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Supradegeneracy, Anti-Supradegeneracy, and the Second Law of Thermodynamics

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HIGHLIGHTS

Supradegeneracy is argued to subvert the Second Law under certain conditions. But the simple supradegenerate system that we consider does not, even though it fulfills two conditions that we hypothesize. This online paper is a corrected revision of the print version.

ABSTRACT

Supradegeneracy—degeneracy $G\,(E)$ increasing with increasing energy E faster than the Boltzmann factor $e^{-E/kT}$ decreases with increasing E—has been investigated with respect to its possibly engendering challenges to the Second Law of Thermodynamics. Supradegeneracy *alone* does *not* challenge the Second Law: Systems manifesting supradegeneracy yet compliant with the Second Law are ubiquitous. If there is to be even the possibility that a system manifesting supradegeneracy can challenge the Second Law, *additional* requirements over and above supradegeneracy *per se* must *also* be fulfilled. We hypothesize what *prima facie* seem to be the two most obvious of these additional requirements. We then consider a simple system manifesting supradegeneracy and also fulfilling these two requirements. At least for the system that we consider, the answer seems to be negative: The Second Law seems *not* challenged. But understanding why the answer is at least apparently negative for the supradegenerate system that we consider may help in understanding of what at least *prima facie* seem to be positive results via analyses, including computer simulations but to the best knowledge of the author at the time of this writing not yet experimental tests, of other supradegenerate systems: of what is the *minimal complete set* of *additional* requirements—over and above supradegeneracy *per se*—that must be fulfilled by a supradegenerate system if it is to challenge the Second Law. Moreover, *even if* it turns out that *all* supradegenerate systems do *not* challenge the Second Law, they could still be useful *even within* its strictures. The same principles apply with respect to both supradegeneracy and *anti*-supradegeneracy [degeneracy $G(E)$ decreasing with increasing energy E], so a brief discussion of anti-supradegeneracy suffices. It is followed by proposal of simple experimental tests of our system: I hope, albeit probably in vain, to be proven *wrong*: Only *experiments*—the final arbiter—can decide the issue for sure! Concluding remarks are provided describing implications *if* the Second Law could be violated *by any means whatsoever* (supradegeneracy, anti-supradegeneracy, and/or otherwise).

KEYWORDS

Degeneracy, supradegeneracy, anti-supradegeneracy, Second Law of Thermodynamics, additional requirements, Boltzmann distribution, canonical distribution, Boltzmann factor, law of isothermal atmospheres, spontaneous momentum flow

I. INTRODUCTION

The probability $P(E)$ that a particle in thermodynamic equilibrium with a heat reservoir at temperature T has a given energy E is proportional to (i) the degeneracy $G(E)$ of the energy level E of the *particle*, i.e., the number of states comprising this level, and (ii) the Boltzmann factor $e^{-E/kT}$, where k is Boltzmann's constant. The Boltzmann factor $e^{-E/kT}$ is proportional to the degeneracy $G'(E_{\text{total}} - E)$ of the energy level $E_{\text{total}} - E$ of the *heat reservoir*, corresponding to the particle having energy E and hence the heat reservoir having energy $E_{\text{total}} - E$; the total energy of the particle-plus-heat-reservoir system being E_{total}. Thus

$$P(E) = \frac{G(E)\, e^{-E/kT}}{\sum G(E)\, e^{-E/kT}} = \frac{G(E)\, G'(E_{\text{total}} - E)}{\sum G(E)\, G'(E_{\text{total}} - E)} = \frac{GG'}{\sum GG'} = \frac{G''}{\sum G''}. \tag{1}$$

In Equation (1), the unprimed quantities refer to the particle, the primed ones to the heat reservoir, and the double-primed ones to the combined particle/heat-reservoir system. The third step of Equation (1) shortens notation. The degeneracies in the numerators of Equation (1) are those of *specific*, i.e., *individual*, energy levels; the sums in the denominators of Equation (1) are over *all* energy levels. The last step of Equation (1) assumes weak coupling between the particle and the heat reservoir, which is obtained in most if not all practicable particle/heat-reservoir systems, and which we assume. [If the coupling is not weak: (i) the states of the particle and heat reservoir are at least somewhat correlated, so $G' < GG'$ and (ii) owing to the interaction energy between the particle and the heat reservoir, E_{total} is slightly less than the sum of the energies of the particle and the heat reservoir.]

Supradegeneracy—degeneracy $G(E)$ of the energy level E of the *particle* increasing with increasing energy E faster than the Boltzmann factor $e^{-E/kT}$ decreases with increasing E—has been investigated with respect to its possibly engendering challenges to the Second Law of Thermodynamics (Sheehan & Schulman, 2019; Sheehan, 2019, 2020a, 2020b, 2001–2022, 2018–2022).

