Univariate Calculus, Integration and Series: Introduction to Thermodynamics

1 Introduction to Differentiation

Why do we care about derivatives?

Derivatives in natural science are widely used as they help understanding some phenomena. Some of the most common case uses of derivatives are:

- Rate of change: Chemistry deals with many dynamic processes that evolve over time.
- Optimization: Derivatives are widely use to find minima or maxima of functions.

The derivative of a function $f(x)$ at a point x is the slope of the straight line tangent to $f(x)$ at x. In the limiting process, the derivative of $f(x)$ at a point x is defined as,

$$f'(x) = \frac{df(x)}{dx} = \frac{dy}{dx} = \lim_{\Delta x \to 0} \frac{f(x+\Delta x) - f(x)}{\Delta x} \tag{1}$$

Fig. 1 illustrates the limiting process for when $\Delta x \to 0$. Eq. 1 is also know as the definition of the **ordinary derivate**.

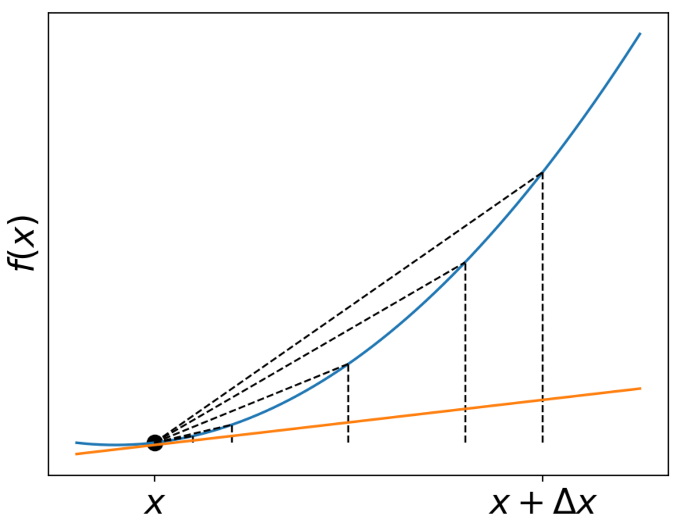

Figure 1: An illustration of the limiting process in the definition of the derivative for $f(x)$.

Exercise: Let's compute the derivative of $f(x) = x^2$ using Eq. 1.

$$\begin{aligned} f'(x) &= \lim_{\Delta x \to 0} \frac{(x+\Delta x)^2 - x^2}{\Delta x} = \lim_{\Delta x \to 0} \frac{\cancel{x^2} + 2x\Delta x + \Delta x^2 \cancel{- x^2}}{\Delta x} & (2) \\ &= \lim_{\Delta x \to 0} \frac{\Delta x(2x+\Delta x)}{\Delta x} = \lim_{\Delta x \to 0} 2x + \Delta x = 2x + \cancel{\lim_{\Delta x \to 0} \Delta x} & (3) \\ &= 2x & (4) \end{aligned}$$

Exercise: Let's compute the derivative of the so called function `ReLU` (rectified linear unit), $f(x) = max(0, x)$ using Eq. 1. For this exercise, we will consider three scenarios, 1) x is positive $x \in \mathbb{R}^+$, 2) x is negative $x \in \mathbb{R}^-$, and 3) $x = 0$.

1. x is positive:

$$f'(x) = \lim_{\Delta x \to 0} \frac{\max(0, x + \Delta x) - \max(0, x)}{\Delta x} = \lim_{\Delta x \to 0} \frac{\cancel{x} + \Delta x - \cancel{x}}{\Delta x} = 1. \tag{5}$$

2. x is negative:

$$f'(x) = \lim_{\Delta x \to 0} \frac{\max(0, x + \Delta x) - \max(0, x)}{\Delta x} = \lim_{\Delta x \to 0} \frac{0 - 0}{\Delta x} = 0. \tag{6}$$

3.1 x is equal to zero and $\Delta x \in \mathbb{R}^+$:

$$f'(x) = \lim_{\Delta x \to 0} \frac{\max(0, x + \Delta x) - \max(0, x)}{\Delta x} = \lim_{\Delta x \to 0} \frac{\Delta x}{\Delta x} = 1. \tag{7}$$

3.2 x is equal to zero and $\Delta x \in \mathbb{R}^-$:

$$f'(x) = \lim_{\Delta x \to 0} \frac{\max(0, x + \Delta x) - \max(0, x)}{\Delta x} = \lim_{\Delta x \to 0} \frac{0}{\Delta x} = 0. \tag{8}$$

As we can observe, the derivative $f'(x)$ when $x = 0$ has two different possible values,

$$f'(x = 0) = \begin{cases} 1 \text{ for } \Delta x \in \mathbb{R}^+ \\ 0 \text{ for } \Delta x \in \mathbb{R}^- \end{cases} \tag{9}$$

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When the derivative of a function has two different possible values, the function is **discontinuous**.

