Thermodynamics and contact geometry
Lecture 3: Thermodynamics

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Introduction

Now we are ready to talk about thermodynamics. This lecture is based on

- ▶ R. Hermann, *Geometry, Physics, and Systems*, Dekker (1973), Chapter 6.
- ▶ J.W. Gibbs, *Graphical methods in the thermodynamics of fluids*, Trans. Conn. Acad. 1873, II, 309–342.
- ▶ D.V. Schroeder, *An Introduction to Thermal Physics*, Pearson (2000).

The paper by Gibbs is very old, but well worth a read. Hermann made the following remark in his book:

After much reading on the subject, I would say that Gibbs understood, in about 1870, the mathematics of thermodynamics - even in its most "modern" form - better than almost all of the authors who followed him.

Quantities and relations

We will assume that at each state of a thermodynamical system, five quantities are given:

- ▶ v,   the volume,
- ▶ p,   the pressure,
- ▶ T,   the temperature,
- ▶ e,   the energy,
- ▶ s,   the entropy.

We also have some quantities that do not depend on the state, but on the path taken when passing from one state to another:

- ▶ W,   the work done,
- ▶ Q,   the heat received.

The first law

The first law of thermodynamics is a statement about energy conservation. It says that the change of energy of a system, when passing from one state to another, is equal to the heat received by the system minus the work done by it.

The infinitesimal version of this statement is often written $de = \delta Q - \delta W$. If we assume that the work and heat satisfy the equations $\delta W = pdv$ and $\delta H = Tds$, we obtain

$$de = Tds - pdv$$

which the space of states of the system must satisfy. In other words, a thermodynamic system is a (2-dimensional) Legendrian submanifold of the contact manifold $(\mathbb{R}^5, \theta = de - Tds + pdv)$.

Definition (Hermann)

A (simple smooth equilibrium) thermodynamic system is a Legendrian submanifold of the manifold $\mathbb{R}^5(v, p, T, e, s)$ equipped with the contact form $\theta = de - Tds + pdv$.

The ideal gas

Let us look at one of the most famous examples of a Legendrian submanifold in $\mathbb{R}^5$. The ideal gas is given by equations of the form

$$pv = aT, \qquad e = cT.$$

These equations by themselves do not determine a 2-dimensional submanifold in $\mathbb{R}^5$, since there are only two of them, but by using the contact structure we can determine the last equation.

From the contact form $-\frac{1}{T}\theta = ds - \frac{1}{T}de - \frac{p}{T}dv$ we see that the entropy is given by

$$s_e(e, v) = \frac{1}{T(e,v)} = \frac{c}{e}, \qquad s_v(e, v) = \frac{p(e,v)}{T(e,v)} = \frac{a}{v}.$$

The first equation has solution $s(e, v) = c \ln e + C(v)$ while the other equation implies that $C(v) = a \ln v + s_0$.

$$s(e, v) = c \ln e + a \ln v + s_0$$

This is almost the Sackur-Tetrode equation. However, determining s_0 is more difficult.

The ideal gas

It is difficult to draw a 2-dimensional surface situated in a 5-dimensional space. But we can easily display how three quantities are related, for example by plotting a surface in $\mathbb{R}^3(p, v, T)$. If $a = 1$, we have $pv = T$ which gives the following surface:
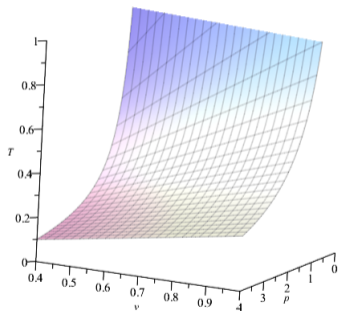

Figure: A plot of the ideal gas in a (p, v, T)-diagram.

The van der Waals gas

Consider an instance of the van der Waals gas[1] given by

$$p = \frac{8T}{3v-1} - \frac{3}{v^2}, \qquad e = 4T - \frac{3}{v}.$$

Then the entropy $s(e, v)$ is a solution to

$$s_e(e, v) = \frac{1}{T(e, v)} = \frac{4v}{ev+3}, \qquad s_v(e, v) = \frac{p(e, v)}{T(e, v)} = \frac{4(2ev^2 - 3v + 3)}{v(3v-1)(ev+3)}.$$

Thus

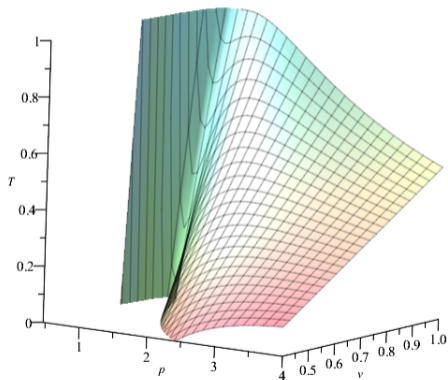$$s(e, v) = 4\ln\left(\frac{ev+3}{v}\right) + \frac{8}{3}\ln(3v-1) + s_0.$$

We can also write

$$s(T, v) = 4\ln(4T) + \frac{8}{3}\ln(3v-1) + s_0 = \ln\left(T^4(3v-1)^{8/3}\right) + s_0'.$$

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[1] See for example arxiv.org/pdf/1402.1205.

