Thermodynamic formulation for a mechanical system satisfying Tsallis statistics

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Outline

- Thermodynamical formalism to describe the dynamical behavior an over-damped mechanical model.
- Go beyond the analysis of a single and isolated system $\Rightarrow$ interactions with exchange of mechanical energy between similar systems.
- Formalism uses definition of pseudo-heat and pseudo-work.
- Together with pseudo-temperature characterize isotherm, adiabatic, isobaric, and isochoric processes.

Outline

- Issue two statements formally analogous to the first and second law of thermodynamics
- Define a Carnot cycle with efficiency expressed in terms of the pseudo-temperatures of the operating heat reservoirs.
- State and prove the Clausius theorem for the system operating an arbitrary reversible cycle $\Rightarrow$ entropy function is derived.
- Analytical expression coincident to that from non-extensive statistical mechanics.

Quotes on thermodynamics

- Every mathematician knows it is impossible to understand an elementary course in thermodynamics (V.I. Arnold).
- A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts (Albert Einstein).

Quotes on thermodynamics

- The law that entropy always increases holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations - then so much the worse for Maxwell's equations. If it is found to be contradicted by observation - well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation (Sir Arthur Stanley Eddington).

Quotes on thermodynamics

- Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more (Arnold Sommerfeld).

Quotes on thermodynamics

- In this house, we obey the laws of thermodynamics!!!

  (Homer Simpson, after Lisa constructs a perpetual motion machine whose energy increases with time).

Introduction

- Thermodynamical entropy: straightforward result of Clausius theorem, a mathematical consequence of enouncements of the Second Law of Thermodynamics.
- Phenomenologically based statements that certain events never occur in nature.
- Statistical entropy related to probability distribution of microstates in the Gibbs ensemble or molecular velocity distribution in Boltzmann's transport equation.
- *Meaning* of entropy $\Rightarrow$ different interpretations from thermodynamical or statistical point of view.

Introduction

- Statistical entropy: arbitrary to a large degree.
- Basic requirements related to convexity and monotonicity satisfied by several families of functions.
- Bolztmann-Gibbs (BG) entropy accepted as *actual* definition $\Rightarrow$ predicted results (including additivity) agree with thermodynamical formalism and experimental records.
- Yet, several sets of experimental data can not be explained by the BG distribution.

Introduction

- In the last decades other statistical entropies have been a proposed by a large number of scientists.
- Renyi entropy, Tsallis q-entropy, superstatistics, ...
- Still missing a concise, successful enough formulation to reproduce experimental results based on simple and well defined microscopic models.

Introduction

- This work $\Rightarrow$ entropy definition along a thermodynamical approach, distinct from quoted works.
- Consider well defined mechanical model with a large number of constituents, proper boundary conditions, and integrate equations of motion with high precision.
- Neglect any effect of the usual temperature T ($\Rightarrow T = 0$).
- Issue two statements based on general mechanical properties of the solutions $\Rightarrow$ first and second law of thermodynamics.

Introduction

- Proof of the analogue of the Clausius theorem for this class of systems.
- Corollary $\Rightarrow$ pertinent form for a new thermodynamic entropy function.
- Entropy can not be derived within the BG formalism, but within Tsallis $q \neq 1$ statistics.

Mechanical model

- N over damped particles moving on a rectangular surface patch oriented along the $(\hat{x}, \hat{y})$ directions:

$$\mu \frac{d\vec{r}_i}{dt} = \sum_{i \neq j = 1}^{N} \vec{J}(\vec{r}_i - \vec{r}_j) + \vec{F}^e(\vec{r}_i). \tag{1}$$

  - $\vec{J}(\vec{r}_i) = f_0 G(|\vec{r}|/\lambda)\hat{r}/2$: short-range repulsive force;
  - λ: typical length scale of the interaction;
  - $\vec{F}^e(\vec{r}_i) = -A(x)\hat{x}$: external force depending only on x and acting along x direction.

Mechanical model

- Confining potential in the x direction $\Rightarrow \phi(x) = \int_0^x A(x')dx'$,
- Motion in the y direction limited by rigid boundaries $U(y) = \delta(y) + \delta(y - L_y)$.
- Linear $A(x) = -\alpha x \Rightarrow$ potential energy of a particle $\phi(x) = \alpha x^2/2$.
- System becomes bounded in the x direction $\Rightarrow$ horizontal confinement depends on α.

