Further information 1

Relations between partial derivatives

A partial derivative of a function of more than one variable, such as $f(x,y)$, is the slope of the function with respect to one of the variables, all the other variables being held constant (see Fig. 2.12). Although a partial derivative shows how a function changes when one variable changes, it may be used to determine how the function changes when more than one variable changes by an infinitesimal amount. Thus, if f is a function of x and y, then when x and y change by $\mathrm{d}x$ and $\mathrm{d}y$, respectively, f changes by

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y \qquad (1)$$

For example, if $f = ax^3y + by^2$,

$$\left(\frac{\partial f}{\partial x}\right)_y = 3ax^2y \qquad \left(\frac{\partial f}{\partial y}\right)_x = ax^3 + 2by$$

Then, when x and y undergo infinitesimal changes, f changes by

$$\mathrm{d}f = 3ax^2y\,\mathrm{d}x + (ax^3 + 2by)\,\mathrm{d}y$$

Partial derivatives may be taken in any order:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \qquad (2)$$

For the function f given above, it is easy to verify that

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = 3ax^2 \qquad \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = 3ax^2$$

In the following, z is a variable on which x and y depend (for example, x, y, and z might correspond to p, V, and T).

Relation no. 1. When x is changed at constant z:

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \tag{3}$$

Relation no. 2 (the inverter).

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y/\partial x)_z} \tag{4}$$

Relation no. 3 (the permuter).

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \tag{5}$$

By combining this relation and Relation no. 2 we obtain **Euler's chain relation:**

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{6}$$

Relation no. 4. This relation establishes whether or not df is an exact differential.

$$df = g(x,y)\,dx + h(x,y)\,dy \text{ is exact if } \left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y \tag{7}$$

If df is exact, its integral between specified limits is independent of the path.

Further information 2

Differential equations

A differential equation is a relation between derivatives of a function and the function itself, as in

$$a\frac{d^2y}{dx^2}+b\frac{dy}{dx}+cy=0 \qquad (1)$$

The coefficients a, b, etc. may be functions of x. The **order** of the equation is the order of the highest derivative that occurs in it, so eqn 1 is a second-order equation. Only rarely in science is a differential equation of order higher than 2 encountered. A solution of a differential equation is an expression for y as a function of x. The process of solving a differential equation is commonly termed 'integration', and in simple cases simple integration can be employed to find $y(x)$. A **general solution** of a differential equation is the most general solution of the equation and is expressed in terms of a number of constants. When the constants are chosen to accord with certain specified **initial conditions** (if one variable is the time) or certain **boundary conditions** (to fulfil certain spatial restrictions on the solutions), we obtain the **particular solution** of the equation. A first-order differential equation requires the specification of *one* boundary (or initial) condition; a second-order differential equation requires the specification of *two* such conditions, and so on.

First-order differential equations may often be solved by direct integration. For example, the equation

$$\frac{dy}{dx}=axy$$

with a constant may be rearranged into

$$\frac{dy}{y}=ax\,dx$$

and then integrated to

$$\ln y=\tfrac{1}{2}ax^2+A$$

where A is a constant. If we know that $y = y_0$ when $x = 0$ (for instance), then it follows that $A = \ln y_0$, and hence the particular solution of the equation is

$$\ln y = \tfrac{1}{2}ax^2 + \ln y_0$$

This expression rearranges to

$$y = y_0 e^{ax^2/2}$$

First-order equations of a more complex form can often be solved by the appropriate substitution. For example, it is sensible to try the substitution $y = sx$, and to change the variables from x and y to x and s. An alternative useful transformation is to write $x = u + a$ and $y = v + b$, and then to select a and b to simplify the form of the resulting expression.

Second-order differential equations are in general much more difficult to solve than first-order equations. The general solutions of many such equations are best found by referring to tables: the *Handbook of mathematical functions*, M. Abramowitz and I.A. Stegun, Dover, New York (1965), is a particularly helpful source of such information. Mathematical software is now capable of finding numerical and, in certain cases, analytical solutions of a wide variety of differential equations.

