temperatures, let alone to approach 0 K, it may be of interest to consider it even if only in principle. Absorption TSRR requires zero work input [24]. Instead, heat Q_H is supplied to the refrigeration apparatus from a hot reservoir at temperature T_H , heat Q_C is extracted by the refrigeration apparatus from a refrigerated system at cold temperature T_C , and heat Q_I is ejected from the refrigeration apparatus at intermediate temperature T_I ($T_H > T_I > T_C$) [24]. By the First Law of Thermodynamics

$$dQ_I = dQ_C + dQ_H. \quad (8)$$

Let the cold temperature of a refrigerated system at a given stage of an absorption-TSRR process be T_C (T_I and T_H assumed fixed). Let dQ_C be the maximum differential increment of heat that the Second Law of Thermodynamics allows to be extracted from this refrigerated system at temperature T_C at the expense of a given differential increment of heat input

dQ_H at temperature T_H , with differential increment of heat $dQ_I = dQ_C + dQ_H$ ejected at temperature T_I . The best possible absorption-TSRR operation and hence the highest possible absorption-TSRR coefficient of performance COP_{abs} allowed by the Second Law of Thermodynamics is in accordance with

$$\begin{aligned}
 dS_{total} &= dS_I + dS_C + dS_H = \frac{dQ_I}{T_I} - \frac{dQ_C}{T_C} - \frac{dQ_H}{T_H} = 0 \\
 \implies \frac{dQ_C + dQ_H}{T_I} - \frac{dQ_C}{T_C} - \frac{dQ_H}{T_H} &= \frac{dQ_C}{T_I} + \frac{dQ_H}{T_I} - \frac{dQ_C}{T_C} - \frac{dQ_H}{T_H} = 0 \\
 \implies dQ_C \left(\frac{1}{T_C} - \frac{1}{T_I} \right) &= dQ_H \left(\frac{1}{T_I} - \frac{1}{T_H} \right) \\
 \implies dQ_C \frac{T_I - T_C}{T_I T_C} &= dQ_H \frac{T_H - T_I}{T_I T_H} \\
 \implies dQ_C \frac{T_I - T_C}{T_C} &= dQ_H \frac{T_H - T_I}{T_H} \\
 \implies COP_{abs} = \frac{dQ_C}{dQ_H} &= \frac{T_C (T_H - T_I)}{T_H (T_I - T_C)} \\
 \implies \lim_{T_C \rightarrow 0K} COP_{abs} &= \frac{T_C (T_H - T_I)}{T_I T_H}. \tag{9}
 \end{aligned}$$

In the second line of Eq. (9) we applied the First Law of Thermodynamics [Eq. (8)]. In the last two lines of Eq. (9) the coefficient of performance COP_{abs} for absorption TSRR is given in general and then in the limiting case $T_C \rightarrow 0K$.

Now let us compare COP_{abs} with COP_{std} . By comparing Eqs. (2) and (9), we obtain

$$\begin{aligned}
 \frac{COP_{abs}}{COP_{std}} &= \frac{\frac{T_C(T_H - T_I)}{T_H(T_I - T_C)}}{\frac{T_C}{T_H - T_C}} = \frac{(T_H - T_I)(T_H - T_C)}{T_H(T_I - T_C)} = \left(1 - \frac{T_C}{T_H}\right) \frac{T_H - T_I}{T_I - T_C} = \left(1 - \frac{T_I}{T_H}\right) \frac{T_H - T_C}{T_I - T_C} \\
 \implies \lim_{T_C \rightarrow 0K} \frac{COP_{abs}}{COP_{std}} &= \frac{T_H - T_I}{T_I} = \frac{T_H}{T_I} - 1. \tag{10}
 \end{aligned}$$

Thus

$$\begin{aligned}
 COP_{abs} &> COP_{std} \text{ if } (T_H - T_I)(T_H - T_C) > T_H(T_I - T_C) \\
 \implies T_H^2 - T_I T_H - T_C T_H + T_C T_I &> T_I T_H - T_C T_H \\
 \implies T_H^2 - 2T_I T_H + T_C T_I &> 0 \\
 \implies T_I(T_C - 2T_H) &> -T_H^2 \\
 \implies T_I(2T_H - T_C) &< T_H^2 \\
 \implies T_I &< \frac{T_H^2}{2T_H - T_C} \\
 \implies T_I &< \frac{T_H}{2 - \frac{T_C}{T_H}} \\
 \implies T_I &< \frac{T_H}{2} \text{ if } T_C \ll T_H. \tag{11}
 \end{aligned}$$

Thus it may be of interest to consider absorption TSRR, even if only in principle, because [24]: (a) It is thermodynamically less costly to supply a *given* quantity of energy input as *heat*, which is sufficient for absorption TSRR, than as *work*, which is required for standard TSRR. (b) If Inequality (11) is fulfilled, then absorption TSRR requires a *smaller* quantity of energy input as *heat* than standard TSRR does as *work*. (c) Some absorption-TSRR systems, notably the Munters/von-Platen system [24] and the Einstein/Szilárd system [25] (which however at least in their original forms cannot attain cryogenic temperatures, let alone approach 0 K), have no moving parts, which minimizes waste of negentropy and free energy via friction while maximizing reliability; also, they operate essentially silently, thus wasting essentially no negentropy and free energy as sound. By Inequality (11), the upper limit of T_I consistent with $COP_{\text{abs}} > COP_{\text{std}}$, i.e., with absorption TSRR requiring less heat input than standard TSRR does work input for given T_H and T_C , never falls below $T_H/2$ even in the limit $T_C \rightarrow 0$ K. Hence even after T_C has been reduced sufficiently that the last lines of Eqs. (2), (9), and (10) and Inequality (11) are applicable, if $T_I < T_H/2$ then the quantities of Q_H , dQ_H/dt , and $Q'_H = \int \frac{dQ_H}{dt} dt$ required for absorption TSRR are *smaller* than those of W , P , and W' , respectively, required in accordance with Eqs. (4), (5), and (7), respectively, for standard TSRR — besides being thermodynamically less costly *per given quantity*. Thus it seems that perhaps we should not *a priori* rule out that approaching or even attaining $T_C = 0$ K may be easier, at least in principle even if not in practice, via absorption TSRR, or perhaps via some variant or modification thereof, than via standard TSRR.

Nevertheless, for T_I finitely greater than 0 K (of course $T_I > T_C$) the advantage of absorption TSRR over standard TSRR is finite. Hence we should restate the first paragraph of Sect. 2.2 with respect to absorption TSRR: The heat input Q_H required to cool any finite sample of matter (and/or of energy such as equilibrium blackbody radiation) maintained within a fixed finite volume V or at fixed finite pressure P from any initial finite fixed relatively hot ambient temperature T_H to $T_C = 0$ K via absorption TSRR is *finite* — indeed for typical room-temperature T_H and for typical laboratory-size samples typically *small*. Hence the unattainability formulation of the Third Law of Thermodynamics does *not* forbid attainment of 0 K via absorption TSRR *by requiring infinite* Q_H for the process. Rather, it forbids *attainment* of 0 K via absorption TSRR by forbidding the utilization of the required *finite*, typically *small*, Q_H . While COP_{abs} as per Eq. (9) is the theoretical maximum allowed by the Second Law of Thermodynamics, for well-designed real-world absorption TSRR systems the actual COP_{abs} is not more than a few times smaller this theoretical maximum, and this small numerical factor in no way contravenes our result.

But *even if* $T_C = 0$ K could be *precisely attained*, whether via standard, absorption, or other TSRR, the question of *maintaining* $T_C = 0$ K discussed in Sect. 2.3 is still open. *Even if* $T_C = 0$ K could be *precisely attained*, whether via standard, absorption, or other TSRR, whether or not it is *maintainable* for finitely longer than the infinitesimally short time allowed in accordance with Eqs. (6) and (7) and the associated discussions is still open. But least in principle even if not in practice *if* $T_C = 0$ K can be *attained*, then *maintaining* $T_C = 0$ K, whether this is possible only for infinitesimally short time or for finite time, may be more easily achievable via absorption TSRR than via standard TSRR.

2.5. Brief remarks concerning one-time-expansion ERR

One-time-expansion ERR can, at least in principle, be achieved via a sample of gas at ambient pressure at Earth's surface (or the surface of any other planet with an

atmosphere) being transported to a vacuum (either to a vacuum chamber on the planet or to the vacuum of space), and there being allowed to expand adiabatically. For a given expansion ratio, maximum cooling is attained via a perfect (reversible) adiabatic expansion, wherein the decrease in thermal (momentum-space) entropy exactly offsets the increase in configurational (position-space) entropy owing to expansion. But even an irreversible adiabatic expansion is ERR, because even in an irreversible adiabatic expansion only energy and not entropy is extracted from the gas. But in an irreversible adiabatic expansion some thermal (momentum-space) entropy is created within the gas, so that the decrease in thermal (momentum-space) entropy only partially offsets the increase in configurational (position-space) entropy owing to expansion, and hence refrigeration is less efficient, with less cooling per given expansion ratio, than in the perfect (reversible) case. It might be argued that no vacuum that the gas expands into is perfect and hence its expansion cannot continue indefinitely. But in an ever-expanding Universe (with no steady-state-theory-type “replacement”) the surrounding vacuum becomes ever more perfect. But (except perhaps for an ever-expanding Universe), a one-time infinite expansion is as physically impossible and physically unrealizable as an infinite number of finite operations.

It might also be argued that a one-time infinite operation, for example a one-time infinite adiabatic expansion of a gas after infinite time in an ever-expanding Universe (with no steady-state-theory-type “replacement”), or of the photon gas comprising the cosmic background radiation after infinite time in an ever-expanding Universe (with no steady-state-theory-type “replacement”), *can* via ERR attain 0 K. But this requires *infinite* resources — *infinite* volume and *infinite* time. Hence it does not contravene the conclusion that absolute zero 0 K *cannot* be attained with *finite* resources — not only classically but even in the quantum regime [6–8] that we will consider in Sect. 3. Hence we do not employ one-time-expansion ERR in this chapter. [In Sect. 3 we will very briefly discuss but not employ another type of ERR that does not require infinite volume (and that is part of a QCR method) for cooling to 0 K, but which still encounters another difficulty with respect to cooling to 0 K.]