The van der Waals gas

Let us plot the relation between p, v, T in $\mathbb{R}^3$.

Different ways of representing the thermodynamic system

Let L be a Legendrian submanifold of the contact manifold $(\mathbb{R}^5, \theta)$. There are several different ways to represent it. In particular, one can (at least locally) choose any pair of the five thermodynamic quantities as coordinates on L.

For example, if we choose (v, s) as coordinates, then L can be given as a parametrized submanifold:

$$(v, s) \mapsto (v, s, p(v, s), T(v, s), e(v, s)).$$

Of course, the functions $p(v, s), T(v, s), e(v, s)$ are not arbitrary. If $e(v, s)$ is fixed, the other two functions are completely determined.

We see that if L is Legendrian with respect to $\theta = de - T ds + p dv$, then $e_v(v, s) = -p(v, s)$ and $e_s(v, s) = T(v, s)$.

(p, v)- and (s, T)-coordinates

We look at two other possible choices of coordinates. Assume that L is given by $e(p, v), s(p, v), T(p, v)$. In these coordinates, we have for $\theta = de - Tds + pdv$

$$
\begin{aligned}
\theta|_L &= e_p(p, v)dp + e_v(p, v)dv - T(p, v)(s_p(p, v)dp + s_v(p, v)dv) + pdv \\
&= (e_p(p, v) - T(p, v)s_p(p, v))dp + (e_v(p, v) - T(p, v)s_v(p, v) + p)dv = 0.
\end{aligned}
$$

The three functions that define L satisfy a system of two partial differential equations:

$$
e_p(p, v) = T(p, v)s_p(p, v), \qquad e_v(p, v) - T(p, v)s_v(p, v) + p = 0.
$$

Now assume that L is given by $e(T, s), p(T, s), v(T, s)$. Then we have

$$
\begin{aligned}
\theta|_L &= e_T(T, s)dT + e_s(T, s)ds - Tds + p(T, s)(v_T(T, s)dT + v_s(T, s)ds) \\
&= (e_T(T, s) + p(T, s)v_T(T, s))dT + (e_s(T, s) + p(T, s)v_s(T, s) - T)ds = 0.
\end{aligned}
$$

Again we obtain two systems of partial differential equations.

"Thermodynamic partial derivatives"

In the thermodynamic literature one often comes across expressions like $\left(\frac{\partial e}{\partial p}\right)_v$. This notation arises because the partial derivatives are taken on the 2-dimensional manifold L. When we compute the partial derivative along one of the coordinate functions, we must also specify the other coordinate. In this case we have chosen the coordinates (p, v). The expression $\left(\frac{\partial e}{\partial p}\right)_v$ means that e is considered as a function of p and v.

In this notation, the two systems on the previous slide is written

$$\left(\frac{\partial e}{\partial p}\right)_v - T\left(\frac{\partial s}{\partial p}\right)_v = 0, \qquad \left(\frac{\partial e}{\partial v}\right)_p - T\left(\frac{\partial s}{\partial v}\right)_p + p = 0$$

and

$$\left(\frac{\partial e}{\partial T}\right)_s + p\left(\frac{\partial v}{\partial T}\right)_s = 0, \qquad \left(\frac{\partial e}{\partial s}\right)_T + p\left(\frac{\partial v}{\partial s}\right)_T - T = 0.$$

Maxwell relations

For a thermodynamic system L, we have $\theta|_L = 0$ where $\theta = de - Tds + pdv$. Taking the exterior derivative of θ gives

$$d\theta = d(de) - dT \wedge ds + dp \wedge dv.$$

Now, use s and v as coordinates so that L is given by $T = T(s, v)$, $p = p(s, v)$, $e = e(s, v)$. We then have

$$dT = \left(\frac{\partial T}{\partial s}\right)_v ds + \left(\frac{\partial T}{\partial v}\right)_s dv, \quad dp = \left(\frac{\partial p}{\partial s}\right)_v ds + \left(\frac{\partial p}{\partial v}\right)_s dv,$$

so that $d\theta|_L = 0$ becomes

$$
\begin{aligned}
0 &= \left[\left(\frac{\partial T}{\partial s}\right)_v ds + \left(\frac{\partial T}{\partial v}\right)_s dv\right] \wedge ds - \left[\left(\frac{\partial p}{\partial s}\right)_v ds + \left(\frac{\partial p}{\partial v}\right)_s dv\right] \wedge dv \\
&= \left[\left(\frac{\partial T}{\partial v}\right)_s + \left(\frac{\partial p}{\partial s}\right)_v\right] dv \wedge ds.
\end{aligned}
$$

Because of this we have the relation $\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v$ which holds for every L.

