Part IA: Mathematics for Natural Sciences A
Examples Sheet 13: Exact differentials, algebra of differentials, and applications in thermodynamics

Model Solutions

Please send all comments and corrections to jmm232@cam.ac.uk.

Differentials: basic definitions

1. We define the *differential* df of the function $f(x, y, ...)$ to be the infinitesimal (first-order) change in the function when its arguments are changed by an infinitesimal amount, $f(x + dx, y + dy, ...)$.

(a) Show that for a function of two variables, we have:

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

(b) Hence, find the differentials of the following functions:

(i) $\exp(-1/(x + y))$, (ii) $\sinh(x)/\sinh(y)$, (iii) $\sqrt{x^2 + y^2}$, (iv) $\arctan(y/x)$, (v) x^y.

➫ **Solution:**

(a) Expanding the function in a Taylor series for fixed dy, and small dx, we have:

$$f(x + dx, y + dy) = f(x, y + dy) + dx\frac{\partial f}{\partial x}(x, y + dy) + \cdots .$$

Now expanding this expression in a Taylor series for fixed dx, and small dy, we have:

$$f(x, y + dy) = f(x, y) + dy\frac{\partial f}{\partial y}(x, y) + \cdots \qquad \text{and} \qquad dx\frac{\partial f}{\partial x}(x, y + dy) = dx\frac{\partial f}{\partial x}(x, y) + \cdots ,$$

where in the second equation we used the fact that $dxdy$ is a second-order quantity, and hence small. This leaves us with the first-order *multivariable Taylor expansion*:

$$f(x + dx, y + dy) = f(x, y) + \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \cdots .$$

Hence, the change in f, namely $f(x + dx, y + dy) - f(x, y)$, is given to first-order by:

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

as required.

(b) For each of the given functions:

(i) We have:

$$d(e^{-1/(x+y)}) = \frac{1}{(x + y)^2}e^{-1/(x+y)}dx + \frac{1}{(x + y)^2}e^{-1/(x+y)}dy.$$

(ii) We have:
$$d\left(\frac{\sinh(x)}{\sinh(y)}\right) = \frac{\cosh(x)}{\sinh(y)}dx - \frac{\sinh(x)\cosh(y)}{\sinh^2(y)}dy.$$

(iii) We have:
$$d\left(\sqrt{x^2+y^2}\right) = \frac{x}{\sqrt{x^2+y^2}}dx + \frac{y}{\sqrt{x^2+y^2}}dy.$$

(iv) We have:
$$d\left(\arctan\left(\frac{y}{x}\right)\right) = -\frac{y/x^2}{1+(y/x)^2}dx + \frac{1/x}{1+(y/x)^2}dy = -\frac{y}{x^2+y^2}dx + \frac{x}{x^2+y^2}dy.$$

(v) We have:
$$d(x^y) = yx^{y-1}dx + \ln(x)x^y dy.$$

Exact differentials, and exact ordinary differential equations

2. Let $\omega = P(x,y)dx + Q(x,y)dy$ be a differential form.

(a) What does it mean to say that ω is *exact*? Define also a *potential function* for a given exact differential form.

(b) Show that $\partial P/\partial y = \partial Q/\partial x$ is a necessary condition for ω to be an exact differential form.

➭ **Solution:**

(a) We say that ω is an *exact* differential form if there exists a *potential function* f satisfying $df = \omega$.

(b) Suppose that indeed ω is exact, so that there exists a potential f satisfying $df = \omega$. Writing out the differential df explicitly, we then have:
$$\frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy = P(x,y)dx + Q(x,y)dy.$$

Comparing coefficients, we see that:
$$\frac{\partial f}{\partial x} = P(x,y), \qquad \frac{\partial f}{\partial y} = Q(x,y).$$

Taking a second derivative in each case, we have:
$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial P}{\partial y}, \qquad \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial Q}{\partial x}.$$

The result follows from the symmetry of mixed partial derivatives, giving:
$$\frac{\partial P}{\partial y} = \frac{\partial Q}{\partial x}.$$

Remarkably, this condition is not only *necessary*, but it is also *sufficient*, provided that we work on an appropriate domain with sufficiently nice functions.

3. Determine whether the following differential forms are exact or not. In the cases where the differential forms are exact, find appropriate potential functions f.

(a) $ydx + xdy$, (b) $ydx + x^2dy$, (c) $(x+y)dx + (x-y)dy$.