We note that, not unlike an irreversible adiabatic expansion of a gas, a polytropic expansion thereof intermediate between adiabatic and isothermal can achieve refrigeration, albeit less efficiently, with less cooling per given expansion ratio, than a perfect (reversible) adiabatic one. A polytropic expansion intermediate between adiabatic and isothermal can be construed as ERR, because only energy and not entropy is *extracted from* the gas. Thermal (momentum-space) entropy is *imported into* the gas during a polytropic expansion, so that the decrease in thermal (momentum-space) entropy only partially offsets the increase in configurational (position-space) entropy owing to expansion, and hence refrigeration is less efficient than in the perfect (reversible) adiabatic case. The only difference between an irreversible adiabatic expansion and a polytropic one intermediate between adiabatic and isothermal is that thermal (momentum-space) entropy is generated within the expanding gas in the former case and imported into it in the latter. [Of course, additional irreversibilities can result in thermal (momentum-space) entropy being generated within the expanding gas during a polytropic expansion intermediate between adiabatic and isothermal, thus rendering refrigeration still less efficient.]

Perfect (reversible) one-time-expansion adiabatic ERR of our gas, or even imperfect (irreversible) adiabatic or even polytropic (intermediate between adiabatic and isothermal)

ERR thereof, yields rather than costs work. Of course, this does not count the work that it costs to evacuate its vacuum chamber or to transport it to the vacuum of space.

Of course, except perhaps for the cooling of or in an ever-expanding Universe (with no steady-state-theory-type “replacement”), the difficulties of *maintaining* cold as opposed to merely *attaining* it apply with respect to one–time-expansion ERR as with respect to standard and absorption TSRR. These difficulties also apply with respect to CSRR, QCR, and another type of ERR that is part of a QCR method, all to be considered in Sect. 3.

3. The quest for absolute zero via configurational-entropy-reduction refrigeration (CSRR)

In Sect. 3 we consider the quest for absolute zero, $T_C = 0\text{ K}$, via configurational-entropy-reduction refrigeration (CSRR), which localizes a refrigerated system in the position part of phase space (in position space for short), as opposed to thermal-entropy-reduction refrigeration (TSRR), which localizes it in the momentum part of phase space (in momentum space for short). Standard TSRR requires extraction of energy from a refrigerated system via *heat* during at least *some* step of the refrigeration process. It may also entail extraction of energy from a refrigerated system via work (recall Sect. 2.1). In absorption TSRR energy is extracted from a refrigerated system continuously via heat, but never via work (recall Sect. 2.4). By contrast, CSRR entails *no* extraction of energy from a refrigerated system *either via heat or via work*. CSRR requires finite work input to *attain* $T_C = 0\text{ K}$, even if this work input is employed differently than the work input in standard TSRR as per Sect. 2.2, or than high-temperature heat input in absorption TSRR as per Sect. 2.4 CSRR shares with TSRR the difficulties of *maintaining* $T_C = 0\text{ K}$ as per Sect. 2.3 and the last paragraphs of Sects. 2.4 and 2.5. But in Sect. 3 let us focus mainly on prospects for and limitations on the quest for *attaining* $T_C = 0\text{ K}$ via CSRR, comparing these prospects and limitations with those via TSRR. We postpone remarking on the difficulties of *maintaining* $T_C = 0\text{ K}$ via CSRR until the last two paragraphs of Sect. 3.5.

3.1. Questioning the unattainability formulation of the Third Law of Thermodynamics in toto

The unattainability formulation of the Third Law of Thermodynamics *in toto* — not merely any particular limit(s) imposed thereby — has been questioned [1]. Above all, the question of the attainability of 0 K in a finite number of finite operations (perhaps even in one) by *any method* whatsoever, and hence the status of the unattainability formulation of the Third Law of Thermodynamics in its *strongest* mode, according to which this is impossible, remains open [1,26–28]. Even so, the question of whether or not 0 K is attainable by *any method* whatsoever is sometimes stated to be only of academic interest [27], and it is also sometimes stated that there may be “profound problems [22]” concerning attaining “absolute thermal isolation [22],” i.e., perfect insulation [23], and that infinitely precise measurements [22] may be required to *perfectly verify* [22] that *precisely* 0 K has actually been attained [22].

Yet it has been shown that 0 K may be attainable in a finite number of finite operations (perhaps even in one) via quantum-control-refrigeration (QCR) methods, specifically, employing quantum coherence [1]. This challenges the *strongest-mode* unattainability

formulation of the Third Law of Thermodynamics, which forbids the attainment of 0 K by *any method* whatsoever [1].

In Sect. 3.2, we will first consider CSRR via positional isolation by means of weighing of entities that happen to be in the ground state. Perhaps in principle, even if not in practice, at least *prima facie* this seems to be the simplest possible method of CSRR. So perhaps it may elucidate at least some of the problems of attaining 0 K, and if 0 K can be attained of *verifying* [22] that 0 K has been attained, more easily than the more technically advanced and more practical QCR methods discussed in Ref. [1], which are much more amenable to realization using currently-available technology [1]. We then consider CSRR via positional isolation, by means of a Stern-Gerlach apparatus, of entities that happen to be in the ground state. Our consideration of CSRR via a Stern-Gerlach apparatus will be with reference to a specific one of the QCR methods [1], but we will not employ this or any other QCR method *per se*. In this regard, in the sixth paragraph of Sect. 3.2 we will briefly discuss but not employ another type of ERR than that discussed in Sect. 2.1 and especially in Sect. 2.5, which entails reduction of a refrigerated system's *nonthermal* energy but not of its entropy.

Thus irrespective of the status of TSRR with respect to the unattainability formulation of the Third Law of Thermodynamics, there also exist CSRR methods, which we will consider in this Sect. 3. Even if, as will turn out to at least apparently be the case, even CSRR methods are limited by the strongest-mode unattainability formulation of the Third Law of Thermodynamics, they at least seem to be closer to breaking through this limit than TSRR methods. The ultimate limitation that the unattainability formulation of the Third Law of Thermodynamics can wield in its strongest mode seems to be *purely* dynamic as opposed to *thermodynamic* — the energy-time uncertainty principle. Thus *exact* attainment of 0 K may be protected against *any* type of refrigeration: TSRR, CSRR, ERR, QCR, or otherwise (or any combination thereof). But the only slightly less ambitious goal of attainment of 0 K *for all practical purposes* seems to be within reach.

3.2. Absolute zero via CSRR (for example isolation in position space by weighing or by Stern-Gerlach apparatus)?

Consider System A comprised of N identical harmonic oscillators, in thermodynamic equilibrium with a heat reservoir at temperature T , an average $\langle n \rangle$ of which are in the ground state. (Averaging is denoted by enclosure within angular brackets.) Let ΔE be the gap between adjacent energy states of any given oscillator. Let T be low enough so that the probability of even one of the harmonic oscillators being in its second or higher excited states is negligible. In accordance with the Boltzmann distribution, the probability \mathbb{P}_{A1} of any given System-A oscillator being in its first excited state is $e^{-\Delta E/kT}$ times the probability \mathbb{P}_{A0} of being in its ground state. (Note: Probability \mathbb{P} should not be confused with power P .) Hence, normalizing yields $\mathbb{P}_{A0} \doteq \langle n \rangle / N = 1 / (1 + e^{-\Delta E/kT})$ and $\mathbb{P}_{A1} \doteq (N - \langle n \rangle) / N = 1 - (\langle n \rangle / N) = 1 - [1 / (1 + e^{-\Delta E/kT})] = e^{-\Delta E/kT} / (1 + e^{-\Delta E/kT}) \doteq e^{-\Delta E/kT}$. [The dot-equal sign (\doteq) means “very nearly equal to.”] Of course, T being small enough so that the probability of even one of the harmonic oscillators being in its second or higher excited states is negligible typically implies that $\mathbb{P}_{A1} \ll 1$. But if N is moderately but not excessively large this can obtain consistently with $N\mathbb{P}_{A1} = N - \langle n \rangle$, the average number of oscillators in the first excited state, exceeding unity.

An oscillator in the first excited state has a mass exceeding that of one in the ground state by $\Delta E/c^2$, and, letting g be the local acceleration due to gravity, a weight exceeding that of one in the ground state by $g\Delta E/c^2$. (From now on we take c to be the speed of light in vacuum, or if so noted the speed of given waves, not the prefactor defined in Sect. 2.3.) Thus (in principle!) the oscillators in the ground state in our original System A at temperature T can be positionally isolated by weighing from those in the first excited state therein — creating in only one operation (albeit consisting of n weighing steps) Subsystem B comprised of n oscillators ($n \leq N$), all of which are in the ground state. *Prima facie* it seems that Subsystem B is therefore indeed at the absolute zero of temperature, 0 K. Moreover such positional isolation can in principle be executed via employment only of work interactions and hence with zero heat transfer, either into our ground-state-only Subsystem B or otherwise.

The required work is modest. The entropy — more correctly, *negentropy* — cost of isolating the first of the n ground-state oscillators is $\Delta S_{\text{isol},1} = k \ln \frac{N}{n}$. The negentropy cost of isolating the second of the n ground-state oscillators is $\Delta S_{\text{isol},2} = k \ln \frac{N-1}{n-1}$, with 1 subtracted from N in the numerator of the argument of the logarithm because after the first oscillator has been isolated there are 1 fewer total oscillators left in our original System A and in the denominator thereof because there are 1 fewer ground-state oscillators left therein. The negentropy cost of isolating the third of the n ground-state oscillators is $\Delta S_{\text{isol},3} = k \ln \frac{N-2}{n-2}$, of isolating the j th ($1 \leq j \leq n$) $\Delta S_{\text{isol},j} = k \ln \frac{N-(j-1)}{n-(j-1)} = k \ln \frac{N-j+1}{n-j+1}$, of isolating the n th and last $\Delta S_{\text{isol},n} = k \ln \frac{N-n+1}{n-n+1} = k \ln (N-n+1)$. Note that the negentropy cost of isolating ground-state oscillators increases with each one isolated and is highest for the last one isolated. Recalling that T is the temperature of our original System A, the work required to isolate the j th of the n ground-state oscillators is $W_{\text{isol},j} = T\Delta S_{\text{isol},j} = kT \ln \frac{N-j+1}{n-j+1}$. Thus, if at temperature T on average $\langle n \rangle$ of the N harmonic oscillators comprising our original System A are in their ground states, the expectation values of the total negentropy cost $\Delta S_{\text{isol},\text{total}}$ and total work cost $W_{\text{isol},\text{total}} = T\Delta S_{\text{isol},\text{total}}$ of isolating all ground-state oscillators into Subsystem B are, to sufficient accuracy, given by and bounded from above in accordance with:

$$\begin{aligned} \langle \Delta S_{\text{isol},\text{total}} \rangle &= \sum_{j=1}^{\langle n \rangle} \langle \Delta S_{\text{isol},j} \rangle = k \sum_{j=1}^{\langle n \rangle} \ln \frac{N-j+1}{\langle n \rangle - j + 1} < \langle n \rangle k \ln (N - \langle n \rangle + 1) \\ \implies \langle W_{\text{isol},\text{total}} \rangle &= T \langle \Delta S_{\text{isol},\text{total}} \rangle = kT \sum_{j=1}^{\langle n \rangle} \Delta S_{\text{isol},j} = kT \sum_{j=1}^{\langle n \rangle} \ln \frac{N-j+1}{\langle n \rangle - j + 1} < \langle n \rangle kT \ln (N - \langle n \rangle + 1). \quad (12) \end{aligned}$$