In the infinite limit when $\Delta x \to 0$, we can defined as,

$$dy = f'(x)dx, \tag{10}$$

where dy and dx are known as the **differentials**.

2 Common derivatives

In real-life, one usually consult a table or memorize the most common derivatives. Later in the course we will see that the derivative of more complicated functions can be simplified using the **chain rule**. For the following derivatives we assume a is a constant, and $f(x)$ and $g(x)$ both are functions of x.

1. **Derivative of a constant**

$$\frac{da}{dx} = 0 \tag{11}$$

2. **Derivative of a sum**

$$\frac{d\, f(x) + g(x)}{dx} = \frac{d\, f(x)}{dx} + \frac{d\, g(x)}{dx} \tag{12}$$

3. **Derivative of a polynomial**

$$\frac{d\ x^n}{dx} = nx^{n-1} \tag{13}$$

4. **Derivative of trigonometric functions**

$$\begin{aligned}
\frac{d\ \cos(x)}{dx} &= -\sin(x) && (14)\\
\frac{d\ \sin(x)}{dx} &= \cos(x) && (15)
\end{aligned}$$

5. **Derivative of logarithm**

$$\frac{d\ \ln(x)}{dx} = \frac{1}{x} \tag{16}$$

6. **Derivative of exponential**

$$\frac{d\ e^x}{dx} = e^x \tag{17}$$

With the previous list of derivatives one can derive the derivate of,

1. **Derivative of** $af(x)$

$$\frac{d\ af(x)}{dx} = a\frac{d\ f(x)}{dx} + f(x)\cancel{\frac{d\ a}{dx}} = a\frac{d\ f(x)}{dx} \tag{18}$$

2. **Derivative of of the ratio between two functions**

$$\begin{aligned}
\frac{d\ \frac{f(x)}{g(x)}}{dx} &= \frac{d\ f(x)g(x)^{-1}}{dx} = g(x)^{-1}\frac{d\ f(x)}{dx} + f(x)\frac{d\ g(x)^{-1}}{dx} && (19)\\
&= g(x)^{-1}\frac{d\ f(x)}{dx} + f(x)(-1)g(x)^{-2}\frac{d\ g(x)}{dx} && (20)\\
&= \left(\frac{g(x)}{g(x)}\right)\frac{\frac{d\ f(x)}{dx}}{g(x)} - \frac{f(x)\ \frac{d\ g(x)}{dx}}{g(x)^2} && (21)\\
&= \frac{g(x)\frac{d\ f(x)}{dx} - f(x)\frac{d\ g(x)}{dx}}{g(x)^2} && (22)
\end{aligned}$$

3 Differentiation for multi-dimensional functions

3.1 Partial Derivatives

In natural sciences, we commonly need functions that depend on multiple variables to describe a phenomenon. For example, in thermodynamics the equation of state depends on temperature T, pressure P and the number of mols of a substance n, $f(T,P,n)$. Similarly, we can define the derivate of a multi variable function with respect to (w.r.t.) one of its variables, this is known as **partial derivative** and it is defined as,

$$\left(\frac{\partial f(x,y)}{\partial x}\right)_y = \lim_{\Delta x \to 0} \frac{f(x+\Delta x, y) - f(x,y)}{\Delta x}, \tag{23}$$

where $(\ )_y$ means that the variable y is considered as a constant. Commonly, we do not use this notation $(\ )_y$ as for functions with large number of variables it makes the writing cumbersome, so we define $\frac{\partial f(x,y)}{\partial x} = \left(\frac{\partial f(x,y)}{\partial x}\right)_y$.

Eq. 23 is analogous to the definition of the ordinary derivative (Eq. 1). The only difference is the different used symbol, $\frac{d}{dx} \to \frac{\partial}{\partial x}$. We can also consider the partial derivative of $f(x, y)$ but w.r.t. y,

$$\left(\frac{\partial f(x,y)}{\partial y}\right)_x = \frac{\partial f(x,y)}{\partial y} = \lim_{\Delta y \to 0} \frac{f(x, y+\Delta y) - f(x,y)}{\Delta y}. \tag{24}$$

The list of ordinary derivatives can be used also in partial derivatives.

