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Addendum to"Nonequivalence of the Nernst-Simon and unattainability statements of the third law of thermodynamics"

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An additional potential objection is noted to the recent argument that the Nernst-Simon and unattainability statements of the third law of thermodynamics are *not* equivalent, but rather make *independent* assertions about the kinds of Hamiltonians found in nature. Although valid in a limited sense, the objection does not invalidate the conclusions reached there and illustrates several significant points about the importance of the thermodynamic limit in considerations of the third law.

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I. INTRODUCTION

Recently it has been argued [1] that the Nernst-Simon and unattainability statements of the third law of thermodynamics are *not* equivalent, as is often assumed, but rather that they make *independent* statements about the kinds of Hamiltonians found in nature. The ideal Bose gas in one, two, and three dimensions was used as a concrete example of a familiar substance illustrating the nonequivalence of the statements. Several possible objections to this example were raised, and it was argued that they do not detract from the correctness of the position taken. Additional counterexamples were produced in the form of thermodynamic equations of state which satisfy the first and second laws of thermodynamics and the Nernst-Simon statement but violate the unattainability statement. The essence of the argument was that thermodynamically consistent equations of state can be constructed, satisfying the first and second laws and the Nernst-Simon statement of the third, for which it is possible, by decreasing the molar volume at fixed temperature, to reduce the molar entropy to zero while the pressure remains bounded. The Hamiltonian and equation of state of the ideal Bose-Einstein gas was given as an example.

There is an additional possible objection that might be raised to the ideal Bose-Einstein gas as a counterexample to the equivalence of the Nernst-Simon and unattainability statements. The objection, although technically valid in one sense, does not invalidate the conclusions of [1], but, rather, actually illustrates the point made there. Moreover, it also illustrates several significant points about the importance of taking the thermodynamic limit in considerations of the third law, a point made earlier by Griffiths [2]. In [1], results were used for the ideal Bose-Einstein gas obtained in the *thermodynamic limit* ($N \to \infty$ with $v = V/N$ and T or $u = U/N$ or $s = S/N$ held constant, or, equivalently, $V \to \infty$ with μ and T held constant), where N is the number of particles, V is the volume, U is the internal energy, S is the entropy, T is the thermodynamic temperature, and μ is the chemical potential. As a result, the internal energy is extensive [e.g., $U(S, V, N)$ is homogeneous of degree 1 in S, V, N]. Under these conditions, the arguments and conclusions reached in [1] are correct.

II. OBJECTION

The objection might be raised [3] that, for *fixed*, finite N, in order for the volume per particle v to approach zero, the linear dimensions of the container must eventually become small compared to the thermal de Broglie wavelength of a particle,

$$\Lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}, \tag{1}$$

where d is the spatial dimensionality, h is Planck's constant, m is the mass of the particles, and k_B is Boltzmann's constant. When this occurs, so few states are available that the discrete nature of the spectrum of one-particle states becomes important, and sums over states cannot be approximated by integrals. In this limit the internal energy is no longer extensive. For particles in a (hyper)cubic box of edge length L in d dimensions, when $L \ll \Lambda$ the system is essentially restricted to its ground state, and the internal energy becomes just N times the one-particle ground-state energy,

$$U \approx \frac{dh^2 N}{8mV^{2/d}}. \tag{2}$$

One might then object that the "pressure,"

$$P = -\left(\frac{\partial U}{\partial V}\right)_{N,S} \approx \frac{2h^2 N}{8mV^{(d+2)/d}}, \tag{3}$$

diverges as $V \to 0$, the limit required for the entropy to vanish, so that it is not possible to reduce the entropy to zero by decreasing the volume at fixed temperature *while keeping the pressure bounded.* This would seem to indicate that the ideal Bose-Einstein gas does not constitute a counterexample after all. Note, however, that the energy given by (2) is not extensive, and the pressure given by (3) is not intensive, as is usually required of thermodynamic functions. We return to this point in Sec. III.

The relationship between this objection and the conclusions reached in [1] can best be illuminated by asking and answering three questions.

