

Chapter 6

Maxwell relations

6.1 Introduction

Chapter 4 showed that a number of partial derivatives equal a quantity that has a physical meaning and can thus also have a value. It turns out that two different partial derivatives equal the temperature. These partial derivatives thus equal each other. The same applies to partial derivatives that equal $-P$, v and $-s$ (also see table 4.1). These partial relations formed by deriving the four thermodynamic energies once to both its variables while the other is kept constant (e.g. by deriving u to s , a partial derivative is found and by deriving to v , a second partial derivative is found). This way, eight partial derivatives were found, two that equal T , two that equal $-P$, two that equal v and two that equal $-s$.

However, more partial derivatives equal each other. These are determined by differentiating the partial derivatives again, but then differentiating them to a different variable. This results in a mixed derivative (in fact, the expression for the energy is derived twice to both variables ($\frac{\partial^2 f}{\partial x \partial y}$)). James Maxwell was the first person to show these relations between partial derivatives. As such, the relations are called thermodynamic **Maxwell relations**. The method can be applied generally and such relations are also apparent in other scientific disciplines.

6.2 James Clerk Maxwell

The Scottish mathematician and physicist James Clerk Maxwell (figure 6.1a and c) was born in Edinburgh on 13 June 1831. He was the only child of John Clerk Maxwell (land owner, lawyer and inventor) and Frances Kay. At a very young age, little Maxwell already wanted to know how everything worked. After his mother - who was nearly 40 when he was born - passed away in 1839 of stomach cancer, Maxwell was raised by his uncle and aunt.

In 1841, Maxwell attends the prestigious Edinburgh Academy. At age thirteen, he won a maths medal of the Edinburgh Academy and won first prizes for English and poetry. At age 14, as part of a natural sciences project, Maxwell wrote an article on a mechanical way of drawing mathematical curves by using a piece of string and on the properties of an ellipsis and curves that have more than two focal points.

In 1847, at age 16, he leaves the Academy and starts taking classes at University of Edinburgh. However, these classes were not always challenging enough for him. He did a lot more self-studying and when he returned to his father's manor, he often did experiments. He experimented with rudimentary chemical and electromagnetic equipment. However, he was truly fascinated by the property of polarized light. He constructed gelatin blocks and subjected them to different forms of stress. By using a number of polarizing prisms (gifted by notable scientist William Nichol), he looked at the coloured interference rings formed in the gelatinous goo.

In 1850, he left Scotland and went to University of Cambridge. Not even twenty years old and Maxwell is already a very gifted mathematician. In 1854, he graduates as a mathematician from Trinity College (one of Cambridge's most well-known colleges). After his studies, he is granted the

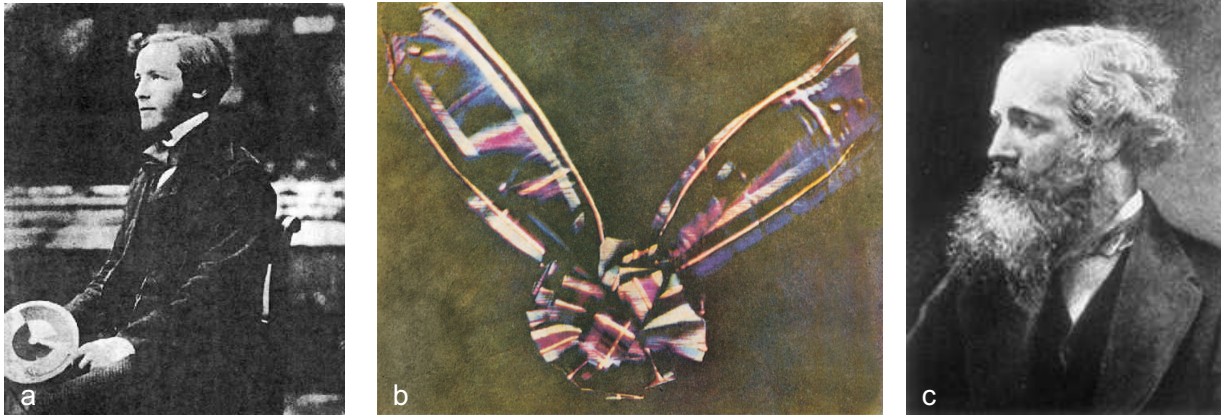


Figure 6.1: a) A young Maxwell at Trinity College in Cambridge. He is holding one of his colour wheels. b) The first permanent colour photo made in 1861 by Maxwell. c) James Clerk Maxwell at older age.

