

On the thermodynamics of classical micro-canonical systems

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Abstract. We study the configurational probability distribution of a mono-atomic gas with a finite number of particles N in the micro-canonical ensemble. We give two arguments why the thermodynamic entropy of the configurational subsystem involves Rényi's entropy function rather than that of Tsallis. The first argument is that the temperature of the configurational subsystem is equal to that of the kinetic subsystem. The second argument is that the instability of the pendulum, which occurs for energies close to the rotation threshold, is correctly reproduced.

1. Introduction

The recent interest in the micro-canonical ensemble [1, 2, 4, 3, 5, 6, 7, 8, 9, 10, 11] is driven by the awareness that this ensemble is the cornerstone of statistical mechanics. Of particular interest is the occurrence of thermodynamic instabilities in closed systems and their relation with phase transitions. The latter are usually studied in the context of the canonical ensemble.

The present paper focuses on the configurational probability distribution of a mono-atomic gas with N interacting particles within a non-quantum-mechanical description. Recently [12], it was proved that this distribution belongs to the q -exponential family [13, 14, 15], with $q = 1 - 2/(3N - 2)$. In the thermodynamic limit $N \rightarrow \infty$ it converges to the Boltzmann-Gibbs distribution. This observation places the statistical physics of real gases into the realm of Tsallis' non-extensive thermostatistics [16, 17]. In the Tsallis community the belief reigns that the Tsallis entropy function is more appropriate than that of Rényi, although both are maximised by the same probability distributions. In favour of this point of view is the Lesche stability [18, 19, 20] of the Tsallis entropy function. Moreover it has been proved that this entropy function is uniquely associated with the q -exponential family (up to a multiplicative and an additive constant). However, it was argued in [12] that for the calculation of thermodynamic quantities the Rényi entropy function is more appropriate. This statement is elaborated in the present work. In addition, it is shown by means of the example of the pendulum

that the stability of the Tsallis entropy function makes it inappropriate to describe instabilities of closed systems.

The pendulum is an interesting example because it has two distinct types of orbits: librational motion at low energy and rotational motion at high energy. The density of states $\omega(U)$ can be calculated analytically (see for instance [21]). It has a logarithmic singularity at the energy U_c , which is the minimum value needed to allow rotational motion — see the Figure 1.

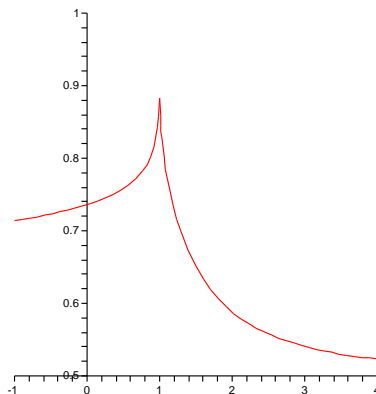


Figure 1. Density of states of the pendulum in reduced units

The thermodynamic quantity central to the micro-canonical ensemble is the entropy $S(U)$ as a function of the total energy U . Therefore, we start with it in the next Section. Sections 3 to 6 discuss the configurational probability distribution and its properties. Section 7 considers the ideal gas as a special case. Section 8 deals with the example of the pendulum. Finally, Section 9 draws some conclusions. The short Appendix clarifies certain calculations.

2. Micro-canonical entropies

The entropy $S(U)$, which is most often used for a gas of point particles in the classical micro-canonical ensemble, is

$$S(U) = k_B \ln \omega(U), \quad (1)$$

where $\omega(U)$ is the N -particle density of states. It is given by

$$\omega(U) = c_N \int_{\mathbb{R}^{3N}} d\mathbf{p}_1 \cdots d\mathbf{p}_N \int_{\mathbb{R}^{3N}} d\mathbf{q}_1 \cdots d\mathbf{q}_N \delta(U - H(\mathbf{q}, \mathbf{p})). \quad (2)$$

Here, \mathbf{q}_j is the position of the j -th particle and \mathbf{p}_j is the conjugated momentum, $H(\mathbf{q}, \mathbf{p})$ is the Hamiltonian. The constant c_N equals $1/N!h^{3N}$. The constant h has the same dimension as Planck's constant. It is inserted for dimensional reasons. This definition goes back to Boltzmann's idea of equal probability of the micro-canonical states and the corresponding well-known formula $S = k_B \ln W$, where W is the number

of micro-canonical states. However, the choice (1) of the definition of entropy has some drawbacks. For instance, for the pendulum the entropy $S(U)$ as a function of internal energy U is a piecewise convex function instead of a concave function [21]. The lack of concavity can be interpreted as a micro-canonical instability [1, 4]. But there is no physical reason why the pendulum should be classified as being unstable at all energies.

