Partial Derivatives, Gradient, Divergence and Chain Rule

Mathematical Tools for Multivariable Calculus

1 Introduction: From One Variable to Multiple Variables

In many scientific problems, a quantity depends on several variables.

For example:

$$z = f(x, y)$$

means that the value of z depends on two independent variables.

Examples in chemistry:

- molecular energy as a function of atomic coordinates;
- concentration depending on position;
- temperature distribution in space.

For one variable:

$$y = f(x)$$

we use the derivative:

$$\frac{dy}{dx}$$

to describe how the function changes.

For multiple variables we need partial derivatives.

2 Partial Derivatives

Consider:

$$f(x, y)$$

The partial derivative with respect to x is written as:

$$\boxed{\frac{\partial f}{\partial x}}$$

It describes the change of the function when x changes while y remains constant.

Similarly:

$$\boxed{\frac{\partial f}{\partial y}}$$

describes the change with respect to y while x remains constant.

2.1 Example: Simple Function

Consider:

$$f(x, y) = x^2 + 3xy + y^2$$

The derivative with respect to x is:

$$\frac{\partial f}{\partial x} = 2x + 3y$$

because y is treated as a constant.
The derivative with respect to y is:

$$\frac{\partial f}{\partial y} = 3x + 2y$$

Therefore:

$$\boxed{\nabla f = \begin{pmatrix} 2x + 3y \\ 3x + 2y \end{pmatrix}}$$

3 The Gradient Vector

The gradient combines all partial derivatives into one vector:

$$\boxed{\nabla f = \begin{pmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \end{pmatrix}}$$

For three dimensions:

$$f(x, y, z)$$

the gradient becomes:

$$\boxed{\nabla f = \begin{pmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial z} \end{pmatrix}}$$

The gradient points in the direction of the largest increase of the function.
Therefore:

$$\boxed{\nabla f = \text{direction of maximum change}}$$

4 Geometrical Meaning of the Gradient

For a surface:

$$z = f(x, y)$$

the gradient describes the slope of the surface.
If:

$$\nabla f = 0$$

then the surface is locally flat.

Such points are called:

$$\boxed{\text{critical points}}$$

They are important in optimization problems.
Examples:

$$\begin{array}{c}\text{molecular energy minimum}\\ \downarrow \\ \nabla E = 0\end{array}$$

5 Partial Derivatives in Three Dimensions

For:

$$f(x, y, z)$$

we have:

$$\frac{\partial f}{\partial x}, \qquad \frac{\partial f}{\partial y}, \qquad \frac{\partial f}{\partial z}$$

Example:

$$f(x, y, z) = x^2 + y^2 + z^2$$

The derivatives are:

$$\frac{\partial f}{\partial x} = 2x$$

$$\frac{\partial f}{\partial y} = 2y$$

$$\frac{\partial f}{\partial z} = 2z$$

Therefore:

$$\boxed{\nabla f = \begin{pmatrix} 2x \\ 2y \\ 2z \end{pmatrix}}$$

6 Higher Order Partial Derivatives

Partial derivatives can also be differentiated again.
For example:

$$f_{xx} = \frac{\partial^2 f}{\partial x^2}$$

and:

$$f_{xy} = \frac{\partial^2 f}{\partial y \partial x}$$

For:

$$f(x, y) = x^2y + 3xy^2$$

we find:

$$f_x = 2xy + 3y^2$$

and:

$$f_{xx} = 2y$$

The mixed derivative is:

$$f_{xy} = 2x + 6y$$

These second derivatives form the basis of the Hessian matrix.

7 Connection with Optimization

Finding extrema requires:

$$\boxed{\nabla f = 0}$$

The gradient tells the direction of change.
The Hessian determines whether the point is:

Hessian	Result
positive definite	minimum
negative definite	maximum
mixed signs	saddle point

This forms the mathematical basis for:

- Newton optimization;
- molecular geometry optimization;
- machine learning algorithms.

8 Vector Fields and Divergence

8.1 Scalar Fields and Vector Fields

A scalar field assigns a single value to every point in space.
Example:

$$T(x, y, z)$$

can represent temperature.
A vector field assigns a vector to every point.
Example:

$$\mathbf{F}(x, y, z) = \begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix}$$

Examples in physics and chemistry:

- velocity field of a fluid;
- electric field;
- diffusion flux.

9 Divergence

The divergence measures how much a vector field spreads out from a point.

For:

$$\mathbf{F}(x, y, z) = \begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix}$$

the divergence is:

$$\boxed{\nabla \cdot \mathbf{F} = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}}$$

The symbol:

$$\nabla \cdot$$

is called the divergence operator.

