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> *"We have to be on our guard against a confusion in terminology. Thermodynamics is usually said to be macroscopic, which is correct to the extent that, say, MTE [macroscopic thermodynamics of equilibrium] has only a single parameter the entropy to account for the microstructure of the system. Yet MTE is not as macroscopic as macromechanics, which ignores the microsctructure altogether." (Tisza)*

Geometric Thermodynamics

Postulate

The states of the thermodynamic system are represented by points in the *configuration space*: a $(k+1)$-dimensional smooth real manifold M with global coordinates $(X_0, X_1, X_2..., X_k)$ known as *extensive variables*, where $U := X_0$ is called the *internal energy* and $S := X_1$ is called the *entropy*.

Geometric Thermodynamics

Postulate

There exists a smooth function f between the extensive variables

$$U = f(S, X_2, ..., X_k) \tag{4}$$

defining a k-dimensional surface in M with the following properties:

- ⓐ f is a first-order homogeneous function of $S, X_2, ..., X_k$:

  $$f(\lambda S, \lambda X_2 ..., \lambda X_k) = \lambda f(S, X_2 ..., X_k) \tag{5}$$

  for every positive real number λ and for all $S, X_2 \ldots, X_k$.
- ⓑ U is a monotonically increasing, surjective function from S to the real numbers, all other variables held fixed.
- ⓒ U is a convex function of its arguments.

Thermodynamic System

Thermodynamic System

A *thermodynamic system* is the pair (M, f), where M is a $(k+1)$-dimensional manifold with global coordinates $U, S, X_2, ..., X_k$ and $U = f(S, X_2, ..., X_k)$ where U is a first-order homogeneous function of its arguments, is a monotonically increasing function of S and is convex.

Some Questions

- Why are we just assuming the existence of the entropy variable?
- How can we recover the ‘orthodox’ first and second laws?
- What does ‘extensive’ mean?
- How are energy and entropy singled out as ‘special’ configuration variables?

Notes on the fundamental relation

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$$dU = TdS + \sum_{i=2}^{k} P_i dX_i$$

where the $P_i := \partial f / \partial X_i$ are called *intensive parameters* with $T := \partial f / \partial S$ called the temperature. Being partial derivatives of f, the P_i are functions of $X_1, ..., X_k$:

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Writing the intensive parameters as such functions, they are known as the *equations of the state*.

Energy and Entropy

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Is this a case of theft over honest toil?

Tisza on theft and toil

There remains, however, a searching question to answer: How do we determine the entropy that appears as an undefined concept by postualtion fiat in MTE? In CKC thermodynamics, great care is taken to construct the entropy from empirical data. The postulation of this concept might seem cavalier to the traditionalist student of the subject, and he may even invoke Bertrand Russell's famous remark contrasting honest work and theft in an apparently similar constellation.

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Similar comment in Uffink's *Bluff your way* which seems to hint at similar sentiment.

Tisza on theft and toil

"Yet such an attitude misses a most important point. Different axiomatizations of the same empirical discipline lead to different theories which enable us to ask and answer different types of questions. In CKC thermodynamics one admits only operational elements into the postulational basis and proceeds from empirical data to the entropy. This concept appears as the culmination of the whole effort, but the theory has not much to tell us about the practical use of the newly won concept.
In contrast, the entropy is a conceptual tool, a means to an end in MTE. The postulational basis is formulated in terms of variables that bring out the intrinsic symmetry of the theory in an elegant form, even though not all of these variables are strictly speaking operational."

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First Law = Energy Conservation?

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Care: In mechanics, energy conservation is the claim that the hamiltonian h is invariant under the phase flow map φ_t associated with the vector field H^a generated by the hamiltonian.
Better: the first law specifies the energy of the thermodynamic system in terms of its degrees of freedom, just like the Hamiltonian does.

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$$\lambda U = f(\lambda S, \lambda X_2, \ldots, \lambda X_k) = \lambda f(S, X_2, \ldots, X_k) \implies U = f(S, \ldots, X_k). \tag{6}$$

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Suggestion: they are simply the variables in terms of which the fundamental relation is defined. Thus extensivity is a purely formal notion.

Concrete Example

Euler's Theorem on Homogeneous functions (Callen, *Thermodynamics*):

$$S = \frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}N$$

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$1/T$ and p/T are determined experimentally. It turns out that μ/T is derivable from $1/T$ and p/T. This is a consequence again of the fundamental relation being homogeneous (See Callen for the mathematical details).