Solution:

(a) We have:

$$\frac{\partial(y)}{\partial y} = 1 = \frac{\partial(x)}{\partial x},$$

so the differential form is exact by the result of Question 2. Let f be a potential, satisfying $df = ydx + xdy$. Then we need:

$$\frac{\partial f}{\partial x} = y, \qquad \frac{\partial f}{\partial y} = x.$$

Integrating the first equation, we have $f(x,y) = xy + g(y)$, where $g(y)$ is an unknown function of y. Differentiating this expression with respect to y, we have:

$$x + g'(y) = \frac{\partial f}{\partial y} = x,$$

which by comparison shows that $g'(y) = 0$, hence $g(y)$ is a constant independent of y. Thus all potential functions are $f(x,y) = xy + c$, where c is an arbitrary constant.

(b) In this case, we have:

$$\frac{\partial(y)}{\partial y} = 1 \neq 2x = \frac{\partial(x^2)}{\partial x},$$

so the differential form is non-exact.

(c) In this case, we have:

$$\frac{\partial(x+y)}{\partial y} = 1 = \frac{\partial(x-y)}{\partial x},$$

so the differential form is exact by the result of Question 2. Let f be a potential, satisfying $df = (x+y)dx + (x-y)dy$. Then we need:

$$\frac{\partial f}{\partial x} = x + y, \qquad \frac{\partial f}{\partial y} = x - y.$$

Integrating the first equation, we see that $f(x,y) = \frac{1}{2}x^2 + xy + g(y)$, where $g(y)$ is an unknown function of y. Differentiating this expression with respect to y, we have:

$$x + g'(y) = \frac{\partial f}{\partial y} = x - y.$$

This shows that $g'(y) = -y$, giving $g(y) = -\frac{1}{2}y^2 + c$, where c is an arbitrary constant independent of both x and y. Thus all potential functions are given by $f(x,y) = \frac{1}{2}x^2 + xy - \frac{1}{2}y^2 + c$, where c is an arbitrary constant.

4. Find all values of the constant a for which the differential form:

$$\left(y^2 \sin(ax) + xy^2 \cos(ax)\right) dx + 2xy \sin(ax) dy$$

is exact. Find appropriate potential functions in the cases where the differential form is exact.

➼ **Solution:** For exactness, we require:

$$\frac{\partial}{\partial y}\left(y^2 \sin(ax) + xy^2 \cos(ax)\right) = 2y\sin(ax) + 2xy\cos(ax) = 2y\sin(ax) + 2axy\cos(ax) = \frac{\partial}{\partial x}\left(2xy\sin(ax)\right).$$

Hence, we see that the only case where the differential form is exact is when $a = 1$. In this case, a potential function f must satisfy:

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy = \left(y^2 \sin(x) + xy^2 \cos(x)\right) dx + 2xy \sin(x) dy.$$

Comparing coefficients, we see that:

$$\frac{\partial f}{\partial x} = y^2 \sin(x) + xy^2 \cos(x), \qquad \frac{\partial f}{\partial y} = 2xy \sin(x).$$

Integrating the second equation (because it looks easier), we see that $f(x, y) = xy^2 \sin(x) + g(x)$, where $g(x)$ is an unknown function of x. Differentiating with respect to x and inserting into the first equation, we have:

$$y^2 \sin(x) + xy^2 \cos(x) + g'(x) = y^2 \sin(x) + xy^2 \cos(x),$$

which shows that $g'(x) = 0$, and hence $g(x)$ is independent of x. Thus all potential functions are $f(x, y) = xy^2 \sin(x) + c$, where c is an arbitrary constant.

5. Let $P(x,y,z)dx + Q(x,y,z)dy + R(x,y,z)dz$ be a differential form in three dimensions. Show that:

$$\frac{\partial P}{\partial y} = \frac{\partial Q}{\partial x}, \qquad \frac{\partial P}{\partial z} = \frac{\partial R}{\partial x}, \qquad \frac{\partial Q}{\partial z} = \frac{\partial R}{\partial y}$$

is a necessary condition for the differential form to be exact. [*It turns out that this is also a sufficient condition, under suitable criteria which you may assume hold*.] Hence, decide whether the following differential forms are exact or not, and find appropriate potential functions in the cases where the forms are exact:

(a) $xdx + ydy + zdz$, (b) $ydx + zdy + xdz$, (c) $2xy^3z^4dx + 3x^2y^2z^4dy + 4x^2y^3z^3dz$.

