# Thermodynamic Geometry

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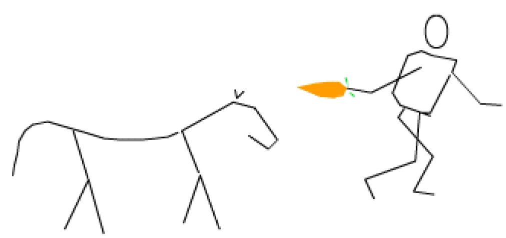


## 1 Introduction

The geometric study of thermodynamics began with Gibbs's reformulation of the theory in terms of equilibrium states rather than processes [1]. The surface of the set of equilibrium states was Gibbs's primary object of study and foreshadowed much of the modern differential geometric theory manifolds.

Gibbs surfaces is where the geometric theory stood when I became a graduate student. The story that I relate in these lectures begins here. This is when Frank Weinhold published a series of five papers [2] based on the following observation: If we interpret differentials as vector quantities, and use the second derivative matrix of the internal energy as a metric, then many of the thermodynamic identities can be interpreted as well known geometric equations, e.g., the Pythagorean theorem, the law of sines, etc. At the time, I was working on another aspect of the geometrical structure related to thermodynamic potentials (briefly mentioned in the last lecture) and reacted to these papers with great skepticism. The geometry of Gibbs seemed to