Exercise: Let's compute the partial derivative of $f(x, y) = ax^2y^3 + be^{xy}$ w.r.t. x and y,

1. w.r.t. x

$$\begin{aligned}\frac{\partial f(x,y)}{\partial x} &= \frac{\partial}{\partial x} ax^2y^3 + \frac{\partial}{\partial x} be^{xy} = ay^3 \frac{\partial}{\partial x} x^2 + b\frac{\partial}{\partial x} e^{xy} && (25)\\ &= ay^3(2x) + bye^{xy} = 2axy^3 + bye^{xy} && (26)\\ & && (27)\end{aligned}$$

2. w.r.t. y

$$\begin{aligned}\frac{\partial f(x,y)}{\partial y} &= \frac{\partial}{\partial y} ax^2y^3 + \frac{\partial}{\partial y} be^{xy} = ax^2 \frac{\partial}{\partial y} y^3 + b\frac{\partial}{\partial y} e^{xy} && (28)\\ &= ax^2(3y^2) + bxe^{xy} = 3ax^2y^2 + bxe^{xy} && (29)\\ & && (30)\end{aligned}$$

If the function $f(x, y)$ now undergoes an infinitesimal change in x and y, we can define the **total differential** of $f(x, y)$ as,

$$df(x,y) = \left(\frac{\partial f(x,y)}{\partial x}\right)_y dx + \left(\frac{\partial f(x,y)}{\partial y}\right)_x dy. \tag{31}$$

Eq. 31 often appears in thermodynamics.

4 Higher-order Derivatives

Functions can also have higher-order derivatives, for example, the kinetic energy is the second derivative of the position. $f(x, y)$ has four different second partial derivatives. Let's first consider the partial derivatives w.r.t. x and y of $\frac{\partial f(x,y)}{\partial x}$; this partial derivative is also a function of x and y.

$$\frac{\partial}{\partial x}\frac{\partial f(x,y)}{\partial x} = \frac{\partial^2 f(x,y)}{\partial x^2} \quad \text{and} \quad \frac{\partial}{\partial y}\frac{\partial f(x,y)}{\partial x} = \frac{\partial f(x,y)}{\partial y \partial x} \tag{32}$$

The partial derivatives of $\frac{\partial f(x,y)}{\partial y}$ w.r.t. x and y are, $f(x, y)$ has four different second partial derivatives. Let's first consider the partial derivatives w.r.t. x and y of $\frac{\partial f(x,y)}{\partial x}$; this partial derivative is also a function of x and y.

$$\frac{\partial}{\partial x}\frac{\partial f(x,y)}{\partial y} = \frac{\partial f(x,y)}{\partial x \partial y} \quad \text{and} \quad \frac{\partial}{\partial y}\frac{\partial f(x,y)}{\partial y} = \frac{\partial^2 f(x,y)}{\partial y^2} \tag{33}$$

Later in the course we will see that for multivariate functions, the second oder derivative is known as the **Hessian**,

$$\mathbf{H}_{f(x,y)} = \begin{pmatrix} \frac{\partial^2 f(x,y)}{\partial x^2} & \frac{\partial f(x,y)}{\partial y \partial x} \\ \frac{\partial f(x,y)}{\partial x \partial y} & \frac{\partial^2 f(x,y)}{\partial y^2} \end{pmatrix} \tag{34}$$

.

Exercise: Let's compute the Hessian of $f(x,y) = ax^2y^3 + be^{xy}$,

$$\frac{\partial^2 f(x,y)}{\partial x^2} = \frac{\partial}{\partial x} 2axy^3 + bye^{xy} = 2ay^3 + by^2e^{xy} \tag{35}$$

$$\frac{\partial f(x,y)}{\partial y \partial x} = \frac{\partial}{\partial y} 3ax^2y^2 + bxe^{xy} = 6axy^2 + be^{xy}(1+xy) \tag{36}$$

$$\frac{\partial f(x,y)}{\partial x \partial y} = 6axy^2 + be^{xy}(1+xy) \tag{37}$$

$$\frac{\partial^2 f(x,y)}{\partial y^2} = 6ax^2y + bx^2e^{xy} \tag{38}$$

Form the prev. equations, we can notice that $\frac{\partial f(x,y)}{\partial y \partial x} = \frac{\partial f(x,y)}{\partial x \partial y}$. This property of the partial derivatives is known as the *Clairaut's theorem*.