

Thermodynamics Far From the Thermodynamic Limit

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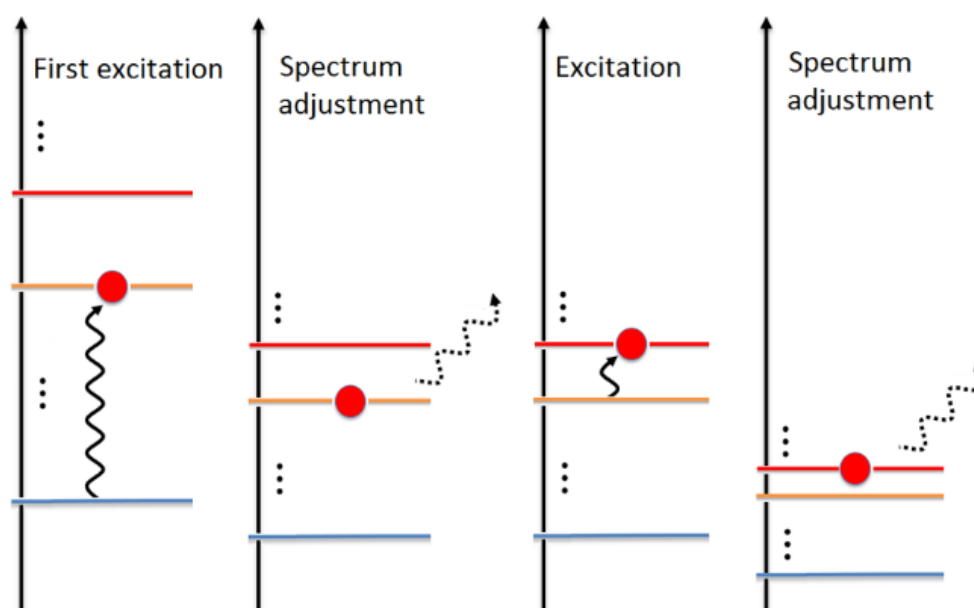
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Abstract

Understanding how small systems exchange energy with a heat bath is important to describe how their unique properties can be affected by the environment. In this contribution, we apply Landsberg's theory of temperature-dependent energy levels to describe the progressive thermalization of small systems as their spectrum is perturbed by a heat bath. We propose a mechanism whereby the small system undergoes a discrete series of excitations and isentropic spectrum adjustments leading to a final state of thermal equilibrium. This produces standard thermodynamic results without invoking system size. The thermal relaxation of a single harmonic oscillator is analyzed as a model example of a system with a quantized spectrum than can be embedded in a thermal environment. A description of how the thermal environment affects the spectrum of a small system can be the first step in using environmental factors, such as temperature, as parameters in the design and operation of nanosystem properties.



1. Introduction

Modern fabrication techniques are producing ever smaller systems that escape the paradigms of classical thermodynamics¹. This has stimulated interest in a quantum description of nonequilibrium processes, a phenomenon which has been studied using fluctuation relations²⁻⁵, quantum Brownian motion⁶, and the *eigenstate thermalization hypothesis* (see e.g. ref. 7). Indeed, the often appealing (see e.g. refs. 8-10) physical properties of *small* systems are intimately related to the discrete nature of their energy spectrum. Nevertheless, quantum systems do have thermal properties which are conditioned by the energy of the available eigenstates and the information these energies provide about the state of the system. Thus, understanding how a small system exchanges energy with a heat bath is crucial to describe how its properties can be affected by the environment.

Models have been proposed that treat the heat bath as a large collection of oscillators connected to the small system through springs (see e.g. refs. 11, 12 and references therein). A simpler approach that may be used to describe how energy spectra, and the resulting physical properties, are affected by thermal environments is extending the theory of temperature-dependent energy levels¹³ that Pathria and Beale refer to in their landmark textbook in Statistical Mechanics (see footnote in page 39 of ref. 14). This theory, first introduced by Rushbrook in 1940¹⁵ and later refined by Elcock and Landsberg in 1956¹³, accounts for the external thermal environment as a perturbation that results in a modified energy landscape. The temperature-dependence of energy levels is directly observable, for example, in semiconducting materials¹⁶, affecting properties of modern nanoscaled semiconductors^{17,18}, often in a manner which strongly deviates from bulk behavior^{19,20}.