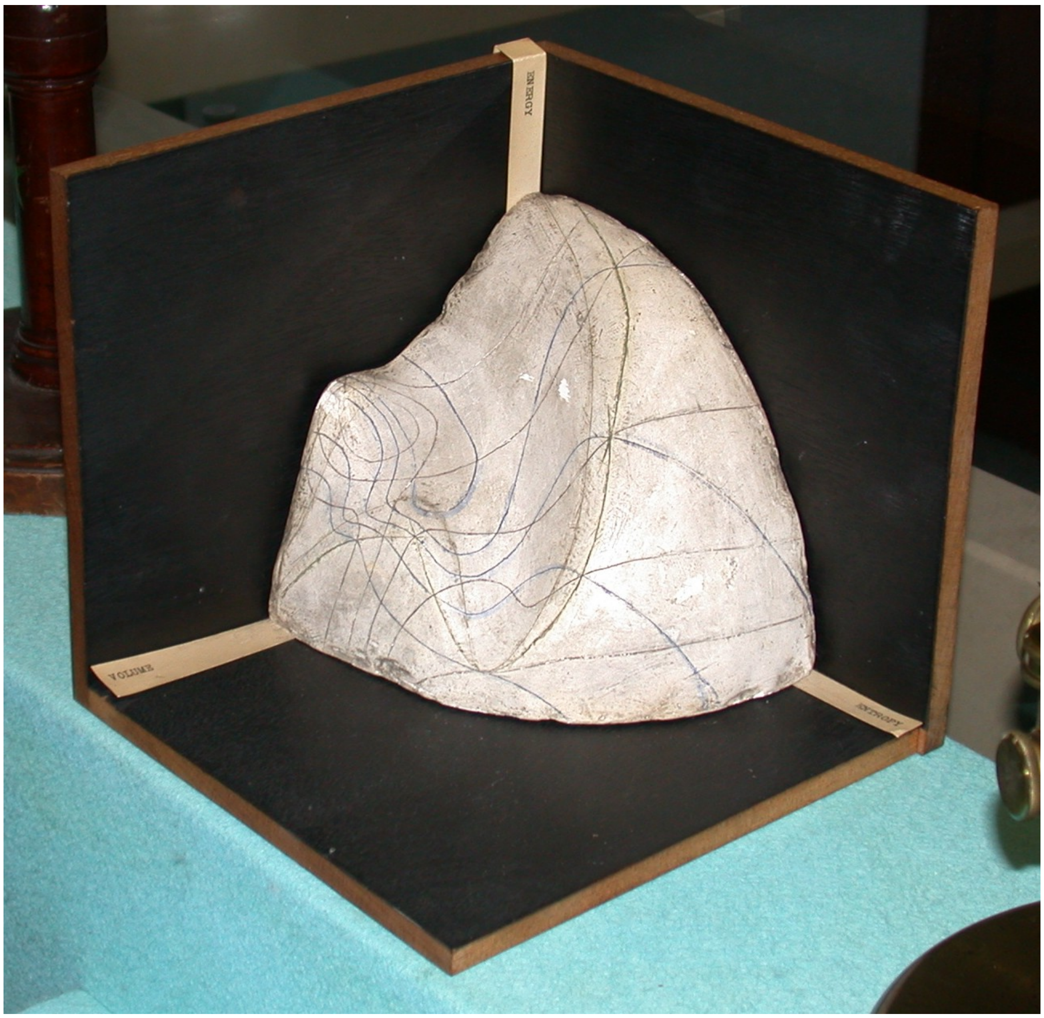



Figure 1: Plaster model of the equilibrium states of water constructed by James Clerk Maxwell and sent as a present to Josiah Willard Gibbs.

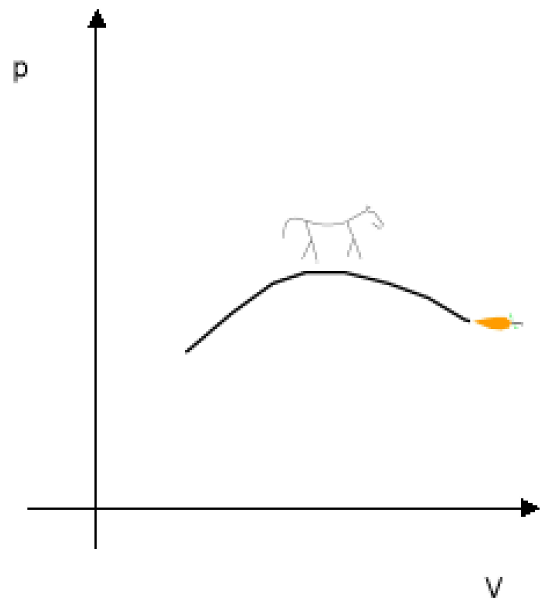
point to an affine rather than a metric structure for the manifold of equilibrium states; there are always many choices for a metric and finding that some identities can be naturally expressed in terms of one is hardly proof of its physical significance. If such a metric really means anything, then finite lengths rather than infinitesimal ones should have meaning. Fortunately, Steve Berry, in whose group Bjarne Andresen and I were both working at the time, did not share my skepticism. He asked me to calculate what such finite distance would look like if we take the metric structure seriously. He then showed them to a shock tube experimentalist (Paul Gait) who recognized one of the formulas (the length of an adiabat) as the change in the flow velocity of a gas when a shock wave passes [3]. This clue led to the more general interpretation of such distances and their intimate relation to dissipation in what was to be called the Horse-Carrot theorems [4, 5, 6], the main topic of these lectures.

# 2 The Horse-Carrot Theorem

Dissipation can be measured by entropy production or by loss of available work. Weinhold worked with the second derivative matrix of the internal energy. As seen below, this metric yields bounds on loss of available work. One early result [7] is that the metrics defined by the second derivative of the internal energy and by the second derivative of the entropy are conformally equivalent, i.e., the energy metric is just the temperature times the entropy metric (not as matrices but as quadratic forms acting on infinitesimal displacements). Below we work almost exclusively with the entropy metric but note that analogous statements can be made for the energy metric.

Let us begin by focusing on a thermodynamic system undergoing a process that we can represent as a sequence of states in its state space of thermodynamic variables. Thus we take what most textbooks would call a quasistatic process of a simple system and ask what the minimum dissipation might mean for such a process. If we are given infinite time, we can make the quasistatic process reversible. More precisely, given a sufficiently large time, we can make the entropy production as small as desired.