(i) Can thermodynamically consistent equations of state be constructed that satisfy the usual requirements of the first and second laws of thermodynamics, including *extensivity* [homogeneity of degree 1 of $U(S,V,N)$ in S, V and N] and *stability* [convexity of $U(S,V,N)$ in S, V and N together, or of P/T in $1/T$ and μ/T together], and which satisfy the Nernst-Simon statement of the third law, but according to which it is possible to reduce the molar entropy to zero at nonzero temperature and bounded pressure by sufficiently decreasing the molar volume?

(ii) Are there Hamiltonians that lead to equations of state of the type in (i) through the usual procedures of statistical mechanics *in the thermodynamic limit*? (There are fairly compelling reasons, elaborated below, for taking this limit *before* posing thermodynamic questions of an equation of state.)

(iii) Are there Hamiltonians that, for *fixed* particle number N, in the canonical ensemble (or any other specified ensemble), lead to vanishing of the total entropy at nonzero temperature and bounded pressure?

The answer to question (i) is unambiguously "yes." All three of the counterexamples in [1] provide demonstrations of this. This is sufficient to establish the nonequivalence of the Nernst-Simon and unattainability statements of the third law through the arguments given there. It should be remarked that the existence of a thermodynamically consistent internal energy per particle, $u(s,v)$, with the required properties *implies* the existence of a thermodynamically consistent *model* internal energy for N particles through the *definition*

$$U(S,V,N) \equiv N u\left(\frac{S}{N},\frac{V}{N}\right), \tag{4}$$

so that equations of state for a finite number of particles can be constructed that satisfy the requirements in (i).

The answer to question (ii) is also "yes," with the ideal Bose-Einstein gas serving as concrete proof by exhibition.

The answer to question (iii) is unknown (at least to the author), but the objection above demonstrates that the ideal Bose-Einstein gas does *not* provide a positive example of such a Hamiltonian.

A consequence of the answer to (iii), above, is that for any *fixed*, finite number of particles, N, an ideal Bose-Einstein gas of N particles, even if it existed, could *not* be used to reduce the absolute temperature to zero if the pressure and volume are both bounded. This does *not* invalidate the principal conclusions of [1], however, but merely changes the status of one of the counterexamples given there. A more careful statement of the assertion in the paragraph containing (1.1) of [1] would have been as follows: The *equations of state* (in the thermodynamic limit) of the ideal quantum gases in d dimensions ($d = 1,2,3,\ldots$) satisfying Bose-Einstein statistics provide illuminating counterexamples of this supposed equivalence.

III. THERMODYNAMIC LIMIT

There are a number of compelling reasons for demanding that the equation of state satisfy extensivity of the energy, e.g., that $U(S,V,N)$ be homogeneous of degree 1 in S, V, and N. This requirement is met in statistical mechanics by taking the *thermodynamic limit* ($N \rightarrow \infty$ with $v = V/N$ and T or $u = U/N$ or $s = S/N$ held constant, or, equivalently, $V \rightarrow \infty$ with μ and T held fixed). Griffiths [2] has argued eloquently for the appropriateness of the thermodynamic limit before the limit $T \rightarrow 0$ in considerations of the third law. Those arguments are cogent with regard to the limit $v \rightarrow 0$, here, as well. Griffiths makes the point that when an investigator measures a property like the heat capacity (or obtains an energy or entropy therefrom), it is *assumed* that the property is extensive, and the investigator divides by the mass or number of particles or moles in order to report a property of the *substance* rather than of a particular experiment. The validity of this assumption can be tested by making measurements on systems with different values of N but the same values of v and T. If it is found that quantities that should be extensive are not, then it is concluded that *finite-size effects* are present, and the experiment is repeated on a larger system (larger N at the same v and T, for example) until the expected extensivity is observed. Alternatively, an extrapolation or fitting may be performed to extract the part of the energy that varies proportionally to N. It is the results for these larger systems, exhibiting extensivity, that are taken to be characteristic of the substance in question. This is precisely what is achieved by taking the thermodynamic limit in statistical mechanics. In this sense, the ideal Bose-Einstein gas in d dimensions *does* have the property that $P(T,v)$ remains bounded and $s(T,v) \rightarrow 0$ as $v \rightarrow 0$, so that it can reasonably be said that the thermodynamic equation of state of the Bose-Einstein ideal gas does provide an example of a violation of the unattainability statement.