Solution: Let $f(x,y,z)$ be a potential function, satisfying $df = Pdx + Qdy + Rdz$. Then:

$$\frac{\partial f}{\partial x} = P, \qquad \frac{\partial f}{\partial y} = Q, \qquad \frac{\partial f}{\partial z} = R.$$

Differentiating the first equation with respect to y, z, the second equation with respect to x, z, and the third equation with respect to x, y, we generate six more equations for the second derivatives:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial P}{\partial y}, \qquad \frac{\partial^2 f}{\partial x \partial z} = \frac{\partial P}{\partial z}, \qquad \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial Q}{\partial x},$$

$$\frac{\partial^2 f}{\partial y \partial z} = \frac{\partial Q}{\partial z}, \qquad \frac{\partial^2 f}{\partial x \partial z} = \frac{\partial R}{\partial x}, \qquad \frac{\partial^2 f}{\partial y \partial z} = \frac{\partial R}{\partial y}.$$

Comparing the relevant mixed partial derivatives, the necessary condition given in the question follows.

For the given functions:

(a) We have $P = x, Q = y, R = z$, which gives:

$$\frac{\partial P}{\partial y} = \frac{\partial P}{\partial z} = 0, \qquad \frac{\partial Q}{\partial x} = \frac{\partial Q}{\partial z} = 0, \qquad \frac{\partial R}{\partial x} = \frac{\partial R}{\partial y} = 0.$$

In particular, the necessary condition derived at the start of the question is satisfied. If $f(x,y,z)$ is a potential, then we have:

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

Integrating the first equation, we have $f(x,y,z) = \frac{1}{2}x^2 + g(y,z)$ for an unknown function $g(y,z)$. Differentiating and inserting into the second equation, we see that:

$$\frac{\partial g}{\partial y} = y \qquad \Rightarrow \qquad g(y,z) = \frac{1}{2}y^2 + h(z),$$

for an unknown function $h(z)$. Overall then, we have $f(x,y,z) = \frac{1}{2}x^2 + \frac{1}{2}y^2 + h(z)$. Differentiating again and inserting into the third equation, we see that:

$$h'(z) = z \qquad \Rightarrow \qquad h(z) = \frac{1}{2}z^2 + c,$$

where c is an arbitrary constant. Thus all potentials satisfy $f(x,y,z) = \frac{1}{2}x^2 + \frac{1}{2}y^2 + \frac{1}{2}z^2 + c$.

(b) This time, we have $P = y, Q = z, R = x$. This implies that:

$$\frac{\partial P}{\partial y} = 1 \neq 0 = \frac{\partial Q}{\partial x},$$

so this differential form is non-exact by the necessary condition derived at the start of the question.

(c) We have $P = 2xy^3z^4, Q = 3x^2y^2z^4, R = 4x^2y^3z^3$. Hence:

$$\frac{\partial P}{\partial y} = 6xy^2z^4 = \frac{\partial Q}{\partial x}, \qquad \frac{\partial P}{\partial z} = 8xy^3z^3 = \frac{\partial R}{\partial x}, \qquad \frac{\partial Q}{\partial z} = 12x^2y^2z^3 = \frac{\partial R}{\partial y},$$

so that indeed the differential form is exact. Let $f(x, y, z)$ be a potential function, satisfying:

$$\frac{\partial f}{\partial x} = 2xy^3z^4, \qquad \frac{\partial f}{\partial y} = 3x^2y^2z^4, \qquad \frac{\partial f}{\partial z} = 4x^2y^3z^3.$$

Integrating the first equation, we have $f(x, y, z) = x^2y^3z^4 + g(y, z)$. Differentiating and inserting into the second equation, we have:

$$3x^2y^2z^4 + \frac{\partial g}{\partial y} = 3x^2y^2z^4 \qquad \Rightarrow \qquad \frac{\partial g}{\partial y} = 0 \qquad \Rightarrow \qquad g(y, z) = h(z).$$

Thus we have $f(x, y, z) = x^2y^3z^4 + h(z)$. Differentiating and inserting into the third equation, we have:

$$4x^2y^3z^3 + h'(z) = 4x^2y^3z^3.$$

This shows $h(z)$ is a constant, and hence all potentials take the form $f(x, y, z) = x^2y^3z^4 + c$ for c an arbitrary constant.

6. Explain what is meant by an *exact first-order ordinary differential equation*, and describe how you can solve one. Show that each of the following first-order differential equations is exact, and hence find their general solution:

(a) $2x + e^y + (xe^y - \cos(y))\dfrac{dy}{dx} = 0$, (b) $\dfrac{dy}{dx} = \dfrac{5x+4y}{8y^3 - 4x}$, (c) $\sinh(x)\sin(y) + \cosh(x)\cos(y)\dfrac{dy}{dx} = 0$.

