Finite Systems in a Heat Bath: Spectrum Perturbations and Thermodynamics

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ABSTRACT: When a finite system is at equilibrium with a heat bath, the equilibrium temperature is dictated by the heat bath and not by the intrinsic thermostatistics of the finite system. If not sufficiently large, it may be necessary for the finite system to change its thermostatistics in order to be at equilibrium with the heat bath. We account for this process by invoking Landsberg's notion of *temperature-dependent energy levels*. We establish that the mismatch between the intrinsic temperature of the excited finite system and that of the heat bath drives a spectrum perturbation which enables thermal equilibrium. We show that the temperature-induced spectrum perturbation is equivalent to Hill's purely thermodynamic subdivision potential. The difference between intrinsic and equilibrium temperature provides us with a measure for how large a system can be before it no longer needs to be regarded as small. The theoretical framework proposed in this paper identifies the role of temperature in a bottom-up thermostatistical description of finite systems.
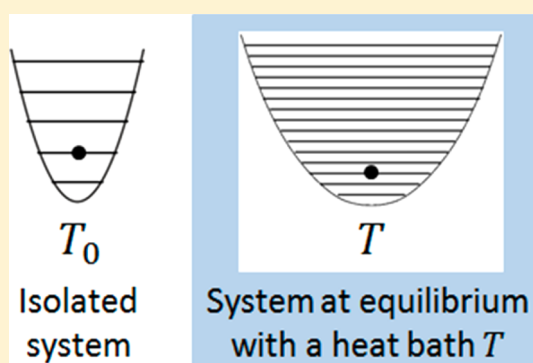
1. INTRODUCTION

A quantum mechanical Hamiltonian dictates the energy levels that are available to a finite system. As the energy spectrum and its degeneracies are quantized, the rate of change of the entropy with respect to the energy must be quantized as well. Although the quantization of this rate of change (i.e., temperature) vanishes in the thermodynamic limit, it is an intrinsic feature of small systems. However, when a finite system comes in thermal contact with a heat bath, the equilibrium temperature becomes fully determined by the heat bath and not by the intrinsic thermostatistics of the finite system itself. In order to adopt the equilibrium temperature, the thermostatistics of the finite system may have to change. This means the energy levels of the system must become effectively dependent on the heat bath temperature.

The effective notion of temperature-dependent energy levels in statistical mechanics is hardly new. It was first introduced by Rushbrook in 1940[1] and later refined by Elcock and Landsberg in 1956.[2] In the decades that followed, this notion was directly invoked to study the temperature dependence of energy gaps in semiconductors,[3] as well as bosonic systems where the standard thermodynamic description breaks down due to strong interactions.[4,5] Temperature-dependent energy levels have since become ubiquitous in the study of semiconductors (see e.g. refs 6 and 7 and references therein) and bosonic systems (see e.g. ref 8 and references therein). More recently, Yamano has proposed the use of temperature-dependent energy levels to describe heat losses in thermoelectrical devices.[9] Temperature-dependent energy levels have also been invoked by information theorists to model thermal systems as information processing systems.[10,11]

In this contribution, we show how temperature-dependent energy levels may be exploited to extend the domain of statistical thermodynamics to include small systems. We describe a process that, driven by the difference between the intrinsic temperature of an excited finite system and that of the heat bath, does work on the spectrum of the finite system to make possible its thermal equilibrium. The intrinsic temperature mismatch is proposed as a measure for how large a finite system needs to be before it no longer needs to be regarded as *small*.

The first comprehensive treatise on the subject of small system thermodynamics was written by Hill in the early 1960s, when he generalized classical thermodynamics to describe increasingly smaller systems.[12,13] Hill's starting point is a homogeneous system with a well-defined temperature. As the system is subdivided into increasingly smaller interacting subsystems, extensivity breaks down. This creates the need for the so-called *subdivision potential*. The descriptive ability of the subdivision potential, however, is limited by the fact that

the small systems are at all times assumed to be purely thermodynamic. This limitation becomes increasingly important as we attempt to describe ever smaller systems[14,15] whose scale-related properties escape the paradigms of classical thermodynamics,[16−19] or nonhomogeneous systems in general.[20]

In this work, we show how the notion of temperature-dependent energy levels extends the descriptive ability of Hill's subdivision potential, which can be interpreted as the heat perturbing the energy levels of a finite system as it is brought into thermal equilibrium with a heat bath. The tools presented in this paper allow for an explicit computation of this potential in arbitrarily small systems with a known density of states.

The paper is structured as follows. In Section 2, we invoke Landsberg's formalism of temperature-dependent energy levels and use it to account for spectrum perturbations in finite systems, and we describe the heat process driving these perturbations. In Section 3, we establish a connection between spectrum perturbations in finite systems and Hill's subdivision thermodynamics. In Section 4, we connect these temperature-dependent perturbations with equilibrium thermostatistics, and we present some examples illustrating how an effectively temperature-dependent spectrum can be used in a thermodynamic description valid across scales. Concluding remarks are given in Section 5.