Isolated system

- Numerical integration of (1) leads to a steady equilibrium $\Rightarrow$ N fixed particles
- Equilibria depend on initial conditions but share macroscopic properties as average linear density in the x direction:

$$\rho_{st}(x) = R\left(x_e^2 - x^2\right). \tag{2}$$

- Average linear density n and potential energy per particle u:

$$n = N/L_y = \int_{-x_e/2}^{+x_e/2} \rho_{st}(x)dx = \frac{4Rx_e^3}{3}, \tag{3}$$

$$u = \frac{1}{n}\int_{-x_e}^{+x_e} \phi(x)\rho_{st}(x)dx = \frac{2\alpha Rx_e^5}{15n}. \tag{4}$$

Isolated system

- (3) and (4): equivalent to the phenomenological equations of state of macroscopic systems like the ideal gas.
- Exhaustive series of numerical integration from which such relationships can be extracted.
- Consistent with theoretical formulation of a suitable non-linear Fokker-Planck for the probability of finding a particle at x.
- $R = \alpha/2a$ and $x_e = (3Na/2\alpha L_y)^{1/3}$ expressed in terms of the system's microscopic parameters.

Isolated system

- Define following variables:

$$\theta = n\pi f_0 \lambda^2 / k, \quad (5)$$

$$\sigma = \frac{1}{10}\left(\frac{3\lambda k\theta}{\alpha}\right)^{2/3}, \quad (6)$$

  - $\theta \sim f_0/\lambda^2$ inter-particle interaction $\Rightarrow$ pseudo temperature;
  - σ depends on inter-particle and external forces $\Rightarrow$ thermodynamic conjugate of α.
  - k "universal" constant.

Isolated system

- Insert (5) into (4) to obtain

$$u = u(\alpha, \theta) = \frac{\left(9\alpha\lambda^2 k^2 \theta^2\right)^{1/3}}{10}. \tag{7}$$

- Insert (5) into (6) to obtain very simple expression for u as function of α and σ

$$u = u(\alpha, \sigma) = \alpha\sigma. \tag{8}$$

Isolated system

- Differential du expressed in terms of $d\alpha$ and $d\theta$

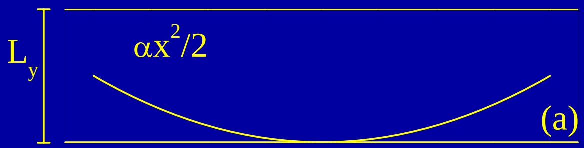
$$du = \frac{1}{30}\left(\frac{3\lambda k\theta}{\alpha}\right)^{2/3} d\alpha + \frac{1}{15}\left(\frac{9\alpha k^2\lambda^2}{\theta}\right)^{1/3} d\theta, \qquad (9)$$

- or $d\alpha$ and $d\sigma$.

$$du = \sigma d\alpha + \alpha d\sigma. \qquad (10)$$

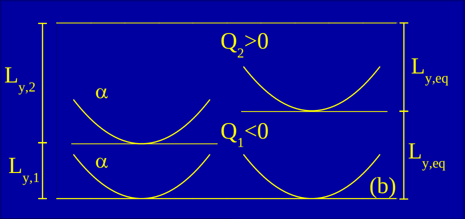
Isolated system

- Schematic representation: vertical height $\sim L_y$; horizontal width $\sim 1/\alpha$ in confining potential.
- System enclosed by rigid, impermeable and adiabatic walls.



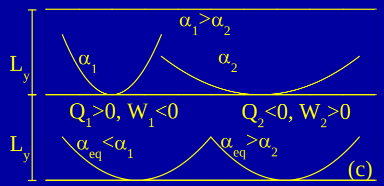
Isochoric process

- Systems 1 and 2 may change their height $L_{y,j} \sim 1/\theta_j$ due to difference in momenta delivered to wall.
- Values of α for both systems and sum $L_{y,1} + L_{y,2}$ remain constant
- $d\alpha = 0$ and $d\theta \neq 0$ or $d\alpha = 0$ and $d\sigma \neq 0$
- The location of the intermediary wall is updated after a small number of integration steps.