The shortcomings of Boltzmann's entropy have been noticed long ago. A slightly different definition of entropy is [22, 23] (see also in [24] the reference to the work of A. Schlüter)

$$S(U) = k_B \ln \Omega(U), \quad (3)$$

where $\Omega(U)$ is the integral of $\omega(U)$ and is given by

$$\Omega(U) = c_N \int_{\mathbb{R}^{3N}} d\mathbf{p}_1 \cdots d\mathbf{p}_N \int_{\mathbb{R}^{3N}} d\mathbf{q}_1 \cdots d\mathbf{q}_N \Theta(U - H(\mathbf{q}, \mathbf{p})). \quad (4)$$

Here, $\Theta(x)$ is Heaviside's function. An immediate advantage of (3) is that the resulting expression for the temperature T , defined by the thermodynamic formula

$$\frac{1}{T} = \frac{dS}{dU}, \quad (5)$$

coincides with the experimentally used notion of temperature. Indeed, there follows immediately

$$k_B T = \frac{\Omega(U)}{\omega(U)}. \quad (6)$$

It is well-known that for classical mono-atomic gases the r.h.s. of (6) coincides with twice the average kinetic energy per degree of freedom. Hence, the choice of (3) as the thermodynamic entropy has the advantage that the equipartition theorem, assigning $k_B T/2$ to each degree of freedom, does hold for the kinetic energy also in the micro-canonical ensemble. Quite often the average kinetic energy per degree of freedom is experimentally accessible and provides a unique way to measure accurately the temperature of the system.

3. The configurational subsystem

The micro-canonical ensemble is described by the singular probability density function

$$f_U(\mathbf{q}, \mathbf{p}) = \frac{1}{\omega(U)} \delta(U - H(\mathbf{q}, \mathbf{p})), \quad (7)$$

where $\delta(x)$ is Dirac's delta function. The normalization is so that

$$1 = c_N \int_{\mathbb{R}^{3N}} d\mathbf{p}_1 \cdots d\mathbf{p}_N \int_{\mathbb{R}^{3N}} d\mathbf{q}_1 \cdots d\mathbf{q}_N f_U(\mathbf{q}, \mathbf{p}). \quad (8)$$

For simplicity, we take only one conserved quantity into account, namely the total energy. Its value is fixed to U .

In the simplest case the Hamiltonian is of the form

$$H(\mathbf{q}, \mathbf{p}) = \frac{1}{2m} \sum_{j=1}^N |\mathbf{p}_j|^2 + \mathcal{V}(\mathbf{q}), \quad (9)$$

where $\mathcal{V}(\mathbf{q})$ is the potential energy due to interaction among the particles and between the particles and the walls of the system. It is then possible to integrate out the momenta. This leads to the configurational probability distribution, which is given by

$$f_U^{\text{conf}}(\mathbf{q}) = \left(\frac{a}{h}\right)^{3N} \int_{\mathbb{R}^{3N}} d\mathbf{p}_1 \cdots d\mathbf{p}_N f_U(\mathbf{q}, \mathbf{p}). \quad (10)$$

The normalization is so that

$$1 = \frac{1}{N!a^{3N}} \int_{\mathbb{R}^{3N}} d\mathbf{q}_1 \cdots d\mathbf{q}_N f_U^{\text{conf}}(\mathbf{q}). \quad (11)$$

The constant a has been introduced for dimensional reasons[‡]. In the limit of an infinitely large system, this configurational system is described by a Boltzmann-Gibbs distribution. However, here we are interested in small systems where an exact evaluation of (10) is necessary. A straightforward calculation yields

$$f_U^{\text{conf}}(\mathbf{q}) = \frac{[U - \mathcal{V}(\mathbf{q})]_+^{3N/2-1}}{\epsilon^{3N/2} \omega(U) \Gamma(3N/2)}, \quad (12)$$

with $\epsilon = h^2/2\pi m a^2$.

