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Eigenstate–Specific Temperatures in Two–Level Paramagnetic Spin Lattices

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ABSTRACT

Increasing interest in the thermodynamics of small and/or isolated systems, in combination with recent observations of negative temperatures of atoms in ultracold optical lattices, have stimulated the need for estimating the conventional, canonical temperature T_c^{conv} of systems in equilibrium with heat baths using *eigenstate–specific temperatures* (*ESTs*). Four distinct ESTs—continuous canonical, discrete canonical, continuous microcanonical, and discrete microcanonical—are accordingly derived for two–level paramagnetic spin lattices (PSLs) in external magnetic fields. At large *N*, the four ESTs are intensive, equal to T_c^{conv}, and obey all four laws of thermodynamics. In contrast, for *N* < 1,000, the ESTs of most PSL eigenstates are non–intensive, differ from T_c^{conv}, and violate each of the thermodynamic laws. Hence, in spite of their similarities to T_c^{conv} at large *N*, the ESTs are not true thermodynamic temperatures. Even so, each of the ESTs manifests a unique functional dependence on energy which clearly specifies the magnitude and direction of their deviation from T_c^{conv}; the ESTs are thus good *temperature estimators* for small PSLs. The thermodynamic uncertainty relation is obeyed only by the ESTs of small canonical PSLs; it is violated by large canonical PSLs and by microcanonical PSLs of any size. The ESTs of population–inverted eigenstates are negative (positive) when calculated using Boltzmann (Gibbs) entropies; the thermodynamic implications of these entropically–induced differences in sign are discussed in light of adiabatic invariance of the entropies. Potential applications of the four ESTs to nanothermometers and to systems with long–range interactions are discussed.

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I. INTRODUCTION

Though temperature is a ubiquitous concept in the physical and biological sciences, its nature and definition have become subjects of fresh debate in the last three decades in two notable contexts: (1) the Feshbach[1]–Kittel[2]–Mandelbrot[3] (FKM) debate regarding the differences between thermodynamic temperatures and so–called "effective temperatures"[2] or "temperature estimators"[3] for systems in contact with small heat baths;[2] and (2) the debate over the thermodynamic legitimacy of negative temperatures in systems with bounded energy spectra,[4-33] which was recently reignited[4-6, 31] by the realization of negative temperatures in optical lattices.[28-32] The FKM[1-3, 34-36] and negative temperature[4-6, 27, 31] debates both address issues central to a number of important topics: (1) the thermodynamics of small systems;[1-3, 34] (2) the thermodynamics of isolated systems;[12, 34, 35, 37-59] (3) the thermodynamic uncertainty relation (TUR);[1-3, 34-36] and (4) quantum thermodynamics,[40, 60] in which the temperatures of individual quantum eigenstates, hereafter designated *eigenstate–specific temperatures (ESTs)*, apply.

In the present study small, two–level paramagnetic spin lattices (PSLs) [7, 9, 11-18, 36, 61-66] are used to address two questions raised in the FKM[1-3] and negative temperature[4-25] debates: (1) "Are the ESTs of PSLs true thermodynamic temperatures or merely good temperature estimators?" and (2) "Are the negative ESTs of population–inverted PSLs thermodynamically legitimate?" We address these questions by characterizing the size– and energy–dependence of four distinct ESTs: (a) Continuous and (b) discrete canonical ESTs, which apply to PSLs in equilibrium with heat baths, and (c) continuous and (d) discrete microcanononical ESTs, which apply to isolated PSLs.

The four ESTs share much in common with the *conventional canonical temperature* T_c^{conv} , which is defined as (1) a parameter which is equal to the temperature T_{bath} of the system's

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heat bath,[2, 67] and (2) the *continuous* rate of change $(\partial U /\partial S_c[U])_{N,V} \big|_{U*}$ of U with respect to the canonical entropy $S_c(U)$ evaluated at the most–probable energy $U*$. The *continuous canonical* and *continuous microcanonical ESTs* are equal to the *continuous* (*i.e.*, instantaneous) rates of change of U with respect to $S_c(U)$ and the microcanonical entropy $S_\mu(U)$ for the *initial* eigenstates [N–j, j] in transitions between adjacent PSL eigenstates with spin quantum numbers j and j+1: $T_c^{j\rightarrow j+1} = (\partial U /\partial S_c[U])_{N,V}\big|_{U_j}$ and $T_\mu^{j\rightarrow j+1} = (\partial U /\partial S_\mu[U])_{N,V}\big|_{U_j}$. The *discrete canonical* and *discrete microcanonical* ESTs $T_{dc}^{j\rightarrow j+1} = (\Delta U /\Delta S_c)_{N,V}\big|_{U_j}$ and $T_{d\mu}^{j\rightarrow j+1} = (\Delta U /\Delta S_\mu)_{N,V}\big|_{U_j}$ are the discrete analogs of the continuous ESTs.

As their name indicates, the ESTs are *eigenstate–specific*; they are equal to the temperatures of specific, individual eigenstates. They thus constitute a distinct contrast to T_c^{conv} = $T_c^{\bar{j}\rightarrow \bar{j}+1}$, which is eigenstate–*non*specific[11, 40, 68] because $\bar{j}$ is equal to the (typically non–integer) *average* value of j over a Boltzmann distribution of eigenstates. Even so, ESTs can provide meaningful estimates of T_c^{conv} in PSLs, particularly when the population distribution is dominated by a single eigenstate (*i.e.*, when $\bar{j} = j$), as occurs for microcanonical (*i.e.*, thermally–isolated) PSLs,[3, 69] PSLs at low temperatures, large PSLs in the $N\rightarrow\infty$, *thermodynamic limit* (TDL),[42, 70-73] and PSLs subjected to repetitive magnetization measurements.[36, 68, 74-78]

This paper is organized as follows. Background materials are provided in Secs. II.A,B. T_c^{conv} and the four ESTs are derived in Secs. II.C,D. The general properties of the ESTs are detailed in Sec. III.A. The *spin–permutation antisymmetries* (*SPAs*) characteristic of positive and negative temperature eigenstates are detailed in Sec. III.B and the supplementary material. The size– and energy–dependencies of the ESTs—with special emphasis on their functional dependence on the *spin–down mole fraction* $X_j = j/N$— are detailed in Sec. III.C and the

supplementary material.   We then detail the adherence of the ESTs to the four laws of thermodynamics (Sec. III.D), the relationships of the ESTs to Boltmann distributions and the TUR, [34, 35] the relationships of the ESTs to temperature–dependent system energy levels (TDSELs)[33] (Sec. III.E), and the FKM debate (Sec. III.F).[1-3, 34-36] The implications of the Boltzmann and Gibbs ESTs for the negative temperature debate[4-6, 27, 31] are detailed in Sec. III.G. We detail the implications of the ESTs for experimental temperature measurements in PSLs[7, 13-17, 22, 54, 63-65, 79-89] (Sec. III.H), the potential utility of ESTs in nanothermometry[60, 83, 84, 90-102] (Sec. III.I), and potential applications of ESTs to systems with long–range interactions[36, 60-62, 66-68, 74, 83, 84, 92-94, 103-106] (Sec. III.J). Finally, a number of issues raised by the present study are detailed in Conclusions and Future Studies.

II. THEORETICAL

A. Properties of Two–Level Paramagnetic Spin Lattices

PSLs are fixed arrays of atoms, ions, or molecules with nuclear[7, 9, 11-17, 63-65, 79, 81, 107] or electron[7, 9, 11-17, 63-65, 79, 87-89, 108-110] spin. *Two–level* PSLs ("PSLs" hereafter), result when each site is comprised of a spin–$\frac{1}{2}\hbar$ nucleus, paramagnetic ion, or free radical with a spin–up (magnetic moment $\mathbf{\mu}$ parallel to external magnetic field $\mathbf{H}$) ground state $\uparrow$ with energy

$$u_{\uparrow} \; = \; - \, \mathbf{\mu} \cdot \mathbf{H} \; = \; - \, \mu H = -\tfrac{1}{2} g \beta H \; = \; -\tfrac{1}{2}\, \varepsilon \tag{1a}$$

and a spin–down ($\mathbf{\mu}$ antiparallel to $\mathbf{H}$) excited state $\downarrow$ with energy

$$u_{\downarrow} \; = \; - \, \mathbf{\mu} \cdot \mathbf{H} \; = \; - \, \mu H = + \tfrac{1}{2}\, g \beta H \; = \; + \tfrac{1}{2}\, \varepsilon \quad , \tag{1b}$$

in which g is the nuclear or electron g factor, and β is the nuclear or electron (Bohr) magneton.[10, 111, 112] For convenience we rescale the single particle energies to $u_{\uparrow} = 0$ and $u_{\downarrow} = \varepsilon$.

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PSLs are characterized by three important features. <u>First</u>, because their spin sites are localized, the sites are *distinguishable*, so that the Pauli Exclusion Principle does not apply.[12] <u>Second</u>, the sites do not interact with each other, so that the total internal energy of an N–particle PSL eigenstate $[N_\uparrow, N_\downarrow] = [N - j, j]$ is equal to the sum of the individual particle energies:[12]

$$U_{PSL} = U_j = N_\downarrow \varepsilon = j\varepsilon. \tag{1c}$$

<u>Third</u>, because $\varepsilon \propto H$, the energy spectra of PSLs are discrete in high fields but become continuous in the $H \rightarrow 0$ limit.