But supradegeneracy *alone* does *not* challenge the Second Law: systems manifesting supradegeneracy yet compliant with the Second Law are ubiquitous. If a system manifesting supradegeneracy is to challenge the Second Law, *additional* requirements over and above supradegeneracy *per se* must *also* be fulfilled. As of this writing, it is not *completely* evident to the author what these additional requirements are. However, re-emphasizing that systems manifesting supradegeneracy yet compliant with the Second Law are ubiquitous, it *is completely evident* that they *must* exist. But we will provide tentative educated guesses, i.e., tentative conjectures, concerning what on the face of it seem to be the two most obvious of these additional requirements.

Any system with sufficiently many degrees of freedom that is compliant with the Second Law is nonetheless supradegenerate with respect to all energies less than its most probable energy (Reif, 2009, sections 2.4, 2.5, 3.7; Kittel, 2004, section 11). And "sufficiently many" does not have to be much larger than unity. The *three*-dimensional Maxwellian distribution for thermal translational kinetic energies—which is certainly within the strictures of the Second Law—manifests $G(E) \propto E^{1/2}$ and hence is supradegenerate with respect to all thermal translational kinetic energies less than the most probable one $kT/2$, at which $E^{1/2}e^{-E/kT}$ is maximized [$P(E)$ *in*creases with increasing E if $0 \le E < kT/2$] (Reif, 2009, section 7.9; Kittel, 2004, section 13). But, by contrast, the *one*-dimensional Maxwellian distribution for thermal translational kinetic energies—which also is certainly within the strictures of the Second Law—manifests $G(E) \propto E^{-1/2}$ and hence is *anti*-supradegenerate with respect to *any* thermal translational kinetic energy [$G(E)$ *de*creases with increasing E and hence $P(E)$ decreases with increasing E *faster* than the Boltzmann factor $e^{-E/kT}$ for *all* E] (Reif, 2009, section 7.10). The *two*-dimensional Maxwellian distribution for thermal translational kinetic energies—which also is certainly within the strictures of the Second Law—manifests $G(E)$ independent of E and hence is a borderline case [$P(E)$ decreases with increasing E exactly as the Boltzmann factor $e^{-E/kT}$ for *all* E] (Garrod, 1995, exercise 1.18).

Thus our two tentative *additional* requirements: (R1) Supradegeneracy must obtain with respect to *one* degree of freedom. (R2) The pertinent energy associated with this *one* degree of freedom must a *potential* energy. R1 is at least partially justified in light of the immediately preceding paragraph. R2 is at least partially justified because, at thermodynamic equilibrium, *kinetic* energy is *in*dependent of position. Hence only *potential* energy can modify probabilities as a function of position (Garrod, 1995, exercises 7.29, 7.30; Tolman, 1987).[1] *Even if* R1 and R2 are among the valid additional requirements, they can*not* be the *only* two, because there exist systems manifesting supradegeneracy and that *also* fulfill them yet do *not* challenge the Second Law. But hopefully our hypothesizing R1 and R2 as *necessary but not sufficient* additional requirements seems at least a step forward. We denote by R* the *minimal complete set* of *additional* requirements (tentatively conjectured to include R1 and R2)—over and above supradegeneracy *per se*—that must be fulfilled by a supradegenerate system if it is to challenge the Second Law.

For example, any spontaneous endothermic (physical, chemical, nuclear, etc.) process manifests supradegeneracy and *also* fulfills both R1 and R2—yet is Second-Law–*compliant*. Let ΔE be the energy difference between a lower-energy reactant configuration and a higher-energy product configuration. Note that: (i) In accordance with R1, the reaction coordinate (the extent of reaction toward completion) represents *one* degree of freedom. (ii) In accordance with R2, ΔE is a *potential*-energy difference: at thermodynamic equilibrium with a heat reservoir at temperature T, both reactant and product species have equal thermal translational *kinetic* energies per degree of freedom. Let G_{rct} and G_{prd} be the degeneracies of the reactant configuration and product configuration, respectively. Then the equilibrium constant for this process if occurring at thermodynamic equilibrium with a heat reservoir at temperature T is

$$K_{\text{eq}} = \frac{G_{\text{prd}}}{G_{\text{rct}}} e^{-\Delta E/kT}. \tag{2}$$

If $\frac{G_{\text{prd}}}{G_{\text{rct}}} > e^{\Delta E/kT}$, $K_{\text{eq}} > 1$: the endothermic process is *spontaneous*, i.e., driven by the Second Law *via supradegeneracy*, *despite* both R1 and R2 *also* being fulfilled. Indeed, if the products are swept away from the reaction vessel, G_{prd} increases almost without limit: Hence for all practical purposes

$$\frac{G_{\text{prd}}}{G_{\text{rct}}} e^{-\Delta E/kT} \to \infty \implies K_{\text{eq}} \to \infty, \tag{3}$$

i.e., the Second Law drives the endothermic process to completion *via extreme supradegeneracy*, *despite* both R1 and R2 *also* being fulfilled.

There are innumerable other examples as well, including the system that we will consider.

In Section II, we consider a simple system manifesting supradegeneracy. At least for the system that we consider, the answer seems to be negative: *despite supradegeneracy* and *despite* both R1 and R2 *also* being fulfilled, the Second Law is at least apparently *not* challenged.