opportunity to do research in Cambridge. Maxwell continued to be fascinated by the origin and impression of colours; an interest that formed during his time at University of Edinburgh when he was one of Forbes' students. By using a spinning top, he showed that white light can form from a mixture of red, green and blue light. His article, *Experiments on Colour*, explains the principle of the colour combination and is presented at the Royal Society of Edinburgh in March 1855. In the same year, Maxwell was appointed a Trinity fellow; an event that occurred much sooner than usual. There, he would teach hydrostatics and optics. However, no more than a few months later, he traded in Cambridge for Aberdeen where he was a professor of natural philosophy at the University of Aberdeen from 1856 to 1860. At the age of 25, he was the youngest professor by far. He worked on teaching and research and it was here where Maxwell looked at a problem that had occupied scientists for centuries: the rings of Saturn phenomenon. It was still unknown how the rings remained stable without breaking apart or floating away from Saturn. The problem was picked as the topic for the 1857 Adams Prize. Over the course of the two years he was working on the problem, he came to the conclusion that the rings could not be solid, because they would not be stable enough. Nor could they be liquid, because that would break them apart as a result of wave motions. As a result, Maxwell concluded that the rings must consist of a large amount of tiny particles that each revolve around Saturn independently. Eventually, Maxwell received the Adams Prize (130 pounds) in 1859 for his essay *On the stability of Saturn's rings*. His work was so detailed and convincing that the commentary of one of the jury members was *It is one of the most remarkable applications of mathematics to physics that I have ever seen*. The fact that Maxwell was right was proven over a hundred years later by the Voyager space flights (around 1980).

In 1858, Maxwell married Katherine Mary Dewar. After a merger between the King's College in Aberdeen and University of Aberdeen, Maxwell's position was made redundant. As a result, he moved to King's College in London in 1860 and took up the position of professor of physics and astronomy. His time in London was probably the most productive of his entire career. In 1860, he received the Royal Society's Rumford Medal for his work in the field of colour. By this time, he used three colour filters to make the first colour photo (this photo can be seen in figure 6.1b), he developed ideas on the viscosity of gases and introduced a system for defining physical quantities that is now known as the dimension analysis.

He was also doing ground-breaking work in the field of electromagnetism and electromagnetic waves at this time. He published several works on the nature of the electromagnetic field. He showed that electricity and magnetism are related and are part of one system. The basic equations named after him are still, to this day, the basic principles of classic electrodynamics. He put forward the idea that light is an electromagnetic wave phenomenon. Based on his basic equations, he was able to theoretically calculate the speed of light. He wrote down his findings in his book *A Treatise on*

electricity and magnetism (1873). Support for Maxwell's suspicion came from Hendrik Lorentz, who was able to accurately describe the refraction of light by means of Maxwell's equations in 1875. In 1884, German physicist Heinrich Hertz (a student of Helmholtz 4.4.1) proved experimentally that light waves and electromagnetic waves exhibit similar behaviour. Thus, he confirmed Maxwell's work. Maxwell's discovery that all findings, experiments and equations that, at that time, were considered to be unrelated from electricity theory, magnetism and even optics fitted into one consistent theory - the theory of the electromagnetic field - is his most important contribution to science. The theory is called the *second great unification in physics*¹.

Maxwell also achieved spectacular results in the field of kinetic gas theory, which was the precursor to static thermodynamics. To this end, he worked with John Herapath, John James Waterston, James Joule and, in particular, Rudolf Clausius (see 6.6). In this field, Maxwell proved to be both an experimenter and a mathematician. He derived a formula for the velocity distribution of gas molecules in a time in which the existence of molecules was still controversial: the Maxwell-Boltzmann distribution (1866). With this formula, he made a connection between classic macroscopic thermodynamics and the microscopic behaviour of the, at the time, speculative gas theory that predicted that only temperature and heat influence the movement of molecules. His approach generalized all prior, established, laws of thermodynamics and explained current observations and experiments better than ever before. In 1871, he derived the Thermodynamic Maxwell relations. Four expressions of equations between double derivatives of thermodynamic energies that describe relations between quantities like temperature, pressure, volume and entropy.

In 1865, he leaves his tenure at King's College in London and goes to live with his wife on his parents' estate. In 1871, he became the first Cavendish professor of experimental physics at University of Cambridge. He was responsible for the construction of the Cavendish laboratory. He passed away due to cancer in Cambridge on 5 November 1879 at the young age of 48. Maxwell is considered to be the 19th-century scientist who had the biggest impact on the 20th century. His contributions to science are considered to be of the same level as those made by Albert Einstein and Isaac Newton. Along with whom they are considered to be the world's greatest physicists. In 1931, at Maxwell's one-hundredth birthday, Einstein described Maxwell's work as *the most profound and the most fruitful that physics has experienced since the time of Newton*.