To see this, consider bringing the system along the quasistatic locus by successively placing it in contact with a very large copy of itself in a state corresponding to a point a little further along the quasistatic locus. This causes the system to equilibrate toward this next state and we then proceed by a sequence of (possibly incomplete) equilibrations. As we make these equilibrations smaller and smaller, the process produces less and less entropy while taking longer and longer. To illustrate this point, we pause for a very simple yet concrete example which makes this basic idea explicit.




*EXAMPLE*: We consider the example of heating a cup of coffee [8]. We do it in the manner suggested above by placing it in contact with a sequence of slightly hotter heat baths. Assuming that our coffee cup has a constant heat capacity, $C$, and that we wish to heat the cup from $T_0$ to $T_f$, we ask for the sequence of $K$ temperatures $T_1$, $T_2$, ..., $T_K = T_f$ such that the $K$ complete equilibrations of the cup starting from $T_{j-1}$ and ending at $T_j$, $j = 1, ...K$ minimize the total entropy production.

The entropy production for step $j$ is

$$(dS_u)_j = dS_{cup} + dS_{room} = C\left(\frac{1}{T} - \frac{1}{T_j}\right)dT. \tag{1}$$

$$(\Delta S_u)_j = \int_{T_{j-1}}^{T_j} dS_u = \int_{T_{j-1}}^{T_j} C\left(\frac{1}{T} - \frac{1}{T_j}\right)dT. \tag{2}$$

If the heat capacity $C$ is constant, the total entropy production $\Delta S_u$ is

$$\Delta S_u = \sum_{j=1}^{K} \Delta(S_u)_j = C \left( ln\frac{T_f}{T_0} - K + \sum_{j=1}^{K} \frac{T_{j-1}}{T_j} \right) \tag{3}$$

which is minimized by the sequence of temperatures

$$T_j = T_0 \left( \frac{T_K}{T_0} \right)^{\frac{j}{K}} \tag{4}$$

with the minimum entropy production given by

$$(\Delta S_u)_{opt} = \frac{C}{2K} \left( ln\frac{T_f}{T_0} \right)^2 \tag{5}$$

This calculation can be made completely generally and gives the discrete version of

**Theorem 1 (Discrete Horse-Carrot Inequality [4])** *In a process of $K$ near equilibrations of a simple system to states along a given quasistatic locus, $K \gg 1$, the entropy production is bounded below by*

$$\Delta S_u \geq \frac{L^2}{2K}. \tag{6}$$

Here $L$ is the thermodynamic length of the path

$$L = \int \sqrt{\sum \frac{\partial S^2}{\partial X_i \partial X_j} dX_i dX_j} \tag{7}$$

and the $X_i$ are a complete set of extensive variables of the thermodynamic system.

A closely related, continuous time version is given by

**Theorem 2 (Horse-Carrot Inequality [5])** *In a sufficiently slow process in which a system traverses a given quasistatic locus, the entropy production is bounded below by*

$$\Delta S_u \geq L^2 \bar{\epsilon}/\tau, \tag{8}$$

*where L is the thermodynamic length of the quasistatic locus, $\tau$ is the duration of the process and $\bar{\epsilon}$ is a mean relaxation time.*

The first lecture will present the details and proofs of these two theorems and discuss their meaning.

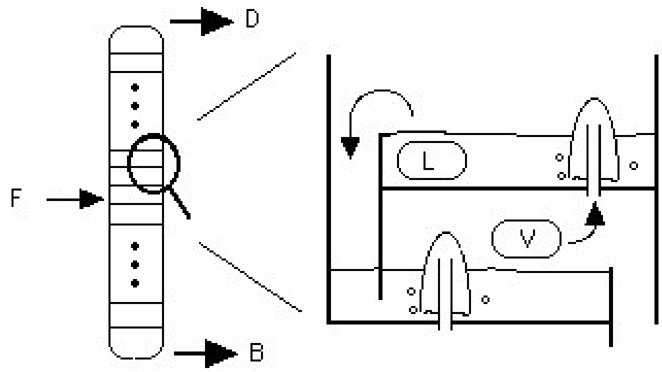



Figure 2: A schematic distillation column with flows: feed $F$, distillate $D$ and bottoms $B$. The close up shows two adjacent trays including overflow tubes for downward flow of liquid $L$ and bubble caps for upward flow of vapor $V$.