Two points: (i) Understanding why the result is at least apparently negative for the supradegenerate system that we consider may help in understanding what at least *prima facie* seems to be positive results obtained via analyses, including computer simulations but to the best knowledge of the author at the time of this writing not yet experimental tests, of other supradegenerate systems (Sheehan & Schulman 2019; Sheehan 2019, 2020a, 2020b, 2001–2022, 2018–2022): of what is the *minimal complete set* of *additional* requirements R* (tentatively conjectured to include R1 and R2)—over and above supradegeneracy *per se*—that must be fulfilled by a supradegenerate system if it is to challenge the Second Law. Moreover (ii) *Even if* the negative result for the supradegenerate system that we consider *does* turn out to be similarly true for *all* systems manifesting supradegeneracy, such systems could still be useful *even within* the strictures of the Second Law (Sheehan & Schulman 2019; Sheehan 2019, 2020a, 2020b, 2001–2022, 2018–2022).

In Section III, implications pertinent to the Second Law are discussed.

In Section IV, we provide a brief discussion of (i) *anti*-supradegeneracy: $G(E)$ *de*creasing with increasing E and hence $P(E)$ decreasing with increasing E *faster* than the Boltzmann factor $e^{-E/kT}$ and (ii) *strong* anti-supradegeneracy: $G(E)$ *de*creasing with increasing E *faster* than the Boltzmann factor $e^{-E/kT}$ and hence $P(E)$ decreasing with increasing E *faster* than the Boltzmann factor $e^{-E/kT}$ *squared*, i.e., faster than $e^{-2E/kT}$. The same principles apply with respect to both supradegeneracy and anti-supradegeneracy (whether strong or not), so a brief discussion of anti-supradegeneracy suffices. We show that modifying our system so as to exploit anti-supradegeneracy (indeed *strong* anti-supradegeneracy)—either alone or together with supradegeneracy—makes no difference in our results.

In Section V, simple experimental tests of the system discussed in Sections II, III, and IV are proposed. I hope, albeit probably in vain, to be proven *wrong*! Only *experiments* can decide the issue for sure: *Experiments* are the final arbiter!

In Section VI, concluding remarks are provided describing implications *if* the Second Law could be violated *by any means whatsoever* [supradegeneracy, anti-supradegeneracy (whether strong or not), and/or otherwise].

II. DESCRIPTION AND DISCUSSION OF OUR SYSTEM

We now describe our simple system manifesting supradegeneracy (and/or *strong anti*-supradegeneracy, as will be discussed in Sections IV and V). Our system consists of a single particle of mass m confined within a closed hollow tube of *constant* internal diameter (and also constant external diameter). An illustration of the tube is shown in Figure 1. The particle could be an atom, molecule, Brownian particle, etc. It is maintained in thermodynamic equilibrium with a heat reservoir at temperature T via collisions with the interior surface of the tube, and is in a uniform gravitational field g (not to be confused with degeneracy G). It can be construed as a one-particle isothermal atmosphere. Generalization to a system containing n like particles (an n-particle isothermal atmosphere) is straightforward. (Of course, if $n > 1$, thermodynamic equilibrium is maintained via interparticle collisions as well as via collisions with the interior surface of the tube, interparticle collisions becoming more important with increasing n.)

The tube (see Figure 1) comprises three segments: Segment 0 is horizontal in its entirety at the datum altitude $z = 0$. Segment 1 is vertical at its join with Segment 0 at the datum altitude $z = 0$. At $z > 0$, Segment 1 curves away from the vertical at an angle $\theta(z)$ that increases monotonically with increasing z, but within the upper bound $\frac{\pi}{2}$ rad. The top of Segment 1, at which $\theta(z) = \theta(z_{max}) < \frac{\pi}{2}$rad, joins with the top of Segment 2, which is vertical in its entirety, at altitude z_{max}. The bottom of Segment 2 vertically joins with Segment 0 at the datum altitude $z = 0$.

Thus the gravitational potential energy $E = mgz$ of our particle relative to the datum altitude $z = 0$ has as its minimum possible value $E_{min} = 0$ and as its maximum possible value $E_{max} = mgz_{max}$. Hence in accordance with R1 and R2 the pertinent energy $E = mgz$ of our system is a *potential* energy (gravitational potential energy) associated with *one* degree of freedom (the vertical direction z).

Because the *entire* tube is of *constant* internal diameter, we avoid the impediments to cyclical motion of the particle owing to, for example, employing as Segment 1 a birch trumpet,[2] i.e., a cone flaring upwards: in particular, flaring upwards fast enough so that its horizontal cross-sectional area $A(z)$ increases with increasing z faster than the Boltzmann factor $e^{-E/kT} = e^{-mgz/kT}$ decreases with increasing z—flaring upwards such that $A(z) = A(z = 0)\, e^{NE/kT} = A(z = 0)\, e^{Nmgz/kT}$ $(N > 1)$: see, in Sheehan (2020b, the paragraph immediately following that containing figure 4 and note 3; 2020a).