B. The Thermodynamic Temperature

The thermodynamic temperature T is equal to the rate of change of internal energy U with entropy S:

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N}. \tag{2a}$$

Hence, when the entropy is analytic in U, ESTs may be obtained via the expression

$$\frac{1}{T(U)} = \left(\frac{\partial S[U]}{\partial U} \right)_{V,N} . \tag{2b}$$

C. The Conventional Continuous Canonical Temperature T_c^{conv}

Using the canonical partition function for a PSL in equilibrium with a heat bath, Kittel[11] obtained expressions for *mean energy*

$$U_{\bar{j}} = \frac{N\varepsilon}{e^{\varepsilon/kT_c^{conv}} + 1} = \bar{j}\varepsilon, \tag{3}$$

and the conventional canonical temperature

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$$T_c^{conv} = T_c^{\bar{j} \to \bar{j}+1} = \cfrac{\varepsilon}{k \ln\left(\cfrac{N\varepsilon - U_{\bar{j}}}{U_{\bar{j}}}\right)} = \cfrac{\varepsilon}{k \ln\left(\cfrac{N - \bar{j}}{\bar{j}}\right)} = \cfrac{\varepsilon}{k \ln\left(\cfrac{1 - X_{\bar{j}}}{X_{\bar{j}}}\right)} \tag{4}$$

as functions of the *average* number of spin–down sites $\bar{j}$ and the *average* spin–down mole

fraction $X_{\bar{j}} = \bar{j}/N$. Eq. (4) is well–behaved for all $\bar{j} \le N$ provided $\bar{j} \ne 0$ or $N/2$[113] and for all $X_{\bar{j}}$

≤ 1 provided $X_{\bar{j}} \ne 0$ or 0.5.[113]

The canonical entropy $S_c(U_{\bar{j}})$ is obtained by integrating $dS_c(U_{\bar{j}}) = dU_{\bar{j}}/T_c(U_{\bar{j}})$ from 0

to $U_{\bar{j}}$, yielding the concave–downward[42, 70-73] expression

$$S_c(U_{\bar{j}}) = \int_0^{U_{\bar{j}}} dS_c(U_{\bar{j}}) = \frac{k}{\varepsilon} \ln\left[\frac{(N\varepsilon)^{N\varepsilon}}{(N\varepsilon - U_{\bar{j}})^{(N\varepsilon - U_{\bar{j}})} U_{\bar{j}}}\right] = k \ln\left[\frac{N^N}{(N - \bar{j})^{(N-\bar{j})} \bar{j}^{\bar{j}}}\right] = S_c(\bar{j}),\text{[11]} \tag{5}$$

which is well–defined provided $0 \le \bar{j} \le N$.[113] Since it is a function of energy, $S_c(U)$ is

microcanonical in character;[11] it can thus also be obtained from the microcanonical partition

function.[10, 112] Even so, $S_c(U)$ differs from the microcanonical entropy $S_\mu(U)$ at finite N, but

converges to $S_\mu(U)$ in the TDL[42, 70-73] (compare Eqs. [5,7]).

D. Eigenstate–Specific Temperatures (ESTs) in PSLs

For Boltzmann–distributed PSLs, the *average* number of spin–down lattice sites $\bar{j} = \overline{N_\downarrow}$

is typically not an integer j.[36, 40] Consequently, $T_c^{conv} = T_c^{\bar{j} \to \bar{j}+1}$ is usually not equal to a

continuous canonical EST $T_c^{j \to j+1}$. The temperature <u>becomes</u> eigenstate–specific when $\bar{j} \to j$.

This *single eigenstate occupancy condition* (*SEOC*) applies in four scenarios: (i) under

microcanonical conditions, in which the PSL is in the single eigenstate it occupied at the

moment it was isolated from its heat bath;[3, 69] (ii) at *low temperatures*, in which only the ground

eigenstate is occupied; (iii) in the *thermodynamic limit* (TDL), in which the Boltzmann

distribution is dominated by its most–probable eigenstate $[N - j*, j*]$;[42, 70-73] and (iv) when PSLs are subjected to *repetitive magnetization measurements* which narrow the eigenstate distribution.[36, 68, 74-78]

Four distinct ESTs may be calculated. The *continuous microcanonical EST* $T_\mu^{j \to j+1} = (\partial U_j/\partial S_\mu[U_j])_{N,V}$ and the *continuous canonical EST* $T_c^{j \to j+1} = (\partial U_j/\partial S_c[U_j])_{N,V}$ are equal to the *derivatives* of U with respect to S_c and S_μ, respectively. They are thus equal to the *tangential slopes* at the points on the U vs. S profiles corresponding to the initial eigenstates $[N - j, j]$ in $j \to j+1$ transitions (see Figs. 1,2). The *discrete microcanonical EST* $T_{d\mu}^{j \to j+1} = (\Delta U^{j \to j+1} / \Delta S_\mu^{j \to j+1})_{N,V}$ and the *discrete canonical EST* $T_{dc}^{j \to j+1} = (\Delta U^{j \to j+1} / \Delta S_c^{j \to j+1})_{N,V}$ are equal to the finite difference slopes between the points on the U vs. S profiles corresponding to the initial $[N - j, j]$ and final $[N - j - 1, j+1]$ eigenstates in the transitions (see Figs. 2a–c).

1. *The Continuous Microcanonical EST* $T_\mu^{j \to j+1}$

The transition energy between energetically adjacent eigenstates in PSLs is equal to

$$\Delta U^{j \to j+1} = \varepsilon = g\beta H \quad . \tag{6}$$

The *microcanonical entropy* $S_\mu(U_j)$ of $[N–j, j]$ is equal to

$$S_\mu(U_j) = k \ln \Omega_j = k \ln\left(\frac{N!}{[N - j]! \, j!}\right) = k \ln\left(\frac{\Gamma[N + 1]}{\Gamma[N - j + 1] \, \Gamma[j + 1]}\right) , \tag{7}$$

in which the gamma function $\Gamma(j+1) = j!$ is introduced to make the entropy a continuous function of j.[114] Taking the derivative with respect to j and inverting the result yields
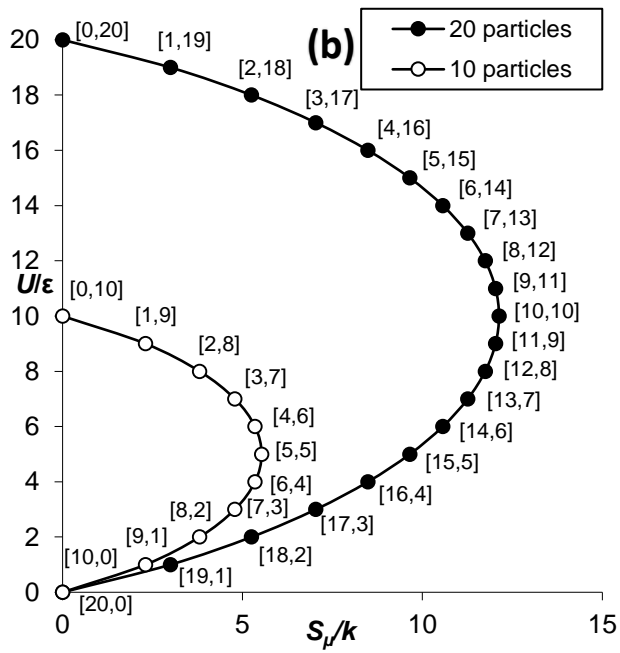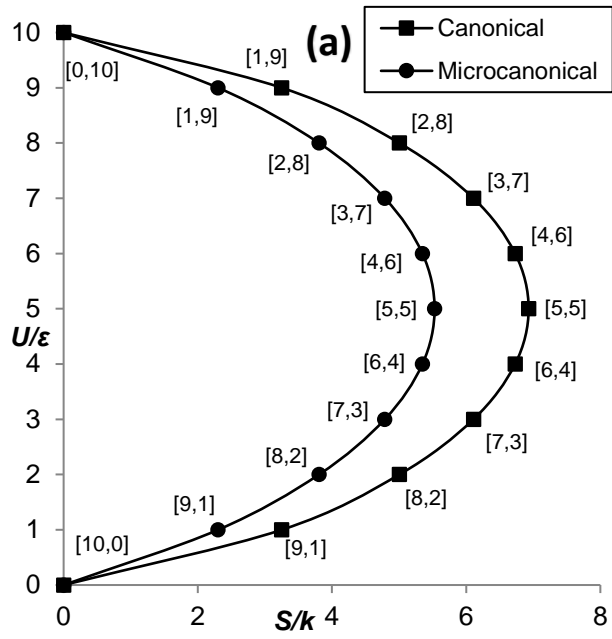
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Fig. 1. (a) Internal energy–entropy profiles for $N = 10$ PSL under microcanonical and canonical conditions. (b) Internal energy–entropy profiles for microcanonical PSLs with $N = 10$ and $N = 20$.
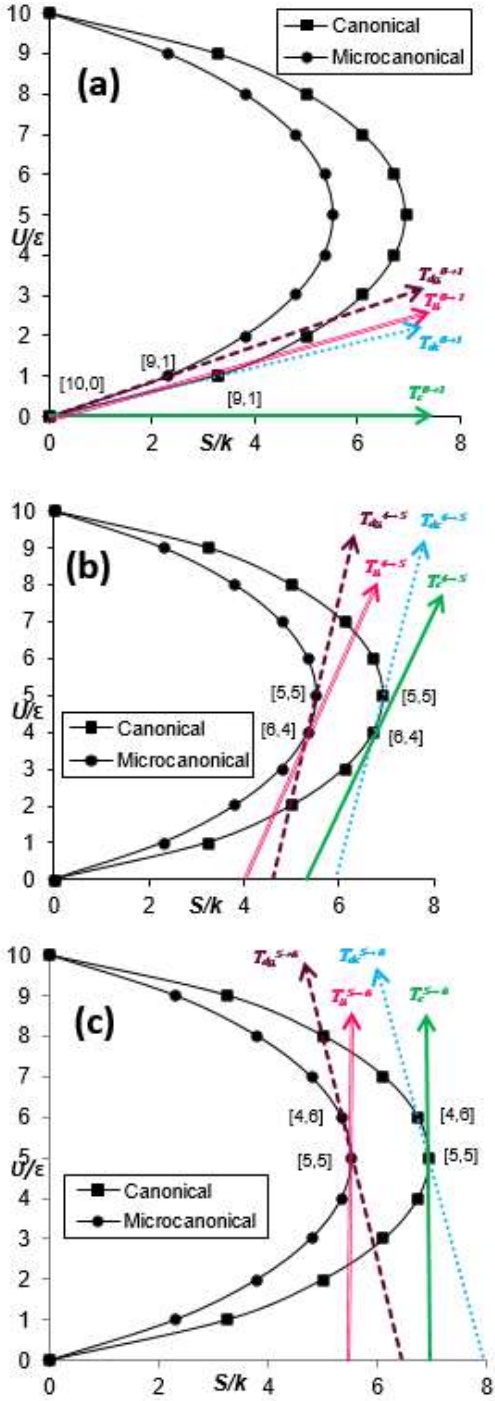
Fig. 2. Continuous microcanonical ($T_\mu^{j \to j+1}$), continuous canonical ($T_c^{j \to j+1}$), discrete microcanonical ($T_{d\mu}^{j \to j+1}$) and discrete canonical ($T_{dc}^{j \to j+1}$) ESTs of the (a) [10, 0] → [9, 1], (b) [6, 4] → [5, 5], and (c) [5, 5] → [4, 6] transitions in an N = 10 PSL. $T_\mu^{j \to j+1}$ and $T_c^{j \to j+1}$ are equal to the slopes of the tangents to the profiles at the initial points in the transitions; $T_{d\mu}^{j \to j+1}$ and $T_{dc}^{j \to j+1}$ are equal to the finite difference slopes between the initial and final points in the transitions.