Solution: An *exact first-order ODE* takes the form:

$$P(x,y) + Q(x,y)\frac{dy}{dx} = 0,$$

where $P(x,y)dx + Q(x,y)dy$ is an exact differential form. Since $P(x,y)dx + Q(x,y)dy$ is exact, we have that it can be written as the differential of a potential function f, $df = P(x,y)dx + Q(x,y)dy$. In the case that $y \equiv y(x)$ is a function of x, as is the case for an ODE, all changes in f are characterised by changes in x only (since these induce changes in y). Hence dividing by dx and taking the limit as $dx \to 0$, we see that:

$$\frac{df}{dx} = P(x,y) + Q(x,y)\frac{dy}{dx} = 0,$$

which shows that the solution of the ODE is $f(x, y(x)) =$ constant.

Now, in practice, we have:

(a) In this case, this equation corresponds to the differential form:

$$(2x + e^y)dx + (xe^y - \cos(y))dy.$$

Seeking a potential, we require:

$$\frac{\partial f}{\partial x} = 2x + e^y, \qquad \frac{\partial f}{\partial y} = xe^y - \cos(y).$$

By inspection, observe that $f(x,y) = x^2 + xe^y - \sin(y)$ is an appropriate potential. Thus the solution is:

$$x^2 + xe^y - \sin(y) = c,$$

for an arbitrary constant c.

(b) Rearranging to standard form, the equation becomes:

$$5x + 4y + (4x - 8y^3)\frac{dy}{dx} = 0$$

The equation corresponds to the differential form $(5x+4y)dx + (4x - 8y^3)dy$. Seeking a potential, we require:

$$\frac{\partial f}{\partial x} = 5x + 4y, \qquad \frac{\partial f}{\partial y} = 4x - 8y^3.$$

By inspection, observe that $f(x,y) = \frac{5}{2}x^2 + 4xy - 2y^4$ is an appropriate potential. Thus the solution is:

$$\frac{5}{2}x^2 + 4xy - 2y^4 = c,$$

for an arbitrary constant c.

(c) In this case, we seek a potential satisfying:

$$\frac{\partial f}{\partial x} = \sinh(x)\sin(y), \qquad \frac{\partial f}{\partial y} = \cosh(x)\cos(y).$$

Again, by inspection observe that $f(x,y) = \cosh(x)\sin(y)$ is an appropriate potential. Thus the solution of the equation is:

$$\cosh(x)\sin(y) = c,$$

for an arbitrary constant c.

7. (a) Show that the differential form $Pdx + Qdy$ can be made exact through multiplication by the integrating factor $\mu(x)$ if and only if:

$$\frac{1}{Q}\left(\frac{\partial P}{\partial y} - \frac{\partial Q}{\partial x}\right)$$

is independent of y.

(b) Hence, find a function μ for which the differential form:

$$\mu[(\cos(y) - \tanh(x)\sin(y))dx - (\cos(y) + \tanh(x)\sin(y))dy]$$

is exact.

(c) Using the result of part (b), solve the differential equation:

$$\frac{dy}{dx} = \frac{\cos(y) - \tanh(x)\sin(y)}{\cos(y) + \tanh(x)\sin(y)}.$$

Solution: (a) Suppose that $\mu P dx + \mu Q dy$ is exact, where $\mu(x)$ is a function of x. Then:

$$\frac{\partial}{\partial y}(\mu P) = \frac{\partial}{\partial x}(\mu Q) \qquad \Rightarrow \qquad \mu(x)\frac{\partial P}{\partial y} = \mu'(x)Q + \mu(x)\frac{\partial Q}{\partial x}.$$

Rearranging, we see that:

$$\frac{\mu'(x)}{\mu(x)} = \frac{1}{Q}\left(\frac{\partial P}{\partial y} - \frac{\partial Q}{\partial x}\right).$$

This implies the necessary condition that the quantity on the right hand side of the equation is independent of y (because the left hand side is independent of y, evidently). On the other hand, if this quantity is independent of y, we can integrate both sides of this equation to obtain an integrating factor:

$$\mu(x) \propto \exp\left(\int \frac{1}{Q}\left(\frac{\partial P}{\partial y} - \frac{\partial Q}{\partial x}\right) dx\right).$$

(b) Here, we have $P = \cos(y) - \tanh(x)\sin(y), Q = -\cos(y) - \tanh(x)\sin(y)$. Hence:

$$\frac{1}{Q}\left(\frac{\partial P}{\partial y} - \frac{\partial Q}{\partial x}\right) = -\frac{1}{\cos(y) + \tanh(x)\sin(y)}\left(-\sin(y) - \tanh(x)\cos(y) + \mathrm{sech}^2(x)\sin(y)\right).$$

