Entropy behavior for isolated systems containing bounded and unbounded states: latent heat at the inflection point

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Abstract

Systems like the Morse oscillator with potential energies that have a minimum and states that are both bounded and extended are considered in this study in the microcanonical statistical ensemble. In the binding region, the entropy becomes a growing function of the internal energy and has a well-defined inflection point corresponding to a temperature maximum. Consequently, the specific heat supports negative and positive values around this region. Moreover, focusing on this inflection point allows to define the critical energy and temperature, both evaluated analytically and numerically. Specifically, the existence of this point is the signature of a phase transition, and latent heat dynamics occur to accomplish the transition. The conditions established below apply to a large variety of potentials, including molecular ones, and have relevance for physics, chemistry, and engineering sciences. As a specific application, we show that the inflection point for the \(H_2\) molecule occurs at \(-1.26\) [eV].

Nomenclature

\begin{align*}
A & \quad \text{Energy parameter defining the potential} \\
\alpha & \quad \text{Distance parameter defining the potential} \\
D & \quad \text{Dimensionless parameter related to the mass} \, M \, \text{of diatomic molecules} \\
U & \quad \text{Internal energy (thermodynamics)} \\
E & \quad \text{Energy spectrum} \\
S & \quad \text{Entropy} \\
T & \quad \text{Temperature} \\
C & \quad \text{Specific heat} \\
K & \quad \text{Kinetic energy} \\
H_2 & \quad \text{Hydrogen molecule}
\end{align*}

1. Introduction

Many physical systems show a change in the concavity of the entropy as a function of the energy with important thermodynamic implications (star, isolated clusters, cluster of 147 sodium atoms, Ar39 cluster, small systems, finite quantum systems, magnetically self-confined plasma [1–7]). The concavity’s point of change—the inflection point—becomes directly related to the divergence of the specific heat. At this point, the temperatures do not change even when heat is supplied. Hence, the conditions for latent heat are satisfied, a signature of a phase transition. This work focuses on studying this inflection point for bounded potentials.

A common application, Morse’s potential is a dressed approximation describing intramolecular interactions that allow for dissociations [8–10]. It has been considered widely in treatments of molecular bonds [11, 12] and...
applications of the Fokker-Planck equations for lasers [13]. Morse’s potential as a function of distance \( x \) (one-dimensional) is given by

\[
V(x) = A(e^{-2\alpha x} - 2e^{-\alpha x}).
\]  

(1)

The positive quantity \( A \) is formally called the dissociation energy and \( \alpha^{-1} \) defines a characteristic length. Note that for \( \alpha x \ll 1 \), the potential \( V(x) \) reduces to the usual harmonic oscillator in the low-energy regime. Furthermore, the associated spectrum is the union of a finite set of levels and the continuum. The discrete energy spectrum \( E \) is [8–10, 14]

\[
E = -A \left[ 1 - 2D \left( n - \frac{1}{2} \right) \right]^2 \quad \text{with} \quad -A(1-D)^2 \leq E < 0,
\]  

(2)

where \( D = \alpha \hbar / \sqrt{8AM} \) is a dimensionless parameter and, for diatomic molecules, \( M \) denotes the reduced mass. Each energy level is labeled by an integer index \( n \) that must satisfy

\[
1 \leq n < \frac{D + 1}{2D}
\]  

(3)

Consequently, for parameter values \( D > 1 \), only dissociated states exist, whereas if \( 0 < D < 1 \), discrete levels occur.

In this study, the calculations and graphs are explicitly related to the \( \text{H}_2 \) molecule. In this instance, we assume [15] \( A \sim 7.61 \times 10^{-11} \) [J] (or \( 4.7563 \) [eV]), \( \alpha \times 10^{-8} \) [1/meter] and therefore, dimensionless quantity \( D \) becomes \( \sim 2.8512 \times 10^{-2} \). Like Morse’s potential here considered, similar treatments can be undertaken for the Poschl-Teller, Hulthen, and Kratzer potentials, or other low-bounded potentials [14] like Van der Waals’.

As mentioned, the energy potential from equation (1) is used in modeling the internal interaction used for diatomic molecules. However, the rotational degrees of freedom will be excluded [16]. Indeed, rotational molecular excitations usually fall in the microwave region of the energy spectrum. Consequently, these energies are of order \( 10^{-5}–10^{-2} \) [eV] which are smaller than the characteristic vibrational energies treated here \( (A \sim 4.7563 \) [eV]).

In this work, we consider the standard entropy definition as related to the number of microscopic configurations for a given macroscopic state, also related to configurational disorder, or complexity. Formally, all thermodynamic quantities like temperature, specific heat, or others can be obtained from entropy. Also, assume that the phase transition supports the use of thermodynamic formalism. Then, the system temperature is determined based on the statistical-thermodynamic long-time average. In fact, we proceed to first obtain the entropy for the systems described by equation (2) and computing the corresponding thermodynamic quantities. As mentioned, particular emphasis will be put on the (negative) specific heat and implication for Morse’s potential.