(If $\langle n \rangle$ is not an integer, then the sums in Eq. (12) are, to sufficient accuracy, construed as encompassing all integers j from 1 up through and including the one immediately below $\langle n \rangle$ and then also encompassing the noninteger $\langle n \rangle$.) The inequalities in Eq. (12), bounding $\langle \Delta S_{\text{isol},\text{total}} \rangle$ and $\langle W_{\text{isol},\text{total}} \rangle = T \langle \Delta S_{\text{isol},\text{total}} \rangle$ from above, are justified because the negentropy cost of isolating ground-state oscillators increases with each one isolated and is highest for the last one isolated. Thus even the upper bounds on the negentropy and work costs are modest. The negentropy and work costs computed in Eq. (12) assume thermodynamic perfection (reversibility). But even given typical imperfection (irreversibility), which is inevitable in practice as opposed to in principle, the upper bounds on the actual negentropy and work costs would typically be only a few times larger, and

hence still modest. The Second Law of Thermodynamics requires that the decrease in entropy associated with localizing ground-state oscillators into Subsystem B be paid for by an increase in entropy elsewhere. The payment for any irreversibilities is most typically via waste heat, which must be dumped anywhere except into Subsystem B. It is best dumped into System A's heat reservoir (not into System A itself). The temperature of this reservoir and hence also of System A itself need not be measurably raised if this heat reservoir is very large and/or is comprised of a substance in its two-phase regime. Of course, this waste heat payment will be larger given imperfect (irreversible) than perfect (reversible) operation, but typically only a few times larger.

Note, first, that this is a CSRR (as opposed to TSRR) operation, entailing only *positional* isolation of the oscillators by weight. The isolation and hence *localization* of the n ground-state oscillators into Subsystem B is in the position, not the momentum, part of phase space. Entropy is the logarithmic measure of delocalization and negentropy the logarithmic measure of localization. The negentropy cost for reversible CSRR by weighing is a *localization* cost paid for by work not heat (although the negentropy cost exacted owing to any irreversibilities is typically via waste heat, which must be dumped anywhere except into Subsystem B — preferably into System A's heat reservoir). Moreover no energy — neither heat nor work — is extracted from either System A or Subsystem B at *any* point during our CSRR process. (Indeed since the oscillators to comprise Subsystem B are in their ground states, energy *cannot* be extracted from them.) This is in contrast with both standard and absorption TSRR (recall Sect. 2 and the first paragraph of this Sect. 3). Second, since the difference in masses and therefore also weights between an oscillator being in its ground or first excited state is finite, we circumvent the objection that infinitely precise measurements [22] would be required to verify [22] that *precisely* 0 K has been attained. Third, while the unattainability formulation of the Third Law of Thermodynamics forbids the expenditure of the typically small amount of work required to attain 0 K via standard TSRR and the expenditure of the typically small amount of high-temperature heat required to attain 0 K via absorption TSRR, it does *not* forbid the expenditure of the typically small amount of work required to attain 0 K via CSRR. Fourth, we stated “in principle!” — i.e., as a thought experiment — no currently-available or even currently-foreseeable practical weighing technology is sensitive enough. This is in contrast to the QCR systems investigated in Ref. [1], which although more complex, are realizable in practice using currently-available technology.

So does our positional isolation of the n ground-state oscillators into Subsystem B at least *prima facie* seem to challenge the strongest-mode unattainability formulation of the Third Law of Thermodynamics [2–5]? If the unattainability formulation of the Third Law of Thermodynamics in its strongest mode *does* forbid attaining 0 K via CSRR, then it must be for *another reason*. As will be discussed in Sects. 3.3–3.5, this other reason is *purely* dynamic rather than *thermodynamic* — the energy-time uncertainty principle, which imposes the requirement of infinite time to attain *precisely* 0 K.

Of the methods discussed in Ref. [1], the one closest to our weighing thought-experiment discussed in the five immediately preceding paragraphs seems to be that discussed in Sect. 3 of Ref. [1] — but employing only the *first step* of that method. Similarly to the weighing thought-experiment example discussed in the five immediately preceding paragraphs, the proposed real system discussed in Sect. 3 of Ref. [1] (System A by our notation) consists of a mixture of atoms, some of which are in the ground state and some in the first excited state. Also as in our weighing thought-experiment, the temperature is assumed low enough so that the probability of occupancy of the second or higher excited states is negligible. This first

step of the method employed in Sect. 3 of Ref. [1] entails positional isolation of atoms in the ground state from those in the first excited state by a Stern-Gerlach apparatus. The subsystem comprised of atoms in the ground state after positional isolation via the Stern-Gerlach apparatus constitutes Subsystem B, our subsystem at the absolute zero of temperature, 0 K. This positional isolation of atoms is a CSRR process. This Stern-Gerlach-apparatus version of our thought experiment may, in accordance with Sect. 3 of Ref. [1], be more realizable experimentally than the weighing version thereof.

In contrast with Sect. 3 of Ref. [1], in the Stern-Gerlach modification of our weighing CSRR method no attempt is made to thence also de-excite the atoms in the first excited state down to the ground state, the *second step* of the QCR method discussed in Sect. 3 of Ref. [1]. It is important to recognize that this *second step* is *neither* a TSRR process *nor* a CSRR process. The entropy of a set of atoms is zero if they are *all in the same quantum state*, irrespective of whether this quantum state is the ground state or not. (But see the last paragraph of the Appendix concerning this point.) In the particular case currently under consideration, we have a set of atoms *all in the first excited state*. Their de-excitation from the first excited state to the ground state maintains their entropy constant at zero. Thus it is *not* an entropy-reduction (SR) process — it is neither a TSRR process nor a CSRR process. It is rather *another type* of refrigeration process, which we have dubbed as *energy-reduction refrigeration (ERR)*: *energy E* but *not* entropy *S* is extracted to de-excite these atoms from the first excited state to the ground state. Thus, as was the case with one-time-expansion ERR which we considered in Sect. 2.1 and especially in Sect. 2.5: (a) this version of ERR yields rather than costs work. But unlike one-time-expansion ERR which we considered in Sect. 2.1 and especially in Sect. 2.5, this version of ERR process does *not* require infinite *volume* to attain 0 K, and (b) the extracted energy *E* is *nonthermal*, because the oscillators are initially all in the first excited state, *not* in a Boltzmann distribution among states. Similarly as is the case with respect to the expenditure of the typically small amount of work required to attain 0 K via CSRR, the unattainability formulation of the Third Law of Thermodynamics does *not* forbid ERR by forbidding the extraction of the typically small amount of *nonthermal* energy required to de-excite these atoms from the first excited state to the ground state. Thus if the unattainability formulation of the Third Law of Thermodynamics in its strongest mode *does* forbid ERR, then, as with CSRR, it must be for *another reason*. As will be discussed in Sects. 3.3–3.5, this other reason is, as with CSRR, *purely* dynamic rather than *thermodynamic* — the energy-time uncertainty principle, which imposes the requirement of infinite *time* to attain *precisely* 0 K.

But, for the moment, not considering the energy-time uncertainty principle, once it has been established and proven that via a CSRR process, entailing isolation in position space rather than in momentum space, e.g., via weighing or employment of a Stern-Gerlach apparatus, that we can be *perfectly* sure that *all n* oscillators in our new ground-state-only Subsystem B really are in the ground state, then this system is indeed at *precisely* 0 K. By contrast, *even not* considering the energy-time uncertainty principle, we can never be *perfectly* sure that all *N* oscillators in our original System A really are in their ground states so long as System A's temperature $T > 0$ is positive, no matter how slightly positive [2–5]. In explanation, let the *N* oscillators in our original System A be in thermal equilibrium with a heat reservoir at positive temperature T so small that the probability of any one given System-A oscillator being in its first excited state is $\mathbb{P}_{A1} \doteq e^{-\Delta E/kT} \lll 1$, and we can neglect the probability of even one of them being in its second excited or higher excited state. Thus, the probability that not even one System-A oscillator is in the first excited state, and hence that all *N* of them are in the ground state, is $\mathbb{P}_{A0}^N = (1 - \mathbb{P}_{A1})^N \doteq \left(1 - e^{-\Delta E/kT}\right)^N$, which for arbitrarily

small positive T and N *not* arbitrarily large simplifies to $\mathbb{P}_{A0}^N \doteq 1 - Ne^{-\Delta E/kT}$. For arbitrarily small positive T , if N is *not* arbitrarily large, \mathbb{P}_{A0}^N can be arbitrarily close to 1, but it can never be *precisely* 1 as is required to attain *precisely* 0 K. If N is arbitrarily large, then the situation is even worse. For then, however large ΔE and however small T , it is certain that at least one System-A oscillator is in its first excited state [28]. But this is a limitation *only* of our *original* System A of N oscillators, *not* of our Subsystem B of n oscillators in their ground state that we have positionally isolated by weighing, by a Stern-Gerlach apparatus, or by any other CSRR method. For arbitrarily small positive T , if N is *not* arbitrarily large, $\langle n \rangle$ can be considerably closer to N than to $N - 1$, so that if we form Subsystem B it would likely — but *not* for sure — contain all N oscillators of System A. The “*not*” in “*not* for sure” is why, if T is positive, no matter how slightly positive, System A is *not* our new ground-state-only Subsystem B.

Positional isolation via pure CSRR is not the only non-TSRR method by which absolute zero might be attained. The attainment of absolute zero via QCR methods [1], of which the specific one discussed in Sect. 3 of Ref. [1] employs first CSRR and then ERR, has been investigated [1]. But positional isolation via pure CSRR seems simpler and easier in principle, even if, via weighing, it may not be realizable in practice. But perhaps as discussed four paragraphs previously, via a Stern-Gerlach apparatus it may be [1]. Its simplicity in principle allows us to focus on attainment of absolute zero per se rather on experimental technical issues. Moreover, as noted three paragraphs previously, the QCR method discussed in Sect. 3 of Ref. [1] employs purely-CSRR positional isolation as its first step; as noted three paragraphs previously, only the de-excitation of atoms still in the first excited state down to the ground state in its second step is an ERR process.