Recall that $1 - \tanh^2(x) = \mathrm{sech}^2(x)$, hence we can rewrite this quotient as:

$$\frac{\tanh(x)\cos(y) + \tanh^2(x)\sin(y)}{\cos(y) + \tanh(x)\sin(y)} = \tanh(x),$$

so indeed this quotient is independent of x. This reveals that the integrating factor is $\mu(x) \propto \exp(\ln(\cosh(x))) = \cosh(x)$, using the integral of $\tanh(x) = \sinh(x)/\cosh(x)$. For this choice of $\mu(x)$, the differential form becomes:

$$(\cosh(x)\cos(y) - \sinh(x)\sin(y))\,dx - (\cosh(x)\cos(y) + \sinh(x)\sin(y))\,dy.$$

A potential for this differential form satisfies:

$$\frac{\partial f}{\partial x} = \cosh(x)\cos(y) - \sinh(x)\sin(y), \qquad \frac{\partial f}{\partial y} = -\cosh(x)\cos(y) - \sinh(x)\sin(y).$$

By inspection, note that $f(x,y) = \sinh(x)\cos(y) - \cosh(x)\sin(y)$ satisfies these equations. Thus the differential form has indeed been made exact.

(c) The equation can be rearranged to the standard form:

$$(\cos(y) - \tanh(x)\sin(y)) - (\cos(y) + \tanh(x)\sin(y))\frac{dy}{dx} = 0.$$

Multiplying through by $\cosh(x)$, we obtain an exact equation, with solution $\sinh(x)\cos(y) - \cosh(x)\sin(y) = c$, as required.

Algebra of differentials

8. Let f, g be functions of (x, y), let a, b be constants, and let $F : \mathbb{R} \to \mathbb{R}$ be any differentiable single-variable function. Prove the following basic properties of differentials:

(a) $d(af + bg) = adf + bdg$, (b) $d(fg) = fdg + gdf$, (c) $d(F(f)) = F'(f)df$.

Hence, without computing partial derivatives, show that if $f(x, y) = \log(xy^2)$, we have $df = dx/x + 2dy/y$. Now, verify that your result is correct by computing the partial derivatives of $f(x, y)$.

➾ **Solution:** Proving the basic properties of differentials, we have:

(a) Note that:

$$\begin{aligned} d(af+bg) &= \frac{\partial}{\partial x}(af+bg)dx + \frac{\partial}{\partial y}(af+bg)dy \\ &= \left(a\frac{\partial f}{\partial x} + b\frac{\partial g}{\partial x}\right)dx + \left(a\frac{\partial f}{\partial y} + b\frac{\partial g}{\partial y}\right)dy \\ &= a\left(\frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy\right) + b\left(\frac{\partial g}{\partial x}dx + \frac{\partial g}{\partial y}\right)dy \\ &= adf + bdg, \end{aligned}$$

as required.

(b) Note that:

$$\begin{aligned} d(fg) &= \frac{\partial}{\partial x}(fg)dx + \frac{\partial}{\partial y}(fg)dy \\ &= \left(\frac{\partial f}{\partial x}g + f\frac{\partial g}{\partial x}\right)dx + \left(\frac{\partial f}{\partial y}g + f\frac{\partial g}{\partial y}\right)dy \\ &= \left(\frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy\right)g + f\left(\frac{\partial g}{\partial x}dx + \frac{\partial g}{\partial y}dy\right) \\ &= df \cdot g + f \cdot dg, \end{aligned}$$

as required.

(c) Finally, note that:

$$\begin{aligned} d(F(f)) &= \frac{\partial}{\partial x}[F(f(x,y))]dx + \frac{\partial}{\partial y}[F(f(x,y))]dy \\ &= \frac{\partial f}{\partial x}F'(f)dx + \frac{\partial f}{\partial y}F'(f)dy && \text{(by single variable chain rule)} \\ &= F'(f)df. \end{aligned}$$

Using the above properties, we have:

$$d\left(\log(xy^2)\right) = \frac{1}{xy^2}d(xy^2) = \frac{1}{xy^2}\left(y^2dx + xd(y^2)\right) = \frac{dx}{x} + \frac{2\,dy}{y}.$$

On the other hand, directly using partial derivatives, we have:

$$d\left(\log(xy^2)\right) = \frac{\partial}{\partial x}\left(\log(xy^2)\right)\,dx + \frac{\partial}{\partial y}\left(\log(xy^2)\right)\,dy = \frac{y^2}{xy^2}dx + \frac{2xy}{xy^2}dy = \frac{dx}{x} + \frac{2\,dy}{y}.$$

9. The period T of a simple pendulum can be approximated by the formula $T = 2\pi\sqrt{l/g}$, where l is the length of the pendulum, and g is gravitational acceleration.