Recently, effectively temperature-dependent Hamiltonians have been considered in stochastic thermodynamics²¹, and an explicitly temperature-dependent Hamiltonian has been used to analyze the dynamics of an optomechanical oscillator embedded in a heat bath²². In recent work²³ we have shown that Elcock and Landberg's theory¹³ of temperature-dependent energy levels provides a thermostistical basis to the renowned *Nanothermodynamics* that Hill introduced in the 1960s²⁴⁻²⁶, where he proposed a new thermodynamic potential to account for non-additive interactions between small systems (for a modern review and applications of Hill's theory see refs. 27,28). In this contribution, we apply Elcock and Landberg's theory¹³ to describe the progressive thermalization of small systems as their spectrum is perturbed by a heat bath. We propose a mechanism whereby the small system undergoes a discrete series of excitations and spectrum adjustments leading towards a state of thermal equilibrium. We show that, while the complete process is irreversible, each of the excitations is locally reversible. Known thermodynamic results, normally produced using the thermodynamic limit, are obtained without reference to system size. As a model example, we analyze a harmonic oscillator embedded in a heat bath, and we show that the thermalization process is affected by the relationship between the heat bath temperature and the fundamental frequency of the oscillator.

The rest of the paper is organized as follows. In Section 2, we present the theory of spectrum thermalization based on temperature-dependent energy levels. In Section 3, we use the theory to

analyze the energy and temperature of a harmonic oscillator as it comes to equilibrium with a thermal environment. Concluding remarks are given in Section 4.

2. A small system in a heat bath

In this section, we describe how the energy landscape available to a small system becomes progressively modified as it exchanges energy with a heat bath. The energy of a small system is characterized by the discrete eigenstructure of its Hamiltonian. As the system absorbs energy from the environment and gets excited to its n^{th} energy level, it adopts a temperature T_n , defined by

$$T_n = \frac{\mathcal{E}_n - \mathcal{E}_{n-1}}{S_n - S_{n-1}}, \quad (1)$$

where \mathcal{E}_n is the n^{th} eigenvalue of the Hamiltonian, and S_n is the associated entropy given by the Boltzmann entropy formula

$$S_n = k_B \ln g_n, \quad (2)$$

where k_B is Boltzmann's constant, and g_n is the degeneracy of the n^{th} energy level.

Due to the quantization of energy and entropy, there is a restricted set of temperatures (1) available for an isolated small system. In order for the system to achieve equilibrium with a thermal reservoir, the quantized energy spectrum must adapt so that (1) can conform to the externally dictated temperature. This brings us to the somewhat unusual notion of temperature-dependent energy levels¹³. The generalization is simple: assuming that the eigenvalues \mathcal{E}_μ of the Hamiltonian can be perturbed by the heat bath temperature (equilibrium temperature) T , then the equilibrium expression for the energy E of the system

$$E = k_B T^2 \sum_{\mu} P_{\mu} \frac{d}{dT} \ln(Z P_{\mu}) \quad \text{with} \quad Z = \sum_{\mu} e^{-\mathcal{E}_{\mu}/k_B T} \quad \text{and} \quad P_{\mu} = Z^{-1} e^{-\mathcal{E}_{\mu}/k_B T}$$

(where sums are taken over the microstates μ corresponding to each energy level, each of which has probability P_{μ}), reduces to¹³

$$E = \sum_{\mu} P_{\mu} \left(\mathcal{E}_{\mu} - T \frac{d\mathcal{E}_{\mu}}{dT} \right), \quad (3)$$

which differs from the usual expression only by the last term in the right hand side. For simplicity, we rewrite this expression as

$$E = \mathcal{E} - T \left\langle \frac{d\mathcal{E}_{\mu}}{dT} \right\rangle, \quad (4)$$

where $\mathcal{E} \equiv \langle \mathcal{E}_{\mu} \rangle$, and $\langle \cdot \rangle$ represents the average over all available microstates μ . Assuming the average $\langle d\mathcal{E}_{\mu}/dT \rangle$ is constant and taking increments on both sides yields

$$T\Delta S = \Delta\mathcal{E} - \left\langle \frac{d\mathcal{E}_\mu}{dT} \right\rangle \Delta T, \quad (5)$$

where the equilibrium temperature T is given by the usual $T = \Delta\mathcal{E}/\Delta S$.