In section 2, in the microcanonical ensemble for vibrational modes, the entropy is calculated for Morse’s potential. Significantly, it has a well characterized inflection point. Furthermore, temperature and specific heat are obtained showing that the latter diverges at the inflection point and is associated with instabilities [17]. Negative and positive heat capacities arise for this potential, being the main topic in this work. Specific applications are realized on the \( \text{H}_2 \) molecule. In section 3, always in the microcanonical, are stated the general requirements on other binding potentials with positive/negative heat capacities. Conclusions appear in the last section.

2. The inflection point for entropy

In this section, we use the concept of entropy defined in the microcanonical ensemble where no external perturbations exist and, equal probability of states is take-up. In fact, it corresponds to a particular case of information entropy. This work assumes that information entropy is equivalent to thermodynamic entropy. Discussions about this topic are well developed in a pivotal reference due to Jaynes [18]. A specific application of information entropy, different from thermodynamic entropy, can be seen in [19].

Consider a set of independent subsystems, for instance, diatomic \( \text{H}_2 \) molecules, each with internal levels modeled according to equation (2). As long as in one spatial dimension the quantum number \( n \) corresponds to the integrated density of states [1], it could be related directly to the entropy by [20, 21] \( S = \kappa \ln(n) \) with \( \kappa \), the Boltzmann constant. This relationship connects microscopic properties with macroscopic ones. For large dimensions other than 1, it is not true that \( n \) corresponds to the integrated density of states; nevertheless, in section 3 we generalize our result for more dimensions and consider other cases with positive/negative specific heat. Upwards, only to accentuate the thermodynamics notation, the formal replacement \( E \rightarrow \bar{U} \) will be assumed. Consequently, from equation (2) the entropy \( \kappa \ln(n) \) (per sub-system) necessarily becomes
where internal energy has a range (figure 1):

\[ U_{\text{min}} \leq U \leq 0, \quad \text{with } U_{\text{min}} = -A(1 - D)^2 \]  

To determine the minimum internal energy \( U_{\text{min}} \), we solve the equation \( S(U_{\text{min}}) = 0 \); for the hydrogen molecule \( U_{\text{min}} \sim -4.4889 \text{ [eV]} \) being distinct from \( -A \) because in this instance \( D \neq 0 \). Likewise, from equation (4), the entropy has range (figure 1)

\[ 0 < S < S_{\text{max}} \quad \text{with } S_{\text{max}} = k \ln \left( \frac{D + 1}{2D} \right), \]

where \( S_{\text{max}} = S(U = 0) \).

Regarding entropy definition, we have used the Boltzmann entropy instead of Gibbs since we are working in the ensemble with constant energy (i.e. a surface in the phase space). Discussions on this subject of descriptions can be followed through references [17, 22–24]. With the parameter values corresponding to the \( H_2 \) molecule, figure 1 shows the variation of the entropy \( S(U) \) which is a growing function of the internal energy \( U \) with an inflection point (dashed line, \( U_c \)). Additionally, also from equation (4), temperature can be obtained as a function of the internal energy (figure 2).

Figure 1. Normalized entropy \( S/k \) as a function of the internal energy \( U \text{[eV]} \) for Morse’s oscillator applied to the \( H_2 \) molecule. An inflection point exists at \( U_c \sim -1.26 \text{ [eV]} \), dashed vertical line, meaning a change in sign of the specific heat.

Figure 2. Temperature \( kT \text{[eV]} \) as a function of internal energy \( U \text{[eV]} \). At \( U_c \) (dashed line) a temperature maximum emerges related to the entropy inflection point (figure 1).

\[
S(U) = k \ln \left[ \frac{1}{2D} \left( D + 1 - \sqrt{\frac{U}{A}} \right) \right].
\]  

(4)
Further, and a main result in this paper, because the entropy concavity is related to the sign of the specific heat through \[ S(U) = -[S'(U)]^2, \] a negative (positive) specific heat necessarily appears for energy values larger (smaller) than \( U_c \).

As in \[17\], this transition in the heat capacity in the microcanonical ensemble echoes instabilities. These become operatives when the systems are not isolated and, in our case, correspond possibly to molecular dissociations.

At volume constant, always from equation \( 4 \), as long as temperature \( T \) is given by the well-known expression in the microcanonical ensemble \[ 16, 20, 21 \] it becomes (figure 2).

\[
\frac{kT}{2A} = \left(D + 1 - \sqrt{\frac{U}{A}}\right) - \sqrt{\frac{U}{A}}. \tag{8}
\]

Explicitly, from equations \(7\) and \(8\) the range of temperatures is \( 0 \leq T \leq T_c \), i.e., there is a maximum for the temperature (figure 2). And at a fixed temperature, the energy becomes multivalued \[18, 19\] opening the route to both positive and negative specific heats, as mentioned.