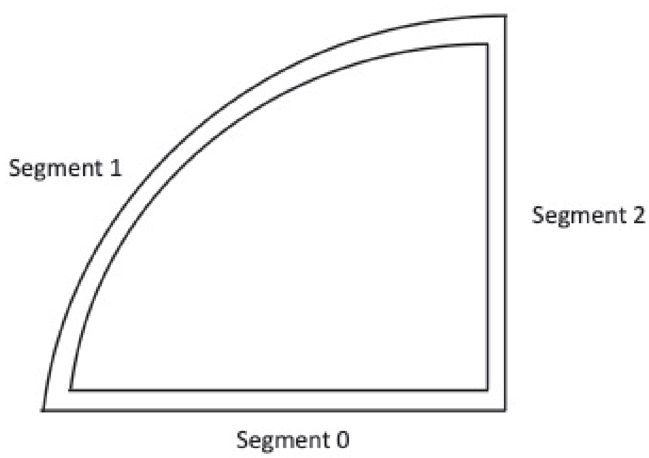

Figure 1. Illustration of the tube.

In Segment 0 and hence at the datum altitude $z = 0$, the probability of the particle being in a given tiny *length* interval dL of the tube is $P_{0,L}dL$. In both Segment 1 and Segment 2, the probability of the particle being in a given tiny *length* interval dL of the tube at altitude z is, in accordance with the law of isothermal atmospheres (Reif, 2009, sections 2.3 and 6.1–6.4, especially section 6.3 subsection "Molecule in an ideal gas in the presence of gravity"; Schroeder, 2000),

$$P_{1,L}(z)\, dL = P_{2,L}(z)\, dL = P_{0,L} e^{-mgz/kT} dL. \tag{4}$$

We note that the law of isothermal atmospheres (Reif, 2009, sections 2.3 and 6.1–6.4, especially section 6.3 subsection "Molecule in an ideal gas in the presence of gravity"; Schroeder, 2000, section 1.2, especially problem 1.16 and problem 3.37, chapter, especially sections 6.1, 6.2, and problem 6.14) is of course a special case of the Boltzmann (or canonical) distribution with $E = mgz$ (Schroeder, 2000, section 6.1, especially p. 223; Reif, 2009, section 6.2, especially p. 205; Kauzmann, 1967). (Of course, the terms "Boltzmann distribution" and "canonical distribution" are synonymous [Schroeder, 2000, section 6.1, especially p. 223; Reif, 2009, section 6.2, especially p. 205; Kauzmann, 2000]).

The terms "barometric equation" (Reif, 2009, section 6.2. especially p. 205) or "hydrostatic equation" (Reif, 2009, section 6.2. especially p. 205; Kauzmann, 2000; Schroeder, 2000, problem 1.16; Wark & Richards, 1999, section 1-5-4; Wallace & Hobbs, 2006; Holton & Hakim, 2013) are sometimes employed to denote hydrostatic equilibrium (Reif, 2009, section 6.2 especially p. 205; Kauzmann, 1967; Schroeder, 2000, problem 1.16; Wark & Richards, 1999, p. 11 and section 6-3-5; Wallace & Hobbs, 2006; Holton & Hakim, 2013), but not necessarily thermodynamic equilibrium (Reif, 2009, sections 2.3 and 6.1-6.4, in section 6.3 see especially subsection "Molecule in an ideal gas in the presence of gravity"; section 6.2 especially p. 205; Schroeder, 2000, section 1.2, especially problem 1.16, problem 3.37, chapter 6, especially sections 6.1 and 6.2 and problem 6.14); Kauzmann, 1967; Wark & Richards, p. 11 and section 6-3-5). Thermodynamic equilibrium necessarily implies hydrostatic equilibrium, but not necessarily vice versa. Thus *any* isothermal atmosphere is at thermodynamic equilibrium and hence necessarily also at hydrostatic equilibrium: This obtains in particular for a one-particle isothermal atmosphere in accordance with Equation (4). By contrast, Earth's atmosphere and oceans are almost always at hydrostatic equilibrium (or at least very nearly so) but not at thermodynamic equilibrium.

Also in accordance with the Boltzmann (or canonical) distribution (Schroeder, 2000, section 6.1 especially p. 223; Reif, 2009, section 6.2 especially p. 205; Kauzmann, 1967, sections 4.4, 4.5, 4.9) in Segment 1, the probability of the particle being in a given tiny *altitude* interval dz of the tube at altitude z is

$$P_{1,z}(z)\,dz = P_{1,L}(z)\left(\frac{dL}{dz}\right)_1 dz$$
$$= P_{0,L}\sec[\theta(z)]\,e^{-mgz/kT}dz. \qquad (5)$$

Supradegeneracy obtains in Segment 1 because [within the restriction $\theta(z_{max}) < \frac{\pi}{2}$ rad] we set

$$\sec[\theta(z)] = e^{Nmgz/kT}\ \ (N>1)$$
$$\Longrightarrow\ P_{1,z}(z)\,dz = e^{(N-1)mgz/kT}\ \ (N>1). \qquad (6)$$

