

Chapter 2

Thermodynamics and partial derivatives

2.1 Introduction

To understand the importance of partial derivatives and their relation to thermodynamics, we begin with an example. Hikers are going for a mountain hike in the Alps and bring along a bag of crisps (compressible, closed volume) that they have bought in the Netherlands (see figure 2.1). Once they arrive at the top of the mount at a height of 2000 metres, it turns out the bag of crisps has popped open. How is this possible and how can this be prevented? The pressure at 2000 metres is lower than the pressure at sea level where the bag of crisps was made and where it has a normal volume. If the pressure outside of the bag decreases then the bag will expand. At a certain point, the volume of the bag increases so much that it tears. If the crisps producers wants their bag to survive a trip to the Alps, it is thus important that they know the bag's volume at a range of pressures. However, it is possible that more parameters will influence the bag's volume. For instance, the temperature will also change when hiking high up in the mountains.

To further investigate this problem and solve it, it needs to be translated into more thermodynamic and mathematical terms, such as: *A system consisting of a compressible volume with air is brought from state 1, with corresponding quantities like v_1 , P_1 and T_1 to state 2, with corresponding quantities like v_2 , P_2 and T_2 . Find a relation that gives the volume v of the system as a function of the pressure P , the temperature T and any other parameters that matter.*

We will come back to this problem at the end of this chapter. The following is more theory on the terms and tools of thermodynamics and mathematics that are required to solve this problem.

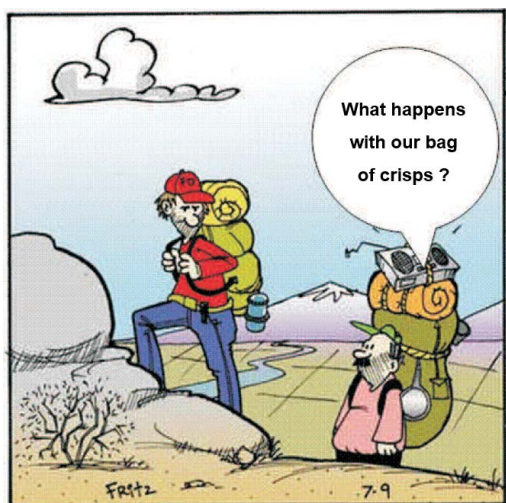


Figure 2.1: Change of temperature and pressure affect the volume.

2.2 Mathematics of partial derivatives

One of the postulates of thermodynamics says that the state of a simple¹ compressible system or substance can be fully described by two independent intensive² quantities. All other quantities can be expressed in terms of the two independent quantities. Mathematically, this can be expressed as

$$f = f(x, y) \quad (2.1)$$

where x and y are the two independent quantities that describe the state and f is a third quantity (that depends on the other two). Such a relation between quantities is called a state equation in thermodynamics, i.e. an equation that records the state of the system. In the case of the crisps, the system is the volume of the bag of crisps and the two quantities that describe the system are the pressure and the temperature; the state equation is expressed by $v(P, T)$. However, this relation still needs to be found. When it is known, the problem will have been solved.

When a system changes from state A (the bag of crisps at sea level) to state B (the bag of crisps in the mountains) (this is called a process in thermodynamics), then the quantities that describe the system change (different pressure and temperature). How they change during this transition can be mathematically described by means of the state equation. The differential of the function describing the state plays an important part in this. The differential designates an infinitesimal change of the state. In describing the transition from state A to state B, it is assumed that the system always only changes so slightly that the differential of the state equation can describe the change (in thermodynamic terms, the system is in a quasi-equilibrium).

