

# 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

$$dW = pdV = R dT - \frac{RT}{p} dp. \quad (5)$$

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:

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

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

$$\text{so} \quad (8)$$

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

$$dW = -\frac{R}{p} \left( T_1 - \frac{\Delta T}{\Delta p} p_1 \right) dp \quad (10)$$

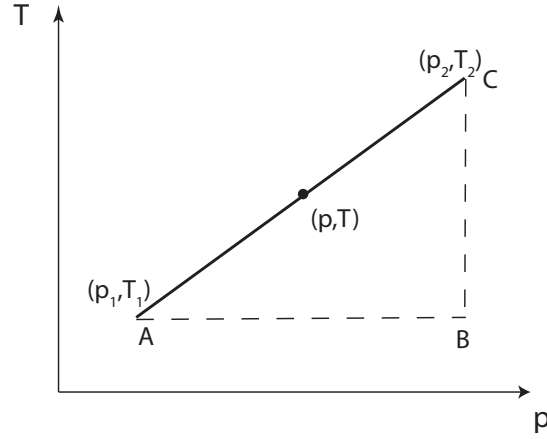


Figure 1: Path in  $p, T$  plane for thermodynamic process.

Now we can calculate the change in volume and the work done in the process:

$$V_2 - V_1 = \int_{AC} dV = R(T_1 - \frac{\Delta T}{\Delta p} p_1) \frac{1}{p} \Big|_{p_1}^{p_2} = R \frac{T_2 p_1 - T_1 p_2}{p_1 p_2} \quad (11)$$

$$W_1 - W_2 = \int_{AC} p dV = R(T_1 - \frac{\Delta T}{\Delta p} p_1) \ln p \Big|_{p_1}^{p_2} = R \frac{T_2 p_1 - T_1 p_2}{p_2 - p_1} \ln \frac{p_2}{p_1} \quad (12)$$

2. Path ABC: Note along AB  $dT = 0$ , while along BC  $dp = 0$ .

$$\begin{aligned} V_2 - V_1 &= \int_{ABC} \left( \frac{\partial V}{\partial T} \right)_p dT + \left( \frac{\partial V}{\partial p} \right)_T dp = \int_{p_1}^{p_2} \left( \frac{\partial V}{\partial p} \right)_T dp + \int_{T_1}^{T_2} \left( \frac{\partial V}{\partial T} \right)_p dT \\ &= \int_{p_1}^{p_2} \frac{-RT_1}{p^2} dp + \int_{T_1}^{T_2} \frac{R}{p_2} dT = R \frac{T_2 p_1 - T_1 p_2}{p_1 p_2} \end{aligned} \quad (13)$$

$$W_2 - W_1 = \int_{p_1}^{p_2} p \left( \frac{\partial V}{\partial p} \right)_T dp + \int_{T_1}^{T_2} \frac{RT}{V} \left( \frac{\partial V}{\partial T} \right)_p dT = -RT_1 \ln \frac{p_2}{p_1} + R(T_2 - T_1)$$

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 *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

$$dV = M dp + N dT, \quad \text{with } M = \frac{R}{p} \text{ and } N = -\frac{RT}{p^2} \quad (14)$$

$$\frac{\partial M}{\partial p} = -\frac{R}{p^2} \quad \frac{\partial N}{\partial T} = -\frac{R}{p^2}, \quad (15)$$

which is indeed exact, whereas

$$dW = M'dp + N'dT \quad M' = R \quad ; \quad N' = -\frac{RT}{p} \quad (16)$$

$$\frac{\partial M'}{\partial p} = 0 \quad \frac{\partial N'}{\partial T} = -\frac{R}{p}, \quad (17)$$

is not. This is a demonstration (we won't use the word proof) that 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  $f(x, y, \dots)$ , together with a constraint  $g(x, y, \dots) = 0$ , to imagine you are solving the *unconstrained* problem of finding the minimum of  $F(x, y, \dots; \lambda) = f(x, y, \dots) + \lambda g(x, y, \dots)$ . 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

$$F = x^2 + y^2 + z^2 + \lambda(x - 2y - 2z - 3) \quad (18)$$

and set all the derivatives equal to zero:

$$\frac{\partial F}{\partial x} = 2x + \lambda = 0 \quad (19)$$

$$\frac{\partial F}{\partial y} = 2y - 2\lambda = 0 \quad (20)$$

$$\frac{\partial F}{\partial z} = 2z - 2\lambda = 0 \quad (21)$$

$$\frac{\partial F}{\partial \lambda} = x - 2y - 2z - 3 = 0. \quad (22)$$

Note the equation  $\partial F/\partial \lambda = 0$  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

$$2y + 4x = 0 \quad (23)$$

$$2z + 4x = 0 \quad (24)$$

$$x - 2y - 2z - 3 = 0, \quad (25)$$

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:

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

Ex :

$$I = \int_x^{2x} \frac{e^{xt}}{t} dt \quad (27)$$

$$\frac{dI}{dx} = \frac{e^{x \cdot 2x}}{2x} \cdot 2 - \frac{e^{x \cdot x}}{x} \cdot 1 + \int_x^{2x} e^{xt} dt \quad (28)$$

$$= \frac{2}{x} (e^{2x^2} - e^{x^2}) \quad (29)$$

### 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:

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

$$\text{heat absorbed} \quad \text{heat capacity const. } p \quad \text{latent heat.} \quad (31)$$

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

$$dU \equiv dQ - dW \quad (32)$$

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

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  $df = p dx + q dy$ , 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

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

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