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$$T_{\mu}^{j \to j+1} = \frac{\varepsilon}{k \left(\Psi_0 [N - j + 1] - \Psi_0 [j+1] \right)} = \frac{\varepsilon}{k \left(\sum\limits_{p=1}^{N-j} \frac{1}{p} - \sum\limits_{p=1}^{j} \frac{1}{p} \right)} \ , \tag{8a}$$

in which $\Psi_0(x)$ is the digamma function.[68, 115] Eq. (8a) is well–defined for all $0 \le j \le N$[113]

provided $j \ne N/2$. As a function of the spin–down mole fraction, $T_{\mu}^{j \to j+1}$ is equal to

$$T_{\mu}^{j \to j+1} = \frac{\varepsilon}{k \left(\Psi_0 \left[(1 - X_j) N + 1 \right] - \Psi_0 \left[X_j N + 1 \right] \right)} = \frac{\varepsilon}{k \left(\sum\limits_{p=1}^{N(1-X_j)} \frac{1}{p} - \sum\limits_{p=1}^{NX_j} \frac{1}{p} \right)} \ , \tag{8b}$$

which is well–behaved for all $0 \le X_j \le 1$[113] provided $X_j \ne 0.5$. $T_{\mu}^{j \to j+1}$ approaches $\mp\infty$ in the limits

as $j \to (N/2)^{\pm}$ and $X_j \to 0.5^{\pm}$.

2. The Continuous Canonical EST $T_c^{j \to j+1}$

When $\bar{j}$ is equal to the spin–down quantum number j of an eigenstate $[N–j, j]$, the

thermodynamic functions become eigenstate–specific. Under these conditions, eigenstate–

specific energy, temperature, and entropy expressions are obtained by substituting j for $\bar{j}$ in Eqs.

(3,4a,b,5), yielding

$$U_j = \frac{N\varepsilon}{e^{\varepsilon/kT_c} + 1} = j\varepsilon \ , \tag{9}$$

and the concave–downward[42, 70-73] entropy expression

$$T_c^{j \to j+1} = \frac{\varepsilon}{k \ln \left(\dfrac{N\varepsilon - U_j}{U_j} \right)} = \frac{\varepsilon}{k \ln \left(\dfrac{N - j}{j} \right)} = \frac{\varepsilon}{k \ln \left(\dfrac{1 - X_j}{X_j} \right)} \ , \tag{10}$$

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$$S_c(U_j) = \frac{k}{\varepsilon} \ln\left[\frac{(N\varepsilon)^{N\varepsilon}}{(N\varepsilon - U_j)^{(N\varepsilon - U_j)} U_j^{U_j}}\right] = k \ln\left[\frac{N^N}{(N-j)^{(N-j)} j^j}\right] = S_c(j) . ^{11} \qquad (11)$$

Eq. (10) is well–behaved for all $j \le N$ provided $j \ne 0$ or $N/2$,[113] and for all $0 \le X_j \le 1$ provided $X_j \ne$

0 or 0.5.[113] $T_c^{j \to j+1}$ approaches zero in the limits as $j \to 0^+$ and $X_j \to 0^+$; it approaches $\mp\infty$ in the

limits as $j \to (N/2)^\pm$ and $X_j \to 0.5^\pm$.

3. The Discrete Microcanonical EST $T_{d\mu}^{j \to j+1}$

$T_{d\mu}^{j \to j+1}$ is obtained by combining Eq. (2a,6,7) to yield

$$T_{d\mu}^{j \to j+1} = \left(\frac{\Delta U^{j \to j+1}}{\Delta S_{d\mu}^{j \to j+1}}\right)_{V,N} = \frac{\varepsilon}{k \ln\left[\dfrac{N\varepsilon - U_j}{U_j + \varepsilon}\right]} = \frac{\varepsilon}{k \ln\left(\dfrac{N-j}{j+1}\right)} = \frac{\varepsilon}{k \ln\left[\dfrac{N(1-X_j)}{X_j N + 1}\right]} , \qquad (12)$$

which is well–behaved for $0 \le j < N$[113] and $j \ne (N-1)/2$ and for $0 \le X_j < 1$[113] and $X_j \ne 0.5(1 -$

$1/N)$. $T_{d\mu}^{j \to j+1}$ approaches $\mp\infty$ in the limits as $j \to (N-1)/2^\pm$ and $X_j \to 0.5(1 - 1/N)^\pm$.[116]

4. The Discrete Canonical EST $T_{dc}^{j \to j+1}$

$T_{dc}^{j \to j+1}$ is equal to the finite difference ratio

$$T_{dc}^{j \to j+1} = \frac{\Delta U^{j \to j+1}}{\Delta S_c^{j \to j+1}} = \frac{\varepsilon}{k \ln\left[\dfrac{(N-j)^{(N-j)} j^j}{(N-j-1)^{(N-j-1)}(j+1)^{(j+1)}}\right]} =$$

$$\frac{\varepsilon}{k \ln\left[\dfrac{(N[1-X_j])^{(N[1-X_j])} (NX_j)^{NX_j}}{(N[1-X_j - 1/N])^{(N[1-X_j-1/N])}(NX_j + 1)^{(NX_j+1)}}\right]} , \qquad (13)$$

in which $\Delta U^{j \to j+1}$ and $\Delta S_c^{j \to j+1}$ are obtained using Eqs. (6,11). Eq. (13) is well–behaved

provided $0 \le j < N$[113, 117] and $j \ne (N-1)/2$ and provided $0 \le X_j < 1$[113, 117] and $X_j \ne 0.5(1 - 1/N$.

$T_{dc}^{j \to j+1}$ approaches $\mp\infty$ in the limits as $j \to (N–1)/2)^{\pm}$[116] and $X_j \to 0.5(1 – 1/N)^{\pm}$.[116] Eq. (13) is to

our knowledge the first derivation of *discrete canonical* temperatures in any context.

III. RESULTS AND DISCUSSION

A. Positive, Infinite, and Negative Absolute Temperatures in PSLs

Conventional absolute (Kelvin) temperatures T_c^{conv} are (1) *positive* because the

translational entropy of an ideal gas increases monotonically with increasing energy,[118] (2) *finite*

because for entropically–monotonic systems infinite temperatures occur only in the limit of

infinite energy, (3) *continuous* because the energetic splittings between the translational energy

levels of ideal gases are small,[118] and (4) *intensive* (*i.e.*, independent of *N*) because typical

systems are large ($N \geq 10^{18}$]), and because ideal gas particles are non–interacting.[36, 60-62, 66-68, 74,

83, 84, 92-94, 103-106] In contrast to those of ideal gases, the entropies of PSLs[7-9, 11-20, 63-65, 79] and other

energetically–bounded systems[7, 21-25, 28-32] increase with energy for eigenstates with energies

between the ground ($U = 0$) and median energy ($U = N\varepsilon/2$), but decrease upon further increases

in energy. Hence, the ESTs are *positive*, *infinite*, and *negative* for $U_j < N\varepsilon/2$, $U_j = N\varepsilon/2$, and

(population–inverted) $U_j > N\varepsilon/2$ eigenstates,[7-9, 11-17, 20] respectively (see Figs. 1,2).

Negative spin temperature (*i.e.*, population–inverted) PSL eigenstates are populated

under two conditions: (i) upon rapid 180° rotation of an external magnetic field, which permutes

the spin–up and spin–down states;[8, 9, 12, 15] and (ii) upon repetitive magnetization measurements.[68,

74-77] Neither of these conditions involves direct thermal heating: Population inversions can be

achieved only through non–thermal means.[7-9, 11-18, 21-32, 36, 61-66]

B. Spin Permutation Antisymmetries (SPAs)

ESTs change sign upon permuting the spin–up and spin–down spin sites; that is, they

manifest *spin permutation antisymmetry.* The most significant manifestation of spin permutation

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antisymmetry is the difference in the *j* values for which the continuous and discrete ESTs become infinite (see Table I and the supplementary material).[119]

C. Impact of System Size and Spin–Down Mole Fraction on EST Values

Temperature is typically *intensive*, so that $T = T(U)$. Because the energy of PSLs is extensive, non–intensive temperatures $T(U,N)$ occur when the entropy is *non–extensive*, in which case the *N*–dependence of the energy numerator in Eq. (2a) is not cancelled by a comparable *N*–dependence in the entropy denominator. Non–intensive temperatures occur in *small* systems, in which *finite–size effects*[36, 40, 60, 68, 83, 84, 92, 93] are important, and in systems with *long–range interactions*.[36, 60-62, 66-68, 74, 83, 84, 92-94, 103-106]

Because the spin sites in PSLs are non–interacting, it follows that non–intensive ESTs in PSLs originate exclusively from finite–size effects. Although these effects are well–known,[36, 40, 60, 68, 83, 84, 92, 93] we report here a previously unrecognized non–intensive temperature behavior which depends functionally on X_j in small PSLs.[120, 121]

The ESTs may be grouped into triads comprised of sets of three types of energetically–adjacent ($j = aN - 1$, aN, and $aN + 1$) eigenstates: (1) *Constant–X_j* eigenstates, for which $X_j = a$ is *constant* with increasing *N*; (2) *Increasing–X_j* eigenstates, for which $X_j = a - 1/N$ *increases* with increasing *N*; and (3) *Decreasing–X_j* eigenstates, for which $X_j = a + 1/N$ *decreases* with increasing *N*. The constant $0 \le a \le 1$ is specific to a given triad.

