Fundamental Approaches to the 2nd Law of Thermodynamics:

A first and a second view

Pedro Campos

28/7/2018

Outline

Laws of Thermodynamis

- "Zeroth Law - Common Sense"

- "Zeroth Law - Common Sense"
- "First Law - You can brake even" (if you don't lose energy, you can't gain energy)

Laws of Thermodynamis

- "Zeroth Law - Common Sense"
- "First Law - You can brake even" (if you don't lose energy, you can't gain energy)
- "Second Law - You can brake even at $0K$"

Laws of Thermodynamis

- "Zeroth Law - Common Sense"
- "First Law - You can brake even" (if you don't lose energy, you can't gain energy)
- "Second Law - You can brake even at $0K$"
- "Third Law - You can't get to $0K$"

Lec 1 | MIT 5.60 Thermodynamics & Kinetics, Spring 2008

Different Formalisms of the 2nd Law

- "No process is possible the sole result of which is that heat is transferred from a body to a hotter one" (Clausius).

Different Formalisms of the 2nd Law

- "No process is possible the sole result of which is that heat is transferred from a body to a hotter one" (Clausius).
- "No process is possible the sole result of which is that a body is cooled and work is done" (Kelvin (and Planck)).

Different Formalisms of the 2nd Law

- "No process is possible the sole result of which is that heat is transferred from a body to a hotter one" (Clausius).
- "No process is possible the sole result of which is that a body is cooled and work is done" (Kelvin (and Planck)).
- "In any neighborhood of any state there are states that cannot be reached from it by an adiabatic process" (Carathodory).

Authors of the Original Paper

Figure: Elliott Lieb and Jakob Yngvason

Thermodynamic States

Possible Measures:

- Empirical Temperature (Intensive)
- Pressure (Intensive)
- Internal Energy (Extensive)
- Volume (Extensive)
- ...

Thermodynamic States

Possible Measures:

- Empirical Temperature (Intensive)
- Pressure (Intensive)
- Internal Energy (Extensive)
- Volume (Extensive)
- ...

Definition (Thermodynamic State)

A Thermodynamic State of a given thermodynamic system is a vector $X = \left(\xi_1(x), ..., \xi_n(x)\right)$, which represents the measurements that an observer makes.

Equillibrium States

Definition (Equilibrium State)

An Equillibrium State, which will be represent by $X, Y, Z, \ldots$ is a thermodynamic state whose observations are homogeneous, i.e, $\exists c \in \mathbf{R} : \forall x \in \Omega, \xi_i(x) = c$, and if the system isn't perturbed the observation is the same for every instant in the observer proper time.

Equillibrium States

Definition (Equilibrium State)

An Equillibrium State, which will be represent by $X, Y, Z, \ldots$ is a thermodynamic state whose observations are homogeneous, i.e, $\exists c \in \mathbf{R} : \forall x \in \Omega, \xi_i(x) = c$, and if the system isn't perturbed the observation is the same for every instant in the observer proper time.

Definition (State Space)

The state space, Γ is the set of all possible states that a thermodynamic system can reach.

Equillibrium States

Definition (Equilibrium State)

An Equillibrium State, which will be represent by $X, Y, Z, \ldots$ is a thermodynamic state whose observations are homogeneous, i.e, $\exists c \in \mathbf{R} : \forall x \in \Omega, \xi_i(x) = c$, and if the system isn't perturbed the observation is the same for every instant in the observer proper time.

Definition (State Space)

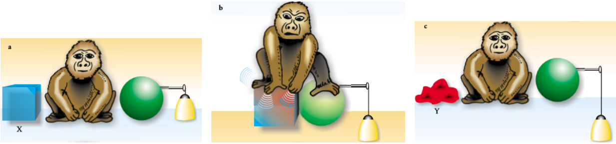
The state space, Γ is the set of all possible states that a thermodynamic system can reach.

The definition that Lieb and Yngvason gave to the state space it's a little dubious, because, as we shall see later, it will be possible to make comparisons between different State Spaces.