If the function depends on one variable only, such as $f = f(x)$, then the derivative of the function is defined as

$$\frac{df(x)}{dx} = \lim_{\Delta x \rightarrow 0} \left(\frac{\Delta f}{\Delta x} \right) = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x)}{\Delta x}. \quad (2.2)$$

Because the state equations in thermodynamics usually contain more than one variable, it is important to look at the differential of a function of multiple variables. Consider a function of two variables, such as $f = f(x, y)$. Now, f depends on both x and y . Sometimes it is useful to look at how f depends on only one of its variables. This is done by changing one variable and keeping others constant and looking at how the function changes. The change of $f(x, y)$ when x changes and y is kept constant is called the **partial derivative** of f to x and is expressed as

$$\left(\frac{\partial f(x, y)}{\partial x} \right)_y = \lim_{\Delta x \rightarrow 0} \left(\frac{\Delta f}{\Delta x} \right)_y = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x}. \quad (2.3)$$

The variable that is kept constant is expressed as a subscript behind the partial derivative³. The symbol ∂ designates a differential change, like the symbol d . The difference is that d presents the **total** derivative of a function to all its variables, whereas ∂ presents the change of the function as a result of only one changing variable (d is called the total differential or total derivative and ∂ is called the partial differential or partial derivative). For independent variables, d and ∂ are equated, but this is not the case for dependent variables. This means that $(\partial x)_y = dx$, because x and y are independent from each other, but $(\partial f)_y \neq df$ because f and y are dependent variables. In general, the partial derivative $(\partial f / \partial x)_y$ has different values for different values of y .

It is now important to get a relation for the total change of $f(x, y)$ for simultaneous changes of x and y . If the independent variables x and y change by Δx and Δy respectively, then the dependent variable f changes with Δf . This can be expressed as

$$\Delta f = f(x + \Delta x, y + \Delta y) - f(x, y). \quad (2.4)$$

¹Simple here means that the system is not influenced by motion, gravitation, electricity and magnetism. These effects, which are the result of external force fields, are usually negligible in thermodynamics.

²An intensive quantity is a quantity that does not depend on the mass or the size of the system, e.g. pressure, temperature and density. Quantities that do depend on the size of the system are called extensive quantities, examples are mass, volume and energy.

³in Calculus, this constant is not expressed; in thermodynamics, it is very important, because there are multiple variables and it is important to know which are constant.

Subtracting and adding $f(x, y + \Delta y)$ results in

$$\Delta f = f(x + \Delta x, y + \Delta y) - f(x, y + \Delta y) + f(x, y + \Delta y) - f(x, y). \quad (2.5)$$

Rewriting this results in

$$\Delta f = \frac{f(x + \Delta x, y + \Delta y) - f(x, y + \Delta y)}{\Delta x} \Delta x + \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y} \Delta y. \quad (2.6)$$

By taking the limits $\Delta x \rightarrow 0$ and $\Delta y \rightarrow 0$ and using the definitions of the partial derivatives, you find that

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy. \quad (2.7)$$

Equation 2.7 is the fundamental relation for the **total differential** of a dependent variable in terms of the partial derivatives to its two independent variables. Equation 2.7 thus shows the total infinitesimal change of quantity f under infinitesimally small changes of x and y . This relation can easily be expanded to multiple variables if necessary.

A vital property of a total differential is that its integrated value depends only on the integration limits and not on the path that is followed. Such a differential is called exact (contrary to an inexact differential that does depend on the path). Quantities whose total differential is exact return to the same value when undergoing a circle process (they are also called state functions); meaning when they are integrated around a closed surface, a circle (circular integral). We will come back to this in chapter 3.

2.3 Partial derivatives for an ideal gas

Now that we know how state changes can be described by means of partial derivatives, we can tackle the problem of the crisps producer. The volume of the bag of crisps is described by the quantities pressure, P and temperature, T , $v(P, T)$. The change in volume for a change in P and T is provided by the total differential of $v(P, T)$:

$$dv = \left(\frac{\partial v}{\partial P} \right)_T dP + \left(\frac{\partial v}{\partial T} \right)_P dT. \quad (2.8)$$

If the air behaves like an ideal gas, then the state equation is provided by

$$v(P, T) = \frac{RT}{P} \quad (2.9)$$

Computing the partial differentials results in

$$\left(\frac{\partial v}{\partial P} \right)_T = -\frac{RT}{P^2} = -\frac{v}{P} \quad \text{and} \quad \left(\frac{\partial v}{\partial T} \right)_P = \frac{R}{P} = \frac{v}{T}. \quad (2.10)$$