4. The variational principle

It was shown in [12] that the configurational probability distribution $f_U^{\text{conf}}(\mathbf{q})$ belongs to the q -exponential family, with $q = 1 - \frac{2}{3N-2}$. This implies [13, 14, 15] that it maximizes the expression

$$I(f) - \theta U^{\text{conf}}(f) \quad (13)$$

for some value of θ , where

$$I(f) = -\frac{1}{1-q} \frac{1}{N!a^{3N}} \int_{\mathbb{R}^{3N}} d\mathbf{q}_1 \cdots d\mathbf{q}_N f(\mathbf{q}) [(f(\mathbf{q}))^{1-q} - 1] \quad (14)$$

with

$$U^{\text{conf}}(f) = \frac{1}{N!a^{3N}} \int_{\mathbb{R}^{3N}} d\mathbf{q}_1 \cdots d\mathbf{q}_N f(\mathbf{q}) \mathcal{V}(\mathbf{q}). \quad (15)$$

This is called the *variational principle*. Note that $I(f)$ is the Tsallis entropy function [16] up to one modification (replacement of the parameter q by $2 - q$). The parameter θ turns out to be given by

$$\theta = \frac{2-q}{1-q} \frac{1}{\epsilon^{2-q} [\Gamma(3N/2) \omega(U)]^{1-q}}. \quad (16)$$

The maximisation of (13) is equivalent to the minimisation of the free energy (using $I(f)$ as the entropy function appearing in the definition of the free energy). Replacing the Boltzmann-Gibbs-Shannon (BGS) entropy function by $I(f)$ is necessary — the configurational probability distribution $f_U^{\text{conf}}(\mathbf{q})$ does *not* maximize the BGS entropy function as a consequence of finite size effects.

[‡] Note that the normalisation here differs from that in [12]

Note that in [14] the definition (14) of the entropy function contains an extra factor $1/(2 - q)$ to fix its normalisation and to make it unique within a class of properly normalised entropy functions. This normalisation factor is not wanted in the present paper because it becomes negative when we use $q = 3$ in the example.

5. Rényi's entropy function

It is tempting to identify the parameter θ of the previous Section with the inverse temperature $\beta = 1/k_B T$ and to interpret (13) as the maximisation of the entropy function $I(f)$ under the constraint that the average energy $U^{\text{conf}}(f)$ equals the given value U^{conf} . However, in [12] an example was given showing that this identification of θ with β cannot be correct in general. It was noted that replacing the Tsallis entropy function by that of Rényi gives a more satisfactory result. This argument is now repeated in a more general setting.

In the present context, Rényi's entropy function of order α is defined by

$$I^\alpha(f) = \frac{1}{1 - \alpha} \ln \left[\frac{1}{N! a^{3N}} \int_{\mathbb{R}^{3N}} d\mathbf{q}_1 \cdots d\mathbf{q}_N f(\mathbf{q})^\alpha \right]. \quad (17)$$

Let $\alpha = 2 - q$. Then (17) is linked to (14) by

$$I^\alpha(f) = \xi(I(f)) \quad (18)$$

with

$$\xi(u) = \frac{1}{q - 1} \ln[1 + (q - 1)u]. \quad (19)$$

Note that

$$\frac{d\xi}{du} = \frac{1}{1 + (q - 1)u}. \quad (20)$$

This derivative is strictly positive on the domain of definition of $\xi(u)$. Hence, $\xi(u)$ is a monotonically increasing function. Therefore, the density $f(\mathbf{q})$ is a maximizer of $I(f)$ if and only if it maximizes $I^\alpha(f)$. This means that from the point of view of the maximum entropy principle it does not make any difference whether one uses the Rényi entropy function or that of Tsallis. However, for the variational principle discussed in the previous Section, and for the definition of the temperature T via the thermodynamic formula (5) the function $\xi(u)$ makes a difference. In the example of the pendulum, discussed further on, the variational principle is not satisfied when using Rényi's entropy function, while it is satisfied when using $I(f)$. Also, the derivation which follows below shows that, when Rényi's entropy function is used, the temperature of the configurational subsystem equals the temperature T of the kinetic subsystem.