3.3. The energy-time uncertainty principle: a *purely* dynamic (*not* thermodynamic) Third-Law limitation under quantum mechanics

We re-emphasize (recall Sect. 3.2, especially the second-to-last paragraph thereof) that the attainment of absolute zero requires *perfect* certainty that our *entire* new n -oscillator Subsystem B is in its ground state — that *all* n oscillators of Subsystem B are in the ground state. But the energy-time uncertainty principle may contravene [29–41]. [Dr. Bernard L. Cohen [29] employs the energy-time uncertainty principle in discussing quantum fluctuations. Dr. Robert Gomer [30] (cited by Dr. Cohen [29]) shows how the position-momentum uncertainty principle can be employed in more limited circumstances. Dr. Mark J. Hagmann [31–35] extends and evaluates Dr. Cohen’s work, and compares it with other works. Drs. Donald H. Kobe and V. C. Aguilera-Navarro [38] provide a derivation from first principles of the energy-time uncertainty relation [38], which they and Drs. Hiromi Iwamoto and Mario Goto employ in a study of tunneling times [39]. Drs. V. V. Dodonov and A. V. Dodonov provide extensive considerations concerning the energy-time uncertainty principle [40]. A heuristic overview is provided by the current author [41].] In order to ensure that *all* n oscillators in Subsystem B really are in the ground state, the best that the energy-time uncertainty principle allows us to do is to isolate each of these oscillators for a sufficiently long time interval Δt pursuant to its being incorporated into Subsystem B, or equivalently to isolate Subsystem B for a sufficiently long time Δt . Let us estimate how long Δt must be. Recall that we let ΔE denote an energy *gap* — in the case currently under consideration the energy *gap* between adjacent states of any given one of our harmonic oscillators. Let $\Delta \mathcal{E}$ denote the magnitude of a *quantum* energy *fluctuation*, and let $\Delta \mathcal{E}$ denote

the magnitude of a *thermal energy fluctuation*. The minimum possible root-mean-square *quantum* fluctuation magnitude that the energy-time uncertainty principle allows in energy $\Delta\mathcal{E}_{\text{rms}}$ during a time interval Δt is $\Delta\mathcal{E}_{\text{rms}} = \hbar/2\Delta t$ [29–41]. (Spontaneously-occurring quantum fluctuations are, or at least tend to be, of minimal possible magnitude, as is required for the macroscopic world being maximally close to classical [29–41].) We require $\Delta\mathcal{E}_{\text{rms}}$ to be much smaller than the typical *upper* limiting root-mean-square magnitude $\Delta\mathcal{E}_{\text{rms}} \approx kT$ of *thermal* energy fluctuations in our original System A. $\Delta\mathcal{E}_{\text{rms}} \approx kT$ is a typical *upper* limiting thermal-energy-fluctuation root-mean-square magnitude because if $N - \langle n \rangle \ll N$ then most oscillators in System A will usually be in the ground state, which requires $\Delta E \gg kT$ and hence at most $\Delta\mathcal{E}_{\text{rms}} \lesssim kT$ and more likely $\Delta\mathcal{E}_{\text{rms}} \ll kT$. But we also require $\Delta E \gg kT$ for the energy gap between adjacent harmonic-oscillator energy states to ensure that probability that the second or higher excited states are occupied can be neglected compared to the already small probability that the first excited state is occupied (recall the first paragraph of Sect. 3.2). Thus all told we require $\Delta\mathcal{E}_{\text{rms}} = \hbar/2\Delta t \ll \Delta\mathcal{E}_{\text{rms}} \lesssim kT \ll \Delta E$. This implies that the strong inequality $\Delta t \gg \hbar/2\Delta\mathcal{E}_{\text{rms}} \gtrsim \hbar/2kT$ and the even stronger one $\Delta t \gg \hbar/2\Delta E$ must be fulfilled [29–41]. But even such a long Δt is not long enough to allow us to be *perfectly* certain that all n oscillators in our new ground-state-only Subsystem B really are in the ground state, but only to be *almost* perfectly certain that they are [29–41]. Thus, our caveat is as follows: In order to be *perfectly* certain that all n oscillators in our new ground-state-only Subsystem B really are in the ground state, each oscillator must be isolated for $\Delta t \rightarrow \infty$ — for infinite time, forever — pursuant to its being incorporated into our new ground-state-only oscillator Subsystem B, or equivalently Subsystem B must be isolated for $\Delta t \rightarrow \infty$. The quantum-mechanical probability \mathbb{P}_{B1} that any one given oscillator isolated for inclusion in our new Subsystem B is in its first excited state decays exponentially or at least quasi-exponentially with increasing Δt in accordance with [29–41]

$$\begin{aligned} \mathbb{P}(\Delta\mathcal{E}\Delta t) &\sim e^{-\Delta\mathcal{E}/\Delta\mathcal{E}_{\text{rms}}} = e^{-2\Delta\mathcal{E}\Delta t/\hbar} \\ \xrightarrow{\Delta\mathcal{E}=\Delta E} \mathbb{P}_{B1} &= \mathbb{P}(\Delta E\Delta t) \sim e^{-\Delta E/\Delta\mathcal{E}_{\text{rms}}} = e^{-2\Delta E\Delta t/\hbar}. \end{aligned} \quad (13)$$

(This exponential or at least quasi-exponential decay is brought out in Ref. [29] and is important implicitly and/or explicitly in Refs. [30–35] and [41]. It is not specifically mentioned but is not inconsistent with Refs. [36–40].) The first line of Eq. (13) expresses the general approximate probability of a quantum energy fluctuation of magnitude $\Delta\mathcal{E}$ persisting for time Δt . In the second line of Eq. (13) $\Delta\mathcal{E}$ is set equal to the energy gap ΔE between adjacent harmonic-oscillator energy states (the gap between the ground and first excited states being of current interest). Thus the probability that any one given Subsystem-B oscillator is in its ground state after isolation for Δt is $\mathbb{P}_{B0} = 1 - \mathbb{P}_{B1} = 1 - \mathbb{P}(\Delta E\Delta t) \sim 1 - e^{-2\Delta E\Delta t/\hbar}$. Hence the probability that all n Subsystem-B oscillators are in their ground states after isolation for Δt is $\mathbb{P}_{B0}^n = (1 - \mathbb{P}_{B1})^n = [1 - \mathbb{P}(\Delta E\Delta t)]^n \sim \left(1 - e^{-2\Delta E\Delta t/\hbar}\right)^n$, which for n not too large and sufficiently large Δt simplifies to $\mathbb{P}_{B0}^n \sim 1 - ne^{-2\Delta E\Delta t/\hbar}$. Thus $1 - \mathbb{P}_{B0}^n \sim ne^{-2\Delta E\Delta t/\hbar}$, which depends only *linearly* on n but decreases *exponentially* (or at least quasi-exponentially) with increasing Δt , soon becomes negligible. But however strongly negligible it becomes, it *never* becomes *precisely* 0 except in the limit $\Delta t \rightarrow \infty$. And $1 - \mathbb{P}_{B0}^n$ is required to be *precisely* 0 — equivalently \mathbb{P}_{B0}^n is required to be *precisely* 1 — if *precisely* 0 K is to be attained and if we are to have *perfect* verification [22] that *precisely* 0 K has been attained.

The difference in masses and therefore also weights of an oscillator being in its ground state as opposed to in its first excited state is finite, thereby, as per the first five paragraphs of Sect. 3.2, circumventing the objection that infinitely precise measurements [22] would be required to verify [22] that *precisely* 0 K has been attained. This objection is similarly circumvented if instead of weighing we employ a Stern-Gerlach apparatus as per the sixth paragraph of Sect. 3.2, in accordance with the first step of the method employed in Sect. 3 of Ref. [1]. But the objection posed by the energy-time uncertainty principle seems to be uncircumventable: *Exact* attainment of 0 K and *perfect* verification [22] that *precisely* 0 K has been attained seems to require infinite time. Thus, the energy-time uncertainty principle may provide additional — quantum-mechanical and hence *purely* dynamic as opposed to *thermodynamic* — protection against *exact* attainment of 0 K and *perfect* verifiability [22] that *precisely* 0 K has been attained, and hence against the unattainability formulation of the Third Law of Thermodynamics in its strongest mode being *precisely* violated. It is not clear whether or not the energy-time uncertainty principle imposes a similar limitation on the QCR systems and methods discussed in Ref. [1]. But owing to the universality of quantum mechanics and hence of the energy-time uncertainty principle, this seems likely to be the case. Indeed owing to the universality of quantum mechanics and hence of the energy-time uncertainty principle, this seems likely to be the case in general, irrespective of the refrigeration method — TSRR, CSRR, ERR, QCR, etc., or any combination thereof — that is employed. This is in accordance with the conclusion reached in Refs. [6–8] via far more technical and mathematical analyses.

Note the *qualitative* — not merely *quantitative* — distinction between the *thermodynamic* (Boltzmann-distribution) probability \mathbb{P}_A discussed in Sect. 3.2 as opposed to the *purely* dynamic (quantum-mechanical) probability \mathbb{P}_B discussed in this Sect. 3.3 *Even if, thermodynamically, exact* attainment of 0 K and *perfect* verification [22] that *precisely* 0 K has been attained *could be* achieved for Subsystem B, the *pure* dynamics of quantum mechanics, specifically the energy-time uncertainty principle, seems to impose the requirement that infinite time must elapse first. [This distinction between *thermodynamic* probabilities as opposed to *purely* dynamic (quantum-mechanical) probabilities should not be confused with the distinction between the derivation of the *thermodynamic* Boltzmann distribution per se in classical as opposed to quantum statistical mechanics. The latter distinction, which we do not consider in this chapter, obtains largely owing to the postulate of random phases being required in quantum but not classical statistical mechanics [42,43].]