Because Segment 2 is vertical in its entirety, in Segment 2 the probability of the particle being in a given tiny *altitude* interval *dz* of the tube at altitude *z* is the same as of it being in a given tiny *length* interval *dL*, i.e., in accordance with the law of isothermal atmospheres (Reif, 2009, sections 2.3 and 6.1–6.4, in section 6.3 see especially subsection "Molecule in an ideal gas in the presence of gravity"; Schroeder, 2000, section 1.2 especially problem 1.16, problem 3.37, chapter 6 especially 6.1 and 6.2 and problem 6.14),

$$P_{2,z}(z)\,dz = P_{2,L}(z)\left(\frac{dL}{dz}\right)_2 dz = [P_{2,L}(z)\times 1]\,dz$$
$$= P_{2,L}(z)\,dL = P_{0,L}e^{-mgz/kT}dz. \qquad (7)$$

Degeneracy *G* (*z*) corresponding to any given tiny *altitude* interval $z-\frac{1}{2}dz \le z \le z+\frac{1}{2}dz$ is proportional to the *length dL* of tube in this tiny *altitude* interval *dz*, i.e.,

$$G(z) \propto dL(z) = \frac{dL(z)}{dz}dz = \sec[\theta(z)]\,dz. \qquad (8)$$

At altitude *z* in Segment 1,

$$G_1(z) = G_1(z=0)\sec[\theta(z)] = G_1(z=0)\,e^{Nmgz/kT}\ \ (N>1) \qquad (9)$$

By contrast, in Segment 2,

$$G_2(z) = G_2(z=0) = G_1(z=0) = \text{ constant}. \qquad (10)$$

Thus: (i) By Equations (5), (6), (8), and (9), $P_{l,z}(z)$ *increases* with increasing *z*—supradegeneracy (Sheehan, & Schulman 2019; Sheehan 2019, 2020a, 2020b, 2001–2022, 2018–2022)! But by Equations (4), (7), and (10), $P_{2,z}$ (*z*) *decreases* with increasing *z* in accordance with the law of isothermal atmospheres [Equation (3)]. But (ii) by Equations (4), (7), and (10), *both* $P_{l,L}$ (*z*) *and* $P_{2,L}$ (*z*) *decrease* with *increasing z at the same rate* as $P_{2,z}$ (*z*)—in accordance with the law of isothermal atmospheres [Equation (4)] (Reif, 2009, sections 2.3 and 6.1–6.4, section 6.3 see especially subsection "Molecule in an ideal gas in the presence of gravity"; Schroeder, 2000, section 1.2 especially problems 1.16 and 3.37, chapter 6, especially sections 6.1, 6.2, problem 6.14).

III. IMPLICATIONS PERTINENT TO THE SECOND LAW OF THERMODYNAMICS

Now the uppermost question pertinent to the Second Law of Thermodynamics is: Will the particle spontaneously circulate, manifesting spontaneous momentum flow (Zhang & Zhang, 1992)—flow that is both (i) sustaining and (ii) robust, i.e., capable of surviving disturbances and of restoring itself if it is destroyed (Zhang & Zhang, 1992)—either ascending in Segment 1, descending in Segment 2, and completing the (clockwise) circuit by returning to the bottom of Segment 1 via Segment 0—or in the opposite (counterclockwise) direction? It doesn't seem so. *Even though* $P_{l,z}$ (*z*) *in*creases with increasing *z* as per Equations (5), (6), (8), and (9)—supradegeneracy (Sheehan, & Schulman, 2019; Sheehan 2019, 2020a, 2020b, 2001–2022, 2018–2022)! —and $P_{2,z}$ (*z*) *de*creases with increasing *z* in accordance with the law of isothermal atmospheres [Equation (4)] as per Equations (4), (7), and (10) (Reif, 2009, sections 2.3 and 6.1–6.4, in section 6.3 see especially the subsection entitled "Molecule in an ideal gas in the presence of gravity"; Schroeder, 2000, section 1.2, especially problems 1.16 and 3.37, chapter 6, especially sections 6.1, 6.2, problem 6.14). And *even though* because the *entire* tube is of *constant* internal diameter, we avoid the impediments to cyclical motion of the particle owing to employing as Segment 1 a birch trumpet,[2] i.e., a cone flaring upwards such that its horizontal cross-sectional area *A* (*z*) increases with increasing *z* as $e^{Nmgz/kT}$ (*N* > 1): see Sheehan (2020b, the paragraph immediately following that containing figure 4, and note 3). And *even though* both R1 and R2 are *also* fulfilled. Because the particle, if allowed to move through a horizontal tube segment, Segment *H* (*z*), connecting Segments 1 and 2 at *any* altitude *z*, would tend to drift in the direction of increasing P_L (*z*)—*not* in the direction of increasing P_z (*z*): P_L (*z*)—*not* P_z (*z*)—is the driver. But, repeating Equation (4), at *any* altitude *z*,