2. TEMPERATURE-DEPENDENT ENERGY LEVELS: STATISTICAL MECHANICS AND FINITE SYSTEM THERMODYNAMICS

We start by presenting the basic statistical mechanical framework which allows the spectrum of a system to be perturbed by the equilibrium temperature. The equilibrium temperature T_r of a thermal system r is defined as $T_r = \partial E_r / \partial S_r$, where

$$E_r = k_B T_r^2 \sum_\mu P_{r,\mu} \frac{\partial}{\partial T_r} \ln(Z_r P_{r,\mu}) \tag{1}$$

$$S_r = -k_B \sum_\mu P_{r,\mu} \ln P_{r,\mu} \tag{2}$$

the index μ labels the available microstates, k_B is Boltzmann's constant, $P_{r,\mu} = Z_r^{-1} e^{-\mathcal{E}_{r,\mu}/k_B T_r}$, the $\mathcal{E}_{r,\mu}$ are the system's energy levels, and Z_r is the usual partition function.[21] We now consider an interacting collection of M such systems (not necessarily identical) at equilibrium. The composite system has temperature $T = T_1 = T_2 = \cdots = T_M$. We would like to enforce size extensity by having an independent thermodynamic description for each subsystem. The subsystems, however, might interact with one another. To address this issue, we shall apply a thermodynamic description where the internal energy contributed by each subsystem is perturbed by the heat bath made up of all other subsystems. To this end, we adopt the formalism introduced by Elcock and Landsberg,[2] which allows for the energy levels of a system to be perturbed by the temperature of the heat bath.

Although energy levels corresponding to the eigenvalues of a quantum mechanical Hamiltonian are intrinsically temperature-independent, the energy levels that dictate the average internal energy of a physical system must be effectively temperature-dependent.[1,2] When this temperature dependence is considered, the energy (1) and the entropy (2) of subsystem r (with energy levels $\mathcal{E}_{r,\mu}$) are given by the following expressions:[2]

$$E_r = k_B T^2 \sum_\mu P_{r,\mu} \frac{\partial}{\partial T} \ln(Z_r P_{r,\mu}) = \sum_\mu P_{r,\mu}\left(\mathcal{E}_{r,\mu} - T\frac{\partial \mathcal{E}_{r,\mu}}{\partial T}\right) \tag{3}$$

$$S_r = -k_B \sum_\mu P_{r,\mu} \ln P_{r,\mu} = k_B \ln Z_r + \frac{E_r}{T} + \sum_\mu P_{r,\mu} \frac{\partial \mathcal{E}_{r,\mu}}{\partial T} \tag{4}$$

which only differ from the usual expressions by the incidence of the last terms. We can express them as

$$\mathcal{E}_r = E_r + T\left\langle \frac{\partial \mathcal{E}_{r,\mu}}{\partial T} \right\rangle \tag{5}$$

$$\mathcal{S}_r = S_r - \left\langle \frac{\partial \mathcal{E}_{r,\mu}}{\partial T} \right\rangle \tag{6}$$

where $\mathcal{E}_r \equiv \langle \mathcal{E}_{r,\mu} \rangle$, $\mathcal{S}_r \equiv E_r/T + k_B \ln Z_r$ and, for simplicity, $\langle \cdot \rangle$ represents the average over all microstates μ.

When a finite system is in equilibrium with a heat bath, the system is in reality a subsystem of a larger thermodynamic system. The subsystem, small as it might be, must exhibit an equilibrium temperature which is on par with that of the heat bath. However, if the finite system under consideration is too small, a standard thermostatistical description may not yield a valid relation between the system's quantized energy and its externally determined equilibrium temperature. As we shall see below, this problem can be circumvented by allowing the energy spectrum $\mathcal{E}_{r,\mu}$ of system r to be effectively temperature-dependent and perturbed by the heat bath T as shown in expression (5). This allows us to modify the finite system's energy function so that it becomes properly characterized by the equilibrium temperature.

2.1. Spectrum Perturbations and the Second Law of Thermodynamics. The equilibrium temperature T of subsystem r is defined by

$$T \equiv T_r = \frac{\partial E_r}{\partial S_r} \tag{7}$$

with E_r and S_r given by (1) and (2), respectively. We invoke (5) and write this temperature in terms of $\partial \mathcal{E}_r / \partial S_r$:

$$T = T_0\left(\frac{\frac{\partial \mathcal{E}_r}{\partial T} - \left\langle \frac{\partial \mathcal{E}_{r,\mu}}{\partial T} \right\rangle}{\frac{\partial \mathcal{E}_r}{\partial T}}\right) \tag{8}$$

where

$$T_0 \equiv \frac{\partial \mathcal{E}_r}{\partial S_r} \tag{9}$$

Expression (8) shows how the intrinsic Boltzmann temperature T_0, which is obtained by simply analyzing the spectrum $\{\mathcal{E}_{r,\mu}\}$ of system r, is modified in the presence of energy perturbations caused by a heat bath T. Such fluctuations vanish when the system approaches the macroscopic limit and its heat capacity $\partial \mathcal{E}_r / \partial T$ becomes much larger than the spectrum perturbation $\langle \partial \mathcal{E}_{r,\mu} / \partial T \rangle$. In this limit, both temperatures become equal.

It is worth noting that, although different, both temperatures T and T_0 analyzed in the present work stem from Boltzmann's definition of entropy. Meanwhile, expression (8) is reminiscent

of eq 14 in ref 22, which connects the intrinsic Boltzmann temperature T_0 with the Gibbs temperature T_G. Both expressions differ only in that the temperature T is replaced with the Gibbs temperature T_G, and $\langle \partial \mathcal{E}_{r,\mu}/\partial T \rangle$ is replaced with k_B. Indeed, the Gibbs temperature proposed in ref 22 provides a correct thermodynamic description only in the special cases where $\langle \partial \mathcal{E}_{r,\mu}/\partial T \rangle = k_B$, such as the example in Section 4.2 below; for for a more comprehensive assessment of the results in ref 22, please refer to refs 23−27.