Adiabatic Accessibility

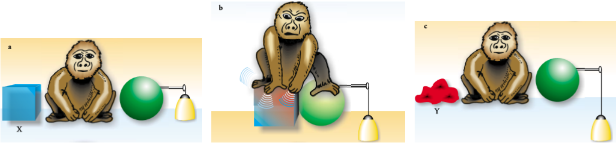
Physicists Definition

We say that a equilibrium state Y is adiabatically accessible from X, and we write $X \prec Y$, if it's possible to get from X to Y through the interaction between a system and a device assisted by a weight, so that the system returns to its initial state and the weight either went up or down.



Physicists Definition

We say that a equilibrium state Y is adiabatically accessible from X, and we write $X \prec Y$, if it's possible to get from X to Y through the interaction between a system and a device assisted by a weight, so that the system returns to its initial state and the weight either went up or down.



Notation

If $X \prec Y$ and $Y \prec X$ we write $X \overset{A}{\sim} Y$.
If $X \prec Y$ but $Y \not\prec X$ we write $X \prec\prec Y$.

State Space Algebra

We can define two operations in the state space, the compositions and the scale copy.

State Space Algebra

We can define two operations in the state space, the compositions and the scale copy.

Composition

The composition of two states X and Y, elements of Γ_1 and Γ_2 resp., is the compound state (X, Y) element of $\Gamma_1 \times \Gamma_2$. Moreover, the composition is commutative, i.e, $(X, Y) = (Y, X)$.

State Space Algebra

We can define two operations in the state space, the compositions and the scale copy.

Composition

The composition of two states X and Y, elements of Γ_1 and Γ_2 resp., is the compound state (X, Y) element of $\Gamma_1 \times \Gamma_2$. Moreover, the composition is commutative, i.e, $(X, Y) = (Y, X)$.

Remark

Note that the compound system can be a composition of finitely many states, because you can consider, for example, $\Gamma_2 = \Gamma_3 \times \Gamma_4$. In this case, we consider this operation, associative, i.e.
$(X, (Y, Z)) = ((X, Y), Z) = (X, Y, Z)$.

Scale Copy

Let X be a state of Γ. We define λX with $\lambda > 0$ as the state where the measures that represent extensive properties are scalled by a factor λ, and the intrinsic roperties remain the same.λX is called the scaled copy of X. The set of the scaled copies, by a factor λ of every element of Γ is denoted as $\lambda\Gamma$.

Entropy Principle

There is a real-valued function on all states of all systems (including compound systems) called entropy and denoted by S such that the following holds.

- Monotonicity. When X and Y are comparable states then $X \prec Y$ if and only if $S(X) \leq S(Y)$.
- Additivity and extensivity. If X and Y are states of some (possibly different) systems and if (X, Y) denotes the corresponding state in the compound system, then the entropy is additive for these states, i.e. $S(X, Y) = S(X) + S(Y)$. S is also extensive, i.e. for or each $\lambda > 0$ and each state X and its scaled copy $\lambda X \in \lambda\Gamma$

$$S(\lambda X) = \lambda S(X)$$

.