Maxwell relations

The relation we found is one of the Maxwell relations. Some others are

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p, \qquad \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p, \qquad \left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v.$$

Heat capacities

The heat capacity of a system is the following quantity:

$$C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T}.$$

This quantity depends of course on the point in L, but also on the path taken as ΔT approaches 0. The two common versions of this quantity is C_p which is found by fixing p and varying T, while the other one is C_v which is found by fixing v and varying T. Since $\delta Q = de + \delta W = de + p \, dv$, we have

$$C_p = \left(\frac{\partial e}{\partial T} \right)_p + p \left(\frac{\partial v}{\partial T} \right)_p, \qquad C_v = \left(\frac{\partial e}{\partial T} \right)_v.$$

Wouldn't it be nice if they were written in the same coordinates?

Change of coordinates

On the previous slide, the functions C_p, C_v were written in different coordinates. Let us try to write also C_v in terms of (T, p)-coordinates. We have

$$(\partial_T)_v = A(\partial_T)_p + B(\partial_p)_T,$$
$$(\partial_v)_T = C(\partial_T)_p + D(\partial_p)_T,$$

for some functions A, B, C, D. In order to determine A, B, C, D we require the following:

$$(\partial_T)_v T = 1, \qquad (\partial_T)_v v = 0, \qquad (\partial_v)_T T = 0, \qquad (\partial_v)_T v = 1.$$

$$A = 1, \quad A\left(\frac{\partial v}{\partial T}\right)_p + B\left(\frac{\partial v}{\partial p}\right)_T = 0, \quad C = 0, \quad C\left(\frac{\partial v}{\partial T}\right)_p + D\left(\frac{\partial v}{\partial p}\right)_T = 1$$

The solution is

$$A = 1, \qquad B = -\frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_T}, \qquad C = 0, \qquad D = \frac{1}{\left(\frac{\partial v}{\partial p}\right)_T}.$$

Change of coordinates

In the end, we are left with the following:

$$(\partial_T)_v = (\partial_T)_p - \frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_T}(\partial_p)_T,$$

$$(\partial_v)_T = \frac{1}{\left(\frac{\partial v}{\partial p}\right)_T}(\partial_p)_T.$$

In particular, we see that

$$C_v = \left(\frac{\partial e}{\partial T}\right)_v = \left(\frac{\partial e}{\partial T}\right)_p - \frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_T}\left(\frac{\partial e}{\partial p}\right)_T.$$

Exercise: Show that we have, for the ideal gas, $C_p = c + a$ and $C_v = c$. (Remember that states of an ideal gas satisfies the equations $e = cT$, $v = aT/p$.)

Change of state

Let L be the Legendrian submanifold of $\mathbb{R}^5$ corresponding to a thermodynamic system. A continuous change from one state to another forms a curve γ on L. We define the work done by the system along γ and the heat absorbed by the system along γ as

$$W = \int_\gamma p\,dv, \qquad Q = \int_\gamma T\,ds.$$

If the path is a circuit (starting point is the same as end point), then since $de = \delta Q - \delta W$ and $\int_\gamma de = 0$, we have $W = Q$. Let D be the domain in L enclosed by γ.

By Green's theorem, we have in (p, v)- and (T, s)-coordinates

$$W = \oint_\gamma p\,dv = \iint_D dp\,dv = \oint_\gamma T\,ds = \iint_D dT\,ds = Q.$$

Thus the work (and heat) of a circuit is equal to the area it encloses, in both (p, v)- and (T, s)-coordinates. This makes such coordinates on L convenient choices.

# The Carnot cycle (an ideal heat engine)

The Carnot cycle consists of 4 steps:

1. Isothermal expansion: The gas is connected to the hot reservoir making T fixed at T_H. It does work by moving the piston upwards while absorbing heat from the reservoir. The entropy increases from its starting value s_1.

2. Adiabatic expansion: The gas is isolated from the reservoirs, but continues doing work (pushing the piston) until T reaches T_C. The entropy is kept fixed at s_2.

3. Isothermal compression: The gas is connected to the cold reservoir, making T fixed at T_C. Work is being done on the gas, moving the piston downwards and heat is transferred to the reservoir. The entropy decreases to s_1.