Concrete Example

The fundamental relation of the ideal gas is:

$$S = \left(\frac{3}{2}R\frac{N}{U}\right)U + \left(\frac{NR}{V}\right)V - \left(R\ln\left[\frac{N^{5/2}}{VU^{3/2}}\right] - K\right)N.$$

Monotonicity

Monotonicity implies that the fundamental relation may be written as

$$S = g(U, X_2, ..., X_k)$$

where the function g results from rearranging

$$U = f(S, X_2, ..., X_k)$$

to make S the subject.
Former: *entropy representation*
Latter: *energy representation*

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- No process exists where heat spontaneously flows from cold to hot.
- No process exists which can completely convert heat to work.
- The entropy change in a (spontaneous) process from one state to another is always greater than or equal to zero.
- The rate of change of entropy is greater than or equal to zero.

Equilibrium and the Second Law

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But what is equilibration and equilibrium in thermodynamics?

Equilibrium

Equilibrium

When a system suffers a change in its surroundings, it will usually be seen to undergo change. If the bulb of a thermometer is placed in a beaker of warm water, the mercury will begin to expand and will start to rise in the capillary. After a time, however, the system will be found to reach a state where no further change takes place and it is then said to have come to thermodynamic equilibrium. (Adkins)

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The most essential primitive concept in classical thermodynamics is that of equilibrium. A system is said to be in equilibrium when it ceases to interact with its immediate surroundings and when all conceivable subsystems within it cease to interact with each other. In other words, a system is said to be in equilibrium if it remains unchanged when its external boundary, or any internal boundary, suddenly becomes adiabatic. It is postulated that any thermodynamic system can be in equilibrium, and that any isolated system reaches equilibrium after a sufficient lapse of time. (Kestin)

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Remarks:

- this version of the law is just as much to do with energy as it is to do with entropy by virtue of the invertibility of the fundamental relation.
- It makes unavoidable use of the concept of 'composite system'.

Equilibrium and the Second Law

K-Equilibrium

Let (M, f) be a thermodynamic system with variables $X_0, ..., X_k$ which is composed of n subsystems $(M^{(i)}, f^{(i)})$ for $i = 1, 2$ such that $X_K^{(1)} + X_K^{(2)} = X_K$ for all $K = 0, ..., k$. Then the values of the variables $X_K^{(i)}$ which are attained on the removal of the internal constraint are those such that the energy of the composite system satisfies

$$U(X_0, ..., X_k) = \inf_{X_K^{(1)} + X_K^{(2)} = X_K} \{U^{(1)}(X_0^{(1)}, ..., X_k^{(1)}) + U^{(2)}(X_0^{(2)}, ..., X_k^{(2)})\}.$$

If this condition on the subsystems' extensive quantities is satisfied we say that the composite system is in equilibrium with respect to the variables X_K, or more briefly, in K-equilibrium.

Composite Systems and the Second Law

"We turn now to a methodological problem connected with the fact that the [geometric] formalism deals only with states of equilibrium while nontrivial results can be obtained only if processes are considered at least to a limited extent. The nature of this problem is illustrated by the following paradox: How are we to give a precise meaning to the statement that entropy tends toward a maximum, whereas entropy is defined only for systems in equilibrium? Thus in an isolated simple system the entropy is constant, if it is defined at all.
This difficulty is resolved in a natural way by the artifice of composite systems that enables us to deal with more or less constrained equilibria." (Tisza)

Convexity and the Second Law

Convexity

The function $f(X_1, ..., X_k)$ is convex iff, for all i and for any values $X_i', X_i'' \geqslant 0$ and for any $\alpha \in (0,1)$:

$$f(\alpha X_1' + (1-\alpha) X_1'', ..., \alpha X_k' + (1-\alpha) X_k'') \leqslant \alpha f(X_1', ..., X_k') + (1-\alpha) f(X_1'', ..., X_k'')$$

Wightman states that the function f is convex if and only if it satisfies

$$f(X_1, ..., X_k) = \ \inf \{ f(X_1', ..., X_k') + f(X_1'', ..., X_k'') \} \tag{7}$$

such that $X_i = X_i' + X_i''$.

Summary

- What is entropy? What role does it play in the various formulations of thermodynamics?
- The second law and how it is inextricably linked to the notions of equilibrium and composite system. Is there a logical hierarchy here?
- What happens if we relax some of the assumptions which it is postulated the fundamental relation has? (monotonicity, convexity, homogeneity) Should the fundamental relation of a thermodynamic system have these properties by definition?
- How is equilibrium to be defined in thermodynamics? Is it a primitive concept? Does its temporal nature hinder its representation in the thermodynamic formalism?