6. Configurational thermodynamics

Let us now calculate the value of Rényi's entropy function for the configurational probability distribution (10). One has

$$I^\alpha(f_U^{\text{conf}}) = \frac{1}{q-1} \ln \left[\frac{1}{N!a^{3N}} \int_{\mathbb{R}^{3N}} d\mathbf{q}_1 \cdots d\mathbf{q}_N (f_U^{\text{conf}}(\mathbf{q}))^{2-q} \right]. \quad (21)$$

Use now that (see (12))

$$(f_U^{\text{conf}}(\mathbf{q}))^{1-q} = \frac{U - \mathcal{V}(\mathbf{q})}{\epsilon [\Gamma(3N/2)\epsilon\omega(U)]^{1-q}}. \quad (22)$$

Then (21) simplifies to

$$I^\alpha(f_U^{\text{conf}}) = \ln \Gamma \left(\frac{3N}{2} \right) \epsilon\omega(U) - \left(\frac{3N}{2} - 1 \right) \ln \frac{U^{\text{kin}}}{\epsilon}. \quad (23)$$

The claim is now that (23), when multiplied with k_B , is the thermodynamic entropy $S^{\text{conf}}(U)$ of the configurational subsystem. Note that $\epsilon = h^2/2\pi ma^2$ is an arbitrary unit of energy. Note also that, using Stirling's approximation and $U^{\text{kin}} = 3N\Omega(U)/2\omega(U)$, (23) simplifies to

$$\begin{aligned} \frac{1}{k_B} S^{\text{conf}}(U) &\simeq \ln \epsilon\omega(U) - \left(\frac{3N}{2} - 1 \right) \ln \frac{\Omega(U)}{\epsilon\omega(U)} \\ &\quad + \left(\frac{3N}{2} - 1 \right) \ln \left(\frac{3N}{2} - 1 \right) - \frac{3N}{2} + \frac{1}{2} \ln 3\pi N. \end{aligned} \quad (24)$$

To support our claim, let us calculate its prediction for the temperature of the configurational subsystem. One finds

$$\begin{aligned} \frac{1}{T^{\text{conf}}} &\equiv \frac{dS^{\text{conf}}}{dU^{\text{conf}}} = k_B \left[\frac{\omega'}{\omega} - \left(\frac{3N}{2} - 1 \right) \frac{1}{U^{\text{kin}}} \right] \frac{dU}{dU^{\text{conf}}} \\ &\quad + k_B \left(\frac{3N}{2} - 1 \right) \frac{1}{U^{\text{kin}}}. \end{aligned} \quad (25)$$

Using (see (26) of [12])

$$\frac{dU^{\text{conf}}}{dU} = 1 - \frac{3N}{2} + \frac{\omega'}{\omega} U^{\text{kin}} \quad (26)$$

this becomes

$$\frac{1}{T^{\text{conf}}} = k_B \frac{3N}{2U^{\text{kin}}} = k_B \frac{\omega}{\Omega} = \frac{1}{T}. \quad (27)$$

This shows that the configurational temperature, calculated starting from Rényi's entropy function, coincides with the temperature T defined by means of the modified Boltzmann entropy (3) and with the temperature of the kinetic subsystem. One concludes that the natural choice of entropy function for the configurational subsystem is Rényi's with $\alpha = 2 - q = 3N/(3N - 2)$.

Finally, let us define a configurational heat capacity by

$$C^{\text{conf}} = \frac{dU^{\text{conf}}}{dT} = T \frac{dS^{\text{conf}}}{dT}. \quad (28)$$

Then one has in a trivial way

$$C = \frac{dU}{dT} = \frac{d}{dT} \left[\frac{3}{2} N k_B T + U^{\text{conf}} \right] = \frac{3}{2} N k_B + C^{\text{conf}}. \quad (29)$$

7. The ideal gas

Let us verify that the expression (23) makes sense even for an ideal gas. In this case the density of states is

$$\omega(U) = \frac{c_N}{\Gamma(3N/2)} V^N (2\pi m)^{3N/2} U^{3N/2-1}. \quad (30)$$

Evaluation of (23) with $U^{\text{kin}} = U$ then gives

$$S^{\text{conf}} = k_B N \ln \frac{V}{Na^3} + k_B \ln \frac{N^N}{N!} \simeq k_B N \ln \frac{eV}{Na^3}. \quad (31)$$

