3 More applications of derivatives

3.1 Exact & inexact differentials in thermodynamics

So far we have been discussing total or “exact” differentials

\[ du = \left( \frac{\partial u}{\partial x} \right)_y \, dx + \left( \frac{\partial u}{\partial y} \right)_x \, dy, \quad (1) \]

but we could imagine a more general situation

\[ du = M(x, y) \, dx + N(x, y) \, dy. \quad (2) \]

If the differential is exact, \( M = \left( \frac{\partial u}{\partial x} \right)_y \) and \( N = \left( \frac{\partial u}{\partial y} \right)_x \). By the identity of mixed partial derivatives, we have

\[ \left( \frac{\partial M}{\partial y} \right)_x = \left( \frac{\partial^2 u}{\partial x \partial y} \right) = \left( \frac{\partial N}{\partial x} \right)_y \] \quad (3)

Ex: Ideal gas \( pV = RT \) (for 1 mole), take \( V = V(T, p) \), so

\[ dV = \left( \frac{\partial V}{\partial T} \right)_p \, dT + \left( \frac{\partial V}{\partial p} \right)_T \, dp = \frac{R}{p} \, dT - \frac{RT}{p^2} \, dp \quad (4) \]

Now the work done in changing the volume of a gas is

\[ dW = pdV = RdT - \frac{RT}{p} \, dp. \quad (5) \]

Let’s calculate the total change in volume and work done in changing the system between two points A and C in \( p, T \) space, along paths \( AC \) or \( ABC \).

1. Path AC:

\[ \frac{dT}{dp} = \frac{T_2 - T_1}{p_2 - p_1} \equiv \frac{\Delta T}{\Delta p} \quad \text{so} \quad dT = \frac{\Delta T}{\Delta p} \, dp \quad (6) \]

\[ \frac{T - T_1}{p - p_1} = \frac{\Delta T}{\Delta p} \quad \Rightarrow \quad T - T_1 = \frac{\Delta T}{\Delta p} (p - p_1) \quad (7) \]

\[ dV = \frac{R}{p} \frac{\Delta T}{\Delta p} \, dp - \frac{R}{p^2} [T_1 + \frac{\Delta T}{\Delta p} (p - p_1)] \, dp = -\frac{R}{p^2} (T_1 - \frac{\Delta T}{\Delta p} p_1) dp \quad (9) \]

\[ dW = -\frac{R}{p} (T_1 - \frac{\Delta T}{\Delta p} p_1) dp \quad (10) \]
Now we can calculate the change in volume and the work done in the process:

\[ V_2 - V_1 = \int_{ABC} dV = R(T_1 - \frac{\Delta T}{\Delta p} p_1) \frac{p^2}{p_1} = R \frac{T_2 p_1 - T_1 p_2}{p_1 p_2} \]  \hspace{1cm} (11)

\[ W_1 - W_2 = \int_{ABC} p dV = R(T_1 - \frac{\Delta T}{\Delta p} p_1) \ln p \bigg|_{p_1}^{p_2} = R \frac{T_2 p_1 - T_1 p_2}{p_2 - p_1} \ln \frac{p_2}{p_1} \]  \hspace{1cm} (12)

2. Path ABC: Note along AB \( dT = 0 \), while along BC \( dp = 0 \).

\[ V_2 - V_1 = \int_{ABC} \left( \frac{\partial V}{\partial T} \right)_p dT + \left( \frac{\partial V}{\partial p} \right)_T dp = \int_{p_1}^{p_2} \left( \frac{\partial V}{\partial p} \right)_T dp + \int_{T_1}^{T_2} \left( \frac{\partial V}{\partial T} \right)_p dT \]

\[ = \int_{p_1}^{p_2} \frac{-R T_1}{p^2} dp + \int_{T_1}^{T_2} \frac{R}{p_2} dT = R \frac{T_2 p_1 - T_1 p_2}{p_1 p_2} \]  \hspace{1cm} (13)

\[ W_2 - W_1 = \int_{p_1}^{p_2} p \left( \frac{\partial V}{\partial p} \right)_T dp + \int_{T_1}^{T_2} \frac{R T}{V} \left( \frac{\partial V}{\partial T} \right)_p dT = -R T_1 \ln \frac{p_2}{p_1} + R(T_2 - T_1) \]