(a) By taking logarithms, show that $dT/T = dl/2l - dg/2g$.

(b) Hence, estimate the percentage change in the period of a pendulum if: (i) the length is increased by 0.1%; (ii) gravitational acceleration increased by 0.2%.

➡ **Solution:**

(a) Taking logarithms, we have:

$$\log(T) = \log(2\pi) + \frac{1}{2}\log(l) - \frac{1}{2}\log(g).$$

Taking the differential of both sides, and using the properties we proved in the previous question, we have:

$$\frac{dT}{T} = \frac{dl}{2l} - \frac{dg}{2g},$$

as required.

(b) (i) If the length is increased by 0.1%, whilst keeping gravitational acceleration constant, we have $dl/l \approx 0.1$ (because the *relative* change in l is 0.1, $(l + dl)/l = 1.01$). Using the equation from part (a), this implied $dT/T \approx 0.05$, implying the period increases by roughly 0.05%.

(ii) Similarly, if the gravitational acceleration increased by 0.2%, we would see that the period would fall by roughly 0.1%.

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10. The magnitude of the gravitational force between two points masses m_1, m_2 which are separated by a distance $r > 0$ in three dimensional space is given by:

$$F(r, m_1, m_2) = \frac{Gm_1m_2}{r^2},$$

where G is a positive constant. Find dF in terms of dr, dm_1 and dm_2. Hence compute the (approximate) fractional change in distance if there is no change in the force, and the masses of both particles increase by 1%.

➡ **Solution:** Similarly to Question 10, taking logarithms is a great idea. We have:

$$\log(F) = \log(G) + \log(m_1) + \log(m_2) - 2\log(r).$$

Taking the differential, we have:

$$\frac{dF}{F} = \frac{dm_1}{m_1} + \frac{dm_2}{m_2} - \frac{2dr}{r},$$

since G is a constant. Rearranging, we have:

$$\frac{dr}{r} = \frac{dm_1}{2m_1} + \frac{dm_2}{2m_2} - \frac{dF}{2F}.$$

If there is no change in the force, and the masses of both particles increase by 1%, then the approximate fractional change in the distance is:

$$\frac{dr}{r} \approx \frac{1}{2} + \frac{1}{2} = 1,$$

i.e. 1% too.

11. The energy, $E(m, v)$, of a relativistic particle of rest mass m and speed v is given by:

$$E = \frac{mc^2}{\sqrt{1 - v^2/c^2}},$$

where c, the speed of light, is a constant.

(a) Find dE in terms of dm, dv.

(b) Two particles, A, B, have equal energy and move at 90% and 91% of the speed of light respectively. Particle A has rest mass m_A. What is the (approximate) difference in the rest masses of the particles, in terms of m_A? Which particle has the larger rest mass?

➺ **Solution:**

(a) Once again, taking logarithms is a fantastic idea. We have:

$$\log(E) = \log(m) + \log(c^2) - \frac{1}{2}\log\left(1 - \frac{v^2}{c^2}\right).$$

Taking the differential, we have:

$$\frac{dE}{E} = \frac{dm}{m} + \frac{2v/c^2}{2(1 - v^2/c^2)}dv = \frac{dm}{m} + \frac{v}{c^2 - v^2}dv.$$

(b) Particle A's velocity is $90c/100$ and particle B's velocity is $91c/100$. Hence the difference in velocities is:

$$dv = \frac{c}{100}.$$

Since the particles have equal energy, $dE = E$. Hence the difference in masses relative to A is approximately:

$$\frac{m_B - m_A}{m_A} = \frac{dm}{m_A} = -\left(\frac{v_A}{c^2 - v_A^2}\right)dv = -\frac{9c/10}{c^2 - (81c^2/100)} \cdot \frac{c}{100} = -\frac{9/10}{19} = -\frac{9}{190}.$$

Thus the approximate difference in rest masses is $9m_A/190$. It follows that the rest mass of particle B is given approximately by:

$$m_B \approx m_A\left(1 - \frac{9}{190}\right) = \frac{181m_A}{190}.$$

The rest mass of B is smaller.

12. The differential of the volume V of a geometrical figure is given by:

$$dV = 2\pi rh dr + \pi r^2 dh,$$

where r and h are non-negative parameters and the volume vanishes when these parameters are zero. Find an expression for the fractional change in volume dV/V for fractional changes in the parameters dr/r and dh/h. Find dV/V if r increases by 1% and h increases by 2%.