Griffiths also makes the point that taking the thermodynamic limit before the limit $T \rightarrow 0$ actually makes more sense from a *practical* point of view as well as being more fundamentally correct. Similar reasoning applies to the limit $v \rightarrow 0$. For example (for a system in a cubic box), while the system falls out of the thermodynamic limiting behavior when the *total* volume V becomes of order Λ^d, with Λ given in Eq. (1) and d the dimensionality, the transition to a thermodynamically degenerate Bose-Einstein gas occurs when the volume *per particle*, v, reaches this limit. For one mole of gas, this amounts to an enormous range (many orders of magnitude) of v (or V) over which P is very nearly equal to $P_0(T)$ given by Eq. (2.9) of [1], and s is decreasing essentially proportionally to the molar volume. If such a gas were actually available, the investigator would choose a sample large enough that the transition to a degenerate Bose-Einstein gas would be readily attainable and would observe the behavior of u, s, and P with v to as small values of v as experimentally obtainable, and then *extrapolate* to $v = 0$ if this seemed justified. (It would, since $P \approx P_0(T)$ would be essentially constant, and $u \approx (d/2)P_0 v$ and

$s \approx [(d+2)/2](P_0/T)v$ would be essentially linear in v.) This would correctly give the thermodynamic limiting behavior. In the event that the investigator were actually able to reach the volume at which the discreteness of levels becomes important, all that would be needed in order to extend closer to $v = 0$ the range of volume per particle over which the thermodynamic limiting formulas apply would be to increase the number of particles in the sample.

For example, for one mole of particles with mass 4 amu in a three-dimensional cubic box at a temperature of 100 K, the system becomes degenerate when $V \approx 0.4$ cm^3 and Bose-Einstein condensation commences when $V \approx 0.15$ cm^3, whereas the discreteness of the quantum states does not become important until $V \approx 10^{-24}$ cm^3 (a cubic box 1 Å on a side). The value of P_0 for this temperature and particle mass is about 27.5 kbar. Taking this as the upper limit of pressure, and 22.4 l mol^{-1} as the upper limit on molar volume, a reversible adiabatic expansion can carry the system from 100 to about 10^{-17} K in a single step. If, instead, a four-kilogram sample is used, the molar volume of the sample can vary from about 10^{-27} cm^3 per mole to 22.4 l mol^{-1} and the final temperature can be as low as 10^{-19} K. Of course, the value of the *total* volume V at which the onset of effects caused by discreteness of the levels occurs does not change with N, but the value of v at which this occurs *does* change, and this allows one to investigate arbitrarily small values of v while still ensuring that the equation of state satisfies the desired extensivity properties.

There is another reason for strongly preferring to work in the thermodynamic limit, or at least in a limit where the discreteness of the levels is unimportant. It is only in this limit that the various ensembles of statistical mechanics give equivalent results. As a particularly striking example of this, note that in the canonical ensemble, for fixed N and V, the entropy vanishes exponentially rapidly as $T \to 0$, whereas in the grand-canonical ensemble, with V fixed and μ adjusted to give a fixed value for the average particle number, $\langle N \rangle$, the entropy *does not vanish* as $T \to 0$. Instead, it approaches the constant value $k_B[\ln(N) + 1]$. This is because, even at $T = 0$, in the grand-canonical ensemble *fluctuations* are allowed in N and the resulting multiplicity of allowed states gives rise to an entropy. Of course, the entropy *per particle* vanishes in the thermodynamic limit, but for a system of fixed, finite size, even the question of whether the Bose-Einstein gas satisfies the *Planck* statement of the third law depends upon which ensemble is used.