The effective temperature-dependence of the equilibrium energy levels leads not only to a modified Boltzmann temperature T. It also extends the second law of thermodynamics to systems with a temperature-dependent spectrum. For a closed system r at equilibrium and constant volume, it shall hold (7) that $T dS_r = d E_r$. Invoking (5), the resulting expression may be written as the second law of thermodynamics in terms of some heat $d\mathcal{E}_r$ added to the system:

$$T dS_r = d\mathcal{E}_r - \left\langle \frac{d\mathcal{E}_{r,\mu}}{dT} \right\rangle dT \tag{10}$$

This expression may also be obtained by combining expressions (9), that is $T_0 dS_r = d\mathcal{E}_r$, and (8) at constant volume. Expression (10) may also be written as

$$T dS_r = \left(\frac{d\mathcal{E}_r}{dT} - \left\langle \frac{d\mathcal{E}_{r,\mu}}{dT} \right\rangle \right) dT = \left(\frac{\frac{d\mathcal{E}_r}{dT} - \left\langle \frac{d\mathcal{E}_{r,\mu}}{dT} \right\rangle}{\frac{d\mathcal{E}_r}{dT}} \right) d\mathcal{E}_r \tag{11}$$

which, recalling that $\mathcal{E}_r \equiv \langle \mathcal{E}_{r,\mu} \rangle$, highlights the fact that entropy is produced as a result of fluctuations.

Like (3) and (4), expression (10) differs from the usual expression only by the last term. This form of the second law of thermodynamics was first proposed by Shental and Kanter while modeling communication channels as thermal systems.[10] They provided a physical interpretation where a part $\langle d\mathcal{E}_{r,\mu}/dT \rangle dT$ of the total heat $d\mathcal{E}_r$ goes to reshaping the energy spectrum, and the rest goes to increasing the entropy of the system. Indeed, if a finite system shall remain at equilibrium with a heat bath T, work must be done on its spectrum every time the equilibrium temperature T changes. The efficiency η of this process may be expressed as the ratio of the work perturbing the spectrum, $\langle d\mathcal{E}_{r,\mu}/dT \rangle dT$, to the total heat available, $d\mathcal{E}_r$:

$$\eta \equiv \frac{\left\langle \frac{d\mathcal{E}_{r,\mu}}{dT} \right\rangle dT}{d\mathcal{E}_r} \tag{12}$$

Invoking (8), this efficiency reduces to

$$\eta = 1 - \frac{T}{T_0} \tag{13}$$

which is the expression for the efficiency of an ideal heat engine operating between the temperatures T and $T_0 > T$ (see e.g. ref 28).

The second law in expressions (10),(11) may be expressed in terms of the efficiency η, or rather the inefficiency $(1 - \eta)$, as

$$T dS_r = d\mathcal{E}_r (1 - \eta) \tag{14}$$

This may be interpreted as follows: As a finite system comes into thermal equilibrium with a heat bath T, an amount of heat

$d\mathcal{E}_r$ is exchanged. This heat excites the system along its intrinsic energy landscape. In the process, the system adopts a quantum state with intrinsic temperature T_0 (see eq 9). The system then relaxes by an energy amount $\eta d\mathcal{E}_r$, which is transformed into the work that changes the spacing between energy levels such that the system finally can adopt the equilibrium temperature T. It is the relative difference between T and T_0 that drives the spectrum perturbation. Indeed, the energy correction in (9) may be expressed as

$$T \left\langle \frac{\partial \mathcal{E}_{r,\mu}}{\partial T} \right\rangle = \eta \frac{d\mathcal{E}_r}{d \ln T} \tag{15}$$

or, equivalently, as

$$T \left\langle \frac{\partial \mathcal{E}_{r,\mu}}{\partial T} \right\rangle = (T_0 - T) \frac{dE_r}{dT} \tag{16}$$

In the limiting case where the heat bath has zero temperature, the quantum system is perfectly isolated in a vacuum, which implies infinitely slow heat exchange ($\eta = 1$) resulting in neither spectrum perturbation nor entropy production over time. In the limiting case when the heat bath has a temperature identical to the intrinsic temperature of the finite system ($\eta = 0$), there is no thermal force, no net heat transfer, no spectrum perturbation (only fluctuations), and the usual second law is recovered. As we shall see below, the ratio T/T_0 may be used as a measure to establish how *small* a finite system is.

3. CONNECTION TO HILL'S NANOTHERMODYNAMICS

In his seminal work in small system thermodynamics[12,13,29] Hill takes an approach inverse to the one above. He starts with a macroscopic, purely thermodynamic system at equilibrium. The system is then partitioned into an ensemble of M subsystems which Hill assumes to be identical. Consider that each of these subsystems contains $\mathcal{N}_r$ particles, has entropy $\mathcal{S}_r$, volume $\mathcal{V}_r$ and energy $\mathcal{E}_r$. If the subsystems did not interact, the composite system would have $\mathcal{N}$ particles, entropy $\mathcal{S}$, volume $\mathcal{V}$ and energy $\mathcal{E}$, given, respectively, by

$$\mathcal{N} = M\mathcal{N}_r, \quad \mathcal{S} = M\mathcal{S}_r, \quad \mathcal{V} = M\mathcal{V}_r, \quad \mathcal{E} = M\mathcal{E}_r \tag{17}$$