Although the ESTs in a given triad converge to the common thermodynamic–limiting value $\varepsilon/k\ln[(1-X_j)/X_j] = \varepsilon/k\ln[(1-a)/a]$, the increasing–$X_j$, constant–$X_j$, and decreasing–$X_j$ eigenstates within each triad manifest different functional *N*–dependencies when $N < 1,000$. This heretofore unreported behavior is demonstrated for continuous canonical ESTs in Eqs.

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(14a,b,c), and for the discrete canonical, continuous microcanonical, and discrete microcanonical ESTs in the supplementary material.

The continuous canonical ESTs

$$T_c^{j \to j+1} = T_c^{aN \to aN+1} = \frac{\varepsilon}{k \ln \left(\frac{1-a}{a} \right)}$$

(14a)

of *Constant–X_j* eigenstates are converged to $\varepsilon/k\ln[(1–a)/a]$ for all N (see Fig. 3b); these ESTs are *inherently* intensive. The continuous canonical ESTs

$$T_c^{j \to j+1} = T_c^{aN-1 \to aN} = \frac{\varepsilon}{k \ln \left(\frac{[1-a]N+1}{aN-1} \right)}$$

(14b)

of *Increasing–X_j* eigenstates are smaller than $\varepsilon/k\ln[(1–a)/a]$ at small N, but *ascend to* this value as $N \to$ ~1,000 (see Fig. 4a). In contrast, the continuous canonical ESTs

$$T_c^{j \to j+1} = T_c^{aN+1 \to aN+2} = \frac{\varepsilon}{k \ln \left(\frac{[1-a]N-1}{aN+1} \right)}$$

(14c)

of *Decreasing–X_j* eigenstates are larger than $\varepsilon/k\ln[(1–a)/a]$ at small N, and *descend to* this value as $N \to$ ~1,000 (see Fig. 4b,c). The continuous microcanonical, discrete microcanonical, and discrete canonical ESTs manifest similar behaviors (see Figs. 3a,c,d, and the supplementary material). These unique small N–dependencies suggest that PSLs may prove effective at characterizing the temperatures of systems smaller than those accessible with most currently available nanothermometers[60, 83, 84, 90-102] (see Secs. III.I, Figs. 3,4, and the supplementary material).

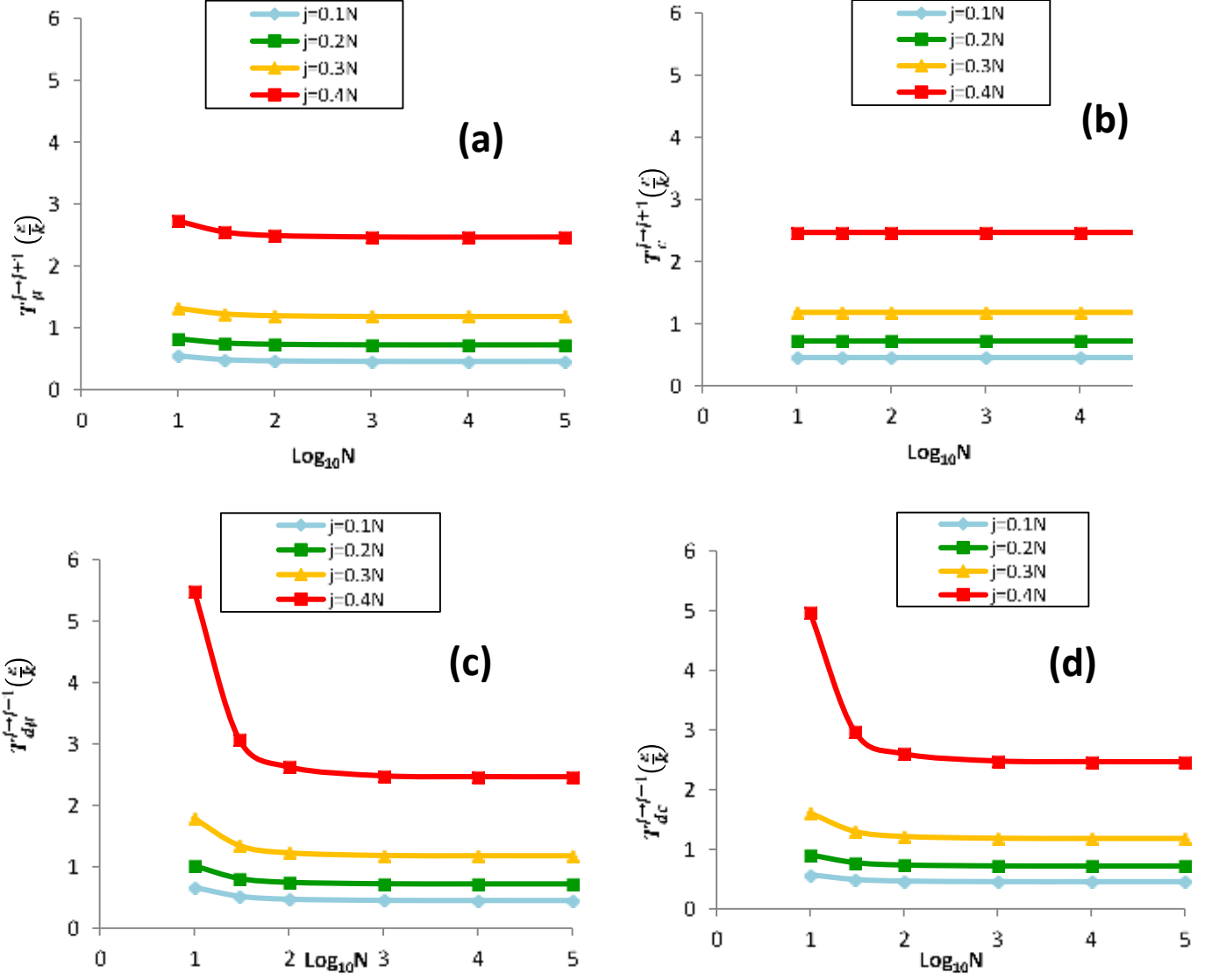**Fig. 3**. *N*–dependence of ESTs for $\Delta j = +1$ transitions originating from $X_j = a$, *Constant–X_j* eigenstates in PSLs: (a) Continuous microcanonical, (b) continuous canonical, (c) discrete microcanonical, and (d) discrete canonical ESTs.
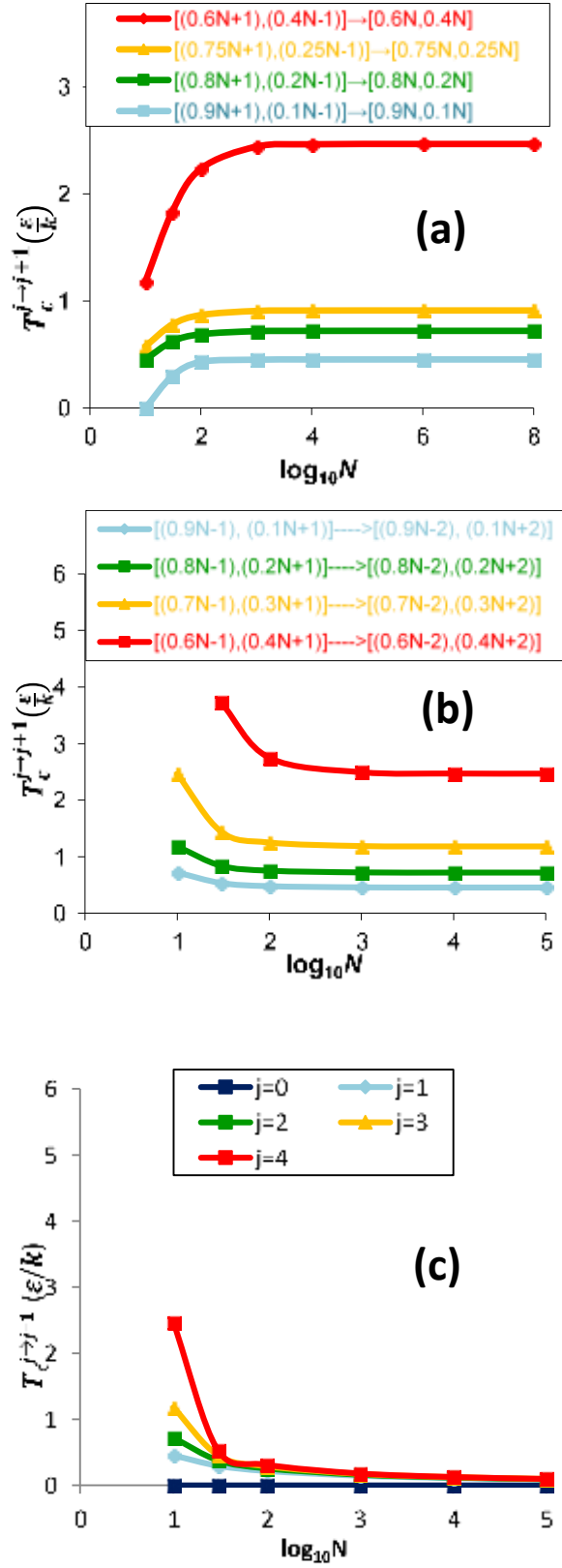
Fig. 4. *N*–dependence of continuous canonical ESTs for Δ*j* = +1 transitions originating from (a) $X_j = a - 1/N$ *Increasing–X_j*; (b) $X_j = a + 1/N$ *Decreasing–X_j*; and (c) $X_j = a/N$ *Decreasing–X_j* eigenstates in PSLs.