6.3 Maxwell relations

To illustrate how deriving the Maxwell relations works, the internal energy will be used as an example again. The differential for the internal energy is $du = Tds - Pdv$. The partial derivatives that follow by deriving the internal energy to both of its variables while the others are fixed are: $T = \left(\frac{\partial u}{\partial s}\right)_v$ and $-P = \left(\frac{\partial u}{\partial v}\right)_s$ (also see equation 4.3). Both partial derivatives can now be derived again to the other variables. This leads to

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial u}{\partial s}\right)_v\right]_s = \left[\frac{\partial}{\partial v}(T)\right]_s = \left(\frac{\partial T}{\partial v}\right)_s \quad \text{and} \quad \left[\frac{\partial}{\partial s}\left(\frac{\partial u}{\partial v}\right)_s\right]_v = \left[\frac{\partial}{\partial s}(-P)\right]_v = -\left(\frac{\partial P}{\partial s}\right)_v. \quad (6.1)$$

Because quantities are continuous state functions (exact differentials), the order of differentiation does not matter (Clairaut's theorem or Schwarz' theorem) and the terms between the square brackets in equation 6.1 are equal

$$\left[\frac{\partial}{\partial v}\left(\frac{\partial u}{\partial s}\right)_v\right]_s = \left[\frac{\partial}{\partial s}\left(\frac{\partial u}{\partial v}\right)_s\right]_v \rightarrow \frac{\partial^2 u}{\partial v \partial s} = \frac{\partial^2 u}{\partial s \partial v} \quad (\text{Theorem of Clairaut or Schwarz}) \quad (6.2)$$

¹The *first great unification in physics* is the universal gravitation theory by Isaac Newton described in his revolutionary work *Principia*. In it, Newton demonstrates that a falling apple and the moon's movement can be attributed to one and the same force: gravitational force. With it, he states that all motion in the entire universe can be described with the classic mechanics he developed (Newton's three laws are: inertia, force changes motion ($F = m \times a$) and action equals - reaction).

and thus

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v. \quad (6.3)$$

Equation 6.3 is the **Maxwell relation** that follows from the differential of the internal energy, u . There are three more Maxwell relations that follow from the enthalpy, h , the Helmholtz energy, a , and the Gibbs energy, g . These four Maxwell relations are provided in table 6.1. The Maxwell relations are quite valuable to thermodynamics, because they offer the possibility of determining a change in entropy - which cannot be measured - by simply measuring the changes in P , T and v .

In chapter 5, a general relation is derived which results in the Maxwell relations (see equation 5.1 and 5.4). In case of the internal energy, M equals T and N equals $-P$ and f, x, y equal u, s, v .

$\begin{aligned} \left(\frac{\partial T}{\partial v}\right)_s &= -\left(\frac{\partial P}{\partial s}\right)_v \\ \left(\frac{\partial T}{\partial P}\right)_s &= \left(\frac{\partial v}{\partial s}\right)_P \\ \left(\frac{\partial P}{\partial T}\right)_v &= \left(\frac{\partial s}{\partial v}\right)_T \\ \left(\frac{\partial v}{\partial T}\right)_P &= -\left(\frac{\partial s}{\partial P}\right)_T \end{aligned}$
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Table 6.1: *Thermodynamic Maxwell relations.*

6.4 Clapeyron equation

The Maxwell relations are commonly used to derive practical, usable thermodynamic relations. An example of this is the **Clapeyron equation**, that can be used to determine the enthalpy change that is linked to a phase transition from the P , T and v values of the saturated state (e.g. the vaporization enthalpy $h_{lv} = h_v - h_l$). This relation can be found from the third Maxwell equation,

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T. \quad (6.4)$$

During the phase transition, the pressure equals the saturation pressure and the temperature equals the saturation temperature. Both are constant during the phase transition and are related to each other ($P_{sat} = f(T_{sat})$). The partial derivative on the left-hand side of equation 6.4 in this case is a total derivative and the left-hand side can be expressed as $(dP/dT)_{sat}$. The right-hand side of equation 6.4 is equal to $(s_{lv}/v_{lv})_{sat}$ for a transition from a fluid to a vapour. When these two terms are placed in Maxwell equation 6.4, then

$$\left(\frac{dP}{dT}\right)_{sat} = \left(\frac{s_{lv}}{v_{lv}}\right)_{sat} \quad \text{with } s_{lv} = s_v - s_l \text{ and } v_{lv} = v_v - v_l. \quad (6.5)$$