Isothermic process

- Both systems have constant height $L_y \sim 1/\theta$
- Confining potential $\sim \alpha_j$ can change.
- Total horizontal width $\sim \alpha_1^{-1/3} + \alpha_2^{-1/3}$ remains constant
- $d\alpha \neq 0$ and $d\theta = 0$ or $d\alpha \neq 0$ and $d\sigma \neq 0$
- Value of α_i and location of potential center periodically updated by least square fits of the density of particles.



Statement of first law

- Identify the heat δQ and work δW transferred to/from the system in an infinitesimal quasi-static process.

$$\begin{aligned} \delta Q &= \alpha d\sigma, \\ \delta W &= \sigma d\alpha. \end{aligned}$$

- State first law:

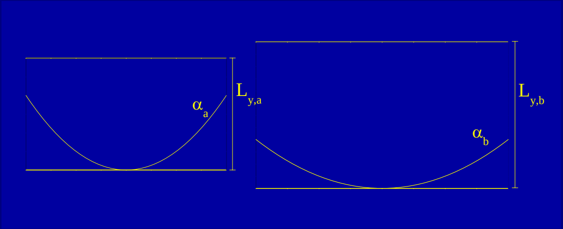
$$du = \delta Q + \delta W \tag{11}$$

Specific processes

- Adiabatic process: $\delta Q = d\sigma = 0$
  $\Delta u_{1\to 2}^{adiab.} = \Delta W_{1\to 2}^{adiab.} = \sigma(\alpha_2 - \alpha_1)$
- Isochoric process: $\delta W = d\alpha = 0$.
  $\Delta u_{1\to 2}^{isoch.} = \Delta Q_{1\to 2}^{isoch.} = \alpha(\sigma_2 - \sigma_1)$.
- Isothermic process: $d\theta = 0$
  $\Delta Q_{1\to 2}^{isoth.} = -2(\sigma_2\alpha_2 - \sigma_1\alpha_1)$ and
  $\Delta W_{1\to 2}^{isoth.} = 3(\sigma_2\alpha_2 - \sigma_1\alpha_1)$,
  $\Delta u_{1\to 2}^{isoth.} = \sigma_2\alpha_2 - \sigma_1\alpha_1$.

Adiabatic process

- Adiabatic process: $dQ = 0$
- Concomitant changes in θ (L_y) and α
- System inflates (deflates) in both x and y directions when $du > 0$ ($du < 0$).

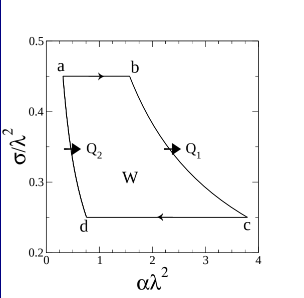


Carnot cycle

- Extend the above thermodynamic framework to introduce pseudo-thermal machine.
- Allow system (1) to operate cycles, by coupling to pseudo-heat and pseudo-work reservoirs in adequate sequence.
- Reservoir $\Rightarrow$ usual thermodynamic meaning: deliver or accept heat (work) from a system without changing thermal (mechanical) properties.
- Reservoir at pseudo-temperature $\theta = \theta_R$ and mechanical features ($\alpha = \alpha_R$) remain the same after interaction with finite size systems.

Carnot cycle

- Two isotherms : (bc) and (da)
- Two adiabat : (ab) and (cd)



Carnot theorem

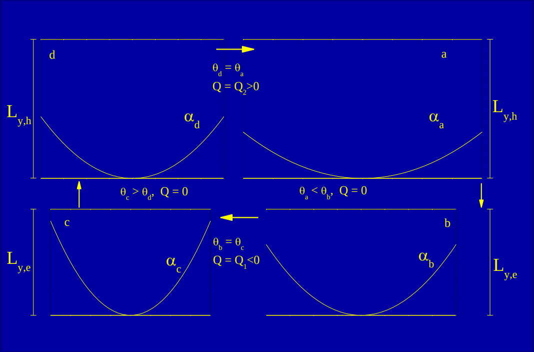
- Carnot cycle has the highest possible efficiency $\eta = \eta_C$ for an engine operating between two pseudo-heat reservoirs at temperatures θ_1 and $\theta_2 (< \theta_1)$.
- η_C depends only on T_1 and T_2, but not on the engine.
- Efficiency of pseudo-Carnot cycle operated by system (1):

$$\eta_C = 1 - \frac{|Q_{34}|}{|Q_{12}|} = 1 - \frac{\theta_2}{\theta_1}. \tag{12}$$