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D. The Four Laws of Thermodynamics and the Thermodynamic Legitimacy of the ESTs

To be thermodynamically legitimate, ESTs must obey the Four Laws of Thermodynamics. As demonstrated below, this condition applies only when ESTs are intensive.

1. *The Zeroth Law*

For small N_A and N_B, the ESTs of two PSLs *A* and *B* differ if $N_A \neq N_B$—even when equilibrium (*i.e.*, $X_{jA} = X_{jB}$) conditions apply. Under such conditions, *A* and *B* can be brought to the same temperature only by adjusting their respective energetic splittings ε_A and ε_B. The Zeroth Law is thus violated by small PSLs; it is obeyed by large PSLs, for which the ESTs are intensive.[122]

2. *The First Law*

The First Law mandates that the energy change $\Delta U^{j \to j+1} = C_V (T_Y^{j+1 \to j+2} - T_Y^{j \to j+1}) = \varepsilon$ for $Y = c, dc, \mu, d\mu$. Using the continuous canonical ESTs of positive ($X_j = 0.2$) and negative ($X_j = 0.8$) temperature eigenstates, we find that $\Delta U = \varepsilon$ for both eigenstates when $N \geq 10^3$, but that when $N = 10$, $\Delta U = 1.411\varepsilon$ for $X_j = 0.2$ and 0.819ε for $X_j = 0.8$. The continuous canonical ESTs are thus consistent with the First Law when *N* is large, but violate this law when *N* is small; comparable behavior is predicted for the other three ESTs. The First Law is thus violated by small PSLs; it is obeyed by large PSLs, for which the ESTs are intensive.

3. *The Second Law*

When "statistical" changes $dS_\Omega = d(k\ln\Omega)$ in the microcanonical entropy are equal to the "thermodynamic" entropy changes $dS_{q/T} = dq/T$, the Second Law is obeyed.[123] This property is used here as a criterion for genuine thermodynamic behavior.

As a working system, we assume a 2*N*–particle microcanonical "super–PSL" A + B comprised of two *N*–particle "sub–PSLs" A and B which exchange energy with each other but

are otherwise thermally isolated. We further assume that the sub–PSLs are initially in hot

(A = [0.7N, 0.3N]) and cold (B = [0.9N, 0.1N]) eigenstates, and that heat flows from A to B until

both sub–PSLs are in their [0.8N, 0.2N] eigenstates. The heat exchange can occur in two ways:

(1) a single–step process

$$([0.7N, 0.3N] \xrightarrow{\ 0.1N\varepsilon\ } [0.9N, 0.1N]) \Rightarrow ([0.8N, 0.2N] + [0.8N, 0.2N]),$$

in which 0.1N heat quanta ε flow instantaneously and isothermally from A to B; and (2) a

sequential, multi–step process

$$\big\{ [0.7N, 0.3N] \xrightarrow{\ \varepsilon\ } [0.9N, 0.1N] \big\} \Rightarrow \big\{ [0.7N + 1, 0.3N - 1] \xrightarrow{\ \varepsilon\ }$$

$$[0.9N - 1, 0.1N + 1] \big\} \Rightarrow \big\{ [0.7N + 2, 0.3N - 2] \xrightarrow{\ \varepsilon\ } [0.9N - 2, 0.1N + 2] \big\} \Rightarrow \ldots \Rightarrow$$

$$\big\{ [0.8N - 1, 0.2N + 1] \xrightarrow{\ \varepsilon\ } [0.8N + 1, 0.2N - 1] \big\} \Rightarrow \big\{ [0.8N, 0.2N]) + [0.8N, 0.2N] \big\},$$

in which 0.1N *individual* heat quanta ε are successively transferred from A to B and the

temperatures of sub–PSLs A and B fall and rise, respectively, with each heat exchange. Since

both processes are temperature–independent and share the same initial and final states, the

entropy changes are identical for both processes:

$$\Delta S_{\Omega,single-step} = \Delta S_{\Omega,multi-step} = \Delta S_{\Omega} = k\ln(\Omega^2_{[0,8N,0.2N]}/\Omega_{[0.7N,0.3N]}\Omega_{[0.9N,0.1N]}) = (0.0647k) \times N.$$

The single–step thermodynamic entropy change

$$\Delta S_{q/T,single-step} = (-0.1N\varepsilon/T_{c_A}^{0.3N \to 0.3N+1} + 0.1N\varepsilon/T_{c_B}^{0.1N \to 0.1N+1}) = (0.1350k) \times N$$

is larger than the multi–step thermodynamic entropy change

$$\Delta S_{q/T,multi-step} = (-\varepsilon/T_{c_A}^{0.3N \to 0.3N+1} + \varepsilon/T_{c_B}^{0.1N \to 0.1N+1}) + (-\varepsilon/T_{c_A}^{0.3N-1 \to 0.3N} + \varepsilon/T_{c_B}^{0.1N+1 \to 0.1N+2}) +$$

$$(-\varepsilon/T_{c_A}^{0.3N-2 \to 0.3N-1} + \varepsilon/T_{c_B}^{0.1N+2 \to 0.1N+3}) + \ldots + (-\varepsilon/T_{c_A}^{0.2N+1 \to 0.2N} + \varepsilon/T_{c_B}^{0.2N-1 \to 0.2N}),$$

which at finite N adopts a value lying between those of $\Delta S_{q/T,single–step}$ and ΔS_Ω. Because they incorporate "excess" entropy contributions originating from the temperature differences between the PSLs, the thermodynamic entropy changes are both larger than ΔS_Ω.

The entropy increases $\Delta S_{q/T} = (-\varepsilon/T_{c_A}^{j_A \to j_A+1} + \varepsilon/T_{c_B}^{j_B \to j_B+1})$ induced by exchanges of individual heat quanta become smaller as the temperatures of the sub–PSLs converge; *i.e.*, as $j_A \to j_B \to j_{final} = 0.2N$. Because the number of heat exchanges in which the values of j_A and j_B are similar increases with increasing N, the average excess entropy per exchange is smallest when N is large. Consequently, $\Delta S_{q/T,multi–step}/\Delta S_\Omega \to 1$ in the TDL: For 10–, 50–, 100–, 500–, and 1,000–particle sub–PSLs initially in $X_{jA} = 0.3$ and $X_{jB} = 0.1$ eigenstates, $\Delta S_{q/T,multi–step}/\Delta S_\Omega = 2.081, 1.209, 1.104, 1.020$, and 1.010, respectively.[123] Hence, $\Delta S_{q/T,multi–step} \to \Delta S_\Omega$ in the TDL; under these conditions, the Second Law is obeyed because the ESTs are intensive. In contrast, since both $\Delta S_{q/T,single–step}$ and ΔS_Ω scale with N, $\Delta S_{q/T,single–step}/\Delta S_\Omega = 2.086$ is constant for all N, so that $\Delta S_{q/T,single–step}$ does not converge to ΔS_Ω in the TDL.

Three conclusions can be drawn from these results. First, from the *standpoint of entropy*, thermodynamics and statistical mechanics are equivalent for PSLs in the TDL because $\Delta S_{q/T,multi–step} \to \Delta S_\Omega$ as N becomes large. Second, from the *standpoint of temperature*, statistical mechanics and thermodynamics are equivalent for PSLs in the TDL because the ESTs become intensive at large N. Third, the Second Law is violated by small PSLs (for which the ESTs are non–intensive), but obeyed by large PSLs (for which the ESTs are intensive).

4. *The Third Law*

Since a PSL in its ground eigenstates $[N,0]$ is a perfect spin crystal, the four ESTs should equal zero for this eigenstate when the Third Law is obeyed. In contrast to this expectation,

however, only the continuous canonical EST $T_c^{0\to1}$ is equal to 0K for all N; $T_\mu^{0\to1}$, $T_{d\mu}^{0\to1}$, and

$T_{dc}^{0\to1}$ are each greater than zero at finite N, and approach zero only in the TDL. Hence, when

$T_\mu^{0\to1}$, $T_{d\mu}^{0\to1}$, and $T_{dc}^{0\to1}$ are applied, the Third Law is violated by small PSLs (for which the ESTs

are non–intensive), but obeyed by large PSLs (for which the ESTs are intensive; see Table I).[6, 124, 125]

E. Relationship of ESTs to Boltzmann Distributions and the TUR

ESTs apply to individual eigenstates regardless of their connection—or lack thereof—to a

Boltzmann distribution. This lack of a necessary connection of ESTs to Boltzmann distributions

makes their similarities to T_c^{conv} both intriguing and useful.

T_c^{conv} is equal to T_{bath} only for canonical PSLs which have remained in contact with an

infinite bath[34-36, 67, 105, 106, 126] for *equilibration timescales t_{equil}* long enough for a Boltzmann

distribution to be established. Since a new eigenstate is populated with each PSL↔bath energy

exchange, many eigenstates are successively occupied, so that the energy and temperature

fluctuate during equilibration. ESTs specify the temperature during the brief *microcanonical

intervals $t_j \ll t_{equil}$* between PSL↔bath energy exchanges. Since T_c^{conv} is effectively an average

of the ESTs weighted by their Boltzmann factors, it generally differs from the ESTs.