Expression (5) is an extended second law of thermodynamics, first proposed by Shental and Kanter while modelling communication channels as thermal systems in their landmark contribution (ref. 29). More recently, Yamano has used this law to describe heat losses in thermoelectrical devices³⁰. This form of the second law of thermodynamics describes the following physical process: As a small system comes into thermal contact with a heat bath T , an amount of heat $\Delta\mathcal{E}$ is absorbed. This heat excites the system along its intrinsic energy/entropy landscape. The system then relaxes isentropically an amount $\langle d\mathcal{E}_\mu/dT \rangle \Delta T$ by simply changing the spacing between the energy levels. The contribution of the heat that increases the entropy of the system is thereby reduced from $\Delta\mathcal{E}$ to $\Delta\mathcal{E} - \langle d\mathcal{E}_\mu/dT \rangle \Delta T$. As we explain below, it is through a series of such excitations and spectrum adjustments that a small system comes to equilibrium with the heat bath.

Figure 1 illustrates how a heat bath progressively *thermalizes* a small system. Upon contact with the heat bath T , the system becomes excited along its quantized energy/entropy landscape until it adopts an energy level \mathcal{E}_n with temperature $T_n > T$. This excitation is followed by an isentropic relaxation that adjusts the system's temperature by simply bringing the energy levels closer together: the energy levels change from the original set $\{\mathcal{E}_j\}$ to become a perturbed set $\{\mathcal{E}_j^{(1)}\}$. As a result, although the system is still in its n^{th} energy level, the temperature is no longer $T_n > T$ given by (1), but instead a lower temperature $T_n^{(1)}$ which is equal to T . As the heat bath continues to emit photons, the system gets excited to the next energy level, now $\mathcal{E}_{n+1}^{(1)}$, and it adopts a temperature $T_{n+1}^{(1)} > T$. After this excitation, a new isentropic relaxation occurs that brings the energy levels even closer together, from the set $\{\mathcal{E}_j^{(1)}\}$ to the denser set $\{\mathcal{E}_j^{(2)}\}$. As a result the temperature of the system is lowered from $T_{n+1}^{(1)} > T$ to a lower $T_{n+1}^{(2)}$ which is equal to T . The process is repeated in a sequence of increasingly smaller excitations to levels $\mathcal{E}_{n+z}^{(z)}$ with temperature $T_{n+z}^{(z)}$ given by

$$T_{n+z}^{(z)} = \frac{\Delta\mathcal{E}}{\Delta S} = \frac{\mathcal{E}_{n+z}^{(z)} - \mathcal{E}_{n+z-1}^{(z)}}{S_{n+z} - S_{n+z-1}} > T, \quad (6)$$

and isentropic relaxations to temperatures $T_{n+z}^{(z+1)}$ obeying

$$T_{n+z}^{(z+1)} = T. \quad (7)$$

At the limit, the energy levels form a continuum and the system fluctuates reversibly in the heat bath.