As in the statistical treatment above, Hill takes into account the problem that extensivity may be broken due to interactions among subsystems. If the subsystems interact, then the total energy must in general be considered a function of the number M of subsystems. In this context Hill defines the so-called *subdivision potential* $\mathbb{E}$, which is the energy required to increase the number of subsystems while keeping constant the extensive state variables ($\mathcal{S}, \mathcal{V}, \mathcal{N}$):

$$\mathbb{E} = \left(\frac{\partial \mathcal{E}}{\partial M} \right)_{\mathcal{S}, \mathcal{V}, \mathcal{N}} \tag{18}$$

From a thermodynamic point of view, $\mathbb{E}$ must vanish in the classical limit, where the energy $\mathcal{E}$ could not vary if ($\mathcal{S}, \mathcal{V}, \mathcal{N}$) were kept constant. However, for Hill's interacting subsystems, the subdivision potential $\mathbb{E}$ and the number M of such identical subsystems become a new pair of conjugate variables. The resulting Euler equation is

$$\mathcal{E} = T\mathcal{S} - p\mathcal{V} + \mu\mathcal{N} + M\mathbb{E} \tag{19}$$

and the subsystem energy is given by

$$\mathcal{E}_r = T\mathcal{S}_r - p\mathcal{V}_r + \mu\mathcal{N}_r + \mathbb{E} \tag{20}$$

Let us now consider that the subsystem described by expression (20) is the same as the system r we considered in expressions (5) and (6) above. Then we may write (5) and (6) as

$$\mathcal{E}_r = E_r + \mathbb{E} \tag{21}$$

$$\mathcal{S}_r = S_r - \frac{\mathbb{E}}{T} \tag{22}$$

with

$$E_r = k_B T^2 \left\langle \frac{\partial}{\partial T}\ln(Z_r P_{r,\mu}) \right\rangle \equiv T\mathcal{S}_r - p\mathcal{V}_r + \mu\mathcal{N}_r \tag{23}$$

$$S_r = -k_B\langle\ln P_{r,\mu}\rangle \equiv \frac{1}{T}\mathcal{E}_r + \frac{P}{T}\mathcal{V}_r - \frac{\mu}{T}\mathcal{N}_r \tag{24}$$

$$\mathbb{E} \equiv T\left\langle \frac{\partial\mathcal{E}_{r,\mu}}{\partial T} \right\rangle \tag{25}$$

The subdivision potential (18) was originally devised by Hill on purely thermodynamic grounds. Expression (25) provides a statistical interpretation of this potential in terms of the spectrum of the new and smaller subsystems which result in each subdivision. Hill's subdivision potential $\mathbb{E}$ is connected to the heat contribution $\langle d\mathcal{E}_{r,\mu}/dT\rangle dT$ that perturbs the energy spectrum in the modified second law (10). Expression (15) shows how the subdivision potential relates to the efficiency η of the spectrum relaxation process described in the previous section. As we shall see below, the subdivision potential remains finite when $\eta = 0$ and it vanishes when $\eta = 1$ (i.e., when the heat bath has no temperature).

4. ENERGY LEVELS AND EQUILIBRIUM THERMODYNAMIC TEMPERATURE

Enabled by the statistical connection (25) we can now look closer into the relation between Hill's subdivision potential $\mathbb{E}$, a finite system's intrinsic temperature T_0, and the equilibrium heat bath temperature T. Consider a finite system r of arbitrary size. Given the number of microstates (or the density of states) ω available to the system, we may find its entropy S_r (up to an additive constant) by applying Boltzmann's entropy formula:

$$S_r = k_B\ln\omega \tag{26}$$

If the dependence of ω on the energy $\mathcal{E}_r$ is known, we may then compute the standard Boltzmann temperature T_0 given by (9). The result is that the energy $\mathcal{E}_r$ is some function f_0 of T_0:

$$\mathcal{E}_r = f_0(T_0) \tag{27}$$

The caloric eq 27 may be generally invalid when the system under consideration is not macroscopic. And, if valid, it will not be extensive unless the thermodynamic limit is assumed. If we consider that the system may be small, and its energy spectrum subject to thermal perturbations due to its equilibrium with the heat bath T, then we express the equilibrium temperature (7) by replacing $\mathcal{E}_r$ with E_r:

$$E_r = f_0(T) \tag{28}$$

At this point, expression (5) can be inserted into (28), resulting in a relation between the energy $\mathcal{E}_r$ and the equilibrium temperature T:

$$\mathcal{E}_r = f_0(T) + T\left\langle \frac{\partial\mathcal{E}_{r,\mu}}{\partial T} \right\rangle \tag{29}$$

As shown by (25), the last term in (29) is analogous to the subdivision potential $\mathbb{E}$ that Hill uses when he considers the small system to be one of many identical interacting subsystems of a larger thermodynamic system. It is a linear correction to the energy function f that shall ensure that $\mathcal{E}_r$ is extensive. It also ensures that a system, however small, which is in equilibrium with a heat bath, is characterized by the bath temperature T.

4.1. Example: Ideal Gas. Consider a monatomic ideal gas of N particles in D dimensions. The density of states $\tilde{\omega}$ depends on the internal energy $\mathcal{E}_r$ as $\tilde{\omega} \propto \mathcal{E}_r^{ND/2-1}$. A standard statistical thermodynamic analysis (eqs 26 and 9 above) of the system gives the following relation between energy and temperature:

$$\mathcal{E}_r = \frac{ND-2}{2}k_B T_0 \tag{30}$$

As expected, this expression works well only for large systems, where the energy is extensive and consistent with the equipartition theorem.