The configurational entropy of an ideal gas does not depend on the total energy or on the mass of the particles, as expected. The total entropy is

$$\begin{aligned} S &= k_B \ln \Omega(U) \\ &= k_B N \ln V + \frac{3}{2} N k_B \ln 2\pi m U \\ &\quad + k_B \ln c_N - k_B \ln \Gamma(3N/2 + 1). \end{aligned} \quad (32)$$

Using Stirling's approximation, (32) simplifies to

$$S \simeq k_B N \left(\ln \frac{eV}{Na^3} + \frac{3}{2} \ln 2\pi \frac{U}{N\epsilon} + \text{constant} \right). \quad (33)$$

This expression coincides with the Sackur-Tetrode equation [25] for an appropriate choice of the constant term. The first term of (33) is the configurational entropy contribution (31), the second term is the kinetic energy contribution.

8. The pendulum

Let us now consider the example of the pendulum. The Hamiltonian reads

$$H = \frac{1}{2I} p^2 - \kappa^2 I \cos(\phi). \quad (34)$$

For low energy $-\kappa^2 I < U < \kappa^2 I$ the motion is oscillatory. At large energy $U > \kappa^2 I$ it rotates in one of the two possible directions. The density of states $\omega(U)$ can be written as

$$\begin{aligned} \omega(U) &= \frac{d}{dU} \frac{2\sqrt{2I}}{h} \int d\phi \sqrt{U + I\kappa^2 \cos \phi} \\ &= \frac{4\pi\sqrt{2}}{h\kappa} \omega_0(U/\kappa^2 I). \end{aligned} \quad (35)$$

with $\omega_0(u)$ given by

$$\omega_0(u) = \frac{1}{2\pi} \int_0^1 dx \frac{1}{\sqrt{x}} \frac{1}{\sqrt{1-x}} \frac{1}{\sqrt{1-u+(1+u)x}} \quad \text{if } -1 < u < 1,$$

$$\omega_0(u) = \frac{1}{2\pi} \int_{-1}^1 dx \frac{1}{\sqrt{1-x^2}} \frac{1}{\sqrt{x+u}} \quad \text{if } 1 < u. \quad (36)$$

See the Figure 1. Note that the integrals appearing in (36) are complete elliptic integrals of the first kind. For simplicity we chose now units in which $\kappa^2 I = 1$ holds. We also fix $h = 4/\kappa$.

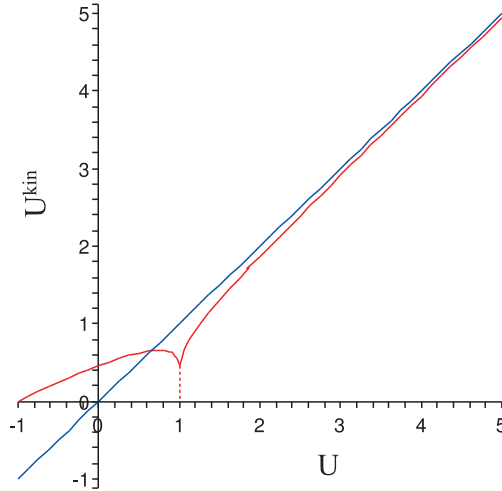


Figure 2. Kinetic energy U^{kin} as a function of energy U

Using the analytic expressions (36), and the expression (6), it is straightforward to make a plot of the temperature T as a function of the energy U . See the Figure 2. Note that it is not a strictly increasing function. Due to the divergence of $\omega_0(u)$ at $u = 1$ the temperature T has to vanish at both $u = -1$ and $u = +1$. Hence it has a maximum in between. As a consequence, the free energy F , which is the Legendre transform of $U(S)$,

$$F(T) = U - TS \quad (37)$$

is a multi-valued function, when calculated by substituting $U(T)$ in (37). See the Figure 3.