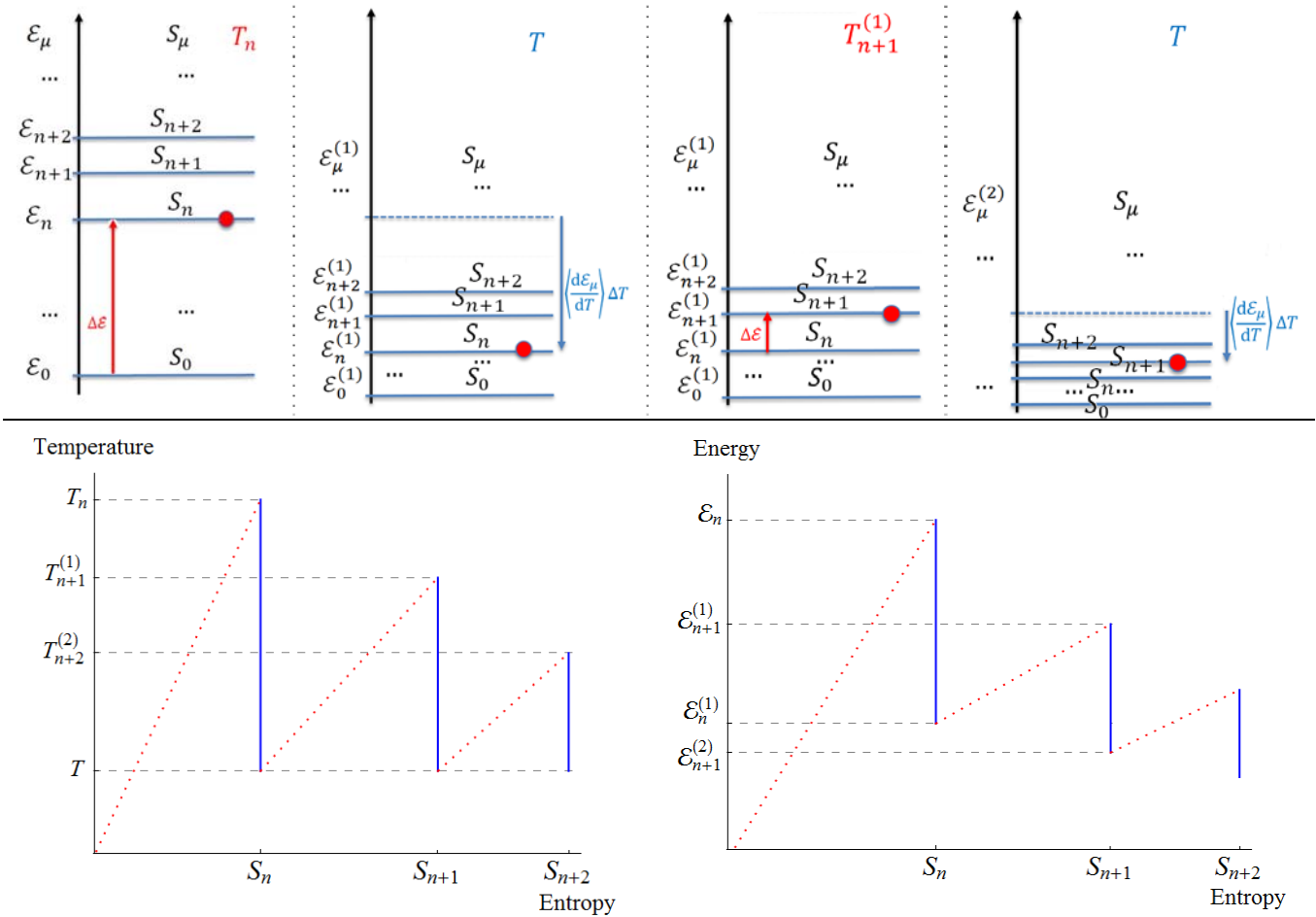


Figure 1. An isolated small system absorbs a photon from a heat bath T . It is thereby excited to a level with energy ϵ_n , entropy S_n given by (2), and temperature $T_n > T$ given by (1). The energy spectrum is thereafter isentropically relaxed from the original set $\{\epsilon_j\}$ to the perturbed set $\{\epsilon_j^{(1)}\}$ in order for the system to adopt the heat bath temperature T given by (7). As a result, the system's energy is isentropically lowered from ϵ_n to $\epsilon_n^{(1)}$. A new photon is absorbed from the heat bath, resulting in a new excitation from level $\epsilon_n^{(1)}$ to $\epsilon_{n+1}^{(1)}$ and a higher temperature $T_{n+1}^{(1)} \in (T, T_n)$ given by (6). The spectrum is thereafter isentropically relaxed from the set $\{\epsilon_j^{(1)}\}$ to the denser set $\{\epsilon_j^{(2)}\}$ in order to newly adopt the heat bath temperature T given by (7). As a result, the system's energy is isentropically lowered from $\epsilon_{n+1}^{(1)}$ to $\epsilon_{n+1}^{(2)}$. After a new excitation, the system is brought from $\epsilon_{n+1}^{(2)}$ to $\epsilon_{n+2}^{(2)}$ and adopts a temperature $T_{n+2}^{(2)} \in (T, T_{n+1}^{(1)})$ given by (6). The process is repeated in a sequence of increasingly smaller energy exchanges until the spectrum becomes a continuum and the small system fluctuates reversibly in the heat bath.