Three conclusions regarding the TUR $\Delta U \Delta(1/T) \geq k$ follow from the temporal properties

of ESTs. <u>First</u>, because the TUR applies only to Boltzmann–distributed systems,[34-36, 67, 105, 106, 126]

and because the *observed* energy and temperature values are equal to the energy and the EST of

the eigenstate occupied at the time of measurement—and hence change with each successive

measurement—ΔU and $\Delta(1/T)$ are both non–zero: The energy and temperature *measurements*

both *fluctuate*, so that the TUR is obeyed by small PSLs in equilibrium with infinite baths.[34-36, 67, 105, 106, 126]

Second, since large canonical PSLs in equilibrium with infinite baths are dominated by their most–probable eigenstate [N–j*, j*],[42, 70-73] each consecutive energy and temperature measurement yields the same values j*ε and $T_c^{j* \to j*+1} = T_c^{conv} = T_{bath}$. The *observed* energy and temperature values are thus both *non–fluctuating*: $\Delta U = \Delta(1/T) = 0$, so that the TUR is violated by *large* canonical PSLs in equilibrium with *infinite* baths.[34-36, 67, 105, 106, 126]

Third, since they are *rigorously* microcanonical, all measurements performed on an isolated PSL yield identical energy and temperature values: $\Delta U = 0$ (by definition) and $\Delta(1/T) = \Delta(1/T_\mu^{j \to j+1}) = 0$ (because the EST is precise). The TUR is thus violated by microcanonical PSLs of any size.

Significantly, this third conclusion disagrees with Mandelbrot,[3] who contended that the TUR applies to a single microcanonical eigenstate "extracted" from a canonical system via thermal isolation. According to Mandelbrot, this eigenstate mysteriously retains the uncertainties in energy and reciprocal temperature of the canonical distribution from which it is extracted. Hence, in agreement with Uffink and van Lith,[34] we conclude that Mandelbrot's arguments regarding the TUR for microcanonical systems are "counterfactual".[127, 128]

The three conclusions above are undergirded by a single unifying feature: *ESTs are thermodynamically accurate and precise only when they are identical to the thermodynamic temperature.* The SEOC applies to *rigorously* microcanonical systems of any size and *effectively* to large canonical systems in equilibrium with infinite baths.[34-36, 67, 105, 106, 126] Since the ESTs converge in the TDL, differences between the ESTs will not be manifest in scenario (iii);

scenarios (i), (ii), and (iv) thus provide the most interesting and important test cases for the utility of ESTs and their applications to the TUR (see Sec. II.D).

F. ESTs and the FKM Debate

The FKM debate[1-3, 34-36] was initiated by Feshbach,[1] who contended that for small systems, T_{system} can be *usefully approximated* provided the range of inverse temperature estimates does not exceed the $\Delta(1/T)$ value specified by the TUR. In response, Kittel[2] contended that T_{system} is defined only for canonical systems—large or small—in equilibrium with large heat baths, in which case $T_{system} = T_{bath} = T_c^{conv}$. Since the large heat capacity of the bath precludes fluctuations in T_{bath},[67, 126] and since the SEOC is effectively satisfied in large baths,[42, 70-73] both T_{system} and T_{bath} are *non–fluctuating*.[2, 34, 67, 105, 106, 126] Mandelbrot[3] took an intermediate position, in which the *actual* reciprocal temperature of a canonical system is equal to T_{bath}, and hence does not fluctuate, but that *estimations* of the reciprocal temperature obtained using *estimators* $k\hat{\beta} = \hat{T}^{-1}$ do fluctuate in accord with the TUR: $\Delta U \Delta(k\hat{\beta}) \geq k$.

The ESTs in the present study—which are analogous to Mandelbrot's temperature estimators—are precise regardless of PSL size. Though they deviate from $T_{bath} = T_c^{conv}$, ESTs provide new insights into many of the issues raised by the FKM debate,[1-3, 34-36] as detailed below.

First, Feshbach was only *partially* correct: The TUR applies to *finite canonical* systems, for which energy and temperature measurements fluctuate. Even so, the TUR applies only when Boltzmann statistics are in effect—and this condition prevails only for systems which are in equilibrium with *infinite baths*.[34-36, 67, 105, 106, 126] Feshbach was thus incorrect to assume that the TUR applies to finite canonical systems in contact with *finite baths*.

Second, Kittel was likewise only *partially* correct: The TUR is violated in *large canonical* systems in equilibrium with *infinite* baths,[34-36, 67, 105, 106, 126] for which energy and temperature measurements are accurate and precise. He was nevertheless incorrect in concluding that T_{system} is *always* equal to T_{bath} for *small canonical* systems in equilibrium with *infinite* baths. T_{system} and T_{bath} are not *necessarily* identical unless the energetic splittings ε_{bath} in the bath are effectively continuous;[2, 34, 67, 105, 106, 126] if $\varepsilon_{bath} > \varepsilon_{PSL}$, small PSLs in contact with infinite baths can violate both the Zeroth Law and the TUR.[121, 129]

Third, Mandelbrot was also only *partially* correct: His temperature estimators obey the TUR under canonical conditions provided the bath is infinite, quasi–continuous, and comprised of non–interacting particles.[34-36, 67, 105, 106, 126] Even so, he was incorrect to conclude that his temperature estimators obey the TUR under microcanonical conditions:[3, 34, 127, 128] The temperatures of microcanonical systems of *any* size are precise—and hence violate the TUR.

G. Boltzmann and Gibbs ESTs and the Negative Temperature Debate

Temperature, entropy and other statistically–derived quantities are *thermodynamically legitimate* when the predictions of statistical mechanics concur with thermodynamic measurements. It is generally assumed that temperature is thermodynamically legitimate when it is *intensive*,[130, 131] and that entropy is thermodynamically legitimate when it is *adiabatically invariant* (*i.e*., constant in reversible, adiabatic processes).[4-6, 27, 132] Because of the intimate relationship between temperature and entropy, these thermodynamic legitimacy requirements raise the question: "Are intensive temperatures synonymous with adiabatically invariant entropies?" The answer to this question revolves around the form of the entropy—Boltzmann or Gibbs—used to calculate temperature, and is partially addressed by the negative temperature debate,[4-6, 27, 31] as detailed below.

The microcanonical *Gibbs* entropy

$$S_{\mu G j} = k \ln \sum_{m=0}^{j} \Omega_m = k \ln \sum_{m=0}^{j} \frac{N!}{(N-m)!m!} \tag{15}$$

for an eigenstate [*N–j, j*] is equal to the logarithm of the *sum* of the microcanonical degeneracies

of all eigenstates of energy *up to and including* [*N–j, j*]. It is commonly assumed that the Gibbs

entropy is an adiabatic invariant for all *N*.[4-6, 27, 132, 133] In contrast, the microcanonical *Boltzmann*

entropies $S_{\mu B j}$ used in Eqs. (12a,b;13,18]) are equal to the the degeneracy Ω_j of the [*N – j, j*]

eigenstate. It is commonly assumed that $S_{\mu B j}$ is not adiabatically invariant for small *N*, but that it

becomes so in the TDL because it converges to $S_{\mu G j}$ as *N* becomes large.[4-6, 27]

Because $S_{\mu B j}$ decreases with increasing energy above the energy median, Boltzmann

ESTs of PSLs are negative for population–inverted eigenstates. In contrast, because $S_{\mu G j}$ of PSLs

increases monotonically with increasing energy for all *j*, the discrete microcanonical Gibbs ESTs

$$T_{d\mu G}^{j\to j+1} = \left(\frac{\Delta U^{j\to j+1}}{\Delta S_G^{j\to j+1}} \right)_{V,N} = \frac{\varepsilon}{k\left(\ln \sum_{m=0}^{j+1} \frac{N!}{(N-m)!m!} - \ln \sum_{m=0}^{j} \frac{N!}{(N-m)!m!} \right)} \tag{16}$$

of PSLs are uniformly positive—even for population–inverted eigenstates.[4, 5, 27]

The thermodynamic legitimacy of Boltzmann entropies and of negative absolute

Boltzmann temperatures in PSLs and other energetically–bounded systems has recently been

challenged, for three reasons: (1) the Gibbs ESTs of PSLs are positive for all eigenstates,

whereas the Boltzmann ESTs are negative for population–inverted eigenstates; (2) negative

absolute temperatures imply that the Boltzmann populations of population–inverted eigenstates

should <u>increase</u> with increasing energy;[8] and (3) Gibbs entropies are *commonly believed* to be

adiabatically invariant, whereas Boltzmann entropies are not.[4-6, 27] Even so, there are strong

reasons to believe that negative absolute temperatures are thermodynamically legitimate, and that Boltzmann temperatures and entropies are preferable to their Gibbs analogs.

First, the Gibbs ESTs of population–inverted eigenstates grow *exponentially* with increasing N,[5] and hence manifest no TDL. This *super–nonintensive* character of the Gibbs ESTs is manifestly non–thermodynamic,[4-6, 27] as it violates both the normal notions of hot and cold[5, 31] and the Zeroth Law of Thermodynamics.[6, 31] In contrast, the Boltzmann ESTs of population–inverted eigenstates are intensive and thermodynamically legitimate in the TDL (see Sec. III.C).[5] Boltzmann ESTs are thus preferable to their Gibbs analogs in PSLs.