Nevertheless, given the *exponential* (or at least quasi-exponential) decay of $1 - \mathbb{P}_{B0}^n \sim ne^{-2\Delta E\Delta t/\hbar}$ [29–41], fulfillment of the *very* strong inequality $\Delta t \gg \hbar/2\Delta E$ does seem to imply that we can be close enough to perfectly certain that all n oscillators in our new Subsystem B really are in the ground state *for all practical purposes*. Hence it seems that we must be content with attainment for all practical purposes as opposed to exact attainment of 0 K and verification for all practical purposes as opposed to perfect verification [22] that *precisely* 0 K has been attained. Thus perhaps the energy-time uncertainty principle provides the ultimate protection against *perfect* violation of the unattainability formulation of the Third Law of Thermodynamics in its strongest mode. But given the *exponential* (or at least quasi-exponential) decay of $1 - \mathbb{P}_{B0}^n \sim ne^{-2\Delta E\Delta t/\hbar}$ [29–41], perhaps, while not *perfectly* violating the strongest-mode unattainability formulation of the Third Law of Thermodynamics, CSRR as opposed to TSRR at least challenges it in the strongest manner that the laws of physics allow. Recall from the sixth and seventh paragraphs of Sect. 3.2 that the specific QCR method discussed in Sect. 3 of Ref. [1] employs first CSRR and then ERR [1], and that we employed the first step of this method for CSRR positional isolation

via Stern-Gerlach apparatus. Recall also that in the last two paragraphs of Sect. 2.3 we have already employed exponential decay in consideration of rendering insulation for a refrigerated system perfect *for all practical purposes*, even if it cannot be *exactly* perfect [23].

3.4. The quest for absolute zero under classical versus quantum mechanics

The energy-time uncertainty principle is of purely quantum-mechanical origin. It does not exist in classical mechanics, whether Newtonian or relativistic. Thus under classical mechanics, whether Newtonian or relativistic, it might seem, at least *prima facie*, that, at least in principle, CSRR via positional isolation by means of weighing as discussed in the first five paragraphs of Sect. 3.2, by means of a Stern-Gerlach apparatus as discussed in the sixth paragraph of Sect. 3.2 (whether or not enhanced via ERR as per the seventh paragraph of Sect. 3.2), or via QCR in general [1], *can* not only attain *precisely* 0 K but also provide *perfect* verification [22] that *precisely* 0 K has been attained — and do both in *finite*, even *arbitrarily short*, time Δt . Hence it may seem, at least *prima facie*, that under classical mechanics, at least in principle, the unattainability statement of the Third Law of Thermodynamics even in its strongest mode *can* be *precisely* violated via CSRR. However, experimentally realizable proposals for attaining 0 K are quantum-mechanical [1]. Indeed the entire Universe is ultimately quantum-mechanical; classical mechanics, Newtonian or even relativistic, being only a limiting approximation. Hence attainment of 0 K *for all practical purposes* and verification [22] that 0 K has been attained *for all practical purposes* is probably the best that can be achieved. Our conclusion seems unalterable even if one accepts the viewpoint expressed by Dr. David Bohm that classical mechanics should be considered in its own right and as prerequisite for quantum mechanics, rather than as a limiting case of quantum mechanics [44]. This is opposed to the more generally accepted viewpoint that classical mechanics should be considered as a limiting case of quantum mechanics. Moreover, even Dr. Bohm expresses the latter viewpoint in his recognition of the Universe as being ultimately quantum-mechanical [45].

Furthermore, classical mechanics imposes its own burden on the quest for absolute zero. While there are instances of quantization even in classical mechanics, for example the discrete allowed frequencies and wavelengths of a vibrating string of finite length [46], of electromagnetic waves within a finite volume [47–49], and of sound waves within a finite volume [47–49], so far as is known energy is always continuous and never quantized in classical mechanics.⁴ Quantization of frequency ν and hence also of wavelength λ , for example the discrete allowed frequencies and wavelengths of a vibrating string of finite length [46], of electromagnetic waves within a finite volume [47–49], and of sound waves within a finite volume [47–49], implies quantization of energy E in *quantum* mechanics in accordance with the *quantum-mechanical* relation $E = h\nu = hc/\lambda$ [50–52]. (Here c is the speed of wave propagation, whether of waves on a string, of light waves, of sound waves, etc. Note for example that for photons ν in a material medium equals ν in a vacuum; both c and λ are smaller in a material medium than in a vacuum by a ratio equal to the index of refraction of the medium.) The relation $E = mc^2 = h\nu = hc/\lambda$ is at the heart of the very closely related Einstein [50–52] and deBroglie [50–52] postulates [50–52]. The relation $E = mc^2$ obtains

⁴ (Re: Entries [48] and [49], Refs. [48] and [49]) Photons of equilibrium blackbody radiation are discussed in Sect. 10.6 and phonons of sound waves in solids in Problem 10.8 of Chap. 10 on pp. 369–371 of Ref. [48]. Both photons and phonons are discussed in Chap. 6 of Ref. [49].

in both classical and quantum relativistic mechanics. But quantization of frequency ν and hence also of wavelength λ does *not* imply quantization of energy E in *classical* mechanics because the relation $E = h\nu = hc/\lambda$ is *strictly quantum-mechanical* [50–52]. There exists *no classical-mechanical* relation such as $E = h\nu = hc/\lambda$ [50–52]. Even in quantum mechanics the relation $E = h\nu = hc/\lambda$ is necessary but not sufficient for discreteness of energy levels as opposed to an energy continuum, for in an infinite volume ν and λ can take on a continuum of values. But given only the additional very mild condition of a finite volume — a fixed finite volume or even an unfixed but always finite volume for example corresponding to maintenance of constant pressure — only discrete values of λ and hence of $\nu = c/\lambda$ will fit therein, thus ensuring discreteness of energy levels under quantum — but not classical — mechanics. This can also be shown via considerations of the Schrödinger equation [53]. Thus so far as is known quantization of energy [50–52] and discrete energy levels [53] can exist under quantum mechanics [50–53], indeed *must* exist under quantum mechanics given finite volume, but *cannot* exist under classical mechanics [50–53]. Hence under classical mechanics, owing to continuity of energy, infinitely precise measurements [2,3,22] would be required to *perfectly* verify [2,3,22] that *precisely* 0 K has been attained [2,3,22]: With an infinitesimal gap between the ground and first excited states, weighing of our harmonic oscillators would have to be infinitely precise. With an infinitesimal gap between the ground and first excited states of atoms an infinitely-sensitive Stern-Gerlach apparatus would be required to separate atoms in the two states. By contrast, under quantum mechanics, owing to discreteness of energy levels [50–53] of a system within a finite volume, measurements of merely finite precision suffice for verification [22] that *precisely* 0 K has been attained.

Thus quantum mechanics, via the energy-time uncertainty principle, imposes the requirement of isolation for infinite time for *perfect* verification [22] that *precisely* 0 K has been attained, but by requiring discreteness of energy levels for a system of finite volume lifts the requirement of infinitely precise measurements [22] to *perfectly* verify [22] that *precisely* 0 K has been attained. By contrast, classical mechanics, since it lacks an energy-time uncertainty principle, lifts the requirement of isolation for infinite time for *perfect* verification [22] that *precisely* 0 K has been attained, but by requiring an energy continuum imposes the requirement of infinitely precise measurements [22] to *perfectly* verify [22] that *precisely* 0 K has been attained. Of these two requirements, the first seems less onerous than the second, because as discussed in Sect. 3.3 the *uncertainty* that *precisely* 0 K has been attained decays *exponentially* (or at least quasi-exponentially) with time [29–41]. This exponential or at least quasi-exponential decay mitigates (albeit does not remove) the requirement of isolation for infinite time under quantum mechanics for *perfect* verification [22] that *precisely* 0 K has been attained. No such decay, exponential, quasi-exponential, or otherwise, mitigates the requirement under classical mechanics for an energy continuum, hence implying that infinitely precise measurements [22] are requisite for perfect verification [22] that *precisely* 0 K has been attained. So at least *prima facie* it seems that quantum mechanics at least brings us closer than classical mechanics to *perfect* verifiability [22] that *precisely* 0 K can be attained.

3.5. Summary: TSRR versus CSRR

In summary, the *thermodynamic* difficulties in *attaining precisely* 0 K via TSRR [2–5] seem to be circumventable via CSRR. By contrast, the *purely* dynamic (quantum-mechanical) limitation imposed by the energy-time uncertainty principle as per Sects. 3.3 and 3.4 is, strictly, not circumventable via either TSRR or CSRR, but this limitation may not be crucial if we do

not insist on *exact* attainment of 0 K and *perfect* verification [22] that *precisely* 0 K has been attained, but are content with attainment of 0 K and verification [22] of its attainment that is perfect for all practical purposes.

Thus it seems that CSRR, based on localization of refrigerated entities in position space, as discussed in Sect. 3, at least brings us *closer* to *exact* attainment of $T_C = 0\text{ K}$ and to *perfect* verification [22] that 0 K has been attained than does TSRR, based on localization of refrigerated entities in momentum space, as discussed in Sect. 2. And CSRR under quantum mechanics (e.g., via weighing or via Stern-Gerlach apparatus), or via QCR methods [1], as opposed to under classical (Newtonian or relativistic) mechanics, seems to bring us the *closest*. (Recall from the sixth and seventh paragraphs of Sect. 3.2 that the specific QCR method discussed in Sect. 3 of Ref. [1] employs first CSRR via Stern-Gerlach apparatus and then ERR [1]; we employed the first, CSRR, step thereof in the sixth paragraph of Sect. 3.2.)

Moreover, *even if* $T_C = 0\text{ K}$ could be *precisely attained* and also its attainment could be *perfectly* verified [22], whether via standard or absorption TSRR, via CSRR, via one-time-expansion ERR as discussed in Sect. 2.1 and especially in Sect. 2.5, via ERR as part of a QCR method as discussed in this Sect. 3, or via other ERR methods, via QCR, etc., or via any combination thereof, the question of *maintaining* $T_C = 0\text{ K}$ as per Sect. 2.3 and the last paragraphs of Sects. 2.4 and 2.5 is still open [23]. *Even if* $T_C = 0\text{ K}$ could be *precisely attained* and also its attainment could be *perfectly* verified [22], the question of whether or not it can be *maintained* for finite time, as opposed to merely the infinitesimally short time allowed in accordance with Eqs. (6) and (7) and the associated discussions, is still open. But least in principle even if not in practice *if* $T_C = 0\text{ K}$ can be *attained*, whether *maintainable* only for an instant or longer, then this may be more easily achievable via CSRR, especially under quantum rather than classical mechanics, than via standard or even absorption TSRR (or any other TSRR). The same is probably true with respect to QCR as opposed to TSRR.