It should be noted that, when an excited energy state with temperature $T_{n+z}^{(z)} > T$ shall relax to T , it faces two choices: either it spits back the exciting photon $\Delta\epsilon$ (*i.e.* it moves to the left in Fig. 1), or it modifies its spectrum by relaxing $\langle d\epsilon_\mu/dT \rangle \Delta T$ (to the right in Fig. 1). Looking at eq. (5), we see that the change in free energy going to the left is equal to the change in free energy going to the right, namely $-\langle d\epsilon_\mu/dT \rangle \Delta T$. This means that the system is equally likely to make either choice. This local reversibility is not at odds with the irreversibility of the total process. As long as the system's spectrum is discrete, it will continue to assimilate finite energy packets from the heat bath. Climbing up the entropy ladder over increasingly smaller energy gaps (to the right) is over time more favorable than it would be to increase the energy at constant entropy (to the left). It has indeed recently been argued that the ultimate cause

behind macroscopic irreversibility can be traced back to an inherent irreversibility in photon-exchange processes between small systems and their environment^{31,32}.

For every step in the process, there is an amount of heat $\Delta\mathcal{E}$ that is absorbed, and an amount of work $\langle d\mathcal{E}_\mu/dT \rangle \Delta T$ done on the spectrum. The efficiency η_z of the z^{th} step is the ratio of the work to the heat, which, invoking (5) and (6) reduces to

$$\eta_z = 1 - \frac{T}{T_{n+z}^{(z)}}. \quad (8)$$

Remarkably, expression (8) is similar to the efficiency of a heat engine operating reversibly between a hot reservoir at temperature $T_{n+z}^{(z)}$ and a cold reservoir at temperature T (see *e.g.* ref. 33). In the thermalization process we describe, an amount $\Delta\mathcal{E} - \langle d\mathcal{E}_\mu/dT \rangle \Delta T$ of heat results in an entropy increase (5), which may be thought of as heat arriving at a cold reservoir. The system releases energy $\langle d\mathcal{E}_\mu/dT \rangle \Delta T$ into the environment by relaxing its spectrum, which may be thought of as work done by the system on the environment. The heat supplied, $\Delta\mathcal{E}$, depends on the difference between the heat bath temperature T and the temperature $T_{n+z}^{(z)}$ of the system's next excited state; this heat, however, is not flowing from hot to cold, it is just a fluctuating exchange between the heat bath (who supplies $\Delta\mathcal{E}$) and the system (who gives back $\langle d\mathcal{E}_\mu/dT \rangle \Delta T$).

As we shall see below, the level n of the first excitation depends on the temperature of the heat bath. It is important to note that the temperature of any finite system is generally greater than the temperature of the heat bath, becoming equal only in the thermodynamic limit, as thoroughly argued by Pyun³⁴ and McFee³⁵. Combining (5) and (6) we see that these two temperatures are related by

$$\frac{T_{n+z}^{(z)}}{T} = \left(\frac{\frac{\Delta\mathcal{E}}{\Delta T}}{\frac{\Delta\mathcal{E}}{\Delta T} - \langle \frac{d\mathcal{E}_\mu}{dT} \rangle} \right), \quad (9)$$

becoming indeed equal as the heat capacity explodes in the thermodynamic limit. Another way of equalizing both temperatures, irrespective of size, is by the thermalization process described above, which turns the spectrum into a continuum and leaves no room for further spectrum perturbations $\langle d\mathcal{E}_\mu/dT \rangle$.