Eventually, the change in volume as a function of the changes in pressure and temperature is found as

$$dv = -\frac{RT}{P^2} dP + \frac{R}{P} dT = -\frac{v}{P} dP + \frac{v}{T} dT. \quad (2.11)$$

Note that in this case the partial derivatives could be determined easily because the state equation of an ideal gas ($Pv = RT$) is known. In general, it will be more difficult to find expressions or values for the partial derivatives. The chapters 5 up to and including 8 will provide tools to determine the values of partial differentials at all times.

2.4 Graphical representation of partial derivatives

Partial derivatives can also be represented graphically. In a graph, the value of the partial derivative is designated by the tangent. This is illustrated by means of the total differential for the volume $v(P, T)$ as provided in equation 2.8. In figure 2.2 v is provided in a three-dimensional plane as a function of P and T for an ideal gas. Here, you see that for a random value of the pressure, P , the volume, v , increases linearly with the temperature, whereas the volume decreases by $1/P$ for a random value of the temperature, T . The highlighted (light-blue) surface contains all possible values of $v(T, P)$ in the range of P and T in the graph.

The continuous (red) line in figure 2.2a is the tangent of the striped (blue) line on the PvT surface in point (P_1, T_1) . This is the change in volume v for a change in pressure P under constant temperature T in point (P_1, T_1) , or $(\partial v / \partial P)_T$. The tangent is thus described by the partial differential.

In figure 2.2b, the situation is displayed somewhat differently. In this case the tangent, the striped (red) line, is located on the incline of the volume v as a function of the temperature T at a constant pressure P in point (P_1, T_1) . For this specific PvT surface (that of an ideal gas), the incline is the same for any temperature. Because $v = RT/P$, the equation for the striped (red) line will be $v = (R/P_1)T = CT$ (C is a constant). The tangent that represents the partial derivative $(\partial v / \partial T)_P = C = R/P_1$ is independent from the temperature T . This in contrast to figure 2.2a where the tangent has a different value in every point, because the incline is not constant. Note that the tangent of the partial derivative (in this case the (red) striped line) becomes steeper as P decreases. This is also apparent in figure 2.2b.

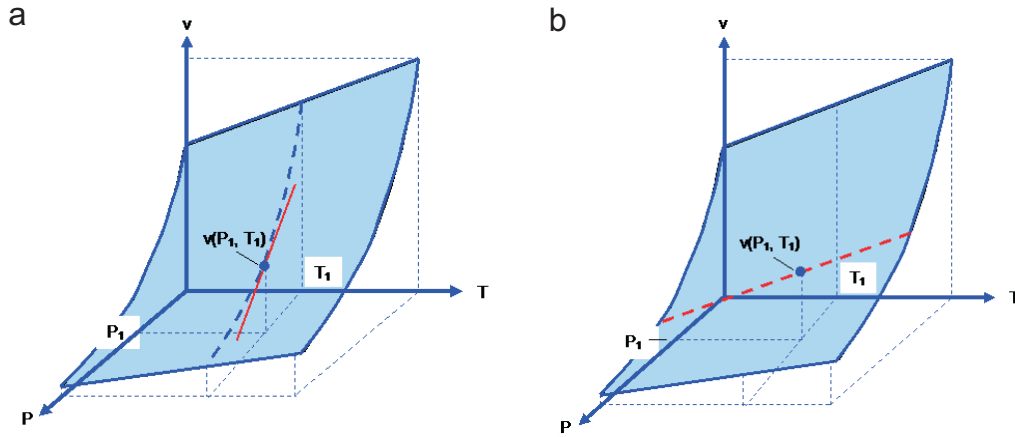


Figure 2.2: a) The incline of $v(P)$ at a constant T for an ideal gas. b) The incline of $v(T)$ at a constant P for an ideal gas.