4. Adiabatic compression: The gas is isolated from the reservoirs, but work is still done on it until the temperature reaches T_H. The entropy is kept fixed at s_1.
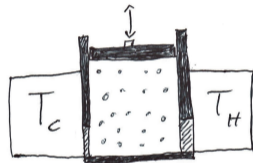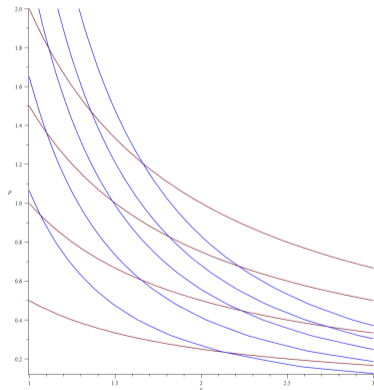
The Carnot cycle

Since the variables T, s take the same values at the end of a cycle as at the beginning, this process traces out a cycle (closed curve) on the Legendrian manifold L defining our system. If we choose (p, v)-coordinates, the cycle looks something like this:
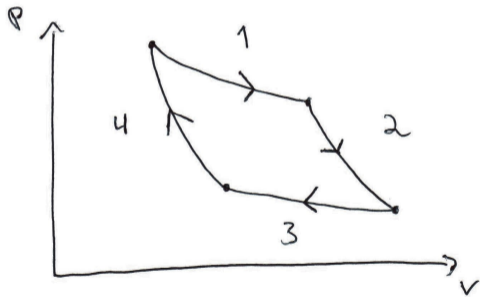
The curves 1 and 3 are curves of constant T while 2 and 4 are curves of constant s.

The Carnot cycle for the ideal gas

For the ideal gas $pv = T, e = T, s = \ln e + \ln v + s_0$, we draw some curves of constant temperature (red) and constant pressure (blue):
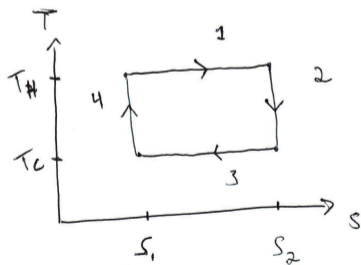
The Carnot cycle

The total work done by the engine during one cycle is equal to the area enclosed by the curve.
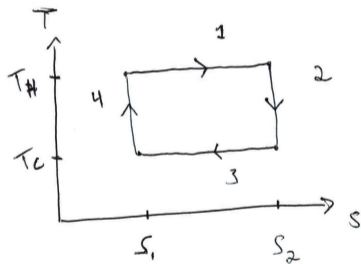
$$W = \iint_D dT\,ds = \iint_D dp\,dv$$

In a TS-diagram, the Carnot cycle takes the following simple form.

Thus $W = (T_H - T_C)(s_2 - s_1)$.

The efficiency of the Carnot cycle

The efficiency of the cycle is defined as $\frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$, where Q_H is the heat absorbed during the cycle, while Q_C is the heat given out.

The figure tells us that $Q_H = T_H(s_2 - s_1)$ while $Q_C = -T_C(s_1 - s_2)$ (since the heat received is $Q = \int_\gamma T ds$). Thus the efficiency of the Carnot cycle is $1 - T_C/T_H$.

Legendre transformations

The quantity $H = e + pv$ is called enthalpy. If we take the exterior derivative of this function, we get

$$dH - de - pdv - vdp = 0.$$

If we remember that $\theta = de - Tds + pdv$ and that $\theta|_L = 0$, we see that

$$(dH - de - pdv - vdp)|_L = (dH - pdv - Tds)|_L$$

This means that instead of considering $(\mathbb{R}^5(v, p, T, e, s), \theta)$, we can consider the manifold $\mathbb{R}^5(v, p, T, e, H)$ with the contact form $dH - vdp - Tds$. This type of transformation is called a Legendre transformation. Notice how v and p changed roles in the contact form.

Another physical quantity is the Gibbs free energy $G = e + pv - Ts = H - Ts$.
Exercise: Show that θ becomes $dG - vdp + sdT$ after the Legendre transformation given by $G = e + pv - Ts$.

A note about adding chemical potentials

So far we only considered Legendrian submanifolds of the space $\mathbb{R}^5(v, p, T, e, s)$. This picture can be generalized by adding chemical potentials. In that case we consider the pair

$$\mathbb{R}^{5+2n}(v, p, T, e, s, \mu_1, ..., \mu_n, \lambda^1, ..., \lambda^n), \qquad \theta = de - Tds - pdv - \mu_i d\lambda^i.$$

Here λ_i measure the concentrations of n different chemical substances, while the conjugates μ_i are called chemical potentials.

Plan for tomorrow

Tomorrow, we will introduce another geometric structure: the metric. And we will see what role it plays in thermodynamics.