It should also be noted that, when all energy levels are pressed together as $z \rightarrow \infty$, then the degeneracy of the $(n+z)^{\text{th}}$ energy level approaches $g_{n+z} + g_{n+z-1} + g_{n+z-2} + \dots + g_0$, and as a result the entropy S_{n+z} (2) becomes

$$k_B \ln \sum_{m \leq n+z} g_m, \quad (10)$$

which is Gibbs' volume entropy. This alternative entropy is known to be equivalent to the Boltzmann entropy (2) in the thermodynamic limit³⁶. The thermalization process described here produces the same result irrespective of system size.

3. Example: Harmonic Oscillator

A harmonic oscillator is a simple example of a small system whose spectrum can be affected by a thermal environment. The harmonic oscillator model can be used to describe a particle whose position is constrained to remain approximately the same, such as an atom in a molecule. A practical example are nanomechanical oscillators, which are very sensitive to thermal noise^{37,38} and can, under controlled temperature conditions, be used as high precision mechanical sensors³⁹. Harmonic effects are also important when modelling electronic-vibrational coupling and band-gap changes in single molecules^{40,41}, modern nanosemiconductors²⁰, and quantum dots⁴².

We consider a single three-dimensional isotropic oscillator with fundamental frequency ω , energy \mathcal{E}_m and degeneracy g_m given, respectively, by

$$\mathcal{E}_m = (m + 3/2)\hbar\omega, \quad (11)$$

$$g_m = (m + 1)(m + 2)/2, \quad (12)$$

where \hbar is the reduced Planck constant and m is a natural number. As the oscillator comes into contact with a heat bath T , it is excited to a temperature $T_n > T$ given by (1). The level n of this first excitation depends on the relationship between the heat bath energy $k_B T$ and the transition energy $\hbar\omega$ of the oscillator. After the first excitation, the system undergoes a series of spectrum relaxations and new excitations, as illustrated in Fig. 1. Each spectrum relaxation adjusts the frequency of the oscillator just enough to reduce the numerator in (1) and have the system adopt temperature T .

If $k_B T$ is small compared to $\hbar\omega$, the first excitation upon contact with the heat bath is small; many spectrum contractions and excitations must follow before the system occupies highly entropic energy levels. On the other hand, if $k_B T$ is large compared to $\hbar\omega$, the first excitation is many levels up, and the thermalization process can start from a higher energy level. The number of thermalization steps needed to achieve a certain T_{system}/T is lower for larger $k_B T/\hbar\omega$. Following the initial excitation, the number z of relaxation-excitation steps needed to achieve $T_{system} \leq (1 + \alpha)T$ is given by

$$z = \begin{cases} 1 + \left\lceil \frac{1}{\alpha} - 2 \frac{k_B T}{\hbar\omega} \right\rceil & \text{if } 0 < \frac{k_B T}{\hbar\omega} \leq 1/\ln \left[\frac{\lceil 1/\alpha \rceil + 1}{\lceil 1/\alpha \rceil - 1} \right] \\ 1 & \text{if } \frac{k_B T}{\hbar\omega} \geq 1/\ln \left[\frac{\lceil 1/\alpha \rceil + 1}{\lceil 1/\alpha \rceil - 1} \right] \end{cases}, \quad (13)$$

where $\lceil x \rceil \equiv \min\{p \in \mathbb{Z} | p \geq x\}$. Figure 2 shows two examples that start the thermalization process from the first excited state (left) and the fourth excited state (right), and come within 10% of the heat bath temperature after 10 and 7 steps, respectively.