9.1 Physical Meaning of Divergence

If:

$$\nabla \cdot \mathbf{F} > 0$$

the field behaves like a source:

$$\boxed{\text{more flow leaves than enters}}$$

If:

$$\nabla \cdot \mathbf{F} < 0$$

the field behaves like a sink:

$$\boxed{\text{more flow enters than leaves}}$$

If:

$$\nabla \cdot \mathbf{F} = 0$$

the field is divergence-free:

$$\boxed{\text{no net creation or destruction}}$$

9.2 Example: Radial Field

Consider:

$$\mathbf{F} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The divergence is:

$$\nabla \cdot \mathbf{F} = \frac{\partial x}{\partial x} + \frac{\partial y}{\partial y} + \frac{\partial z}{\partial z}$$

Therefore:

$$\nabla \cdot \mathbf{F} = 1 + 1 + 1$$

and:

$$\boxed{\nabla \cdot \mathbf{F} = 3}$$

The field behaves everywhere as a source.

10 The Nabla Operator

The operator:

$$\nabla$$

is defined as:

$$\boxed{\nabla = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix}}$$

It can be used in different ways.
Gradient:

$$\boxed{\nabla f}$$

Divergence:

$$\boxed{\nabla \cdot \mathbf{F}}$$

Laplacian:

$$\boxed{\nabla^2 f = \nabla \cdot \nabla f}$$

11 Directional Derivative

The gradient gives the direction of the strongest increase.
However, we often want the rate of change in a specific direction.
This is the directional derivative.
Let:

$$\mathbf{u}$$

be a unit vector.
The directional derivative is:

$$\boxed{D_{\mathbf{u}} f = \nabla f \cdot \mathbf{u}}$$

where:

$$|\mathbf{u}| = 1$$

11.1 Example: Directional Derivative

Consider:

$$f(x, y) = x^2 + y^2$$

The gradient is:

$$\nabla f = \begin{pmatrix} 2x \\ 2y \end{pmatrix}$$

At:

$$(1, 2)$$

we have:

$$\nabla f(1, 2) = \begin{pmatrix} 2 \\ 4 \end{pmatrix}$$

Suppose the direction is:

$$\mathbf{u} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

The directional derivative becomes:

$$D_{\mathbf{u}} f = \nabla f \cdot \mathbf{u}$$

Therefore:

$$= \begin{pmatrix} 2 \\ 4 \end{pmatrix} \cdot \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

giving:

$$\boxed{D_{\mathbf{u}} f = \frac{6}{\sqrt{2}}}$$

12 Relation Between Gradient and Directional Derivative

The directional derivative is:

$$D_{\mathbf{u}} f = \nabla f \cdot \mathbf{u}$$

Using the dot product:

$$\nabla f \cdot \mathbf{u} = |\nabla f||\mathbf{u}| \cos \theta$$

Because:

$$|\mathbf{u}| = 1$$

we obtain:

$$\boxed{D_{\mathbf{u}} f = |\nabla f| \cos\theta}$$

Therefore:

$$\boxed{\text{maximum change occurs when } \mathbf{u} \parallel \nabla f}$$

and:

$$\boxed{D_{\mathbf{u}} f_{\max} = |\nabla f|}$$

13 Chemical and Physical Examples

13.1 Concentration Gradient

A concentration field:

$$c(x, y, z)$$

has gradient:

$$\nabla c$$

which points toward increasing concentration.
Diffusion follows approximately:

$$\mathbf{J} = -D\nabla c$$

where:

- $\mathbf{J}$ is the diffusion flux;
- D is the diffusion coefficient.

The minus sign means diffusion occurs from high to low concentration.

13.2 Electric Field

The electric field is related to potential:

$$V(x, y, z)$$

by:

$$\boxed{\mathbf{E} = -\nabla V}$$

The gradient therefore connects:

$$\boxed{\text{potential energy} \to \text{force}}$$

14 Summary

The main operators are:

$$\boxed{\nabla f = \text{gradient}}$$

$$\boxed{\nabla \cdot \mathbf{F} = \text{divergence}}$$

$$\boxed{D_{\mathbf{u}} f = \nabla f \cdot \mathbf{u} = \text{directional derivative}}$$

Their meaning:

Concept	Meaning
Gradient	direction of fastest increase
Divergence	source or sink behaviour
Directional derivative	change along a chosen direction

15 The Chain Rule for Multivariable Functions

15.1 Why the Chain Rule is Needed

In many scientific problems variables depend on other variables.

For example:

$$z = f(x, y)$$

but:

$$x = x(t), \qquad y = y(t)$$

Therefore z depends indirectly on t:

$$t \to (x, y) \to z$$

The chain rule describes this total dependence.