- Explicit calculation

$$\begin{aligned} Q_{12} &= 2(\sigma_A \alpha_1 - \sigma_B \alpha_2) = 2\sigma_A \alpha_1 (1 - \sqrt{\sigma_A \sigma_B}) \\ Q_{34} &= 2(\sigma_B \alpha_3 - \sigma_A \alpha_4) = 2\sigma_B \alpha_3 (1 - \sqrt{\sigma_B \sigma_A}) \end{aligned}$$

Schematic representation



Second law

- Pushing away the correspondence to usual thermodynamics, state the equivalent of the second law:
- Clausius statement: "It is impossible to have a process in which the only effect is to extract the pseudo-heat (at a low pseudo-temperature or particle density n) and deliver it at a larger temperature (larger particle density n)".
- Kelvin statement "It is impossible to have a process in which the only effect is to extract the pseudo-heat (increase particle density) from a reservoir and convert it entirely into mechanical work (increase the value of α)".

Clausius theorem

- Statements justified from the observation of the numerical results

- State and prove the analogous to the Clausius theorem

$$I = \oint_C \frac{\delta Q}{\theta} = 0, \tag{13}$$

- $C \Rightarrow$ closed curve describing any reversible process

- Equivalent to a cycle in the *PV* or *HM* plane in usual thermodynamics.

Clausius theorem

- Divide closed path in the $\sigma\alpha$ plane into infinitesimal parts labeled by the index i.
- Consider ideal situation where heat can be introduced into/ (extracted from) the system with set of heat reservoirs at specific pseudo-temperatures $\overline{\theta}_i$.
- Consider further reference heat reservoir at arbitrary large temperature θ_0,
- Consider local processes formed by Carnot cycle between reservoirs at θ_0 and $\overline{\theta}_i$.

Clausius theorem

- Replace actual path between (σ_i, α_i) and $(\sigma_{i+1}, \alpha_{i+1})$ by sequence of an adiabat, an isotherm, and another adiabat.
- 1) The pseudo-temperature of original and approximate paths at the initial and final points are the same.
- Three curves are chosen so that work ΔW_i done by the system along the actual and approximate paths are equal.
- Δu_i are equal for both paths $\Leftrightarrow$ depends only on (σ_i, α_i) and $(\sigma_{i+1}, \alpha_{i+1})$.
- $\Rightarrow$ heat flow ΔQ_i between (σ_i, α_i) and $(\sigma_{i+1}, \alpha_{i+1})$ must also be equal.

Clausius theorem

- Approximate path: heat flow only during the isotherm
- Heat exchanged only at $\overline{\theta}_i$ with $\theta_i \neq \overline{\theta}_i \neq \theta_{i+1}$.
- $\Delta Q'$: heat extracted from (or delivered to) the θ_0 reservoir $\Rightarrow$ by Carnot's theorem,

$$\Delta Q' = \theta_0 \frac{\delta Q_i}{\overline{\theta}_i}. \tag{14}$$

- Sum over all infinitesimal curves:

$$Q' = \sum_i \Delta Q' = \theta_0 \sum_i \frac{\delta Q_i}{\overline{\theta}_i}. \tag{15}$$

Clausius theorem

- Number of curves $\to \infty$,

$$Q' \to \oint_C \Delta Q' = \theta_0 \oint_C \frac{\delta Q}{\overline{\theta}} = \theta_0 \oint_C \frac{\delta Q}{\theta} = \theta_0 I. \tag{16}$$

- Carnot cycle: $\sum_{i=1}^{2} \frac{\delta Q_i}{\theta_i} = 0$ for thermal engine or refrigerator.
- Arbitrary reversible process $\Rightarrow \theta_0 I \leq 0$ and $\theta_0 I \geq 0$.
- Two inequalities only satisfied when $\theta_0 I = 0$.
- Arbitrary path $C \Rightarrow$ *thermodynamic pseudo-entropy s*:

$$s_2 - s_1 = \int_1^2 \frac{\delta Q}{\theta} \tag{17}$$

Clausius theorem

- Explicit result after integration of (17):

$$s = k\left[1 - \frac{1}{5}\left(\frac{9\alpha\lambda^2}{k\theta}\right)\right]. \quad (18)$$

- Same expression derived for system (1) by non-linear Fokker-Planck equation within nonadditive statistical mechanics.

- $\Rightarrow$ developed thermodynamic approach necessarily has statistical counterpart in Tsallis framework.