$$P_{1,L}(z)\,dL = P_{2,L}(z)\,dL = P_0e^{-mgz/kT}dL. \qquad (11)$$

Thus P_L (*z*) is *constant* within *any* such horizontal tube segment, Segment *H* (*z*), at *any* altitude *z*—and equal to $P_{l,L}(z) = P_{2,L}(z)$ at this altitude *z*. Hence if there is a horizontal tube segment, Segment *H*(*z*), connecting Segments 1 and 2 at *any* altitude *z*, the particle would be *equally likely* to drift either from Segment 1 to Segment 2 or vice versa: random Brownian motion. [Segment 0 is Segment *H* (*z* = 0). Even though $\theta(z_{max}) < \frac{\pi}{2}$ rad at the top of Segment 1 *per se*, there must be at least a tiny horizontal region at its join with the top of Segment 2, at altitude z_{max}. Alternatively, we can construe a short horizontal tube segment, Segment H (z_{max}), connecting the tops of Segments 1 and 2 at altitude z_{max}.] Hence the particle's motion *anywhere* within our closed tube would be random Brownian motion: It would *not* spontaneously circulate: either ascending in Segment 1, descending in Segment 2, and completing the (clockwise) circuit by returning to the bottom of Segment 1 via Segment 0—or in the opposite (counterclockwise) direction. It would *not* manifest the spontaneous momentum flow (Zhang & Zhang, 1992) that would be required to challenge the Second Law.

It doesn't seem to matter whether there is only one particle in our tube—a one-particle isothermal atmosphere—or an isothermal atmosphere comprising two, three, or many particles. As per Equations (4) and (11), the smoothed-out long-time-average density of *one* particle as a function of altitude z in our tube corresponds to thermodynamic equilibrium (Reif, 2009, sections 2.3 and 6.1–6.4, in section 6.3 see especially the subsection entitled "Molecule in an ideal gas in the presence of gravity,", section 6.2 especially p. 205; Schroeder, 2000, problem 1.16; Kauzmann, 2000; Wark & Richards, 1999, p. 11 and section 6-3-5) and hence also to hydrostatic equilibrium (Reif, 2009, section 6.2; Kauzman, 1967; Schroeder 2000, problem 1.16; Wark & Richards, 1999, section 1-5-4; Wallace & Hobbs, 2006, section 3.2; Holton & Hakim, 2013, section 1.4.1).

Thus also the density of an isothermal atmosphere comprising two, three, or many such particles as a function of altitude z in our tube would correspond to thermodynamic equilibrium (Reif, 2009, sections 2.3 and 6.1–6.4, in section 6.3 see especially the subsection "Molecule in an ideal gas in the presence of gravity", section 6.2 especially p. 205; Schroeder, 2000, problem 1.16; Kauzmann, 2000; Wark & Richards, p. 11 and section 6-3-5) and hence also to hydrostatic equilibrium (Reif, 2009, section 6.2 especially p. 205; Kauzmann, 2000; Schroeder, 2000, problem 1.16; Wark & Richards, 1999, section 1-5-4; Wallace & Hobbs, 2006; Holton & Hakim, 2013).

Thus also the density of *any* isothermal fluid (gas or liquid) as a function of altitude z in our tube would correspond to thermodynamic equilibrium and hence also to hydrostatic equilibrium). If there is only one particle in our tube, thermalization occurs via collisions with the inner wall of the tube; if there are $n > 1$, via interparticle collisions as well as via collisions with the inner walls of the tube (interparticle collisions becoming more important with increasing n)—but this seems to make no difference. That is why spontaneous momentum flow (Zhang & Zhang, 1992) can*not* be manifested, irrespective of the nature or density of the fluid (gas or liquid) in our tube. (We re-emphasize that thermodynamic equilibrium necessarily implies hydrostatic equilibrium but not necessarily vice versa).

Thus, at least in our system, supradegeneracy apparently does *not* challenge the Second Law of Thermodynamics—*despite* both R1 and R2 *also* being fulfilled. But it seems to be an open question whether or not this negative result is similarly true for *all* systems manifesting supradegeneracy, especially given that analyses, including computer simulations but to the best knowledge of the author at the time of this writing not yet experimental tests, of other supradegenerate systems at least *prima facie* seem to yield positive results (Sheehan & Schulman, 2019; Sheehan, 2019, 2020a, 2020b, 2001–2022, 2018–2022). The crucial question seems to be: What is the *minimal complete set* of *additional* requirements R* (tentatively conjectured to include R1 and R2)—over and above supradegeneracy *per se*—that must be fulfilled by a supradegenerate system if it is to challenge the Second Law?

But *even if* our negative result *does* turn out to be similarly true for *all* systems manifesting supradegeneracy, such systems could still be useful *even within* the strictures of the Second Law (Sheehan & Schulman, 2019; Sheehan, 2019, 2020a, 2020b, 2001–2022, 2018–2022).