Reflexivity

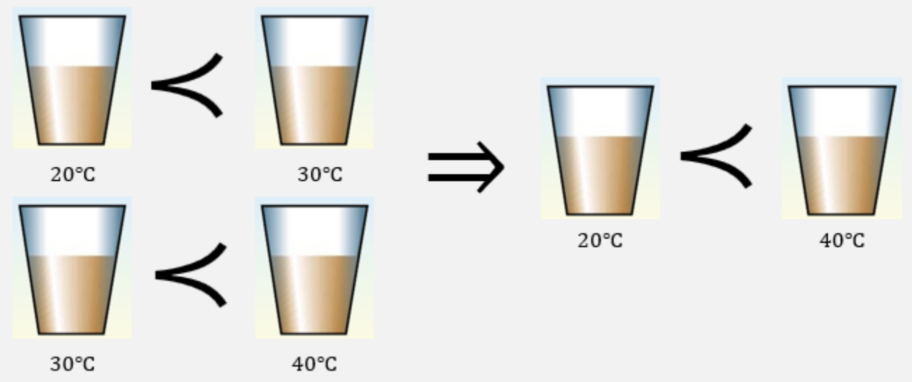
Axiom 1

For all equilibrium state X in Γ, $X \overset{A}{\sim} X$

Transitivity

Axiom 2

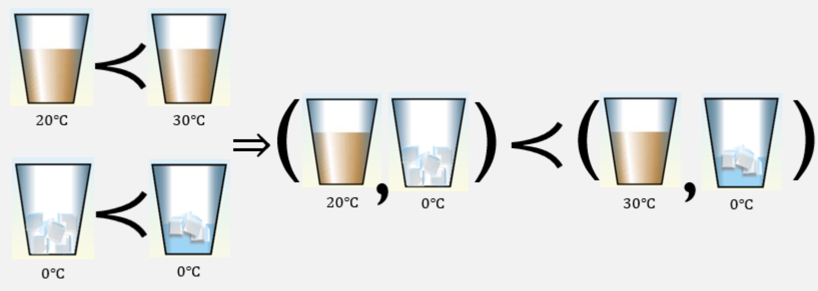
If $X \prec Y$ and $Y \prec Z$ then $X \prec Z$.



Consistency

Axiom 3

If $X \prec X'$ and $Y \prec Y'$ then $(X, Y) \prec (X', Y')$.



Scalling Invariance

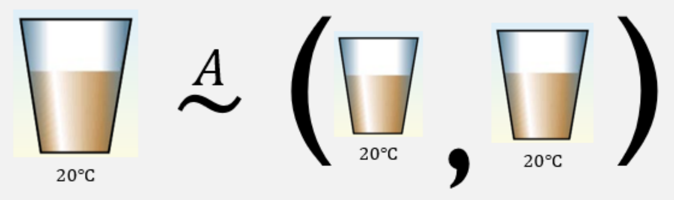
Axiom 4

If $\lambda > 0$ and $X \prec Y$ then $\lambda X \prec \lambda Y$.

Splitting and Recombination

Axiom 5

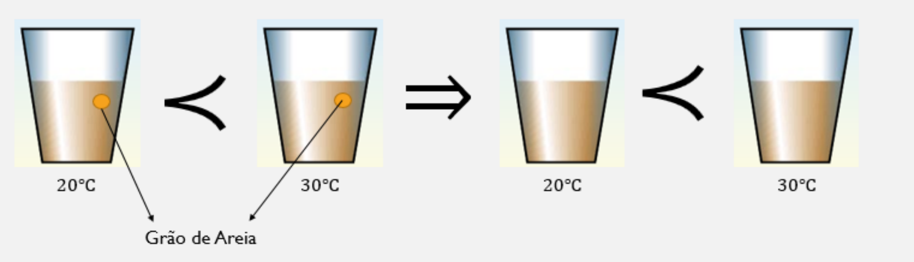
$X \overset{A}{\sim} ((1-\lambda)X, \lambda X)$ for all $0 < \lambda < 1$.



Stability

Axiom 6

If $(X, \varepsilon Z_0) \prec (Y, \varepsilon Z_1)$ for some Z_0, Z_1 and a sequence of εs tending to zero, then $X \prec Y$.



Axiom 7

Assume X and Y are states in the same *convex* state space, Γ. Then, for $t \in [0, 1]$,

$$(tX, (1-t)Y) \prec tX + (1-t)Y.$$

Where the sum is defined by ordinary convex combination of points in the convex set Γ.

Irreversibility

Axiom 8

For each $X \in \Gamma$ there is a point $Y \in \Gamma$ such that $X \prec\prec Y$.

Comparison Hypothesis

Definition

We say that the Comparison Hypothesis (CH) holds for a state space Γ if all pairs of states in Γ are comparable, i.e., $\forall X, Y \in \Gamma, X \prec Y$ or $Y \prec X$.

Theorems

Theorem

The Entropy Principle is equivalent to Axioms 1 *to* 6 *and CH. Moreover this entropy function on* Γ *is unique up to affine equivalence, i.e.,* $S(X) \to aS(X) + b$ *with* $a > 0$.