But the issue of *maintenance* [23] seems *inseparable* from that of *verifiability* [22]. For, as discussed in Sects. 3.3 and 3.4, the energy-time uncertainty principle requires $\Delta t \rightarrow \infty$ for perfect verifiability that $T_C = 0\text{ K}$ has been attained, which is obviously incompatible with $T_C = 0\text{ K}$ being maintained only for an instant, or even for any finite number of instants, in accordance with Eqs. (6) and (7) and the associated discussions. If $T_C = 0\text{ K}$ can be maintained only for an instant, or even for any finite number of instants, then the energy-time uncertainty principle seems to preclude verification *even for all practical purposes* that $T_C = 0\text{ K}$ has actually been attained. Thus verification [22] *even for all practical purposes* that $T_C = 0\text{ K}$ has actually been attained seems to require insulation [23] that is perfect for all practical purposes as per Sect. 2.3.

3.6. What if: Better-than-perfect refrigeration?

The Second Law of Thermodynamics forbids better-than-perfect refrigeration, in which the total entropy change is negative. Yet the universal validity of the Second Law of Thermodynamics has been seriously questioned [54–58], albeit with the understanding that even if not universally valid at the very least it has a very wide range of validity [54–58]. Thus *what if* better-than-perfect refrigeration is possible, whether via TSRR, CSRR, ERR, QCR, etc., or any combination thereof? (ERR entails zero entropy change; hence it could be part, but not the entirety, of a better-than-perfect refrigeration process, if such can exist [54–58]. Recall from the sixth and seventh paragraphs of Sect. 3.2 that the specific

QCR method discussed in Sect. 3 of Ref. [1] employs first CSRR and then ERR [1]: we employed the first, CSRR, step thereof in the sixth paragraph of Sect. 3.2.) For example, what if CSRR-isolation of our Subsystem-B oscillators could be achieved at smaller negentropy and work cost than in accordance with Eq. (12)? Unfortunately, *even if* better-than-perfect refrigeration in contravention of the Second Law of *Thermodynamics* is possible, the *purely* dynamic limitations discussed in Sects. 3.3–3.5 still obtain for both TSRR and CSRR (as well as for ERR, QCR, etc., or any combination of refrigeration methods). Thus at least *prima facie* it seems that *even if* the Second Law can be contravened [54–58] and hence better-than-perfect refrigeration is possible, owing to the energy–time uncertainty principle the strongest-mode unattainability statement of the Third Law could still be violated only for all practical purposes and not perfectly. And this considers *only* the difficulties of *attaining* $T_C = 0$ K. *Even if* the Second Law of Thermodynamics can be contravened [54–58] and hence better-than-perfect refrigeration is possible, the difficulties in *maintaining* $T_C = 0$ K for longer than an infinitesimal time, discussed in Sect. 2.3, the last paragraphs of Sects. 2.4 and 2.5, and the last two paragraphs of Sect. 3.5, may preclude verification [22] *even for all practical purposes* that $T_C = 0$ K has actually been attained — unless insulation [23] that is perfect for all practical purposes as per Sect. 2.3 is possible.

4. Hot true and cold effective negative Kelvin temperatures

4.1. Hot true negative Kelvin temperatures

Negative Kelvin temperatures certainly exist [59–63]. But *true* negative Kelvin temperatures are *hotter* than $T = \infty$ K, not colder than $T = 0$ K [59–62]. *True* negative Kelvin temperatures exist only in systems with an upper bound in energy, wherein $T = (\partial E/\partial S)_{V,N} < 0$ obtains if enough energy is pumped into such a system so that its high-energy state is more populated than its low one — a population inversion [59–62]. [As per standard notation, the subscript “ V, N ” denotes fixed volume and number of entities (most typically atoms or molecules).] The temperature of *any* system can, at least in principle, be raised to $T = \infty$ K via energy pumped into the system as heat and/or as work. But unless a heat reservoir at a negative Kelvin temperature is available, energy must be pumped into a system as work rather than as heat, i.e., *nonthermally*, if the system’s temperature is to be raised to negative Kelvin values, because heat input from a heat reservoir at a positive Kelvin temperature can never raise a system’s temperature above $T = \infty$ K, which corresponds to all of the system’s states being uniformly populated — just short of a population inversion [59–62].

Consider, for simplicity, a 2-energy-level system with both levels nondegenerate. A total of N entities (typically atoms whose nuclei can manifest spin aligned either parallel or antiparallel to an external magnetic field) can be distributed among these 2 energy levels. At $T = +0$ K, the probability is unity that all N entities are in the lower level and hence the system’s entropy is minimized at $S = 0$. As energy is pumped into the system (as heat and/or as work), its temperature $T = (\partial E/\partial S)_{V,N}$ increases through increasing positive values and its entropy increases. At $T = +\infty$ K = $-\infty$ K, each entity has a probability of 1/2 of being in either level and hence the system’s entropy is maximized at $S = Nk \ln 2$. As more energy is pumped into the system (as work only unless a heat reservoir at $T = -0$ K is available), its temperature $T = (\partial E/\partial S)_{V,N}$ increases through decreasing negative values from $T = -\infty$ K to $T = -0$ K and its entropy decreases, until at $T = -0$ K the probability is unity that all N entities are in the upper level and hence the system’s entropy is again minimized at $S = 0$.

It should be noted that the concept of hot negative Kelvin temperature can meaningfully be applied for 2-energy-level systems [63], whether or not either level or both are degenerate — but *only* for 2-energy-level systems [63]. For systems with 3 or more energy levels, wherein population need not be a monotonic function of level (multiple population inversions are possible with 4 or more levels), the concept of hot negative Kelvin temperature becomes unwieldy and contrived [63].⁵

It has been remarked [59–62] that there are advantages in defining temperature via $1/T = -(\partial S/\partial E)_{V,N}$, because by this definition the numerical value of a system's temperature always increases monotonically with its increasing ability to spontaneously deliver heat to its surroundings or equivalently with its decreasing ability to spontaneously accept heat from its surroundings, whether temperature defined via $T = (\partial E/\partial S)_{V,N}$ is positive or negative [59–62]. But temperature defined via $T = (\partial E/\partial S)_{V,N}$ has the advantages of numerical proportionality to temperature as measured by an ideal-gas thermometer and to average thermal kinetic energy per molecular translational degree of freedom of ideal-gas molecules in the classical (nonquantum) regime. So we employ the definition $T = (\partial E/\partial S)_{V,N}$ in this chapter.

4.2. Cold effective negative Kelvin temperatures

Insofar as is known, *true* negative Kelvin temperatures that are *colder* than $T = 0\text{ K}$ do not exist. Nevertheless, we can still consider *effective* negative Kelvin temperatures that are *colder* than $T = 0\text{ K}$ — linearly extrapolating the Kelvin temperature scale downwards through $T = 0\text{ K}$ to negative *effective* values. Such cold *effective* negative Kelvin temperatures *do* exist. Consider, for example, the effective wind-chill temperature \mathcal{W} on Neptune, at the level in Neptune's atmosphere where the pressure is 1 bar, approximately 1 atm. The wind-chill temperature \mathcal{W} is the temperature that calm air must have to produce the same chilling effect as moving air — wind — at speed \mathcal{V} , all other things being equal. The *true* mean temperature (without wind chill) at the 1 bar level on Neptune is approximately $T = 72\text{ K} = -201\text{ }^\circ\text{C} = -330\text{ }^\circ\text{F}$ [65]. The standard *formula* for wind-chill temperature \mathcal{W} employed by the U. S. A. National Weather Service is [66]

$$\mathcal{W} = \left[0.6215T_{\circ\text{F}} + (0.4275T_{\circ\text{F}} - 35.75) \mathcal{V}_{\text{mi/h}}^{0.16} + 35.74 \right] ^\circ\text{F}. \quad (14)$$

In Eq. (14), the wind speed \mathcal{V} is that at the 5 ft (typical face) level, based on reduction owing to surface friction of wind speed measured at the standard 10 m or 33 ft level to the 5 ft level [66]. (Over flat open ground or over open water, this reduction in wind

⁵ (Re: Entry [63], Ref. [63]) In Ref. [63], Dr. Peter Atkins doesn't seem to explicitly state that negative Kelvin temperatures are hotter than $\infty\text{ K}$, not colder than 0 K . He admits the possibility of attaining 0 K via noncyclic processes, but as we showed in Sect. 3 of this chapter *purely* dynamic — as opposed to *thermodynamic* — limitations may contravene. On pp. 103–104 of Ref. [63], he correctly states that the third law of thermodynamics is “not really in the same league” as the zeroth, first, and second laws, and that “hints of the third law of thermodynamics are already present in the consequences of the second law,” but that the Third Law of Thermodynamics is “the final link in the confirmation that Boltzmann's and Clausius's definitions refer to the same property.” But his statement that “we need to do an ever increasing, and ultimately infinite, amount of work to remove energy from a body as heat as its temperature approaches absolute zero” neglects the rapid decrease in specific heat as absolute zero is approached as discussed in Sect. 2 of this chapter.

speed is typically small.⁶⁾ For the given temperature $T = 72 \text{ K} = -201^\circ\text{C} = -330^\circ\text{F}$ at the 1 bar level on Neptune [65], even with a slow (by Neptune standards) $\mathcal{V} = 50 \text{ mi/h}$ wind, Eq. (14) yields $\mathcal{W} = -500^\circ\text{F} = -296^\circ\text{C} = -22 \text{ K}$. [A wind speed of $\mathcal{V} = 50 \text{ mi/h}$ is chosen so that our example is more “Earthlike.” Typical wind speeds on Neptune are considerably higher than 50 mi/h (See Ref. [65].) But according to Eq. (14), the chilling effect of wind increases at a decreasing rate with increasing wind speed: $(\partial\mathcal{W}/\partial\mathcal{V})_T = \left[0.16 (0.4375T_{\text{°F}} - 35.75) \mathcal{V}_{\text{mi/h}}^{-0.84}\right]^\circ\text{F} / (\text{mi/h})$. Hence \mathcal{W} decreases only very slowly at wind speeds above 50 mi/h , at least assuming that if not Eq. (14) in its entirety then at least this aspect of Eq. (14) retains at least approximate validity at Neptune-like temperatures. The singularity in $(\partial\mathcal{W}/\partial\mathcal{V})_T$ at $\mathcal{V} = 0 \text{ mi/h}$ is sufficiently weak that it has no effect on values of \mathcal{W} itself.] Since standard atmospheric pressure at sea level on Earth is approximately 1 bar, for illustrative purposes and for argument’s sake let us assume that the standard wind chill *formula* [Eq. (14)] retains at least approximate validity at the 1 bar level on Neptune, especially since the atmospheric density of 0.45 kg/m^3 at the 1 bar level on Neptune is at least comparable to that at the 1 bar level on Earth. (We will appraise this assumption later in this Sect. 4.2, especially in the second-to-last paragraph thereof.) The temperature in Neptune’s atmosphere at the 0.1 bar level is $T = 55 \text{ K} = -218^\circ\text{C} = -361^\circ\text{F}$ [65]. Since Eq. (14) was derived for standard conditions (1 bar atmospheric pressure on Earth), its accuracy may be reduced if it is applied at the 0.1 bar level on Neptune. If we nevertheless apply it at the 0.1 bar level on Neptune, we obtain, even with a slow (by Neptune standards) $\mathcal{V} = 50 \text{ mi/h}$ wind, $\mathcal{W} = -544^\circ\text{F} = -320^\circ\text{C} = -47 \text{ K}$.