If we consider the system under analysis may be small, and its energy spectrum subject to thermal perturbations due to a heat bath T, then its equilibrium temperature (7) is not given by (30). In order to find the equilibrium temperature T we follow steps (27)−(29) above and write an expression for the energy $\mathcal{E}_r$ in terms of the heat bath temperature T:

$$\mathcal{E}_r = \frac{ND-2}{2}k_B T + \left\langle \frac{\partial\mathcal{E}_{r,\mu}}{\partial T} \right\rangle T \tag{31}$$

The second term in the right-hand side is a linear correction to the energy that shall ensure extensivity, in this case

$$T\langle\partial\mathcal{E}_{r,\mu}/\partial T\rangle = k_B T \tag{32}$$

which, inserted into (31) gives us the extensive equipartition result for the ideal gas:

$$\mathcal{E}_r = \frac{ND}{2}k_B T \tag{33}$$

The correction (32) can be recovered from expressions (15) and (33), and it can be identified with Hill's subdivision potential $\mathbb{E}$ via (25). From the perspective of Hill's top-down thermodynamics, an ideal gas is an example of a large system that can be subdivisioned into increasingly smaller non-interacting subsystems. In an ideal gas, the subsystems are from the beginning assumed to only have elastic interactions, and the only cost of devising a subdivision process is having to repartition the energy equally among all subsystems. In this case Hill's subdivision adjustment (25) is simply given by $\mathbb{E} = k_B T$.

Although the temperature T_0 in (30) characterizes a nonextensive energy, the temperature assignment in (33) yields an extensive energy irrespective of system size. Both temperatures are related by the following expression:

$$\frac{T}{T_0} = \frac{ND-2}{ND} \tag{34}$$

The relative deviation between both temperatures provides us with a metric to determine how small a finite system is. Expression (34) shows that an ideal gas need not consist of

many particles before the extensive approximation (33) provides an accurate description. It should be noted that, although T and T_0 become identical in the large system limit (where $\eta = 0$), the correction energy (15) does not vanish as, in this limit, $\mathcal{E}_r$ becomes infinite; the contribution k_BT, however, becomes negligible as system size increases. The correction energy vanishes completely only when the system is perfectly isolated ($T = 0$, $\eta = 1$, $\mathcal{E}_r = 0$); in this case, there is no heat bath, and the system's energy is simply given by its intrinsic temperature (30).

4.2. Example: Two-Level Systems. We consider next a system r of N two-level noninteracting particles with energy levels 0 and ϵ. At any given moment there are $n \leq N$ particles in the upper energy state, and the total internal energy $\mathcal{E}_r$ of the system is given by

$$\mathcal{E}_r(n) = n\epsilon \qquad (35)$$

The number of microstates for a given configuration is given by

$$\omega(N, n) = \frac{N!}{(N - n)!n!}$$

In this case, we have the luxury of being able to find the exact temperature, T_0, by simply replacing the differentials in (9) with finite difference operators:

$$T_0(N, n) = \frac{\mathcal{E}_r(N, n) - \mathcal{E}_r(N, n - 1)}{S(N, n) - S(N, n - 1)} \qquad (36)$$

In principle, (36) could have been written with forward, central, or backward differences.[30] However, the central difference method is not exact, because the entropy is only defined for integer values of n. The forward difference assigns positive temperature to the state with $n = 0$, which contravenes the third law of thermodynamics. The backward difference (36), however, is well-defined and it complies with the third law (note that $\omega(N, -1)$ is zero). The resulting temperature T_0 is given by

$$T_0 = \frac{\mathcal{E}_r}{nk_B\ln[N/n - 1 + 1/n]} \qquad (37)$$

As discussed earlier, the energy spectrum of a finite system may be subject to thermal perturbations due to a heat bath T. The system's equilibrium temperature T is connected to the isolated intrinsic temperature T_0 through the correction energy $T\langle\partial\mathcal{E}_{r,\mu}/\partial T\rangle$ or the equivalent Hill's subdivision potential $\mathbb{E}$. In order to find the subdivision potential we may, as before, follow steps (27)−(29) and write

$$\mathcal{E}_r = nk_BT\ln[N/n - 1 + 1/n] + \mathbb{E} \qquad (38)$$

The subdivision potential $\mathbb{E}$ that makes the energy extensive while keeping the temperature of the small system compatible with that of the macroscopic supersystem (i.e., with the macroscopic limit of (37)) is given by

$$\mathbb{E} = nk_BT\ln\left[1 - \frac{1}{N - n + 1}\right] \qquad (39)$$

which yields the usual size-extensive relation between energy $\mathcal{E}_r$ and temperature T:

$$T = \frac{\mathcal{E}_r}{nk_B\ln[N/n - 1]} \qquad (40)$$

with $\mathcal{E}_r = n\epsilon$.

The subdivision potential (39) can be recovered from expressions (25), (15), and (40), and it has a magnitude strictly smaller than $Nk_BT/(N - n)$. As expected, when N is large, the contribution from the subdivision potential becomes insignificant compared to the energy $\mathcal{E}_r$.

From the perspective of Hill's subdivision thermodynamics, successive imaginary subdivisions of a two-level system would lead to many identical, non interacting, two-level systems, each with an equal number of particles in the upper state, and each with an equal number of particles in the lower state. Every time there is a new subdivision, the equipartition of the energy among the identical subsystems reduces the total multiplicity. This eliminates extensivity and creates the need for an adjusting subdivision potential.