Still another reason for preferring to work in the limit in which the discreteness of the levels is unimportant is that when this condition is violated the properties depend upon the *shape* of the container as well as its volume. For example, the energy and pressure given in Eqs. (2) and (3) with $d = 3$ are appropriate for a *cubic* container. If, instead, one considers a container of square cross section of edge length L_1 and variable height L_2, the behavior is quite different. (This geometry would be at least as natural as the cubic container for investigating variable volume.) Provided that all dimensions are large compared to the thermal de Broglie wavelength Λ, the behavior is identical to that for the cubic box under the same conditions. However, when L_2 becomes small compared to Λ while L_1 remains fixed greater than Λ, the behavior becomes quite different than that for the cubic box with edge length small compared to Λ. In this limit, the "pressure" is different on the square faces of the container than on its rectangular walls, and the energy consists of two quite distinct contributions, one from the ground-state energy of a particle in a one-dimensional box and the other characteristic of a two-dimensional Bose-Einstein gas. Moreover, the entropy does not vanish even in the limit $v \to 0$. It is, however, again the case that the internal energy and entropy are *subextensive*, scaling proportionally to a power less than 1 of the number of particles.

The following trap is, perhaps, worth a cautionary note. One might be tempted to suppose that the problem with the ideal Bose-Einstein gas Hamiltonian could be dealt with by simply shifting the energy of every state downward by the same constant amount, equal to the ground-state energy of the system. This gives a ground-state energy that is identically zero and therefore a ground-state pressure that is zero also, thereby eliminating the divergent pressure. This shift has no effect whatever on the thermodynamic limiting behavior, since the ground-state energy per particle determined by Eq. (2) vanishes in that limit anyway. Unfortunately, for fixed finite N, when the dimensions of the container are comparable to or less than Λ, this leads to a pressure that is not always decreasing with increasing V at fixed N and T. [The pressure must fall from $P_0(T)$, when $V \gg \Lambda^d \gg v$ to zero when $V \ll \Lambda^d$.] Thus, the equation of state no longer satisfies the convexity requirements of stability in this regime. This is just one more example of the perils of trying to extract thermodynamically sensible behavior from statistical mechanics when one is not (essentially) in the thermodynamic limit. Given the nonequivalence of ensembles in this regime, the interpretation of this behavior requires some care, but it does not seem likely that the result would be useful in clarifying the third law of thermodynamics.

IV. DISCUSSION

In Sec. IV of [1] it was suggested that the most fruitful interpretation of the counterexamples presented there was that the Nernst-Simon and unattainability statements are *not* equivalent as thermodynamic statements, and that they make *independent* statements about the kinds of Hamiltonians found in nature. That conclusion, it seems to me, remains correct and unaffected by the objection raised above. The issue in question is whether the ideal-gas Hamiltonian with Bose-Einstein statistics is to be placed in the category of Hamiltonians excluded by or allowed by the unattainability statement of the third law of thermodynamics.

One may take either of two points of view regarding the role of the ideal Bose-Einstein gas. From the point of view of one raising the objection in Sec. II, the ideal Bose-

Einstein gas Hamiltonian for fixed, finite N does *not* lead to a violation of the unattainability statement, and therefore is not disallowed by that statement. Therefore, from this point of view, the ideal Bose-Einstein gas is not itself an example of the nonequivalence of the Nernst-Simon and unattainability statements, although its equation of state in the thermodynamic limit provides a thermodynamic example of the nonequivalence.

Alternatively, one might argue that, in order to ensure that the equation of state is independent of the amount of material and the shape of the container in which it is measured and independent of the ensemble in which it is calculated, it seems reasonable to insist that the thermodynamic properties of a substance be specified as those obtained in the thermodynamic limit. If this is agreed to, then the ideal Bose-Einstein gas can itself be said to provide a counterexample demonstrating the nonequivalence of the Nernst-Simon and unattainability statements of the third law of thermodynamics.

In *any* case, however, the thermodynamic limiting features can be used to construct a *model* counterexample that does this by the procedure outlined in Eq. (4).

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[1] J. C. Wheeler, Phys. Rev. A **43**, 5289 (1991).

[2] *The Third Law in Statistical Mechanics*, in *A Critical Review of Thermodynamics*, edited by E. B. Stuart, B. Gal-Or, and A. J. Brainard (Mono Book Corp., Baltimore, 1970).

[3] I became aware of this objection after [1] had been accepted for publication as the result of a private communication from R. G. Petschek. The point was raised independently by W. D. Harris (private communication).