16 Chain Rule in One Variable

For:

$$y = f(x)$$

and:

$$x = g(t)$$

we have:

$$y = f(g(t))$$

The derivative is:

$$\boxed{\frac{dy}{dt} = \frac{dy}{dx}\frac{dx}{dt}}$$

The change propagates through the intermediate variable.

17 Chain Rule for Two Variables

Consider:

$$z = f(x, y)$$

where:

$$x = x(t), \qquad y = y(t)$$

The total derivative becomes:

$$\boxed{\frac{dz}{dt} = \frac{\partial f}{\partial x}\frac{dx}{dt} + \frac{\partial f}{\partial y}\frac{dy}{dt}}$$

In vector notation:

$$\boxed{\frac{dz}{dt} = \nabla f \cdot \frac{d\mathbf{x}}{dt}}$$

where:

$$\mathbf{x} = \begin{pmatrix} x \\ y \end{pmatrix}$$

17.1 Example

Let:

$$f(x, y) = x^2 + y^2$$

and:

$$x(t) = t^2$$

$$y(t) = \sin(t)$$

First calculate the partial derivatives:

$$\frac{\partial f}{\partial x} = 2x$$

and:

$$\frac{\partial f}{\partial y} = 2y$$

The derivatives of the variables are:

$$\frac{dx}{dt} = 2t$$

and:

$$\frac{dy}{dt} = \cos(t)$$

Therefore:

$$\frac{df}{dt} = 2x(2t) + 2y\cos(t)$$

Substitution gives:

$$\boxed{\frac{df}{dt} = 4t^3 + 2\sin(t)\cos(t)}$$

18 Chain Rule in Several Dimensions

For:

$$f(x_1, x_2, \ldots, x_n)$$

where each variable depends on t:

$$x_i = x_i(t)$$

we have:

$$\boxed{\frac{df}{dt} = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} \frac{dx_i}{dt}}$$

In vector form:

$$\boxed{\frac{df}{dt} = \nabla f \cdot \frac{d\mathbf{x}}{dt}}$$

19 The Jacobian Matrix

For a transformation:

$$\mathbf{y} = \mathbf{f}(\mathbf{x})$$

with:

$$\mathbf{x} = (x_1, x_2, \ldots, x_n)$$

and:

$$\mathbf{y} = (y_1, y_2, \ldots, y_m)$$

the Jacobian matrix is:

$$\boxed{J = \frac{\partial(y_1, \ldots, y_m)}{\partial(x_1, \ldots, x_n)}}$$

Explicitly:

$$J = \begin{pmatrix} \frac{\partial y_1}{\partial x_1} & \frac{\partial y_1}{\partial x_2} & \cdots \\ \frac{\partial y_2}{\partial x_1} & \frac{\partial y_2}{\partial x_2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

The Jacobian describes how small changes transform:

$$\boxed{d\mathbf{y} = J\, d\mathbf{x}}$$

20 Total Differential

For:

$$f(x, y)$$

the total differential is:

$$\boxed{df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy}$$

For three variables:

$$\boxed{df = f_x dx + f_y dy + f_z dz}$$

This describes the change of a function caused by small changes in all variables.

21 Application: Reaction Coordinates in Chemistry

A molecular energy can depend on many coordinates:

$$E = E(x_1, x_2, \ldots, x_N)$$

where:

$$x_i$$

are atomic coordinates.
Along a reaction coordinate:

$$s$$

the energy changes as:

$$\boxed{\frac{dE}{ds} = \nabla E \cdot \frac{d\mathbf{x}}{ds}}$$

This is the energy change along a molecular pathway.
The condition:

$$\frac{dE}{ds} = 0$$

corresponds to stationary points:

$$\boxed{\text{reactants, products or transition states}}$$

22 Application: Coordinate Transformations

In chemistry and physics we often change coordinates.
Example:
Cartesian coordinates:

$$(x, y, z)$$

can be transformed into spherical coordinates:

$$(r, \theta, \phi)$$

The Jacobian is needed when transforming derivatives and integrals.
For example:

$$dV = dx\, dy\, dz$$

becomes:

$$\boxed{dV = r^2 \sin\theta\, dr\, d\theta\, d\phi}$$

The factor:

$$r^2 \sin\theta$$

is the determinant of the Jacobian.

23 Summary

The chain rule describes how changes propagate:

$$\boxed{\text{change in output} = \text{local sensitivity} \times \text{change in input}}$$

Important formulas:

$$\boxed{\frac{dz}{dt} = \nabla f \cdot \frac{d\mathbf{x}}{dt}}$$

$$\boxed{d\mathbf{y} = J d\mathbf{x}}$$

$$\boxed{df = \sum_i \frac{\partial f}{\partial x_i} dx_i}$$

Applications:

optimization
molecular dynamics
reaction coordinates
coordinate transformations