It is *important* to note that the negative result for the system that we consider does *not* depend on whether or not z_{max}, the altitude at the top of our system at the join of Segments 1 and 2, is high enough for suprathermality (Sheehan & Schulman, 2019; Sheehan, 2019, 2020a, 2020b, 2001–2002, 2018–2002), i.e., for $E_{max} = mgz_{max} \gg kT$ to obtain. That P_L (z) is *constant* within *any* horizontal tube segment, Segment H (z), at *any* altitude z and equal to $P_{1,L}$ (z) = $P_{2,L}$ (z) at this altitude z—implies only random Brownian motion. And this implication is *in*dependent of the value of z_{max} and hence of $E_{max} = mgz_{max}$. Indeed, *even if* our particle *could* spontaneously circulate (Zhang & Zhang 1992) in challenge to the Second Law—according to our results it can*not*—this too would have been *in*dependent of the value of z_{max} and hence of $E_{max} = mgz_{max}$. [But if we wish for suprathermality to be obtained without requiring an inconveniently large z_{max} in Earth's gravitational field, see Sheehan (2020b, note 3), our particle should be massive, e.g., a Brownian particle rather than an atom or molecule of gas. If the Brownian particle is suspended in a fluid, then m should be construed as its *net* mass after subtracting the buoyant force provided by the fluid. The mass of a Brownian particle, or even its *net* mass if it is suspended in a fluid, can easily be large enough to avoid an inconveniently large z_{max} in Earth's gravitational field.] Thus the operation of supradegenerate systems in general, and in particular whether any such systems turn out to challenge the Second Law or all such systems operate within the strictures of the Second Law, does not *in principle* depend on whether or not suprathermality obtains—even if *in practice* suprathermality facilitates more efficient operation, whether in challenge to the Second Law or within its strictures (Sheehan & Schulman 2019; Sheehan 2019, 2020a, 2020b, 2001–2022, 2018–2022).

IV. ANTI-SUPRADEGENERACY

To recapitulate, we dub as *anti*-supradegeneracy $G(E)$ *de*creasing with increasing E and hence $P(E)$ decreasing with increasing E *faster* than the Boltzmann factor $e^{-E/kT}$. And we dub as *strong* anti-supradegeneracy $G(E)$ *de*creasing with increasing E *faster* than the Boltzmann factor $e^{-E/kT}$ and hence $P(E)$ decreasing with increasing E *faster* than the Boltzmann factor $e^{-E/kT}$ *squared*, i.e., faster than $e^{-2E/kT}$. In our system $E = mgz$ so we can, equivalently, employ $G(z)$ and$P(z) = e^{-mgz/kT}$.

Consider the system shown in Figure 1 *inverted*, i.e., *upside down*. In the inverted Segment 1, $G(z)$ not merely *de*creases with increasing z but does so *faster* than the Boltzmann factor $e^{-mgz/kT}$, and hence $P_{l,z}(z)$ decreases with increasing z not merely faster than the Boltzmann factor $e^{-mgz/kT}$ but faster than the Boltzmann factor $e^{-mgz/kT}$ *squared*, i.e., *faster* than $e^{-2mgz/kT}$: not merely anti-supradegeneracy but *strong* anti-supradegeneracy. Or consider a tube comprising an upright Segment 1 as shown in Figure 1 *and* an inverted Segment 1. Then *both* (i) $P_{l,z}(z)$ *in*creases with increasing z in the upright Segment 1: supradegeneracy! *and* (ii) $P_{l,z}(z)$ *de*creases with increasing z *faster* than $e^{-2mgz/kT}$ in the inverted Segment 1: *strong* anti-supradegeneracy! Yet exploiting *either* supradegeneracy *or* anti-supradegeneracy (even as in our system *strong* anti-supradegeneracy)—or even exploiting *both* supradegeneracy *and* anti-supradegeneracy (even as in our system *strong* anti-supradegeneracy)—does *not* seem to contravene compliance with the Second Law. Because, still, irrespective of $P_{l,z}(z)$, whether employing an upright Segment 1, an inverted Segment 1, or even *both* an upright Segment 1 *and* an inverted Segment 1, $P_{l,L}(z)$—*not* $P_{l,z}(z)$—is the driver. And $P_{l,L}(z)$ still—in *all* cases—decreases with increasing z *exactly* as the Boltzmann factor $e{-}^{mgz/kT}$ as per the law of atmospheres [Equation (4)] (Reif, 2009, sections 2.3 and 6.1–6.4, section 6.3, especially the subsection "Molecule in an ideal gas in the presence of gravity"; Schroeder, 2000, section 1.2, especially problem 1.16, problem 3.37, chapter 6, especially sections 6.1 and 6.2 and problem 6.14). Thus our result of Section III—that our particle would execute only random Brownian motion—*not* (either clockwise or counterclockwise) spontaneous momentum flow (Zhang & Zhang, 1992)—remains *un*changed.