Second, Gibbs entropies are not *necessarily* adiabatically invariant. Recently, based on the N–dependence of the chemical potential, Tavassoli and Montakhab[133] have recently demonstrated that neither the Gibbs nor the Boltzmann entropies are adiabatic invariants in *any* system for *any* value of N.[5, 31, 133] Hence, neither S_{G_j} nor S_{B_j} give perfect statistical mechanical–thermodynamic equivalence for thermodynamic observables. It is thus not possible to establish a direct correlation between temperature intensivity and entropic adiabatic invariance. Even so, Boltzmann ESTs obey the four laws of thermodynamics when they are intensive (see Sec. III.D), whereas the Gibbs ESTs of population–inverted eigenstates are non–thermodynamic. Hence, *intensivity of temperature is a more important criterion for thermodynamic legitimacy than adiabatic invariance of the entropy.*

H. ESTs and Earlier Experimental Temperature Measurements with Nuclear PSLs

With few exceptions,[5, 54, 85] temperature has been characterized with T_c^{conv} in previous studies of PSLs.[7, 9, 11-18, 63-65, 79, 89] Because PSLs containing more than 10^{21} nuclei of each element were used in the earlier studies,[13-17, 64, 65, 79, 134] these PSLs were in the TDL. Hence, the (unreported) nuclear spin ESTs are effectively identical to the (reported) conventional canonical

nuclear spin temperatures. ESTs thus provide no new insights into the temperatures of the large

PSLs utilized in previous studies; the principal utility of ESTs lies in their application to studies

of *small* PSLs, which may find application in nanothermometry, as detailed below.

I.   ESTs and Nanothermometry

An experimental thermometry setup in which a small PSL–based nanothermometer

(PSLnt) can yield accurate measurements of the temperature of a canonical system, provided five

conditions are satisfied. <u>First</u>, to ensure that the PSLnt does not perturb the system temperature,

the size and heat capacity of the PSLnt must both be *small compared to those of the system*.

<u>Second</u>, to ensure that the bath temperature remains constant during system–bath energy

exchanges, the size and heat capacity of the bath must be *large compared to those of the system.*

<u>Third</u>, the system–bath interaction $\hat{H}'_{system-bath}$ must be large enough to allow the system to

equilibrate with the bath, but small enough to prevent the nanothermometer from perturbing the

energies of the system eigenstates;[135, 136] *i.e.*, the bath must be *weakly–coupled to the system.*

<u>Fourth</u>, the system–PSLnt interaction $\hat{H}'_{system-PSLnt}$ must be large enough to allow the PSLnt to

equilibrate with the system, but small enough to preclude changes in the energies of the

eigenstates of the system and the PSLnt;[135, 136] *i.e*, the PSLnt must be *weakly–coupled to the*

system. <u>Fifth</u>, to ensure that it measures the temperature of the system exclusively, with minimal

inaccuracies induced by the bath, the PSLnt must be effectively uncoupled from the bath; *i.e.*,

$\hat{H}'_{bath-PSLnt} \sim 0.$

Provided the five conditions above are satisfied, the canonical temperatures of both the

system and the PSLnt may be characterized following equilibration. Since the net magnetization

of a PSLnt is proportional to its energy, the temperature of the PSLnt may be assessed by

measuring its net magnetization, *ipso facto* yielding the system temperature in accord with the Zeroth Law.

For measuring microcanonical temperatures, we propose a setup utilizing a PSLnt which is similar to the "minimal quantum thermometer" proposed by Dunkel and Hilbert.[4] Provided the first and third conditions above are satisfied, such a setup should yield reliable measurements of the microcanonical Gibbs temperature of a system. Since the microcanonical system is isolated, it will initially be in a single eigenstate. If the PSLnt is first prepared in a (preferably) very low energy state with well–defined initial magnetization by magnetic cooling[68, 76, 77] and then brought into contact with the system under constrained conditions in which the combined energy of the system and the PSLnt is constant, then upon equilibration the magnetization of the PSLnt will change. The initial microcanonical temperature of the system may then be inferred by noting the change in the net magnetization of the PSLnt.

Our results regarding the impact of $N_{PSL} = N_{nt}$ on the four ESTs have two important implications for PSLnts. <u>First</u>, because the four ESTs of a given PSL eigenstate are typically intensive for $N \geq 10^3$, our results suggest a *minimum temperature intensivity size limit* of $N \sim 10^3$ particles—significantly smaller than the sizes of most existing magnetic nanoparticle ($N \geq 10^6$)[98-102], paramagnetic salt ($N \geq 10^{20}$)[95] and optical ($N \geq 10^6$)[96, 98] nanothermometers. Assuming a PSLnt must be no more than one–tenth the size of its target system, PSLnts could yield reliable intensive temperatures for systems as small as 10^4 particles, potentially resulting in a 1,000–fold reduction in the size of target systems accessible with the smallest currently available magnetic nanothermometers.[98-102] <u>Second</u>, because the X_j–dependent deviations of the ESTs from their thermodynamic–limiting values are monotonic with decreasing N, reliable—albeit non–

J. ESTs in Systems with Long–Range–Interactions

Since the spins of PSLs are non–interacting, it follows that the deviations of the ESTs of small PSLs from their thermodynamic–limiting values originate exclusively from finite–size effects.[36, 40, 60, 68, 83, 84, 92, 93] (see Sec. III.B). Since inter–particle interactions also give rise to non–intensive temperatures,[36, 60-62, 66-68, 74, 83, 84, 92-94, 103-106] any contrasts between the temperatures of PSLs and those of comparably–sized systems with long–range spin–spin interactions will provide new insights into the relative impact of finite–size effects and inter–particle interactions on temperature non–intensivity.

IV. CONCLUSIONS AND FUTURE STUDIES

Four types of eigenstate–specific temperatures—continuous canonical, continuous microcanonical, discrete canonical, and discrete microcanonical—have been derived for two–level paramagnetic spin lattices. To our knowledge, this study constitutes the first detailed application of continuous microcanonical and discrete canonical ESTs to PSLs.[137]

Our results lead us to conclude the following. *First*, the Boltzmann ESTs of small $(N \leq 10^3)$ PSLs deviate from their thermodynamic–limiting values in previously unreported ways which differ depending on whether the spin–down mole fraction X_j increases, decreases, or remains constant with increasing N. Because these X_j–dependencies are monotonic in N, PSL–based nanothermometers can in principle provide meaningful temperature estimates for systems containing fewer than 10^3 particles.

Second, although the four Boltzmann ESTs of PSLs are not true thermodynamic temperatures, they are useful *temperature estimators* for the full eigenstate spectrum of small

PSLs. Gibbs ESTs are also useful temperature estimators—but only for positive temperature eigenstates; for population–inverted eigenstates, Boltzmann ESTs provide reliable temperature estimates, whereas the Gibbs ESTs do not.

Third, the thermodynamic uncertainty relation[34, 35] is violated by microcanonical PSLs of any size and by large canonical PSLs in equilibrium with infinite baths; it is obeyed only by finite canonical PSLs in equilibrium with infinite baths.[34-36, 67, 105, 106, 126] Temperature measurements are thus *non–fluctuating* in microcanonical PSLs of any size, non–fluctuating and thermodynamically *accurate* in large canonical PSLs,[42, 70-73, 126] and fluctuating and thermodynamically *approximate* in finite canonical PSLs.

Fourth, intensivity of temperature is a more important criterion for genuine thermodynamic behavior than adiabatic invariance of the entropy.[5, 133]

Collectively, our results suggest that ESTs will provide insights into a number of important current topics, including (1) the relative impacts of finite–size effects,[36, 40, 60, 68, 83, 84, 92, 93] and long–range interactions[36, 60-62, 66-68, 74, 83, 84, 92-94, 103-106] on thermostatistical behavior, (2) the eigenstate thermalization hypothesis,[138, 139] (3) the potential impact of temperature–dependent system energy levels on the thermodynamic uncertainty relation;[33, 121, 129] and (4) nanothermometry.[60, 83, 84, 90-102]

VI. SUPPLEMENTARY MATERIAL

See supplementary material for details regarding (A) the spin–permutation antisymmetries of the ESTs[119] and (B) the impact of spin–down mole fraction X_j on the continuous microcanonical, discrete canonical, and discrete microcanonical ESTs of constant–X_j, Increasing–X_j, and Decreasing–X_j eigenstates.[120, 121]

VII. ACKNOWLEDGEMENTS

VIII. TABLES

TABLE I. Continuous microcanonical,[a] continuous canonical,[b] discrete microcanonical,[c] and discrete canonical[d] ESTs for $j \to j + 1$ transitions[e] in two–level, 10–particle PSLs, illustrating differing spin permutation antisymmetries for continuous and discrete ESTs (see supplementary material).

Transition[e] $[N - j, j] \to [N - j - 1, j + 1]$	$T_{\mu}^{j \to j+1}\left(\dfrac{\varepsilon}{k}\right)$ [a]	$T_{c}^{j \to j+1}\left(\dfrac{\varepsilon}{k}\right)$ [b]	$T_{d\mu}^{j \to j+1}\left(\dfrac{\varepsilon}{k}\right)$ [c]	$T_{dc}^{j \to j+1}\left(\dfrac{\varepsilon}{k}\right)$ [d]
$[10, 0] \to [9, 1]$	0.3414	0 [f]	0.4343	0.3076
$[9, 1] \to [8, 2]$	0.5468	0.4551	0.6649	0.5704
$[8, 2] \to [7, 3]$	0.8211	0.7213	1.019	0.9053
$[7, 3] \to [6, 4]$	1.316	1.180	1.787	1.609
$[6, 4] \to [5, 5]$	2.727	2.466	5.485	4.966
$[5, 5] \to [4, 6]$	$\pm \infty$ [g]	$\pm \infty$ [h]	-5.485	-4.966
$[4, 6] \to [3, 7]$	-2.727	-2.466	-1.787	-1.609
$[3, 7] \to [2, 8]$	-1.317	-1.180	-1.020	-0.9053
$[2, 8] \to [1, 9]$	-0.8211	-0.7213	-0.6649	-0.5704
$[1, 9] \to [0, 10]$	-0.5468	-0.4551	-0.4343	-0.3076

[a]Continuous microcanonical ESTs of $j \to j + 1$ transitions, as given by Eq. (8a,b;B3,B7,B12) and calculated using easycalculation.com/digammafunction.php.