Theorems

Theorem

The Entropy Principle is equivalent to Axioms 1 *to* 6 *and CH. Moreover this entropy function on* Γ *is unique up to affine equivalence, i.e.,* $S(X) \to aS(X) + b$ *with* $a > 0$.

Corollary

If $X, Y, Z \in \Gamma, X \prec Y \prec Z$ *with* $X \prec\prec Z$ *and we define* $S(X) = 0$ *and* $S(Z) = 1$, *then:*

$$S(Y) = sup\{\lambda : ((1-\lambda)X, \lambda Z) \prec Y\} = inf\{\lambda : Y \prec ((1-\lambda)X, \lambda Z)\}$$

.

Theorems

Definition (Forward Sector)

The forward sector of X is the set $A_X := \{Y \in \Gamma : X \prec Y\}$.

Theorems

Definition (Forward Sector)

The forward sector of X is the set $A_X := \{Y \in \Gamma : X \prec Y\}$.

Theorem

Assume axioms 1 to 7 for $\Gamma \subset \mathbf{R}^n$ and consider the following statements:

1. *Existence of Irreversible processes: For every $X \in \Gamma$ there is a $Y \in \Gamma$ with $X \prec\prec Y$.*
2. *Caratheodory's Principle: In every neighborhood of every $X \in \Gamma$ there is a $Z \in \Gamma$ with $X \not\prec Z$.*

Then (1) implies (2) always. If forward sectors in Γ have interior points, then (2) implies (1).

Theorems

Theorem

Forward Sectors are convex sets

Theorems

Theorem

Forward Sectors are convex sets

Theorem (Concavity of Entropy)

Let Γ be a convex state space. Assume the axioms 1 to 7, and CH for multiple scaled copies of Γ. Then the entropy S is a concave function on Γ.

Our Philosophy

- Generalize the ideas of Lieb and Yngvason.
- Localize the theory.
- Consider the existence of restrictions on the state space.

The First Law of Thermodynamics

We start by given a precise definition of what is the adiabatic acessibility, which is something that is missing in Lieb's Theory. First of all, we assume that $\Gamma = (U, V_1, ..., V_n) : F(U, V_1, ..., V_n) = 0 \subseteq \mathbf{R}^{n+1}$ is a $n+1$ dimensional manifold, where F is some constraint that can limit the states that can be reached. Now lets recall the first law of thermodynamics.

Definition

The first law of thermodynamics

$$dU = \delta Q - \delta W$$

establishes a relation between the internal energy of a system and the energy supplied to the system, both in the form of heat and in the form of work.

Notice that $dU, \delta Q$ and δW are 1-forms. We write δW instead of dW, because the line integral might depend on the path.

Adiabatic Accessibility

Definition (Adiabatic Accessibility)

Given a state space Γ and two elements of this space, X, Y, we say that Y is adiabatically acessible from X, and write $X \prec Y$, if exits a path connecting X and Y, satisfying the relation $du = -\delta W$.

New Axiom

New Axiom 7

Let A be an open set of $\mathbf{R}^{n+1}$ and $B = A \cap \Gamma$. Fix $X \in int(B)$. We axiomatize that exists a set $\mathcal{C}$, of continuous maps $\gamma : [0,1] \to B$ such that:

1. $X \in int(\gamma([0,1]))$;
2. γ is right-differentiable and $\{d^+\gamma(t) : \gamma \in \mathcal{C}\} \cong A$;
3. $\forall Y \in B, \exists \gamma \in \mathcal{C} : Y \in \gamma([0,1])$.
4. $(t\gamma(0), (1-t)\gamma(1)) \prec \gamma(t)$.

New Axiom

New Axiom 7

Let A be an open set of $\mathbf{R}^{n+1}$ and $B = A \cap \Gamma$. Fix $X \in int(B)$. We axiomatize that exists a set $\mathcal{C}$, of continuous maps $\gamma : [0,1] \to B$ such that:

1. $X \in int(\gamma([0,1]))$;
2. γ is right-differentiable and $\{d^+\gamma(t) : \gamma \in \mathcal{C}\} \cong A$;
3. $\forall Y \in B, \exists \gamma \in \mathcal{C} : Y \in \gamma([0,1])$.
4. $(t\gamma(0), (1-t)\gamma(1)) \prec \gamma(t)$.