One powerful approach commonly used to lay siege to second-order differential equations is to express the solution as a power series:

$$y = \sum_{n=0}^{\infty} c_n x^n \tag{2}$$

and then to use the differential equation to find a relation between the coefficients. This approach results, for instance, in the Hermite polynomials that form part of the solution of the Schrödinger equation for the harmonic oscillator. All the second-order differential equations that occur in this text can be found tabulated in compilations of solutions, and the specialized techniques that are needed to establish the form of the solutions may be found in mathematical texts.

A **partial differential equation** is a differential in more than one variable. An example is

$$\frac{\partial^2 y}{\partial t^2} = a\frac{\partial^2 y}{\partial x^2} \tag{3}$$

with y a function of the two variables x and t. In certain cases, partial differential equations may be separated into ordinary differential equations. Thus, the Schrödinger equation for a particle in a two-dimensional square well (Section 12.2) may be separated by writing the wavefunction, $\psi(x, y)$, as the product $X(x)Y(y)$, which results in the separation of the second-order partial differential equation into two second-order differential equations in the variables x and y. A good guide to the likely success of such a **separation of variables** procedure is the symmetry of the system.

A common approach to the solution of awkward differential equations that appear to have no analytical solutions is to adopt a numerical procedure. Software packages are now readily available that can be used to solve almost any equation numerically. The general form of such programs to solve $df/dx = g(x)$, for instance, replaces the infinitesimal quantity $df = g(x)\,dx$ by the small quantity $\delta f = g(x)\,\delta x$, so that

$$f(x + \delta x) \approx f(x) + g(x)\,\delta x \tag{4}$$

and then proceeds to step along the x-axis numerically, generating $f(x)$ as it goes. The actual algorithms adopted are much more sophisticated than this primitive scheme, but stem from it.

Further information 3

Undetermined multipliers

Suppose we need to find the maximum (or minimum) value of some function f that depends on several variables $x_1, x_2, \ldots, x_n$. When the variables undergo a small change from x_i to $x_i + \delta x_i$ the function changes from f to $f + \delta f$, where

$$\delta f = \sum_i^n \left(\frac{\partial f}{\partial x_i}\right)\delta x_i \tag{1}$$

At a minimum or maximum, $\delta f = 0$, so then

$$\sum_i^n \left(\frac{\partial f}{\partial x_i}\right)\delta x_i = 0 \tag{2}$$

If the x_i were all independent, all the δx_i would be arbitrary, and this equation could be solved by setting each $(\partial f/\partial x_i) = 0$ individually. When the x_i are not all independent, the x_i are not all independent, and the simple solution is no longer valid. We proceed as follows.

Let the constraint connecting the variables be an equation of the form $g = 0$. For example, in Chapter 19, one constraint was $n_0 + n_1 + \cdots = N$, which can be written

$$g = 0, \text{ with } g = (n_0 + n_1 + \cdots) - N$$

The constraint $g = 0$ is always valid, so g remains unchanged when the x_i are varied:

$$\delta g = \sum_i \left(\frac{\partial g}{\partial x_i}\right)\delta x_i = 0 \tag{3}$$

Because δg is zero, we can multiply it by a parameter, λ, and add it to eqn 2:

$$\sum_i^n \left\{\left(\frac{\partial f}{\partial x_i}\right) + \lambda\left(\frac{\partial g}{\partial x_i}\right)\right\}\delta x_i = 0 \tag{4}$$

This equation can be solved for one of the δx, δx_n for instance, in terms of all the other δx_i. All those other δx_i $(i = 1, 2, \ldots n-1)$ are independent, because there is only one constraint on the system. But here is the trick: λ is arbitrary; therefore we can choose it so that the coefficient of δx_n in eqn 4 is zero. That is, we choose λ so that

$$\left(\frac{\partial f}{\partial x_n}\right) + \lambda\left(\frac{\partial g}{\partial x_n}\right) = 0 \tag{5}$$

Then eqn 4 becomes

$$\sum_i^{n-1}\left\{\left(\frac{\partial f}{\partial x_i}\right) + \lambda\left(\frac{\partial g}{\partial x_i}\right)\right\}\delta x_i = 0 \tag{6}$$