When a fast rotating pendulum slows down due to friction then its energy decreases slowly. The average kinetic energy, which is the temperature $\frac{1}{2}k_B T$, tends to zero when the threshold U_c is approached. In the Figure 3, the continuous curve is followed. The pendulum goes from a stable into a metastable rotational state. then it switches to an unstable librating state, characterised by a negative heat capacity. Finally it goes through the metastable and stable librational states. The first order phase transition cannot take place because in a nearly closed system the pendulum cannot get rid of the latent heat. Neither can it stay at the phase transition point because a coexistence of the two phases cannot be realised.

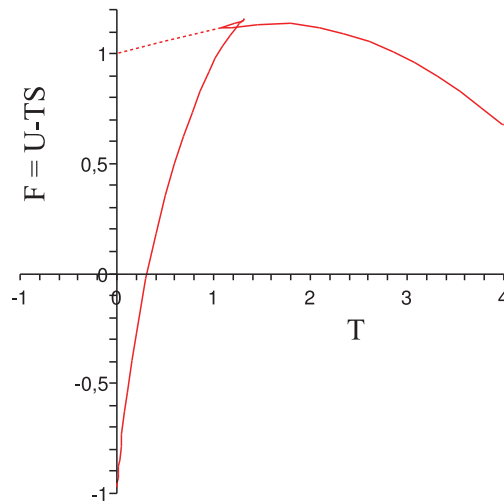


Figure 3. Free energy of the pendulum

9. The configurational free energy of the pendulum

For the example of the pendulum the number of degrees of freedom $3N$ in the expression for the non-extensivity parameter q has to be replaced by 1, so that $q = 3$ results. This is an anomalous value because $0 < q < 1$ has been assumed in the main part of the paper. See the Appendix for a discussion of the modifications needed to treat this situation.

It remains true that the configurational probability distribution $f_U^{\text{conf}}(\phi)$ maximizes the Rényi entropy with $\alpha = 2 - q = -1$ within the set of all probability distributions having the same average potential energy U^{conf} . Next, using

$$\frac{1}{T^{\text{conf}}} \equiv \frac{dS^{\text{conf}}}{dU^{\text{conf}}} \quad (38)$$

as the definition of the temperature T of the configurational subsystem, one can plot the configurational free energy as a function of T . See the Figure 4.

One observes the same behaviour as in the Figure 3. The main difference is that in the rotational phase the configurational free energy is a convex rather than a concave function of the temperature T . This implies that the configurational entropy S^{conf} is a decreasing function of T and that the heat capacity $C^{\text{conf}} = T(dS^{\text{conf}}/dT)$ is negative. This is not in contradiction with the physical intuition that the fluctuations in potential energy decrease with increasing energy U . The instability of the configurational subsystem in the rotational phase is more than compensated by the stability of the kinetic subsystem, so that the free energy $F(T)$ of the total system is concave.

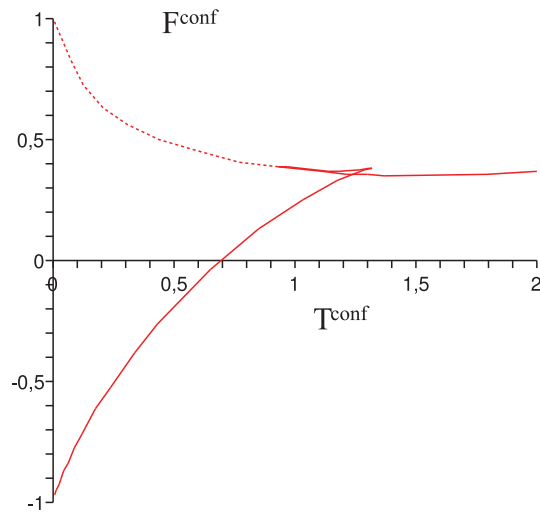


Figure 4. Configurational free energy of the pendulum

10. Conclusions

In a previous paper [12] we have shown that the configurational probability distribution $f_U^{\text{conf}}(\mathbf{q})$ of a real mono-atomic gas with N particles always belongs to the q -exponential family, with $q = 1 - \frac{2}{3N-2}$. In the same paper it was argued, based on one example, that for the definition of the configurational temperature T the entropy function of Rényi is better suited than that of Tsallis. Here we show in the Section 6 that the same result holds for any real gas with a Hamiltonian of the usual form (9).