Note the change in \( V \) is independent of the path – the volume is characteristic of a point \((p, T)\) in equilibrium – but the work done in the process is not! What’s the difference? In the system with \( p, T \) as independent variables, \( dV \) is an \textit{exact differential}, while \( dW \) is not. How can you see the difference? Go back and examine the forms we had for \( dV \) and \( dW \) in (4) and (5). In the case of \( dV \), we had

\[ dV = M dp + N dT, \quad \text{with} \quad M = \frac{R}{p} \quad \text{and} \quad N = -\frac{R T}{p^2} \]  \hspace{1cm} (14)

\[ \frac{\partial M}{\partial p} = -\frac{R}{p^2} \quad \text{and} \quad \frac{\partial N}{\partial T} = -\frac{R}{p^2}, \]  \hspace{1cm} (15)
which is indeed exact, whereas

\[ dW = M' dp + N' dT \quad M' = R \quad N' = \frac{-RT}{p} \]  

(16)

\[ \frac{\partial M'}{\partial p} = 0 \quad \frac{\partial N'}{\partial T} = \frac{-R}{p}; \]  

(17)

is not. This is a demonstration (we won’t use the word proof) that for a for a thermodynamic process involving changes in the \( p - T \) plane, the volume of the system is a ”state variable”, i.e. (for 1 mole of gas) it simply depends on what \( p \) and \( T \) are; if you have specified \( p, T \), you know the volume of the system. The change in volume between two points will therefore always be \( V_2 - V_1 \) independent of which path is chosen. The work done in the same process is however not independent of the path of integration.

### 3.2 Maxima/minima problems with constraints (Lagrange multipliers)

I’m going to make a mathematical detour before coming back to thermodynamics, in order to give you some tools you need to solve homework problems. In physics we often need to find the extrema of a function of several variables subject to a constraint of some kind. In math, a simple example would be the distance function in 3-space, \( d = \sqrt{x^2 + y^2 + z^2} \). Of course the minimum of this function over all 3-space is just 0, achieved at \( x = y = z = 0 \). But suppose we were to look for the minimum of \( d \) over the ”constrained” set of points defined by the plane \( x - 2y - 2z = 3 \)? The usual way to proceed is often the simplest, if it works: express \( y = y(x) \), then set \( dy/dx = 0 \) and solve. But sometimes one can’t solve for \( y(x) \) explicitly, so one can try the method of implicit differentials (see Boas ch. 4), or use an elegant technique called the method of Lagrange multipliers (Joseph Lagrange (1736-1813) was a French mathematical physicist).

The idea is, if you can express the problem in terms of the minimization of a function \( f(x, y, \ldots) \), together with a constraint \( g(x, y, \ldots) = 0 \), to imagine you are solving the unconstrained problem of finding the minimum of \( F(x, y, \ldots; \lambda) = f(x, y, \ldots) + \lambda g(x, y, \ldots) \). Then you can simply treat \( \lambda \) as an additional variable, and minimize with respect to it as well. In the process of solving the problem, you eliminate \( \lambda \) from the solution.