Warning: This axiom is under construction

Important Theorem

Theorem

Assuming axioms 1 to 6, the new axiom 7, axiom 8 and CH, then Caratheodory's Principle doesn't imply the Concavity of the Entropy everywhere.

Sketch of the proof

Notation

- We write $\gamma_{[X,Y]}$ if $\gamma(0) = X$ and $\gamma(1) = Y$.
- Let $S_\gamma = S \circ \gamma$ the entropy along the curve γ.

Sketch of the proof

Notation

- We write $\gamma_{[X,Y]}$ if $\gamma(0) = X$ and $\gamma(1) = Y$.
- Let $S_\gamma = S \circ \gamma$ the entropy along the curve γ.

Lemma

If $Y \in \gamma_{[X,Z]}([0,1])$ and $Y \prec Z$ then $X \prec Y$.

Sketch of the proof

Notation

- We write $\gamma_{[X,Y]}$ if $\gamma(0) = X$ and $\gamma(1) = Y$.
- Let $S_\gamma = S \circ \gamma$ the entropy along the curve γ.

Lemma

If $Y \in \gamma_{[X,Z]}([0,1])$ and $Y \prec Z$ then $X \prec Y$.

Lemma

With these axioms and CH, Existence of Irreversible Processes implies Caratheodory's Principle.

Sketch of the proof

Notation

- We write $\gamma_{[X,Y]}$ if $\gamma(0) = X$ and $\gamma(1) = Y$.
- Let $S_\gamma = S \circ \gamma$ the entropy along the curve γ.

Lemma

If $Y \in \gamma_{[X,Z]}([0,1])$ and $Y \prec Z$ then $X \prec Y$.

Lemma

With these axioms and CH, Existence of Irreversible Processes implies Caratheodory's Principle.

Lemma

If S is concave then Γ is convex.

We constructed a theory where the Caratheodory's Principle holds, but Γ isn't convex.

Under which circumstances is the entropy concave?

Theorem

If the domain is convex, then S is concave.

Under which circumstances is the entropy concave?

Theorem

If the domain is convex, then S is concave.

Theorem

For very state $X \in \Gamma$ exists a neighborhood where S is concave except sates in $\partial\Gamma$ where the curvature is negative.

Remarks

According to the Radamacher's theorem, which states that if a function is convex, then is differential almost everywhere, there is temperature almost everywhere, since the temperature is given by

$$\frac{1}{T}(X) = \partial_U S(X)$$

Remarks

According to the Radamacher's theorem, which states that if a function is convex, then is differential almost everywhere, there is temperature almost everywhere, since the temperature is given by

$$\frac{1}{T}(X) = \partial_U S(X)$$

If we assume that S is twice differentiable, we can define a Pseudo-Riemannian Metric, as

$$g_{ij} = -\partial^2_{x_i x_j} S,$$

where $\mathbf{x} = (U, V^n)$.

Open Problems

- What properties can we infer about state space with the use of metrics?
- Is our state space geodesically convex?
- What is the physical meaning of the states in the boundary where the curvature is negative? Is it even possibel to have such points?
- If we consider spaces which the states aren't at equilibrium. How far can we get with this formalism?

References

- Stephen Kronwith. *Convex Manifolds of Nonnegative Curvature.* Journal of Differential Geometry
- Theodore Frankel. *The Geometry of Physics An Introduction.* Cambridge University Press
- Elliott H. Lieb, and Jakob Yngvason. *The Physics and Mathematics of the Second Law of Thermodynamics.* Physics Reports 310(1999) 1-96
- Andre Thess. *The Entropy Principle: Thermodynamics for the Unsatisfied.*
- R. Tyrrell Rockafellar. *Convex Analysis.* Springer
- George Ruppeiner. *Riemannian geometry in thermodynamic fluctuation theory.*
- Manfredo Perdigão do Carmo. *Geometria Riemanniana.* IMPA