It is well-known that Rényi's entropy function and that of Tsallis are related because each of them is a monotone function of the other. Hence, from the point of view of the maximum entropy principle the two entropy functions are equivalent. However, from the point of view of the variational principle (this is, the statement that the free energy is minimal in equilibrium) the two are not equivalent. This raises the need to distinguish between them. The result of the Section 6 then suggests that from a thermodynamic point of view Rényi's entropy function is the preferred choice.

A further indication in the same direction comes from stability considerations. In the literature of non-extensive thermostatics one studies the notion of Lesche stability [18, 19, 20]. Tsallis' entropy function is Lesche-stable while Rényi's is not. The present paper focusses on thermodynamic stability, by which one usually understands the positivity of the heat capacity.

A well-known property of the Boltzmann-Gibbs distribution is that it automatically leads to a positive heat capacity and that instabilities such as phase transitions are only possible in the thermodynamic limit. The entropy function which is maximised by the Boltzmann-Gibbs distribution is that of Boltzmann-Gibbs-Shannon (BGS). The Boltzmann-Gibbs distribution is known in statistics as the exponential family. Its

generalisation, needed here, is the q -exponential family. Both Tsallis' entropy function and that of Rényi are maximised by members of the q -exponential family. However, only Tsallis' entropy function shares with the BGS entropy function the property that the heat capacity is always positive — this has been proved in a very general context in [13]. For this reason, one can say that the Tsallis' entropy function is a stable entropy function. We have shown in the present paper with the explicit example of the pendulum that Rényi's entropy function is not stable in the above sense.

The example of the pendulum was chosen because it exhibits two thermodynamic phases. At low energy the pendulum librates around its position of minimal energy. At high energy it rotates in one of the two possible directions. In an intermediate energy range the time-averaged kinetic energy drops when the total energy increases. If the kinetic energy is taken as a measure for the temperature then the pendulum is a simple example of a system with negative heat capacity. Hence, it is not such a surprise that, if we look for an instability, that we find it in this system. But this also means that Rényi's entropy function is able to describe the instability of the pendulum, while Tsallis' entropy function is not suited for this task. This is again an indication that Rényi's entropy function is an appropriate candidate for a statistical definition of the thermodynamic entropy of small systems.

Appendix

The configurational probability distribution of the pendulum is given by

$$f_U^{\text{conf}}(\phi) = \frac{a\sqrt{I/2}}{h\omega(U)\sqrt{U + I\kappa^2 \cos \phi}}. \quad (\text{A.1})$$

It maximizes Rényi's entropy function with $\alpha = -1$. The maximal value equals

$$\begin{aligned} S^{\text{conf}}(U) &= \frac{1}{2}k_B \ln \frac{1}{a} \int d\phi \frac{1}{f_U^{\text{conf}}(\phi)} \\ &= \frac{1}{2}k_B \ln \frac{h\omega(U)}{a^2\sqrt{I/2}} \int d\phi \sqrt{U + I\kappa^2 \cos \phi} \\ &= \frac{1}{2}k_B \ln \frac{h^2}{Ia^2} \omega(U)\Omega(U). \end{aligned} \quad (\text{A.2})$$

Therefore the inverse of the configurational temperature is given by

$$\begin{aligned} \frac{1}{T^{\text{conf}}} &= \frac{dS^{\text{conf}}}{dU^{\text{conf}}} \\ &= k_B \frac{\omega(U)^2 + \omega'(U)\Omega(U)}{2\omega(U)\Omega(U)} \frac{dU}{dU^{\text{conf}}}. \end{aligned} \quad (\text{A.3})$$

But note that

$$\begin{aligned} \frac{dU^{\text{conf}}}{dU} &= \frac{d}{dU} \left(U - \frac{\Omega(U)}{2\omega(U)} \right) \\ &= \frac{\omega'(U)\Omega(U) + \omega^2(U)}{2\omega^2(U)}. \end{aligned} \quad (\text{A.4})$$

Hence (A.3) becomes

$$\frac{1}{T^{\text{conf}}} = k_{\text{B}} \frac{\omega(U)}{\Omega(U)}. \quad (\text{A.5})$$

This shows that the temperature of the configurational subsystem coincides with that of the kinetic subsystem — see (6).

It is now straightforward to make the parametric plot of Figure 4 by plotting T as a function of U on the horizontal axis, and $F = U - TS$ on the vertical axis.

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