Now the $n-1$ variations δx_i *are* independent, so the solution of this equation is

$$\left(\frac{\partial f}{\partial x_i}\right) + \lambda\left(\frac{\partial g}{\partial x_i}\right) = 0 \qquad i = 1, 2, \ldots n-1 \tag{7}$$

But eqn 5 has exactly the same form as this equation, so the maximum or minimum of f can be found by solving

$$\left(\frac{\partial f}{\partial x_i}\right) + \lambda\left(\frac{\partial g}{\partial x_i}\right) = 0 \qquad i = 1, 2, \ldots n \tag{8}$$

The use of this approach was illustrated in the text for two constraints and therefore two undetermined multipliers λ_1 and λ_2 (α and $-\beta$).

The multipliers λ cannot always remain undetermined. One approach is to solve eqn 5 instead of incorporating it into the minimization scheme. In Chapter 19 we used the alternative procedure of keeping λ undetermined until a property was calculated for which the value was already known. Thus, we found that $\beta = 1/kT$ by calculating the internal energy of a perfect gas.

Further information 4

Classical mechanics

We shall see how classical mechanics describes the behaviour of objects in terms of two equations. One equation expresses the fact that the total energy is constant in the absence of external forces. The other equation expresses the response of particles to the forces acting on them.

1 The trajectory in terms of the energy

The total energy of a particle is the sum of the **kinetic energy**, E_K, the energy arising from the motion of the particle, and **potential energy**, $V(x)$, the energy arising from the position of the particle in a field of force:

$$E = E_K + V(x) \tag{1}$$

The force, F, is related to the potential energy by

$$F = -\frac{dV}{dx} \tag{2}$$

According to this expression, the direction of the force is towards decreasing potential energy (Fig. 1). The kinetic energy of a particle of mass m travelling with a speed v is

$$E_K = \tfrac{1}{2}mv^2 \tag{3}$$

It is often convenient to express kinetic energy in terms of the **linear momentum, $\boldsymbol{p}$**. The linear momentum is a vector quantity (that is, it has direction as well as magnitude, like the velocity, $\boldsymbol{v}$). The magnitude of the linear momentum, p, is related to the speed, v, of the particle by

$$p = mv \tag{4}$$

harmonic motion is found by substituting the expression for the force, eqn 16, into Newton's equation, eqn 10. The resulting equation is

$$m\frac{d^2x}{dt^2} = -kx \tag{17}$$

and a solution is

$$x(t) = A\sin\omega t \qquad p(t) = m\omega A\cos\omega t \qquad \omega = \left(\frac{k}{m}\right)^{1/2} \tag{18}$$

(To verify the solution for x, substitute it into the differential equation; the expression for the momentum is obtained from $p = m\mathrm{d}x/\mathrm{d}t$.) These expressions show that the position of the particle varies **harmonically** (that is, as $\sin\omega t$) with a frequency $\nu = \omega/2\pi$. They also show that the particle is stationary ($p = 0$) when the displacement, x, has its maximum value, A, which is called the **amplitude** of the motion.

The total energy of a classical harmonic oscillator is proportional to the square of the amplitude of its motion. To confirm this remark we note that the kinetic energy is

$$E_K = \frac{p^2}{2m} = \frac{(m\omega A\cos\omega t)^2}{2m} = \tfrac{1}{2}m\omega^2A^2\cos^2\omega t \tag{19a}$$

Then, because $\omega = (k/m)^{1/2}$, this expression may be written

$$E_K = \tfrac{1}{2}kA^2\cos^2\omega t \tag{19b}$$

The force on the oscillator is $F = -kx$, so it follows from the relation $F = -\mathrm{d}V/\mathrm{d}x$ that the potential energy of a harmonic oscillator is

$$V = \tfrac{1}{2}kx^2 = \tfrac{1}{2}kA^2\sin^2\omega t \tag{20}$$

The total energy is therefore

$$E = \tfrac{1}{2}kA^2\cos^2\omega t + \tfrac{1}{2}kA^2\sin^2\omega t = kA^2 \tag{21}$$