Ex: Coming back to our problem with the plane, let’s first make our life a bit easier by recalling that if we minimize \( d' = x^2 + y^2 + z^2 \), the square root will also
be a minimum. So define

\[ F = x^2 + y^2 + z^2 + \lambda(x - 2y - 2z - 3) \]  

(18)

and set all the derivatives equal to zero:

\[
\frac{\partial F}{\partial x} = 2x + \lambda = 0 \tag{19}
\]

\[
\frac{\partial F}{\partial y} = 2y - 2\lambda = 0 \tag{20}
\]

\[
\frac{\partial F}{\partial z} = 2z - 2\lambda = 0 \tag{21}
\]

\[
\frac{\partial F}{\partial \lambda} = x - 2y - 2z - 3 = 0. \tag{22}
\]

Note the equation \(\frac{\partial F}{\partial \lambda} = 0\) is always just the constraint equation itself. Now we have a problem with 4 equations and 4 unknowns, and it can be solved. The usual idea is to eliminate the constraint as quickly as possible. The first eqn. tells us that \(\lambda = -2x\), so

\[
2y + 4x = 0 \tag{23}
\]

\[
2z + 4x = 0 \tag{24}
\]

\[
x - 2y - 2z - 3 = 0, \tag{25}
\]

which we can solve to find \((x, y, z) = (1/3, -2/3, -2/3)\).

3.3 Differentiation of integrals

Leibnitz’ rule for differentiating integrals:

\[
\frac{d}{dx} \int_{u(x)}^{v(x)} f(x, t)dt = f(x, v) \frac{dv}{dx} - f(x, u) \frac{du}{dx} + \int_{u(x)}^{v(x)} \left( \frac{\partial f}{\partial x} \right) dt. \tag{26}
\]

Ex:

\[
I = \int_{x}^{2x} \frac{e^{xt}}{t} dt \tag{27}
\]

\[
\frac{dI}{dx} = \frac{e^{x2x}}{2x} \cdot 2 - \frac{e^{x^2}}{x} \cdot 1 + \int_{x}^{2x} e^{xt} dt \tag{28}
\]

\[
= \frac{2}{x} (e^{x^2} - e^{x^2}) \tag{29}
\]
3.4 Laws of thermodynamics

Let’s come back to the idea of exact and inexact differentials in thermodynamics. Here’s another example of an inexact differential:

$$\underbrace{dQ}_{\text{heat absorbed}} = c_p \underbrace{dT}_{\text{heat capacity const.}} + \underbrace{\Lambda_p \, dp}_{\text{latent heat}}.$$  \hfill (30)

We showed already that the work done is also not an exact differential, however the combination of the two is:

$$dU \equiv dQ - dW$$

$$= \left[ c_p - p \left( \frac{\partial V}{\partial T} \right)_p \right] dT + \left[ \Lambda_p - p \left( \frac{\partial V}{\partial p} \right)_T \right] dp.$$  \hfill (33)

This is called the internal energy, and this equation is sometimes referred to as the 1st law of thermodynamics, expressing energy conservation, i.e. the change in internal energy of a gas in a thermodynamic cycle goes either into heating the system ($dQ$ is the infinitesimal heat absorbed by the system) or into doing work (done by the system).

Another exact differential is $dS = dQ/T$.

Remark 1: sometimes you will see the notation $\bar{d}Q$ and $\bar{d}W$ for infinitesimal heat absorbed and work done. This is just a more careful notation to remind you that they are inexact differentials.

Remark 2: since the work done in a thermodynamic process depends on the path, it is really nonsense what I wrote above “$W_2 - W_1$”. You are to think of this as the work performed by the system in the process of going $1 \rightarrow 2$, but $W_2$ and $W_1$ have no independent meaning, since they are not characteristic of a macrostate.

3.5 Legendre transformation

If for a function $f(x, y)$ we have the differential $df = pdx + qdy$, where $p$ and $q$ are equal to $\partial f/\partial x$ and $\partial f/\partial y$, respectively, we might ask the question, how do we make a simple change of variables to a new function $g(x, q)$ with $q$ one of the independent variables? We simply make use of the fact that

$$d(f - qy) = df - dq \, y - q \, dy = p \, dx + q \, dy - dq \, y - q \, dy = p \, dx - y \, dq.$$  \hfill (34)

This function is by definition associated with an exact differential $dg$. You explored this on the HW for various thermodynamic quantities.