# 3 Staged Steady-State Processes

Applications of the Horse-Carrot theorem were not quick to materialize. In fact, it was a 1997 comment by a graduate student (Eitan Geva, who has since made important contributions to quantum thermodynamics in finite time) that spurred me to pursue a serious search for applications. The result was a version of the discrete Horse-Carrot Theorem [6] in which, surprisingly, the "system" consisted of the flows (!) in the steady state process. The only example that has been calculated in detail is fractional distillation, for which the large $K$ limit turned out to be rather a mild constraint. Already for $K = 15$ the bound, and the prescribed optimum, performed surprisingly well [9]. This was later explained by Jim Nulton's theorem [10] showing that the prescribed optimum is correct to a higher order than the truncations involved would lead one to expect.

The second lecture will discuss the generalized Horse-Carrot Theorem for steady-flow processes and the fact that the truncation gives higher order than expected.

# 4 Fluctuation Theory

A natural question to ask was how this metric structure looks from a statistical mechanical perspective. Rather early in the process of uncovering this structure we were led to the following theorem:

**Theorem 3 (Statistical Mechanical Length [11])** *The length of a path measured microscopically or macroscopically are equal.*

The metric at this level is still the second derivative of the entropy $S = \sum p_i ln(p_i)$. This metric, in the hands of Diosi and Ruppeiner, has made a significant impact on the theory of fluctuations [12, 13]. It turns out that for large fluctuations, corrections must be made to the Einsteinian theory. This becomes important only near the critical point, where fluctuations become large. The initial impetus was provided by George Ruppeiner's computational experiments in Ising lattices near the critical point. His framework involves a nice physical picture of fluctuations inside fluctuations inside fluctuations ... (see figure 3).

He was able to use a path-integral formalism in which $1/V$ plays the role of time and the likelihood of a path is the length of a path as measured by thermodynamic distance. A very similar theory, more elegant but less physically motivated, was advanced by Diosi and coworkers [12] which analyzed the underlying stochastic processes in terms of a covariant partial differential equation instead of path integrals. The interpretation supported by these considerations is that the thermodynamic length of a process may be thought of as the number of fluctuations needed to traverse the process. This point was eloquently made by Wootters [14].

# 5 Pot Pourri

It is difficult to plan a series of lectures for an audience as yet unmet. (I have this same difficulty at the beginning of each semester.) How much details will the audience want/need? The last lecture will elaborate on and fill in certain details from the previous three. If this appears superfluous, there is plenty of additional topics:

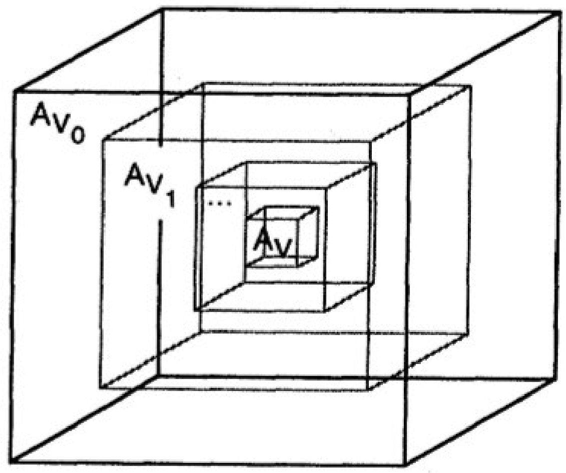



Figure 3: Hierarchy of subsystems $A_{V_1} \supset A_{V_2} \supset ... \supset A_V$. Each subsystem feels only the state of its immediate surrounding neighbor.

- Quantum mechanical version of thermodynamic length [15].
- Fisher information and the theory of large fluctuations [16].
- Generalized thermodynamic potentials and contact geometry [17].

How much of these topics will be covered, given the alloted time and the curiosity of the audience, remains to be seen.

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