➠ **Solution:** The volume must depend on r, h, so must be a function $V(r, h)$. We are essentially given its partial derivatives:

$$\frac{\partial V}{\partial r} = 2\pi rh, \qquad \frac{\partial V}{\partial h} = \pi r^2.$$

Integrating the first equation directly, we have:

$$V(r, h) = \pi r^2 h + g(h),$$

for some arbitrary function $g(h)$. However, this must be consistent with the second equation. Differentiating, the solution we just found, we have:

$$\frac{\partial V}{\partial h} = \pi r^2 + g'(h),$$

so we see that we need $g'(h) = 0$. Thus, $g(h)$ is actually a *constant*, completely independent of h too. We see that:

$$V(r, h) = \pi r^2 h + c.$$

We are given the volume vanishes when both parameters are zero, which fixes the volume as $V(r, h) = \pi r^2 h$ (this is in fact the volume of a cylinder with radius r and height h).

Now, take logarithms of $V(r, h) = \pi r^2 h$ to get:

$$\log(V) = \log(\pi) + 2\log(r) + \log(h).$$

Taking the differential, we have:

$$\frac{dV}{V} = \frac{2dr}{r} + \frac{dh}{h},$$

which is the required expression. If r increases by 1% and h increases by 2%, this equation shows that V increases by approximately 4%.

Applications in thermodynamics

13. A thermodynamic system can be modelled in terms of four fundamental variables, pressure p, volume V, temperature T, and entropy S. Only two of these variables are independent, so that any pair of them may expressed as functions of the remaining two variables. The *fundamental thermodynamic relation* tells us that for any given system, the differential of the internal energy U of the system is related to the differentials of the entropy and volume via:

$$dU = TdS - pdV.$$

(a) Give a physical interpretation of each of the terms in the fundamental thermodynamic relation.

(b) From the fundamental thermodynamic relation, prove Maxwell's first relation:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

(c) By defining an appropriate thermodynamic potential, show that $-SdT - pdV$ is an exact differential. Deduce Maxwell's second relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

(d) Through similar considerations, derive the remaining Maxwell relations:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p, \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p.$$

Solution:

(a) dU is the 'infinitesimal' change in internal energy of a system under a transition between equilibrium states. The term $-pdV$ represents macroscopic mechanical energy transfer (if the system expands, it does work on the surroundings, transferring energy from the system to the environment). The term TdS represents energy transfer through heat, corresponding to the increase in microscopic energy from increased 'disorder' of a system (the entropy).

(b) This is obvious because $dU = TdS - pdV$ is an exact differential. Hence:

$$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial p}{\partial S}\right|_V,$$

as required.

(c) Since $d(TS) = TdS + SdT$, we can write:

$$dU = d(TS) - SdT - pdV \qquad \Rightarrow \qquad d(U - TS) = -SdT - pdV.$$

This shows that $-SdT - pdV$ is exact with potential $F = U - TS$, the *Helmholtz free energy*. The Maxwell relation follows immediately from exactness.

(d) Since $d(pV) = pdV + Vdp$, we can write:

$$dU = TdS - d(pV) + Vdp \qquad \Rightarrow \qquad d(U + pV) = TdS + Vdp.$$

This shows that $TdS + Vdp$ is exact with potential $H = U + pV$, the *enthalpy*. The third Maxwell relation follows immediately from exactness. Similarly, using $d(TS) = TdS + SdT$, we have:

$$d(U + pV) = d(TS) - SdT + Vdp \qquad \Rightarrow \qquad d(U + pV - TS) = -SdT + Vdp.$$

This shows that $-SdT + Vdp$ is exact with potential $G = U + pV - TS$, the *Gibbs free energy*. The Maxwell relation follows immediately from exactness.

14. A classical monatomic ideal gas has equations of state:

$$pV = nRT, \qquad S = nR\log\left(\frac{VT^{3/2}}{\Phi_0}\right)$$

where n is the amount of substance in moles, which we consider constant, R is the gas constant, and Φ_0 is a constant which depends on the type of gas.

(a) Using the fundamental thermodynamic relation, show that the internal energy of the gas is $U = \frac{3}{2}nRT$.

(b) By appropriately expressing each pair of thermodynamic variables in terms of the remaining pair, verify Maxwell's relations for this thermodynamic system.