The equilibrium temperature T in the extensive expression (40) is related to the intrinsic isolated temperature T_0 in (37) by the size and state of the system as follows:

$$\frac{T}{T_0} = \frac{\ln\left[\frac{N - n + 1}{n}\right]}{\ln\left[\frac{N - n}{n}\right]} \qquad (41)$$

Figure 1 shows this ratio of temperatures as a function of N/n for different system sizes. Systems consisting of ∼10 particles
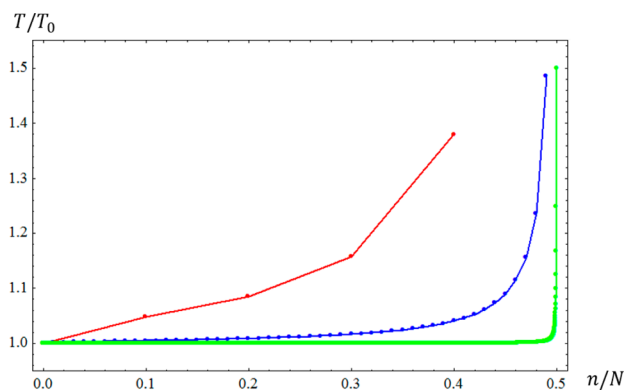
Figure 1. T/T_0 vs n/N for a two-level system of size $N = 10$ (red), $N = 100$ (blue), and $N = 10^5$ (green).

can hardly be approximated by T and should therefore be regarded as small. As N gets larger, a greater portion of energy states may be accurately described by (40), which can be a good fit for systems as small as $N \sim 100$, provided n is not near $N/2$. This limitation is not surprising, considering that the fully extensive approximation (40) presents a singularity at $n = N/2$. This is not the case for the exact expression (37), which is well-defined in every energy regime. Indeed, as N grows large the ratio converges to

$$\frac{T}{T_0} \xrightarrow{N \gg 1} 1 + \frac{1}{N - 2n} \qquad (42)$$

suggesting that, regardless of size, all systems become *small* (i.e., not accurately described by classical thermodynamics) in the vicinity of $n = N/2$.

It should be noted that, in cases where $n > N/2$, both (40) and (37) yield negative absolute temperatures, which are a unique feature of systems where the multiplicity of higher energy configurations may be lower than that of lower lying states.[21] Negative absolute temperatures have indeed been

measured in systems that may be modeled as a collection of independent two-level systems.[31−34]

4.3. Example: Einstein Solid. We consider next an Einstein solid r with N three-dimensional oscillators and q energy units of size ϵ. The internal energy is given by

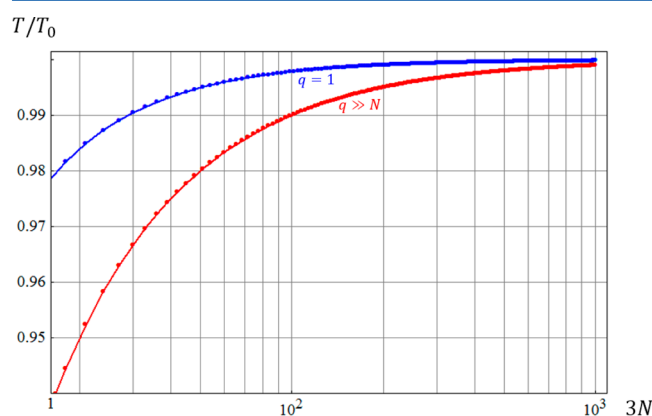$$\mathcal{E}_r(q) = q\epsilon,$$

and the number of microstates by

$$\omega(q) = \frac{(q + 3N - 1)!}{q!(3N - 1)!}$$

Applying the same recipe as in the previous example we obtain

$$\mathcal{E}_r = qk_B T_0 \ln[1 + 3N/q - 1/q] = qk_B T \ln[1 + 3N/q] \tag{43}$$

Figure 2 shows that, for an Einstein solid, there is little discrepancy between the exact vibrational temperature and the

Figure 2. T/T_0 vs $3N$ for an Einstein solid. The upper curve represents the low temperature limit ($q = 1$), and the lower curve the high temperature limit ($q \gg N$).

thermodynamic approximation. In contrast to the two-level system, it takes few oscillators for an Einstein solid to behave as a *large* system. This is owed to the fact that each oscillator may store arbitrary amounts of energy in three degrees of freedom. This means that the number of microstates that are available to any given ($q/3N$) temperature regime is not so dramatically affected by the size of the system.

4.4. Single Quantum Systems. The method we propose in Section 2 may be applied directly to single quantum systems. Consider, for example, a harmonic oscillator r with fundamental frequency ν. Its internal energy $\mathcal{E}_r$ is given by

$$\mathcal{E}_r = (n + 1/2)\hbar\nu \tag{44}$$

The density of states is given by $\tilde{\omega} = 1/\hbar\nu$. As all states have equal multiplicity, an exact analysis (36) would yield infinite temperature. A standard differential thermodynamic analysis (eqs 26 and 9 above) is not very promising either, as it gives the following relation between energy and temperature:

$$\mathcal{E}_r = -k_B T_0 \tag{45}$$

Not surprisingly, this expression is not correct, for standard thermodynamics is not valid for single quantum systems. Indeed, the harmonic oscillator cannot be considered a thermodynamic system, but a small subsystem whose energy spectrum will be subject to thermal perturbations due to a heat bath T. To find a relation between the oscillator's thermal

energy and the equilibrium temperature T (7), we may proceed as before and rewrite the energy $\mathcal{E}_r$ in terms of the heat bath temperature T:

$$\mathcal{E}_r = -k_B T + T\langle \partial \mathcal{E}_{r,\mu}/\partial T \rangle \tag{46}$$