(We have used $\cos^2\omega t + \sin^2\omega t = 1$.) That is, the energy of the oscillator is constant and, for a given force constant, is determined by its maximum displacement. It follows that the energy of an oscillating particle can be raised to any value by stretching the spring to any desired amplitude A. It is important to note that the frequency of the motion depends only on the inherent properties of the oscillator (as represented by k and m) and is independent of the energy; the amplitude governs the energy, through $E = \tfrac{1}{2}kA^2$, and is independent of the frequency. In other words, the particle will oscillate at the same frequency regardless of the amplitude of its motion.

Further information 5

Electrical quantities

The fundamental expression in **electrostatics**, the interactions of stationary electric charges, is the **Coulomb potential energy** of one charge of magnitude q at a distance r from another charge q:

$$V = \frac{qq'}{4\pi\varepsilon_0 r} \tag{1}$$

That is, the potential energy is inversely proportional to the separation of the charges. The fundamental constant ε_0 is the **vacuum permittivity**; its value is $\varepsilon_0 = 8.854 \times 10^{-12}\ \mathrm{J^{-1}\,C^2\,m^{-1}}$. (Note that with r in metres, m, and the charges in coulombs, C, the potential energy is in joules, J.) The potential energy is equal to the work that must be done to bring up a charge q from infinity to a distance r from a charge q'. In a medium other than a vacuum, the potential energy of interaction between two charges is reduced, and the vacuum permittivity is replaced by the **permittivity**, ε, **of the medium**. It is common to express the permittivity as a multiple of the vacuum permittivity, and to write $\varepsilon = \varepsilon_r\varepsilon_0$, where ε_r is the **relative permittivity** (or **dielectric constant**) of the medium. For water at 25°C, $\varepsilon_r = 78.54$.

The potential energy of a charge q in the presence of another charge q' can be expressed in terms of the **Coulomb potential**, ϕ:

$$V = q\phi \qquad \phi = \frac{q'}{4\pi\varepsilon_0 r} \tag{2}$$

The units of potential are joules per coulomb, $\mathrm{J\,C^{-1}}$ so, when ϕ is multiplied by a charge in coulombs, the result is in joules. The combination joules per coulomb occurs widely in electrostatics, and is called a *volt*, V:

$$1\ \mathrm{V} = 1\ \mathrm{J\,C^{-1}}$$

(which implies that 1 V C = 1 J). If there are several charges $q_1, q_2, \ldots$ present in the system, the total potential experienced by the charge q is the sum of the potential generated by each charge:

$$\phi = \phi_1 + \phi_2 + \cdots \quad (3)$$

The electrical force, F, exerted by a charge q on a second charge q' has magnitude

$$F = \frac{qq'}{4\pi\varepsilon_0 r^2} \quad (4)$$

The force is a vector quantity (that is, has direction), and is directed along the line joining the two charges. With charge in coulombs and distance in metres, the force is obtained in newtons.

The motion of charge gives rise to an electric **current**, I. Electric current is measured in *amperes*, A, where

$$1\ \text{A} = 1\ \text{C s}^{-1}$$

If the electric charge is that of electrons (as it is for conduction in metals and semiconductors), then a current of 1 A represents the flow of 6×10^{18} electrons per second. If the current flows from a region of potential ϕ_i to ϕ_f, through a **potential difference** $\Delta\phi = \phi_f - \phi_i$, the rate of doing work is the current (the rate of transfer of charge) multiplied by the potential difference, $I\Delta\phi$. The rate of doing work is called **power**, P, so

$$P = I\Delta\phi \quad (5)$$

With current in amperes and the potential difference in volts, the power works out in joules per second, or *watts*, W:

$$1\ \text{W} = 1\ \text{J s}^{-1}$$

The total energy, E, supplied in an interval Δt is the power (the energy per second) multiplied by the duration of the interval:

$$E = P\Delta t = I\Delta\phi\Delta t \quad (6)$$

The energy is obtained in joules with the current in amperes, the potential difference in volts, and the time in seconds.