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Temperature-dependent energy levels and size-independent thermodynamics

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We show that, by properly adopting the notion of temperature-dependent energy levels,1,2 the standard tools of differential thermodynamics can be used for a consistent thermostatistical description irrespective of system size. In this framework the paradigmatic (yet not always descriptive) large-system limit is no longer a necessary assumption for differential thermodynamics. We present a generalized relation between temperature and internal energy which extends thermodynamics all the way to isolated quantum systems.

The notion of temperature dependent energy levels in statistical mechanics was introduced by Rushbrooke in 19401 and later refined by Elcock and Landsberg in 1956.2 More recently, Shental and Kanter have proposed temperature dependent energy levels to model information processing systems as thermal systems.3

While 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 any physical system must in general be temperature-dependent.1,2 In this work it is shown that, when this temperature-dependence is carefully considered, the standard tools of statistical thermodynamics can be used to provide a consistent thermostatistical description of physical systems irrespective of their size.

The key to the connection between the atomistic, microscopic theory of matter, and macroscopic thermodynamics is the entropy $S$ and its unique relation to the number $\omega$ of microstates:4

$$ S = k_B \ln \omega. \quad (1) $$

When a physical system is in macrostate $\mathcal{M}$, it can be in different microstates, each characterized by an eigenvalue $E_\mu$ of a temperature-independent Hamiltonian. The mean energy $U$ of the system, however, is a temperature-dependent ensemble average:

$$ U = \langle E_\mu \rangle_{\mathcal{M}}, \quad (2) $$

where $\langle \cdot \rangle_\mathcal{M}$ denotes an average over all microstates compatible

with a temperature-determined macrostate $\mathcal{M}$ (this subscript will in the remainder be dropped for convenience). For a system at equilibrium, this mean energy is the same as the internal energy, and the temperature $T$ given by

$$ T^{-1} = \frac{\delta S}{\delta U} \quad (3) $$

Temperature dependent energy levels.—Following [1, 2], the permissible energy levels $E_\mu$ of a physical system are in general temperature-dependent as

$$ E_\mu = E_\mu + T \frac{d E_\mu}{d T} \quad (4) $$

where the $E_\mu$’s form a discrete set of temperature-independent energy levels. The ensemble average $U$ of the levels $E_\mu$ may be given in terms of the ensemble average $\mathcal{E}$ of the $E_\mu$ as follows (see (2.13) in [2]):

$$ U = \mathcal{E} - T \left( \frac{d E_\mu}{d T} \right). \quad (5) $$

Size-independent thermodynamics.—In the following, we show how the notion of temperature-dependent energy levels enables statistical thermodynamics to describe physical systems irrespective of their size. We begin with the example of a monoatomic ideal gas of $N$ particles in $D$ dimensions, whose density of states $\tilde{\omega}$ depends on the internal energy $U$ as follows:

$$ \tilde{\omega}(U) \propto U^{d N D - 1}. $$

Following (1) and (3) the entropy $S$ and temperature $T$ are given by

$$ S = k_B \ln \left[ \frac{N D}{U T^{-1}} \right] + \text{constant}, \quad T^{-1} = \frac{N D - 2 k_B}{2} \frac{1}{U} \quad (6) $$

In the limit where $N \gg 1$ expression (6) yields the expected thermodynamic result that assigns energy $k_B T/2$ to each kinetic degree of freedom. However, in the trivial case where $N=D=1$, a negative temperature results, rendering the thermodynamic analysis unphysical. This problem, however, can be circumvented by substituting (5) into (6):
\[
E = \frac{N\hbar^2}{2I} + \frac{1}{2} k_BT + T \left( \frac{\partial E}{\partial T} \right),
\]
(7)

We can now think of \((\partial E_\mu / \partial T)\) as a parameter given by the single particle boundary condition that \(E = k_BT\) when \(N = D = 1\). This results in \((\partial E_\mu / \partial T) = k_BT\) and

\[
E = \frac{N\hbar^2}{2I} + \frac{1}{2} k_BT, \tag{8}
\]

which is physically descriptive irrespective of system size. The monatomic ideal gas is a generalization of the particle in a box, and, not surprisingly, analysis of a single particle in a box (where \(\omega(U) \propto 1/\sqrt{T}\)) also yields \(E = k_BT\) when \(U\) is the single harmonic oscillator, namely expressions (9) to (11) with \((\partial E_\mu / \partial T) = k_BT\).

The next example we consider is a single quantum harmonic oscillator in one dimension with fundamental frequency \(v\). The internal energy \(U(v) = (n + 1/2)hv\) and density of states \(\omega(v) = 1/hv\) yield the following inverse temperature:

\[
T^{-1} = k_B \left( \frac{dU}{dv} \right)^{-1} \ln \omega = \frac{k_B}{v}.
\]
(9)

As anticipated, this result is unphysical, for standard statistical thermodynamics is a macroscopic theory applicable only to very large systems. However, substituting (5) into (9), we obtain

\[
E = -k_BT + T \left( \frac{\partial E_\mu}{\partial T} \right). \tag{10}
\]

As before, we can think of \((\partial E_\mu / \partial T)\) as a parameter given by a single particle boundary condition, namely \(E = k_BT\) when \(N = 1\). This results in \((\partial E_\mu / \partial T) = 2k_BT\) and (10) becomes

\[
E = k_BT. \tag{11}
\]

Analysis of a single rigid rotor with moment of inertia \(I\), where \(U(Z) = \ell(\ell + 1)\hbar^2/Z^2\), and \(\omega(Z) = (2\ell + 1)2/h^2\), yields results exactly similar to those of the single harmonic oscillator, namely expressions (9) to (11) with \((\partial E_\mu / \partial T) = 2k_BT\). This is consistent considering that both the rigid rotor and harmonic oscillator have two equipartitioned degrees of freedom.