The last term in (46) is a linear adjustment representing the thermal perturbation in the oscillator's spectrum. This perturbation acts directly on the potential, thermalizing even the fundamental frequency. A correction in line with the equipartition theorem is

$$T\langle \partial \mathcal{E}_{r,\mu}/\partial T \rangle = 2k_B T \tag{47}$$

resulting in

$$\mathcal{E}_r = k_B T \tag{48}$$

which is the energy of a diatomic ideal gas consisting of one particle. The correction (47) may be recovered from expressions (15) and (48).

Another example of an isolated quantum system is a rigid rotor with moment of inertia I, quantized energy $j(j + 1)\,\hbar^2/2I$, and density of states $2I/(\hbar^2(2j + 1))$. In this case, we obtain results identical to those of the harmonic oscillator, namely, eqs 45−48. The similarity in the thermal perturbation of the rigid rotor and the harmonic oscillator is consistent with the equipartition theorem.

As a last example of a single quantum system we consider a single particle in a one-dimensional box, with energy $\mathcal{E}_r$ and density of states proportional to $\mathcal{E}_r^{-1/2}$. Not surprisingly, we obtain the expressions of Section 4.2 with $N = D = 1$.

5. CONCLUSION

Assigning a proper relationship between a system's energy and its temperature is crucial to quantifying how it exchanges heat with its surroundings. Yet the standard tools of statistical thermodynamics are based on a series of assumptions (such as the continuity assumption) that do not generally produce meaningful relationships between energy and temperature if the system is too small (see e.g. Sections 4.2 and 4.4 above). In cases where the multiplicity and the energy of each individual microstate are precisely known, exact calculations can result in a discrete set of allowed temperatures (see e.g. expression (37) above). However, finite systems can come into thermal contact with reservoirs having arbitrary temperature. When this happens, the equilibrium temperature is dictated by the heat bath, and not by the intrinsic thermostatistics of the finite system itself. This means that the thermostatistics of the system must change in order to become compatible with the equilibrium temperature. In this work, we describe this process invoking Landsberg's notion of effectively temperature-dependent energy levels in statistical mechanics.[2]

We have established that an excited finite system has an intrinsic temperature which is generally different from the externally determined equilibrium temperature. This temperature difference provides us with a measure for how large a system can be before it no longer needs to be regarded as *small*. We have presented some examples showing that, while a large class of systems need not consist of many particles before they may be treated thermodynamically, some finite systems do exhibit temperatures that differ significantly from the equilibrium heat bath temperature prescribed by classical thermodynamics. This temperature mismatch drives a process that produces an amount of work which is used to perturb the

quantum spectrum of the finite system. It is this temperature-dependent spectrum perturbation which finally makes possible the thermal equilibrium between the finite system and the heat bath. The efficiency of this process is given by (13), which is the maximum efficiency any heat driven process can attain.

We have shown that the aforementioned spectrum perturbation is equivalent to the conversely conceived subdivision potential introduced by Hill in 1962.[12] While our starting point is a quantum system in contact with a heat bath, Hill's starting point is a large homogeneous system with a well-defined temperature, which is later subdivided into increasingly smaller, identical, isothermal, and isoenergetic systems. The interaction between these subsystems creates the need for the so-called subdivision potential. The descriptive ability of the subdivision potential, however, is limited by the fact that the increasingly smaller systems are, despite their decreasing size, at all times assumed homogeneous. We have extended the descriptive ability of Hill's subdivision potential by showing it may be interpreted as the energy needed to perturb the intrinsic energy levels of the small system if it were to isolately assume the macroscopic temperature of the parent super-system. The tools presented in this paper allow for an explicit computation of this potential for finite systems with a known density of states. The theoretical framework proposed in this work identifies the role of temperature in a bottom-up thermostatistical description of small systems.

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Notes

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■ REFERENCES

(1) Rushbrooke, G. S. On the Statistical Mechanics of Assemblies whose Energy-Levels Depend on the Temperature. *Trans. Faraday Soc.* **1940**, *36*, 1055−1062.

(2) Elcock, E. W.; Landsberg, P. T. Temperature Dependent Energy Levels in Statistical Mechanics. *Proc. Phys. Soc., London, Sect. B* **1957**, *70*, 161−168.

(3) Cuden, C. B. *Temperature Dependence of the Energy Gaps in Semiconductors.* Ph.D.Thesis, University of British Columbia, 1969. Available at the following: https://circle.ubc.ca/bitstream/id/128275/UBC_1969_A1.

(4) Bendt, P. J.; Cowan, R. D.; Yarnell, J. L. Excitations in Liquid Helium: Thermodynamic Calculations. *Phys. Rev.* **1959**, *113*, 1386−1395.

(5) Donnelly, R. J.; Roberts, P. H. A theory of temperature-dependent energy levels: Thermodynamic properties of He II. *J. Low Temp. Phys.* **1977**, *27*, 687−736.

(6) Allen, P. B.; Heine, V. Theory of the Temperature Dependence of Electronic Band Structures. *J. Phys. C: Solid State Phys.* **1976**, *9*, 2305−2312.