The standard wind-chill *formula* [Eq. (14)] should not be confused with the standard wind-chill *table* [66]. The standard wind-chill *table* is based on a standard of calm of 3 mi/h (typical walking speed), rather than on the *true* standard of calm $\mathcal{V} = 0 \text{ mi/h}$ in *true* accordance with the standard wind-chill *formula* [Eq. (14)] that we adopt in this Sect. 4.2. Also, the recommended ranges of applicability of the standard wind-chill *table* are $-50^\circ\text{F} < T \leq 50^\circ\text{F}$ and $3 \text{ mi/h} < \mathcal{V} < 110 \text{ mi/h}$ [66]. But we base our calculations of \mathcal{W} on the standard wind-chill *formula* [Eq. (14)], for which no limits on the range of applicability are stated for either T or \mathcal{V} [66]. If there is a sufficiently strong wind on Neptune, then Eq. (14) yields a *cold* negative Kelvin *effective* wind-chill temperature \mathcal{W} .

A physical interpretation is this: In order to produce the same chilling effect as air at temperature $T = 72 \text{ K} = -201^\circ\text{C} = -330^\circ\text{F}$ at the 1 bar level on Neptune [65] with a 50 mi/h wind [65,66], calm air would have to be at temperature $\mathcal{W} = -22 \text{ K} = -296^\circ\text{C} = -500^\circ\text{F}$ — colder than absolute zero, sub-0 K. [The 0.1 bar level on Neptune is colder, but as noted in the first paragraph of this Sect. 4.2, Eq. (14) is likely more accurate if applied at the 1 bar level on Neptune.] The average thermal translational kinetic energy of the air molecules would have to be negative, and hence their average thermal speed imaginary. Our physical interpretation assumes that this super-cold, or hyper-cold, sub-0 K air of our imagination remains an ideal gas, for which the restricted definition of temperature as twice the average thermal kinetic energy $\langle E_{\text{kin}} \rangle$ per molecular translational degree of freedom

⁶ (Re: Entries [66] and [67], Refs. [66] and [67]) An online brochure accessible at Ref. [66] provides more information. Reference [67] augments Ref. [66] with still more information, including references and a few alternative formulas for wind-chill temperature \mathcal{W} . (In Australia the wind-chill temperature \mathcal{W} is dubbed as the apparent temperature \mathcal{AT} .) In this Sect. 4.2 we always calculate \mathcal{W} based on the formula employed by the U. S. A. National Weather Service [Eq. (14)].

divided by Boltzmann's constant, i.e., $T = 2 \langle E_{\text{kin}} \rangle / k$ [68–81], is valid — and is extrapolated as remaining valid even for negative values of $\langle E_{\text{kin}} \rangle$ and T . A necessary, but probably not sufficient, property of our hypothetical super-cold, or hyper-cold, air molecules is that they exert no attractive forces, however weak, on each other, so that they could never condense into a liquid or solid. (This could obtain, at least for all practical purposes, if the average distance between real air molecules is more than a few orders of magnitude larger than typical molecular sizes of $\sim 10^{-10}$ m to $\sim 10^{-9}$ m — but then of course the density would be much lower than the $0.45 \text{ kg} / \text{m}^3$ obtaining at the $1 \text{ bar} \approx 1 \text{ atm}$ level on Neptune.) Our physical interpretation seems limited to this restricted definition of temperature. There seems to be no obvious way of extending our physical interpretation of cold negative *effective* (wind-chill) Kelvin temperature \mathcal{W} in terms of the most general definition of *true* Kelvin temperature, i.e., $T = (\partial E / \partial S)_{V,N}$ [68–81]. Even for *true* (not *effective*) *nonnegative* Kelvin temperatures, the restricted definition of temperature $T = 2 \langle E_{\text{kin}} \rangle / k$ [68–81] is valid if and only if, as is the case of ideal gases, $\langle E_{\text{kin}} \rangle$ is directly proportional to T [68–81]. There exist excellent in-depth discussions of the concept of temperature, especially concerning the point that “Temperature is deeper than average kinetic energy.” [78,79]. Nevertheless, although taking temperature as proportional to average thermal kinetic energy per molecular translational degree of freedom is not the most general concept [78,79], it suffices to serve as one of the elements in an important derivation of Boltzmann's principle relating entropy and probability [80,81] and in an important generalization of the relation between entropy and heat [82].⁷

It has been argued [83] that Eq. (14) for wind-chill temperature \mathcal{W} is only an approximation [83], and that even as an approximation it is valid only at Earth-like or “human” temperatures [83]. Thus, even though Eq. (14) is likely more accurate if applied

⁷ (Re: Entries [71–77], Refs. [2], [3], [4], [48], [49], [76], and [77]) It is usually stated that the definition of temperature in terms of the Carnot efficiency of a reversible heat engine yields only a ratio of the two temperatures of the hot and cold reservoirs, not the one temperature of either reservoir considered individually, as does $T = (\partial E / \partial S)_{V,N}$, and as does even the more restricted $T = 2 \langle E_{\text{kin}} \rangle / k$ for the special case of ideal-gas reservoirs. To obtain actual values of temperature by this method rather than just the ratio of two temperatures, it is usually stated that the temperature of at least one of the two reservoirs must be ascertained by other means, most typically by allowing one reservoir to attain thermodynamic equilibrium with water at its triple point. This is discussed in Entries [71–75]. Thermodynamic equilibrium with water at its triple point is likewise employed to fix the temperature scale of ideal-gas thermometers, as discussed in Entry [75]. However, Refs. [76] and [77] describe how this requirement for a water-triple-point (or any other heat reservoir) is overcome, at least in principle even if not in practice, by employing a sequence of ideal, reversible, Carnot engines, the cold reservoir for engine \mathbb{N} serving as the hot reservoir for engine $\mathbb{N} + 1$, with the heat input for engine $\mathbb{N} + 1$ to that for engine \mathbb{N} being in a fixed ratio r ($0 < r < 1$), and with each engine doing an equal amount of work. Then the last engine in the sequence *must* have a cold reservoir at $T = 0 \text{ K}$, thus dispensing with the requirement of a water-triple-point or other standardizing heat reservoir. Of course, this considers only the Second-Law aspect of the problem; according to the unattainability formulation of the Third Law, especially in its strongest mode, a cold reservoir at *precisely* $T = 0 \text{ K}$ is impossible. But perhaps a cold reservoir at *arbitrarily close to* 0 K or even *sufficiently close to* 0 K suffices to thus dispense, even if not perfectly then at least for all practical purposes, with requiring a water-triple-point or other standardizing heat reservoir. [One point concerning Sect. 58 of Ref. [77]: Consider, as in Sect. 58 of Ref. [77], a heat engine operating between a heat source at positive Kelvin temperature and a heat sink at *true* (not merely *effective*) *cold* negative Kelvin temperature *if true* (not merely *effective*) *cold* negative Kelvin temperatures could exist — *if* the Kelvin temperature scale *could* be linearly extrapolated downwards through $T = 0 \text{ K}$ to *true* (not merely *effective*) negative values. Contrary to what is stated in Sect. 58 of Ref. [77], such a heat engine, *if* it could exist, would *not* discard more heat to its heat sink than it received from its heat source, thereby violating the First Law of Thermodynamics (conservation of energy). It would discard *negative* heat, i.e., it would *extract* heat, from its heat sink — in addition to extracting heat from its heat source as does a standard heat engine. Its work output (neglecting friction and other irreversibilities) would equal the heat it extracts from its heat source *plus* the heat it extracts from its heat sink. Thus its efficiency as usually defined = (work output) \div (heat extracted from heat source *alone*) $> 100\%$, consistent with the First Law of Thermodynamics, but of course *inconsistent* with the Second and Third Laws.

at the 1 bar level on Neptune than at the 0.1 bar level on Neptune, we cannot be sure of its accuracy even at the 1 bar level on Neptune [83]. Moreover, it has also been argued [83] that \mathcal{W} is more correctly expressed as W / m^2 of heat loss flux rather than as the temperature of calm air that would have the same chilling effect as moving air — wind — at speed \mathcal{V} [83]. Indeed, many if not most national weather services *do* express \mathcal{W} as W / m^2 of heat loss flux rather than as the temperature of calm air that would have the same chilling effect. (The national weather services of the U. S. A. [66], Canada [67], and Australia [67] employ wind-chill formulas for the temperature of calm air that would have the same chilling effect.) But *if* wind chill is expressed as the temperature of calm air that would have the same chilling effect [66,67], *then* irrespective of the equation for \mathcal{W} that even if not exactly correct is at least a good approximation at the 1 bar level on Neptune, be that Eq. (14) or otherwise, it seems inescapable that in order to produce the same chilling effect as a sufficiently strong wind at sufficiently cold but still positive Kelvin temperatures, calm air *must* be colder than 0 K. Thus it seems inescapable that the *effective* (wind-chill) Kelvin temperature \mathcal{W} must then be colder than 0 K even if no *actual* temperature can be colder than 0 K.

This would obtain even more strongly for a helium atmosphere, which remains gaseous at a pressure of 1 bar at Kelvin temperature T which, while still positive, is nevertheless much colder than the value $T = 72 \text{ K} = -201^\circ\text{C} = -330^\circ\text{F}$ obtaining at the 1 bar level on Neptune or even than the value $T = 55 \text{ K} = -218^\circ\text{C} = -361^\circ\text{F}$ obtaining at the 0.1 bar level on Neptune [65,84,85].⁸ While recognizing the caveats discussed in the immediately preceding paragraph, nevertheless for illustrative purposes and for argument's sake let us assume that the standard wind chill *formula* [Eq. (14)] retains at least approximate validity for gaseous helium at a pressure of 1 bar. At a pressure of 1 bar, the common isotope of naturally-occurring helium, ${}^2\text{He}^4$, is gaseous at $T = 5 \text{ K} = -268^\circ\text{C} = -450^\circ\text{F}$, and the rare isotope of naturally-occurring helium (which fortunately can be produced artificially [84]), ${}^2\text{He}^3$, is gaseous at $T = 4 \text{ K} = -269^\circ\text{C} = -452^\circ\text{F}$ [84,85]. Again taking $\mathcal{V} = 50 \text{ mi/h}$, for $T = 5 \text{ K} = -268^\circ\text{C} = -451^\circ\text{F}$ Eq. (14) yields $\mathcal{W} = -118 \text{ K} = -391^\circ\text{C} = -671^\circ\text{F}$, and for $T = 4 \text{ K} = -269^\circ\text{C} = -452^\circ\text{F}$ Eq. (14) yields $\mathcal{W} = -119 \text{ K} = -392^\circ\text{C} = -674^\circ\text{F}$.