We note that the concepts of supradegeneracy and anti-supradegeneracy (albeit without being dubbed with these names) have been considered previously (Denur, 2012). It was shown that the average fluctuating energy $\langle E \rangle$ above the ground state of a single particle confined to a single classical degree of freedom in thermodynamic equilibrium with a heat reservoir at temperature T can be much larger or much smaller than kT (Denur, 2012). But the larger $\langle E \rangle$ is, the more spatially delocalized the particle must be (Denur, 2012), and thus the greater the thermodynamic cost of overcoming its delocalization (Denur, 2012). Hence these previous considerations (Denur, 2012) were compliant with the Second Law (Denur, 2012).

V. SIMPLE EXPERIMENTAL TESTS OF OUR SYSTEM

It would be easy enough to bend a piece of transparent glass or plastic tubing into the shape described in the first four paragraphs of Section II and shown in Figure 1. And it would be equally easy to invert it—or to bend a piece of transparent glass or plastic tubing into an upright-plus-inverted Segment 1—as described in Section IV. An isothermal atmosphere consisting of a single Brownian particle, or of any number n of them, could be placed in the tube. *Both* isothermality (and hence thermodynamic equilibrium) *and* observability of the Brownian particle(s) could be ensured by *uniform* illumination of the *entire* tube. It would then be a simple matter to observe whether (a) the Brownian particle(s) spontaneously circulate (either clockwise or counterclockwise) (Zhang & Zhang, 1992), manifesting spontaneous momentum flow (Zhang & Zhang 1992), which is *not* compliant with the Second Law, or (b) whether they manifest only random Brownian motion, which *is*. I hope for (a), but probably in vain: realistically, we expect the result to be (b). *Probably*, but as of this writing *not certainly*, in vain: Only *experiments* can decide the issue for sure! *Experiments* are the final arbiter!

VI. CONCLUDING REMARKS: IMPLICATIONS *IF* THE SECOND LAW IS VIOLATED

As has been stated by Sheehan (2018, 2020b, 2022), *if* the Second Law of Thermodynamics could be violated—*by any means whatsoever* [supradegeneracy, anti-supradegeneracy (whether strong or not), and/or otherwise]—the implications would be revolutionary (Sheehan, 2018, 2020b, 2022)—indeed, more than revolutionary (Sheehan, 2018, 2020b, 2022).

All current energy sources and technologies—not only nonrenewable ones but also renewable ones (except photosynthesis)—could be rendered obsolete overnight (Sheehan, 2018, 2020b, 2022). Even so-called "renewable" current energy sources require continual *free*-energy (exergy) input paid for by the temperature difference between the hot solar photosphere and the cold depths of space. Also, even so-called "renewable" current energy sources, both directly via sunlight and indirectly via wind, rivers, ocean currents, waves, ocean thermal energy conversion (with a few exceptions, e.g., OTEC[3]) require expensive storage systems (Sheehan 2018, 2020b, 2022). Moreover, even so-called "renewable" current energy sources (including OTEC[3]) have environmental impacts, including the environmental impacts pertaining to disposal of worn-out materials and equipment: Reversing the degradation of worn-out materials and equipment may be entropically impracticable. By contrast, Second-Law violators require *zero* input, because *the same heat can be recycled, used over and over again, forever*—with no storage systems required (Sheehan, 2018, 2020b, 2022). With rare exceptions such as the launching of spacecraft and construction (e.g., of buildings, bridges, etc.), work is frictionally degraded to heat on short timescales, indeed, most usually, continually. If the Second Law is violated, wherever and whenever work is frictionally degraded to heat, *the same heat can be recycled back to work, used over and over again, forever*—with no storage systems required. *A fixed, finite quantity of heat can thus do an infinite amount of work!* Some of this work could be employed to reverse the degradation of worn-out materials and equipment—hence no disposal required either (Sheehan, 2018, 2020b, 2022). And it has been stated that systems violating the Second Law are approaching commercialization (Sheehan, 2018, 2020b, 2022).

But, that being said, we should also note that: "If the second law should be shown to be violable, it would nonetheless remain valid for the vast majority of natural and technological processes" (Cápek & Sheehan, 2005).

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NOTES

1. Strictly, relativistic gravitational equilibrium vertical temperature gradients should be accounted for: See Garrod (1995, exercises 7.29 and 7.30) and Tolman (1987). At thermodynamic equilibrium, temperature increases downwards in any gravitational field. But these vertical temperature gradients are utterly negligible for the system that we discuss and for all systems discussed in the cited references. Moreover, the gravitational redshift reduces the temperature of heat radiated from a hot reservoir at a lower altitude to the temperature of a cold reservoir at a higher altitude by the time this heat reaches the higher altitude of the cold reservoir. Thus what the gravitational temperature gradient giveth, the gravitational redshift taketh away. So the Carnot efficiency is *zero*. Hence relativistic gravitational equilibrium vertical temperature gradients can-*not* be exploited to challenge the Second Law of Thermodynamics.
2. Birch trumpet. https://en.wikipedia.org/wiki/Birch_trumpet
3. Ocean thermal energy conversion. https://en.wikipedia.org/wiki/Ocean_thermal_energy_conversion

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