This still contains the entropy that needs to be removed for the benefit of the enthalpy. This is done through relation 4.4 for dh , from which follows that $Tds = dh - vdP$. A phase transition is an isobaric process and the change in pressure is zero, $dP = 0$, which results in $Tds = dh$. When this is integrated around the area of the phase transition, between the limits l and v , then $h_{lv} = T_{sat}s_{lv}$. Filling this into equation 6.5 results in

$$\left(\frac{dP}{dT}\right)_{sat} = \left(\frac{h_{lv}}{T_{sat}v_{lv}}\right) \quad (6.6)$$

the **Clapeyron equation** is named after the French physicist Émile Clapeyron (1799-1864). It is an important relation that allows for determining the evaporation enthalpy by simply measuring the

specific volume of the saturated fluid and saturated gas and the incline of the saturation curve in the $P - T$ diagram at a specific temperature.

The Clapeyron relation can be applied to any process with a phase transition that takes place at a constant pressure and temperature. In its general form, it is given by

$$\left(\frac{dP}{dT}\right)_{sat} = \left(\frac{h_{12}}{Tv_{12}}\right). \quad (6.7)$$

in which subscripts 1 and 2 indicate the two phases. The Clapeyron relation indicates the incline of the transition line between two phases in a $P - T$ phase diagram (figure 6.2b).

6.5 Clausius-Clapeyron equation

In case of a fluid-vapour (or a solid-vapour) transition, the Clapeyron relation for the specific case of a low pressure can be simplified some more. The specific volume of the liquid phase is much smaller at low pressure than the specific volume in the gas phase, so $v_{lv} = v_v - v_l \approx v_v$. Furthermore, it can be assumed that the vapour behaves as an ideal gas at a low pressure, so $P_{sat}v_v = RT_{sat}$. When these terms are placed in the Clapeyron relation 6.6, then

$$\left(\frac{dP}{dT}\right)_{sat} = \left(\frac{P_{sat}h_{lv}}{T_{sat}^2 R}\right) \quad (6.8)$$

or

$$\left(\frac{dP}{P}\right)_{sat} = \frac{h_{lv}}{R} \left(\frac{dT}{T^2}\right)_{sat} \quad \text{or} \quad \left(\frac{d(\ln P)}{dT}\right)_{sat} = \frac{h_{lv}}{RT_{sat}^2}. \quad (6.9)$$

In this form, the equation is called the **Clausius-Clapeyron equation**. It can be used in the same way as the Clapeyron equation with the exception that the value of the specific volume, which is more difficult to measure, is not required. To consider the fact that the Clausius-Clapeyron relation becomes inaccurate at high pressure when v_v is no longer significantly greater than v_l and vapour also can no longer be approached as an ideal gas.

6.6 Rudolf Julius Emanuel Clausius

The German physician and mathematician Rudolf Julius Emanuel Clausius (figure 6.2a) was born in Köslin in what was then called Prussia (current-day Koszalin, Poland) as Rudolf Gottlieb on 2 January 1822. He went to the school of his father and after a couple of years went to the gymnasium in Stettin (current-day Szczecin). Clausius studied mathematics and physics together with, among others, Heinrich Magnus, Johann Dirichlet and Jakob Steiner at the University of Berlin. He also studied history together with Leopold von Ranke.

He did his exams in 1844 and, three years later, in 1847, he got his doctorate at the University of Halle for a study into optical effects in the atmosphere of the earth. In his thesis on the refraction of light, Clausius states that the blue sky during the day and the different shades of red during dawn and dusk as well as other phenomena that occur in the atmosphere are the result of reflection and refraction of light. Later, Lord Rayleigh would show that these phenomena are the result of the scattering of light. Irrespective of the exact effect that the colour causes, Clausius used a more mathematical approach than his predecessors.

He was appointed a seat as professor of physics at the *Royal Artillery and Engineering School* in Berlin and as 'Privatdozent' at the University of Berlin. His primary and most famous article *Über die bewegende Kraft der Wärme* ("On the Moving Force of Heat and the Laws of Heat which may be Deduced Therefrom") was published in 1850. In this publication on the mechanical theory of heat, Clausius explains the basis of his ground-breaking ideas regarding the second law of thermodynamics. In the article, he shows that there is a discrepancy between the Carnot principle and the concept of energy conservation Clausius reformulated the first two laws of thermodynamics to get rid of this