(7) Patrick, C. E.; Giustino, F. Unified Theory of Electron-Phonon Renormalization and Phonon-Assisted Optical Absorption. *J. Phys.: Condens. Matter* **2014**, *26*, 365503.

(8) Konstantinov, D.; Kimitoshi, K.; Lea, M.; Dykman, M. Ripplonic Lamb Shift for Electrons on Liquid Helium. Presented at APS March Meeting, San Antonio, Texas, March 2−6, 2015. Available at the following: http://meetings.aps.org/link/BAPS.2015.MAR.Q37.10.

(9) Yamano, T. Efficiencies of Thermodynamics when Temperature-Dependent Energy Levels Exist. *Phys. Chem. Chem. Phys.* **2016**, *18*, 7011−7014.

(10) Shental, O.; Kanter, I. Shannon meets Carnot: Generalized Second Thermodynamic Law. *Europhys. Lett.* **2009**, *85*, 10006.

(11) Peleg, Y.; Efraim, H.; Shental, O.; Kanter, I. Mutual Information via Thermodynamics: Three Different Approaches. *J. Stat. Mech.: Theory Exp.* **2010**, *2010*, P01014.

(12) Hill, T. L. Thermodynamics of Small Systems. *J. Chem. Phys.* **1962**, *36*, 3182−3197.

(13) Hill, T. L. *Thermodynamics of Small Systems, Parts I & II*; Dover: New York, 2013.

(14) Reguera, D.; Rubi, J. M.; Vilar, J. M. G. The Mesoscopic Dynamics of Thermodynamic Systems. *J. Phys. Chem. B* **2005**, *109*, 21502−21515.

(15) Lucia, U. A Link between Nano- and Classical Thermodynamics: Dissipation Analysis (The Entropy Generation Approach in Nano-Thermodynamics). *Entropy* **2015**, *17*, 1309−1328.

(16) Jortner, J.; Rao, C. Nanostructured Advanced Materials. Perspectives and Directions. *Pure Appl. Chem.* **2002**, *74*, 1491−1506.

(17) Berry, R. S. The Power of the Small. *Eur. Phys. J. D* **2007**, *43*, 5−6.

(18) Simon, J. M.; Rubi, J. M. Temperature at Small Scales: A Lower Limit for a Thermodynamic Description. *J. Phys. Chem. B* **2011**, *115*, 1422−1428.

(19) Michaelian, K.; Santamaria-Holek, I. Dynamics and Thermodynamics of Nanoclusters. *Entropy* **2015**, *17*, 7133−7148.

(20) Latella, I.; Perez-Madrid, A.; Campa, A.; Casetti, L.; Ruffo, S. Thermodynamics of Nonadditive Systems. *Phys. Rev. Lett.* **2015**, *114*, 230601.

(21) Pathria, R. K.; Beale, P. D. *Statistical Mechanics*, 3rd ed.; Elsevier:Oxford, U.K., 2011.

(22) Dunkel, J.; Hilbert, S. Consistent Thermostatistics Forbids Negative Absolute Temperatures. *Nat. Phys.* **2014**, *10*, 67−72.

(23) Vilar, J. M. G.; Rubi, J. M. Communication: System-Size Scaling of Boltzmann and Alternate Gibbs Entropies. *J. Chem. Phys.* **2014**, *140*, 201101.

(24) Frenkel, D.; Warren, P. B. Gibbs, Boltzmann, and Negative Temperatures. *Am. J. Phys.* **2015**, *83*, 163−170.

(25) Schneider, U.; Mandt, S.; Rapp, A.; Braun, S.; Weimer, H.; Bloch, I.; Rosch, A. Comment on Consistent Thermostatistics Forbids Negative Absolute Temperatures, **2015**, arXiv:1407.4127v1. arXiv.org e-Print archive. Available at the following: http://www.arxiv.org.

(26) Swendsen, R. H.; Wang, J.-S. Gibbs volume entropy is incorrect. *Phys. Rev. E* **2015**, *92*, 020103.

(27) de Miguel, R. Temperature-Dependent Energy Levels and Size-Independent Thermodynamics. *Phys. Chem. Chem. Phys.* **2015**, *17*, 15691−15693.

(28) Castellan, G. W. *Physical Chemistry*, 3rd ed.; Benjamin/Cummings: Menlo Park, CA, 1983; pp 153−162.

(29) Hill, T. L. A Different Approach to Nanothermodynamics. *Nano Lett.* **2001**, *1*, 273−275.

(30) Wada, T.; Scarfone, A. M. Finite Difference and Averaging Operators in Generalized Entropies. *J. Phys: Conf. Series* **2010**, *201*, 012005.

(31) Purcell, E. M.; Pound, R. V. A Nuclear Spin System at Negative Temperature. *Phys. Rev.* **1951**, *81*, 279−280.

(32) Hakonen, P.; Lounasmaa, O. V. Negative Absolute Temperatures: "Hot" Spins in Spontaneous Magnetic Order. *Science* **1994**, *265*, 1821−1825.

(33) Braun, S.; Ronzheimer, J. P.; Schreiber, M.; Hodgman, S. S.; Rom, T.; Bloch, I.; Schneider, U. Negative Absolute Temperature for Motional Degrees of Freedom. *Science* **2013**, *339*, 52−55.

(34) Rapp, A.; Mandt, S.; Rosch, A. Equilibration Rates and Negative Absolute Temperatures for Ultracold Atoms in Optical Lattices. *Phys. Rev. Lett.* **2010**, *105*, 220405.