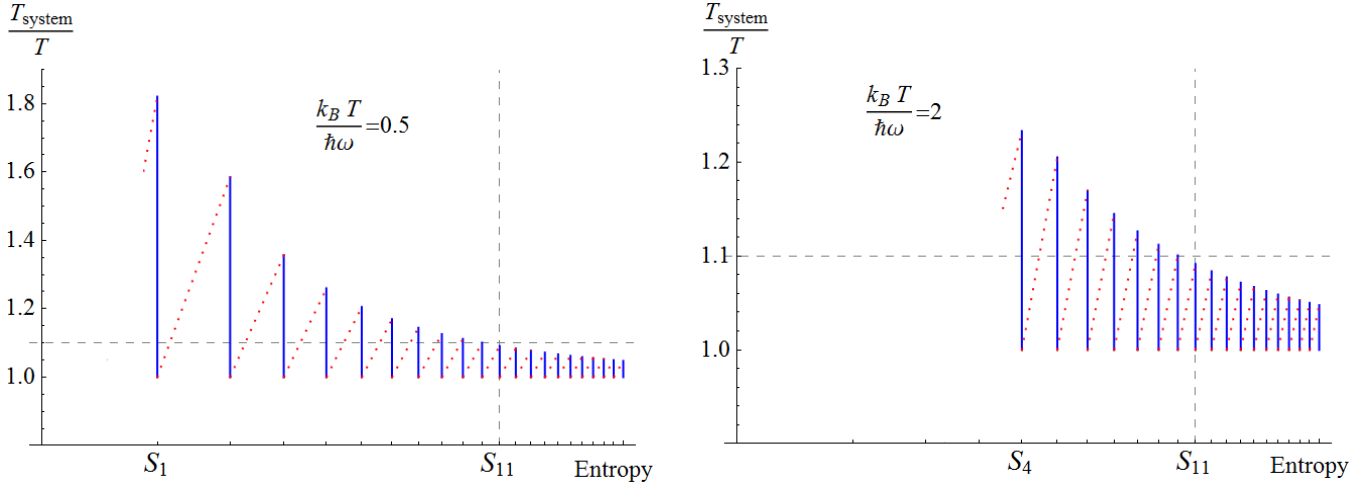


Figure 2. The first steps in the thermalization process of a harmonic oscillator, with $k_B T / \hbar \omega = 0.5$ and $k_B T / \hbar \omega = 2$. When $k_B T / \hbar \omega$ is greater, the thermalization process starts from a higher energy level. Following the initial excitation, the number of relaxation-excitation steps required to achieve a certain T_{system}/T decreases with the ratio $k_B T / \hbar \omega$.

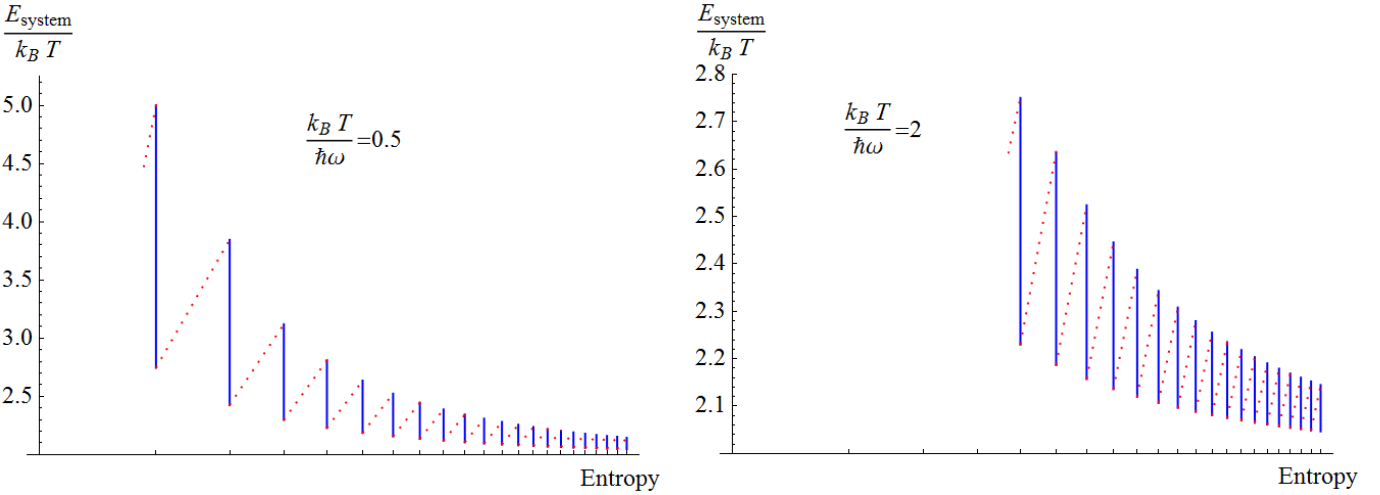


Figure 3. The internal energy of the small system evolves towards an equilibrium value.