We consider next a system of \(N\) two-level non-interacting particles with levels 0 and \(\varepsilon\). At any given moment there are \(n \leq N\) particles in the upper energy state. It follows that the total internal energy of the system is given by \(U(n) = n\varepsilon\). The number of microstates for a given configuration is given by

\[
\omega(n) = \frac{N!}{(N-n)!n!}.
\]

Following (1) and (3), the inverse temperature results in the following expression:

\[
T^{-1} = k_B \left( \frac{dU}{dn} \right)^{-1} \ln n = k_B \left( H[N-n] - H[n] \right),
\]

where \(H[m]\) is the \(m\)th harmonic number. In terms of internal energy \(U\), this expression may be written as

\[
U = n k_BT \left( H[N-n] - H[n] \right). \tag{12}
\]

Substituting (5) into (12), we obtain

\[
E = n k_BT \left( H[N-n] - H[n] \right) + T \left( \frac{\partial E_\mu}{\partial T} \right).
\]

In the single particle limit, when \(N = n = 1\), we obtain \(E = k_BT\) with \((\partial E_\mu / \partial T) = 2k_BT\). We may then write the final expression

\[
E = n \left( \left( H[N-n] - H[n] \right) + 2/n k_BT \right). \tag{13}
\]

This expression shall be valid for all values of \(N\) and \(n\). As \(N\) becomes large it reduces to the usual large-system result by taking Stirling's approximation \(H(x) = \ln[x]\) when \(x >> 1\). It is also worth noting that, as expected, the expression above gives positive temperatures when \(n < N/2\), and negative temperatures when \(n > N/2\). The positive and the negative temperatures become increasingly symmetric as \(N\) grows larger.

As a last example we consider an Einstein solid with \(N\) oscillators and \(q\) energy units of size \(\varepsilon\). The number of microstates is given by

\[
\omega(q) = \frac{(q+N-1)!}{q!(N-1)!},
\]

and the internal energy by \(U(q) = q\varepsilon\). Applying (1) and (3) we obtain for the inverse temperature

\[
T^{-1} = k_B \left( \frac{dU}{dq} \right)^{-1} \ln q = \frac{k_B}{\varepsilon} \left( H[q + N - 1] - H[q] \right),
\]

which may be written as

\[
U = q k_BT \left( H[q + N - 1] - H[q] \right). \tag{14}
\]

Substituting (5) into (14) we obtain

\[
E = q k_BT \left( H[q + N - 1] - H[q] \right) + T \left( \frac{\partial E_\mu}{\partial T} \right).
\]

In the limit when \(N = 1\), the energy simply reduces to \(T(\partial E_\mu / \partial T)\). As \(N\) gets larger, this term becomes increasingly insignificant, and the usual large system result is recovered by taking Stirling's approximation.

**Generalized absolute temperature.**—Inserting (5) into (3), yields a simple relation that connects the standard thermodynamic temperature \(dU/dS\) with the generalized temperature \(d\varepsilon/dS\).

\[
\frac{d\varepsilon}{dS} = \frac{d\epsilon}{dS} \left( 1 - \frac{\epsilon}{k_B T} \right)^{-1}. \tag{15}
\]

When the system is large, the heat capacity \(d\varepsilon/dT\) is much larger than \((\partial E_\mu / \partial T)\) (which is of order \(k_BT\) and both temperatures are equal. However, when systems are small, the standard thermodynamic temperature \(dU/dS\) needs to be corrected. The examples above show that the correction yields a proper thermostatistical description of small systems.

Expression (15) is reminiscent of expression (14) in [5], which is generally incorrect, as it only captures the special cases where \((\partial E_\mu / \partial T) = k_BT\). For a more comprehensive critique of [5], where Dunkel and Hilbert challenge the well-established notion of negative absolute temperatures, the reader is referred to [10—12].

A **generalized second law of thermodynamics.**—For closed systems at constant volume, \(d\varepsilon = dq\) (where \(q\) is the heat added to the system), and (15) results in the generalized second law of thermodynamics proposed by Shental and Kanter for the analysis of information processing systems:

\[
dS = \frac{dq}{\bar{T}} - \frac{1}{\bar{T}} \left( \frac{\partial E_\mu}{\partial T} \right) dT.
\]
This modified second law has been successfully used to model communication channels as thermal systems.  

Conclusions

In this work we show that, by adopting the notion of temperature-dependent energy levels, 1,2,12 the standard tools of differential thermodynamics can be used for a consistent thermostatistical description irrespective of system size. In this framework, the paradigmatic (yet not always descriptive) large-system limit is no longer a necessary assumption for differential thermodynamics. We present a generalized relation between the temperature and the internal energy of a system which extends thermodynamics all the way to isolated quantum systems.

Notes and references

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7 P. Hakonen and O. V. Lounasmaa, Science, 1994, 265, 1821.