[b]Continuous canonical ESTs of $j \to j + 1$ transitions, as given by Eqs. (10;B4,B8,B13).

[c]Discrete microcanonical ESTs of $j \to j + 1$ transitions, as given by Eqs. (12;B5,B9,B14).

[d]Discrete canonical ESTs of $j \to j + 1$ transitions, as given by Eqs. (13;B6,B10,B15).

[e]$N - j$ and j specify the number of spin–up $(U_\uparrow = 0)$ and spin–down $(U_\downarrow = \varepsilon)$ lattice sites, respectively, in a given eigenstate.

[f]Undefined for $j = 0$ but equal to zero in the limit as $j \to 0^+$; *i.e.*, $T_c^{0 \to 1} = \lim_{j \to 0^+} T_c^{j \to j+1} = \lim_{j \to 0^+} \varepsilon/k \ln\left[(N - j)/j\right] = 0$.

[g]Undefined for $j = N/2$, but approaches infinity as $j \to (N/2)^{\pm}$ for all N because the denominator of $T_{\mu}^{j \to j+1} = \varepsilon/k(\Psi[N - j + 1] - \Psi[j+1])$ approaches 0 in this limit, so that $\lim_{j \to (N/2)^{\mp}} T_{\mu}^{j \to j+1} = \pm \infty$ for all *even N*, and hence is inherently intensive (see Eqs. [B3,B7,B12]).

[h]Undefined for $j = N/2$, but approaches infinity as $j \to (N/2)^{\mp}$ for all N because the argument of the logarithm in the denominator of $T_c^{j \to j+1} = \varepsilon/k \ln\left[(N - j)/j\right]$ approaches 1 in this limit, so that $\lim_{j \to (N/2)^{\mp}} T_c^{j \to j+1} = \pm \infty$ for all even N, and hence is inherently intensive (see Eqs. [10;B4]).

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[113]$[N+1, -1] \rightarrow [N, 0]$ and $[0, N] \rightarrow [-1, N+1]$ transitions are not *physically* realistic because $[N+1, -1]$ and $[-1, N+1]$ are not PSL eigenstates. These transitions are accordingly not discussed in the text, though T_c^{conv}, $T_c^{j \rightarrow j+1}$, $T_\mu^{j \rightarrow j+1}$ and $T_{dc}^{j \rightarrow j+1}$ are *mathematically* well–behaved for $j = -1$ and N, as is $T_{d\mu}^{j \rightarrow j+1}$ for $j = N$.

[114]Though an infinite number of analytic functions pass through the factorials of all positive integers, $\Gamma(x)$ is the only function which is uniquely determined for all positive real numbers because—in accord with the Bohr–Mollerup Theorem—it satisfies the conditions $\Gamma(1) = 1$, $\Gamma(x+1) = x\Gamma(x)$, and is logarithmically convex. The gamma function is thus the only reasonable analytic function for representing factorials; see Artin, Emil, "The Gamma Function" in Rosen, M. *Exposition by Emil Artin: A Selection*, History of Mathematics **30** (American Mathematical Society, Providence, RI, 2006).

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[117]$T_{dc}^{j \rightarrow j+1}$ is imaginary for $j = N$, since the argument of the logarithm is negative and $\ln(-1) = i\pi$.

[118]See pp. 10–12 of McQuarrie, D.A., *Statistical Mechanics* (University Science Books, Sausalito, CA, 2000)

[119]de Miguel and Rubi obtain a different—but related—set of spin permutation antisymmetries for the discrete microcanonical ESTs $T_{d\mu}^{j-1 \rightarrow j}$ defined in terms of "backward" $j-1 \rightarrow j$ transitions. Our four ESTs are all defined in terms of "forward" $j \rightarrow j+1$ transitions transitions ("forward" and "backward" terminology taken from Ref. 33 and from T. Wada and A.M. Scarfone, J. Phys. Conf. Ser. **201**, 0125 [2010]).

[120]The X_j–dependence of our forward ($T_{d\mu}{}^{j\to j+1}$) and de Miguel and Rubi's backward ($T_{d\mu}{}^{j-1\to j}$) discrete microcanonical ESTs (see Refs. 33 and 119) are opposite to each other. For example, the values of $T_{d\mu}{}^{j\to j+1}$ are large for small N and fall to their thermodynamic limiting values near N = 1,000 (see Fig. 3c in the revised manuscript), whereas the values of $T_{d\mu}{}^{j-1\to j}$ are small for small N and rise to their intensive, thermodynamic limiting values near N = 1,000 (from our plots of de Miguel and Rubi's $T_{d\mu}{}^{j-1\to j}$ values; data not shown).

[121]The presence of the functional X_j–dependencies in both forward and backward discrete microcanonical ESTs (see Refs. 33, 119) precludes the possibility that these X_j–dependencies originate from temperature–dependent system energy levels (TDSELs), since the Hamiltonians of thermally–isolated systems are not perturbed by bath Hamiltonians.

[122]The continuous canonical ESTs for constant–X_j eigenstates—which are inherently intensive— are the single exception to this rule.

[123]See Eq. (34.7) and surrounding discussion in Becker, R., *Theory of Heat, Second Edition* (Springer–Verlag, New York, NY, 1967).

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[125]Using backward $j = -1 \to j = 0$ transitions (see Refs. 33, 119), de Miguel and Rubi find that the discrete microcanonical temperature of the perfect crystalline (*i.e.*, all–spins–down) PSL ground state [N, 0] is equal to zero: $T_{d\mu}{}^{j-1\to j} = T_{d\mu}{}^{-1\to 0} = 0$, in accord with the Third Law. However, to obtain this result, they must assume that the ground state temperature is equal to that of a transition originating from a non–physical [N+1, –1] "eigenstate" lying below the ground eigenstate. In contrast, we assume that the ground state temperature $T_{d\mu}{}^{j\to j+1} = T_{d\mu}{}^{0\to 1}$ is equal to that of a forward $j = 0 \to j = 1$ transition between the two genuine, physical PSL eigenstates [N, 0] and [N–1, 1]. While the forward continuous canonical EST $T_c{}^{0\to 1}$ is equal to zero for all N, the forward ESTs $T_{d\mu}{}^{0\to 1}$, $T_\mu{}^{0\to 1}$ and $T_{dc}{}^{0\to 1}$ are all greater than zero for finite N and approach zero in the limit of large N. Our results thus indicate that for the ground state in PSLs, forward ESTs are consistent with the Third Law—but generally only in the TDL.

It is interesting to note that for $j = N \to j = N$+1 transitions from the perfect crystalline (*i.e.* all–spins–down), maximum energy eigenstate [0, N] to the non–physical state [–1, N+1] directly above it, backward $T_{d\mu}{}^{j-1\to j}$ values are finite and negative and approach –0 in the thermodynamic limit, whereas forward $T_{d\mu}{}^{j\to j+1}$ values are equal to –0 for all N; *i.e.*, there is a symmetry between the N–dependence of $T_{d\mu}{}^{j-1\to j}$ and $T_{d\mu}{}^{j\to j+1}$ for the [N, 0] and [0, N] eigenstates, which suggests a difference in zero–point energy for backward and forward discrete microcanonical ESTs. This symmetry is related to the spin permutation antisymmetries and may be rooted in the differences in the Second Law for negative and positive temperature eigenstates proposed by Lavenda (see Sec. III.B, the supporting materials, and Ref. 8).

[126]Boltzmann statistics apply only to systems in equilibrium with baths which are infinite ($N_{bath}\to\infty$), energetically quasi–continuous ($\varepsilon\to 0$), and which (generally) lack long–range interactions. For systems in contact with baths which do not satisfy these conditions, Tsallis statistics prevail (see Refs. [67,105,106]). Since the TUR *assumes* Boltzmann statistics, it applies only to finite canonical PSLs in equilibrium with *infinite* baths (see Refs. [34,106]).

[127]This disagreement does not negate the importance of Mandelbrot's contributions to TUR research, for two reasons. First, his results regarding the applicability of the TUR to canonical systems agree with both our results and those of Uffink and van Lith (see Ref. 34). Second, in

assuming that a single eigenstate extracted from a Boltzmann distribution retains the thermostatistical content of the full distribution, Mandelbrot appears to have anticipated the *eigenstate thermalization hypothesis*; see Refs. 138 and 139.

[128]In spite of his mistaken contention that the TUR applies to finite microcanonical systems, Mandelbrot was aware that the TUR fails in the TDL, for which he noted that "temperature fluctuations … are negligibly small" (see Ref. 3). This raises the question: "Did Mandelbrot incorrectly conflate the $N \to \infty$ requirement for a single microcanonical EST to be thermodynamically accurate with the requirements for the TUR to fail?" The answer appears to be no, as Mandelbrot based his arguments on the "zeroth principal of thermodynamics"—not on large N behavior.

[129]When there is a mismatch between energy level spacings of small systems and their heat baths, small canonical systems are able to equilibrate with their heat baths only when the system energy levels are modulated by interaction with the bath (*i.e.*, when TDSELs are operative). In such cases, the mismatch between T_{system} and T_{bath} "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 makes possible the thermal equilibrium between the finite system and the heat bath." (quoted from Ref. 33). This scenario, in combination with the fact that both TDSELs and the TUR by definition apply only to finite canonical systems, raises an interesting question: "Since the energy levels of small canonical systems are perturbed by their baths, do TDSELs contribute to the energy and temperature uncertainties associated with the TUR in such systems?" (see Refs. 34,67,105,106,126). This suggestion seems plausible, particularly because the TUR does not apply to microcanonical (*i.e.*, thermally isolated) systems (see Ref. 121). TDSELs may also play a role in the generation of negative temperature eigenstates in PSLs which are out of "resonance" with their baths ($\varepsilon_{PSL} \neq \varepsilon_{bath}$; see Ref. 68).

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