As the main topic in this work, specific heat, at volume constant, can be calculated directly from equation \(8\) with the standard definition in the microcanonical ensemble \[21\] \( C = \partial U / \partial T \):

\[
C = -k \frac{\sqrt{\frac{U}{A}}}{D + 1 - 2\sqrt{\frac{U}{A}}}, \tag{9}
\]

and directly plotted in figure 4. Divergence occurs at critical energy \( U_c \) defined by equation \(7\). Additionally, when \( U \sim U_{\min} \) and \( D \to 0^+ \) then \( C \sim k \) similar to the usual harmonic oscillator in the canonical ensemble (Dulong-Petit rule). Therefore, presumably at the bottom range of energies, the microcanonical and canonical ensembles are expected to be equivalent.

Figure 5 shows similarly the specific heat but as function of the temperature \( C(T) \). As occur at low energy, at low temperature, the positive branch tends to 1 in good accord with the specific heat for the classical oscillator.

As long as the specific heat is divergent at the inflection point (figure 4), the temperature remains constant (i.e., \( dT/dt = 0 \)) when heat flux exists in that point. That is, a signature of a transition and latent heat \[21\] becomes operative. Finally, the existence of positive and negative specific heats similarly holds for other binding potentials with a minimum in the energy potential (Poschl-Teller, Hulthen, Kratzer, and others \[14\]). The next section formalizes this generalization.

### 3. Generic thermodynamic systems with positive/negative specific heat

For a large variety of systems, including any spatial dimension, the following three statements ensure that the thermodynamic function \( T(U) \) preserves features similar to those in figure 2 for Morse’s oscillator (i.e., there is a temperature maximum). Consequently, positive/negative specific heat occurs around this point.

(a) There is a region corresponding to bounded states with energy \( E < 0 \) and another corresponding to unbounded states with \( E > 0 \).
The potential energy has a minimum, \( V > -A \) with \( A \) as positive parameter. Equivalently, in the binding region, kinetic energy satisfies \( K \leq A \).

Then, in the microcanonical ensemble, seen in figure 1, these systems retain an entropy inflection point in the binding region. Further, from the above mentioned thermodynamic expression involving the entropy \( (C, S^V(U) = -[S'(U)]^2) \), around this point, a change of sign for the specific heat necessarily occurs.

It should be noted that the existence of negative specific heat has been considered, for example, in clusters of sodium atoms near the liquid-solid transition and clusters of \( \text{Ar}_{39} \). More examples include finite systems, hydrophilic interactions, small isolated systems and left-handed structures. However, there is theoretical evidence that in the case of nanoclusters the specific negative heat is the abrupt result of changes in the phase space volume. In this line, Schmidt et al., in an well-dressed series of experiments, determined a negative heat capacity of a Na cluster with 147 atoms for temperatures near the melting temperature of the cluster. Stability and fluctuation-dissipation have been similarly considered and, additionally, discussed under the canonical ensemble framework. Applications to the Potts model were also considered containing a peak similar to the one in figure 2 in the microcanonical ensemble. Other potentials related to diatomic molecules and thermodynamic aspects (canonical ensemble) can be found in references.

However, the nature and origin of negative heat capacity for the systems described by the microcanonical ensemble remain controversial. For instance: (a) it has been argued that negative heat capacity may be the result of the coexistence of metastable states. (b) Large high-energy barriers were trapping the system in a stable state. (c) Breakdown of ergodicity. (d) A particular structure of potential energy in small systems. Besides, in this work, three conditions have been proposed for the possible existence of negative specific heat, particularly in systems with a functional structure similar to Morse’s potential.
Finally, for more clarity, the physical meaning of negative heat capacity became related to the variation of temperatures when the thermodynamic system lost energy (heat). As long as $\delta Q = c\delta T$ (section 2), the system lost heat when the temperature rose, contrary to conventional systems with positive heat capacity. A connection of this process with astronomical events can be established in the so-called gravothermal catastrophe [17] including blackhole [1, 17].

4. Conclusions

In this work, we were mainly occupied with finding the conditions for the existence of positive/negative specific heat for a diversity of systems possessing a minimum in the potential energy with bounded and unbounded states.

Explicit numerical and analytical calculations for the entropy, temperature and specific heat as a function of internal energy were presented with a focus on the Morse oscillator in the microcanonical ensemble. Calculations of the specific heat as a function of the temperature were similarly presented.

In detail, for the Morse oscillator, the entropy possesses a well-defined inflection point, corresponding to a maximum in the temperature and, unavoidably, the specific heat supports negative and positive values in the binding region. The energy separating both branches defines the critical energy (and temperature) associated with instabilities [17]. These instabilities develop outside the microcanonical framework, possibly, as molecular dissociation. Finally, the existence of this point is the signature of a phase transition, and latent heat dynamics occur to accomplish that transition.

For other binding systems with a minimum in potential energy, like the Morse oscillator, the existence of positive and negative specific heat also is expected to occur in the microcanonical ensemble (section 3). Also, we conjecture that the model developed here can be used for the thermodynamic study of different problems with strong indications phase transitions, as described and studied in [43–46].

Finally, as an application, the H$_2$ molecule gas was considered. The critical energy separating both regions of positive and negative specific heat was evaluated as $U_c \sim -1.26$ [eV]. Further thermodynamic variables were evaluated and all graphs in this work were related to this molecule.

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