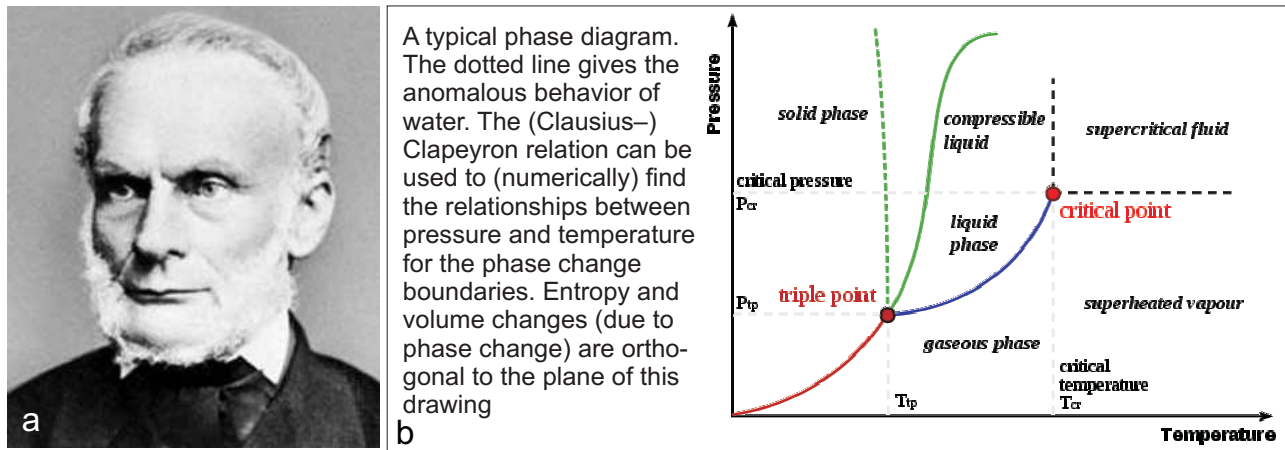


Figure 6.2: a) Rudolf Clausius, one of the founders of thermodynamics and inventor of the concept of entropy. b) Phase diagram, the relation between pressure and temperature for the phase transitions can be found by means of the Clausius-Clapeyron equation.

discrepancy (the third law was described by Walther Nernst between 1906 – 1912). Thanks to his reformulation of Sadi Carnot's principle, otherwise known as the Carnot cycle, he took the theory of heat to a purer and more reliable level. This article was the start of his academic career.

In 1855, he became a professor at ETH Zürich (Swiss Federal Institute of Technology). Clausius introduced the key term of thermodynamics: **entropy**, in 1865. In hindsight, entropy turned out to be very useful to come to a good understanding of the second law. However, because Clausius was not a very clear author, it took quite a while before his terms became commonplace in the scientific world. He provided a mathematical description of the concept of entropy and gave the term its name. Clausius opted for the word *entropy* because of its meaning in Greek. Entropy is derived from the Greek $\epsilon\nu\tau\rho\omicron\pi\iota\alpha$, *en+tropein*, meaning *turning toward* ($\epsilon\nu-$ = in $+\tau\rho\omicron\pi\iota\alpha$ = turning). This indicates that a change of the (energy) content is taking place. He used the dimension Clausius, Cl, which is no longer used. The current dimension of entropy is energy per temperature unit (J/K) in which $1 \text{ Cl} = 1 \text{ cal}/^\circ\text{C} = 4.1868 \text{ Joules per Kelvin (J/K)}$. Thanks to his important contribution to the key concept of entropy, Clausius is considered to be one of the founders of the science of thermodynamics. Two famous statements regarding thermodynamics made by Clausius in 1865 are

- 1: The energy of the universe is constant.
- 2: The entropy of the universe is constantly increasing (striving towards a maximum).

Clausius also derived the *Clausius-Clapeyron* relation from a thermodynamic point of view. This relation, which describes the connection between vapour pressure and temperature, was first described by Émile Clapeyron in 1834. He also came up with the *Inequality of Clausius* that states that the contour integral around Q/T is only zero if the path around which the circle takes place is completely reversible. In other cases, the integral is always smaller, but never bigger.

The Clausius postulate states that it is impossible to have a machine go through a circle process where the only result is the extraction of heat from a heat reservoir at low temperature and the issuing of the same amount of heat to a heat reservoir at a higher temperature. This is possible, however, if work is added to the machine or if a third heat reservoir with an even higher temperature gives off heat to the machine (see Thermodynamics book, Schmidt et al., chapter 8). Examples of applications of the Clausius principle are cooling machines (refrigerators), heat pumps and thermal refrigerators.

In 1869, Clausius moved to Bonn. In 1870, he organized a corps of medic troops in the French-German War, got injured during battle and received the Iron Cross. His wife, Adelheid Rimpham, passed away in 1875 at the birth of their last child and left him behind with their six children. He continued to teach, but had a lot less time for research after this event. Clausius passed away in Bonn on 24 August 1888.