4.3. Limits of the possible

How impossible is the super-cold, or hyper-cold, sub-0 K air of our imagination — but with a true as opposed to merely effective sub-0 K temperature? It is (at the very least, almost) certainly physically impossible, but, at least *prima facie*, it seems not to be logically impossible. The physically impossible at least does not exist and possibly even cannot exist in physical reality, but can exist in the imagination and hence in virtual reality (imagination displayed via a computer). The logically impossible cannot exist — rather than merely does not exist — not only in physical reality, but to boot not even in the imagination and hence not even in virtual reality.

A Euclidean (planar) right triangle that violates the Pythagorean Theorem is not merely physically impossible but logically impossible. Such a triangle cannot exist — rather than merely does not exist — not only in physical reality, but to boot not even in the imagination: it cannot even be imagined; it cannot exist even in virtual reality.

⁸ (Re: Entry [85], Ref. [17]) In Fig. 14-19 (a) on p. 381 of Ref. [17], the normal boiling point of ${}^2\text{He}^3$ is incorrectly shown at a pressure of approximately 1.3 atm instead of at 1 atm.

By contrast, for example, a violation of the First Law of Thermodynamics (conservation of energy) [86,87] is (at least so far as is known [86,87]) physically but not logically impossible — perpetual motion of the first kind can at least be *imagined*; it *can* exist at least in *virtual* reality [86,87]. Indeed even concerning the *physical* impossibility (or possibility?) of violation of energy conservation, we should note that energy conservation has never been rigorously proven in general relativity, and that there have been serious proposals for its possible violation at cosmological distance and time scales [86,87]. But: Any proposed violation of energy conservation should address the difficulty posed by Noether's Theorem [88]. According to Noether's Theorem [88], nonconservation of energy implies that the time-invariance of the fundamental laws of physics must be broken (and vice versa). There isn't much wiggle room — even small changes in the (at least apparent) fine-tuning of at least some of the laws of physics would render life (at least carbon-based life as we know it on Earth) impossible [89–92]. Energy, even free energy or equivalently negentropy, is far from being the only requirement for life. But could Noether's Theorem be satisfied if nascent energy is construed as a new boundary — specifically, initial — condition on the future history of the Universe, thereby preserving the time-invariance of the laws of physics? For example, consider the following thought experiment: What if a mass m subject to local gravitational acceleration g could spontaneously rise through a height Δy to the ceiling — not spontaneously get cooler and rise to the ceiling (on demand rather than via unpredictable and uncontrollable fluctuation), thereby violating the Second Law of Thermodynamics, but just spontaneously rise to the ceiling, thereby violating the First Law of Thermodynamics (energy conservation)? Could the nascent gravitational potential energy $mg\Delta y$ simply be a new boundary — specifically, initial — condition on the future history of the Universe, leaving the time-invariance of the laws of physics intact? Might Noether's Theorem accept payment in the cheap currency of boundary — most typically, initial — conditions instead of the expensive currency of the time-invariance of the laws of physics, and hence not pose any difficulty? [Note: Proposals such as those cited for genuine creation of nascent energy [86,87] should not be confused with proposals for creation of positive mass-energy at the expense of negative energy, typically at the expense of negative gravitational energy [93–101], but in some versions of the steady-state theory [102–107] at the expense of a negative-energy creation field (the C field) [105–107]. (There are difficulties associated with the C field [106,107].] The former proposals [86,87] but not the latter ones [93–107] contravene the First Law of Thermodynamics (conservation of energy).]

Thus since knowledge is imperfect and incomplete, perhaps one should not *a priori* rule out any nonzero probability, however remote, that a logically possible phenomenon might also be physically possible [86,87]. Hence the “Insofar as is known” in the first sentence of Sect. 4.2, the “(at the very least, almost)” in the second sentence of the first paragraph of Sect. 4.3, and the “(at least so far as is known [86,87])” in the first sentence of the third paragraph of Sect. 4.3. Unlike our Pythagorean-Theorem-violating Euclidean (planar) right triangle but like a violation of energy conservation [86,87], our super-cold, or hyper-cold, sub-0 K air can at least be *imagined*.

5. Brief concluding remarks

Hopefully our considerations of and related to absolute zero 0 K have been helpful. In Sect. 2.2, we showed that in principle 0 K can be *attained* at the expense of only a finite, typically small, cost of work via standard TSRR, in Sect. 2.4 at the expense of an even smaller

cost of high-temperature heat via absorption TSRR, and in Sect. 3.1 at the expense of a small cost of work via CSRR, employing weighing or a Stern-Gerlach apparatus. (Recall from the sixth and seventh paragraphs of Sect. 3.2 that the specific QCR method discussed in Sect. 3 of Ref. [1] employs first CSRR and then ERR [1]: we employed the first, Stern-Gerlach-apparatus CSRR, step thereof in the sixth paragraph of Sect. 3.2.) In the standard and absorption TSRR cases, the unattainability formulation of the Third Law of Thermodynamics does not require infinite expenditure of work and heat, respectively to attain 0 K, but forbids the expenditure, respectively, of the required small cost of work and even smaller cost of heat. But in the CSRR cases, it does *not*, even in its strongest mode, forbid the expenditure of the required small cost of work.

But there are also the difficulties of *maintaining* 0 K and of *verifying* [22] that 0 K has even been *attained*, which we discussed in Sect. 2.3, the last paragraphs of Sects. 2.4 and 2.5, and Sect. 3. *Perfectly maintaining* 0 K for more than infinitesimal time requires perfect insulation [23], and *perfectly verifying* [22] that 0 K has even been *attained* requires infinite time. Even given perfect insulation [23] (recall Sect. 2.3) and hence that 0 K can be perfectly *maintained*, the unattainability formulation of the Third Law of Thermodynamics in its *strongest mode*, which forbids attainment of 0 K by *any means* whatsoever, seems inviolable with respect to *perfect* verification [22] that 0 K has been *attained*, because of the infinite-time requirement imposed by the energy-time uncertainty principle. But if we do not insist on *exactly* perfect verification [22] and are willing to accept verification that is perfect *for all practical purposes*, then to this extent the unattainability formulation of the Third Law of Thermodynamics even in its strongest mode *is* challenged. The limitation to “for all practical purposes” is further imposed because as per Sect. 2.3 insulation [23] can be perfect only for all practical purposes. At least in principle and possibly also in practice, CSRR and QCR [1] seem superior to standard TSRR or even absorption TSRR in effecting the challenge to the unattainability formulation of the Third Law of Thermodynamics in its strongest mode, albeit for all practical purposes and not with exact perfection.

Hopefully also our considerations in Sect. 4 of negative Kelvin temperatures, both true ones hotter than ∞ K and effective ones colder than 0 K, have been helpful.

Appendix: A few fine points concerning the Third Law of Thermodynamics

It is generally stated that the Nernst formulation of the Third Law of Thermodynamics, according to which all entropy changes vanish at 0 K, and the unattainability formulation thereof, according to which 0 K is unattainable in a finite number of finite operations, are equivalent. But we should note that there are dissensions to this viewpoint [108–113].⁹

Also, in considering the discreteness of energy eigenstates required by quantum mechanics in any system constrained within a fixed finite volume, or even within an unfixed but always finite volume for example corresponding to maintenance of constant pressure, we did not mention the role of quantum-mechanical Bose-Einstein symmetry or Fermi-Dirac antisymmetry requirements on the allowed wave functions [114]. The gaps between energy

⁹ (Re: Entry [109], Ref. [109] Footnote 5 on p. 494 of Ref. [109] concerns “a residual inequivalence” between the Nernst heat theorem and unattainability principle, with the former construed as more fundamental.

eigenstates at very low temperatures in light of these requirements can be much larger than would be the case in the absence of these requirements [114]. For a typical laboratory macroscopic system, the energy gap ΔE between the ground and first excited state is $\Delta E \sim 10^{-20} \text{ Kk} - 10^{-19} \text{ Kk}$ [114,115]. Yet the entropy and heat capacity of a typical laboratory macroscopic system is, as a rule, already only a very small fraction of the value predicted by classical (as opposed to quantum) statistical mechanics at $T \sim 10 \text{ K}$ [114,115]. It has been noted that at $T \sim 10 \text{ K}$ the energy *per particle* in a typical laboratory macroscopic system is $\sim \Delta E \sim 10^{-20} \text{ Kk} - 10^{-19} \text{ Kk}$ [114,115]. But because the characteristic temperatures of quantum statistical mechanics, for example, the Debye, Fermi-Dirac, and Bose-Einstein temperatures [116], are independent of the size of a system [116], this is a fortuitous result owing to the typical sizes of laboratory macroscopic systems [114,115].

A third formulation of the Third Law of Thermodynamics has also been stated [117], according to which the zero of entropy with a system in its ground energy level (assumed nondegenerate), is as unattainable as 0K itself [117].¹⁰ (If the ground level is G -fold degenerate, then the entropy is $k \ln G$ rather than zero, but this has no effect on our argument.) This third formulation of the Third Law of Thermodynamics has been stated with respect to *thermodynamics*. But, in fact, it ultimately obtains owing to the *pure* (quantum) dynamics of the energy-time uncertainty principle, and with respect to fixing a system *exactly* into *any* of its energy levels in general (not just specifically its ground level), degenerate or not. The energy-time uncertainty principle requires infinite time to *exactly* — with *strictly zero* uncertainty — fix the energy of any system into *any* of its energy levels in general (not just specifically its ground level), degenerate or not.

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¹⁰ (Re: Entries [17] and [117], Refs. [17] and [117]) The detailed discussions concerning the Third Law of Thermodynamics in Ref. [117] are largely deleted in Ref. [17], which provides only a brief mention of the Third Law on p. 217. Reference [117] dubs the Nernst formulation of the Third Law of Thermodynamics as the Nernst-Simon formulation thereof. Reference [17] does not render Ref. [117] obsolete, because Ref. [117] discusses topics not discussed in Ref. [17], and vice versa.

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