The system evolves towards equilibrium with its environment by successively absorbing photons (excitations) and releasing energy (spectrum relaxations). The internal energy of the system evolves accordingly towards an equilibrium value. In the case of a single three-dimensional oscillator, that value is $2k_B T$, as shown in Fig. 3. This value, which may appear to be at odds with the equipartition theorem, is explained in the following.

For an Einstein solid with N three-dimensional oscillators and q energy quanta, the internal energy may be expressed in terms of the equilibrium temperature as

$$qk_B T \ln[1 + 3N/q],$$

which, in the high temperature ($q \gg 1$) limit, becomes $3Nk_B T$. In ref. 23 (eq. 43 therein) we showed that, if the solid is in its m^{th} energy state, then the energy may be also be expressed as

$$qk_B T_m \ln[1 + 3N/q - 1/q],$$

where T_m is not the equilibrium temperature T , but instead the temperature (1) corresponding to the m^{th} state of the unperturbed system. When the system relaxes its spectrum and lowers its m^{th} energy level in order to make T_m equal to T , an amount $k_B T$ of energy is released to the environment. Indeed, if T_m is made equal to T , the last expression becomes $(3N - 1)k_B T$ as opposed to $3Nk_B T$. In ref. 23, we show that the missing $k_B T$ can be identified as the subdivision potential Hill introduced in his top-down nanothermodynamics²⁶.

4. Concluding remarks

Extending the descriptive scope of thermodynamics beyond bulk systems is becoming increasingly relevant as we develop the ability to fabricate ever smaller systems. Understanding how small systems exchange energy with a heat bath is important to describe how their unique properties can be affected by the thermal environment. In this work we have used Elcock and Landsberg's theory of temperature-dependent energy levels¹³ to account for the progressive thermalization of small systems without invoking the thermodynamic limit. We have shown that, as the small system is thermalized, its microcanonical temperature (1) approaches the heat bath's canonical temperature, which is a classical thermostistical result usually reliant on system size. Another thermodynamic result that requires the large system limit is the equivalence between Boltzmann's surface entropy (2) and Gibbs' volume entropy (10); we have shown this equivalence occurs, irrespective of system size, when the system's energy levels are perfectly compressed at the end of the thermalization process. Both the classical thermodynamic limit and the spectrum thermalization process we describe result in an energy continuum. However, the latter is better suited to account for small systems, which can be seen as a subsystem in a larger heterogeneous thermodynamic system.

As a model example that has a quantized energy spectrum and can be embedded in a thermal environment, we have analyzed a single harmonic oscillator. We have shown how the number of steps in the thermalization process is affected by the ratio of the heat bath temperature to the oscillator's fundamental frequency. When the heat bath energy $k_B T$ is small compared to the oscillator's quantum $\hbar\omega$, the system must begin with a small excitation and undergo many spectrum contractions to approach thermal equilibrium. On the other hand, if $k_B T$ is large compared to $\hbar\omega$, the thermalization process can start from a higher energy level and fewer spectrum contractions are needed to approach equilibrium.

Whether or not a system can be considered *small* is not so much a function of its sheer physical size, but most importantly characterized by how it is affected by its surroundings (see *e.g.* refs. 23,43). Truly small systems are always embedded in some kind of environment with which they have non-trivial interactions as they evolve towards equilibrium. As we have shown, the spectrum perturbation caused by the heat bath makes the microcanonical temperature evolve towards the canonical temperature. This idea could be useful, for example, to describe how a nanoparticle comes to thermal equilibrium with a photon gas⁴⁴ and how the temperature of a protein equilibrates with that of the environment⁴³.

In nonequilibrium systems where thermal equilibrium exists, a similar analysis may be used, for example, to explore how a grand-canonical environment perturbs the energy spectrum and drives the evolution of the chemical potential of a small system, something which may be relevant to describe mass transfer processes in biological systems and in chemical reactions. Understanding how the environment affects the spectrum of a small system can be the first step in using environmental factors, such as temperature or chemical potential, as parameters in the design and operation of nanosystem properties.

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