Solution:

(a) The fundamental thermodynamic relation $dU = T(S,V)dS - p(S,V)dV$ expects that T, p are expressed as functions of S, V. In our case, we can rearrange the second equation to give an equation for temperature in terms of S, V:

$$T(S,V) = \left(\frac{\Phi_0}{V}\right)^{2/3} \exp\left(\frac{2S}{3nR}\right).$$

Similarly we can rearrange the first equation to give an equation for pressure in terms of S, V (substituting for $T(S,V)$):

$$p(S,V) = \frac{nRT}{V} = nR\frac{\Phi_0^{2/3}}{V^{5/3}} \exp\left(\frac{2S}{3nR}\right).$$

Now using the fundamental thermodynamic relation, $dU = TdS - pdV$, we know that $\partial U/\partial S = T$ and $\partial U/\partial V = -p$. Hence we have the equations:

$$\frac{\partial U}{\partial S} = \left(\frac{\Phi_0}{V}\right)^{2/3} \exp\left(\frac{2S}{3nR}\right).$$

and:

$$\frac{\partial U}{\partial V} = -nR\frac{\Phi_0^{2/3}}{V^{5/3}} \exp\left(\frac{2S}{3nR}\right).$$

Integrating the first equation, we have:

$$U(S,V) = \frac{3nR}{2}\left(\frac{\Phi_0}{V}\right)^{2/3} \exp\left(\frac{2S}{3nR}\right) + g(V).$$

Differentiating and inserting into the second equation, we have:

$$-nR\frac{\Phi_0^{2/3}}{V^{5/3}} \exp\left(\frac{2S}{3nR}\right) + g'(V) = -nR\frac{\Phi_0^{2/3}}{V^{5/3}} \exp\left(\frac{2S}{3nR}\right),$$

which reveals that $g(V)$ is independent of V. Hence we have:

$$U = \frac{3nR}{2}\left(\frac{\Phi_0}{V}\right)^{2/3} \exp\left(\frac{2S}{3nR}\right) + c = \frac{3}{2}nRT + c.$$

Requiring the energy of the gas to vanish as $T \to 0$, the constant c is fixed to zero, as required.

(b) We have already expressed p, T in terms of S, V it is easy to check that:

$$\frac{\partial T}{\partial V} = -\frac{2}{3}\frac{\Phi_0^{2/3}}{V^{5/3}}\exp\left(\frac{2S}{3nR}\right) = -\frac{\partial p}{\partial S},$$

which verifies the first Maxwell relation.

For the second Maxwell relation, we express p, S in terms of T, V. This is the form used in the question (with $p = nRT/V$). Checking the relation then, we have:

$$\frac{\partial S}{\partial V} = \frac{nR}{V} = \frac{\partial p}{\partial T},$$

which verifies the second Maxwell relation.

For the third Maxwell relation, we express T, V in terms of p, S. Rearranging the first equation in the question, we have $V = nRT/p$, which we can substitute into the second equation in the question, giving:

$$S = nR\log\left(\frac{nRT^{5/2}}{\Phi_0 p}\right) \qquad \Rightarrow \qquad T(p,S) = \left(\frac{p\Phi_0}{nR}\right)^{2/5}\exp\left(\frac{2S}{5nR}\right).$$

This gives:

$$V(p,S) = \frac{nR}{p}\left(\frac{p\Phi_0}{nR}\right)^{2/5}\exp\left(\frac{2S}{5nR}\right).$$

Checking the relation, we note:

$$\frac{\partial T}{\partial p} = \frac{2}{5p}\left(\frac{p\Phi_0}{nR}\right)^{2/5} = \frac{\partial V}{\partial S}$$

which verifies the third Maxwell relation.

For the final Maxwell relation, we express S, V in terms of p, T. Rearranging the first equation in the question, we have $V = nRT/p$. Substituting into the second equation in the question, we have:

$$S(p,T) = nR\log\left(\frac{nRT^{5/2}}{p\Phi_0}\right).$$

Checking the relation, we have:

$$\frac{\partial S}{\partial p} = -\frac{nR}{p} = -\frac{\partial V}{\partial T},$$

which verifies the fourth and final Maxwell relation.

15.

(a) Using the fundamental thermodynamic relation, and the Maxwell relations, prove that:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p.$$

(b) In a van der Waals gas, the equation of state is:

$$p = \frac{RT}{V-b} - \frac{a}{V^2},$$

where a, b, R are constants. Using part (a), derive a formula for U in terms of V, T, assuming that $U \to cT$, for some constant c, as $V \to \infty$.

Solution:

(a) Starting from the fundamental thermodynamic relation $dU = TdS - pdV$, we use the fact that S may be written as a function of V, T to obtain:

$$\begin{aligned} dU &= T\left(\frac{\partial S}{\partial V}\bigg|_T dV + \frac{\partial S}{\partial T}\bigg|_V dT\right) - pdV \\ &= \frac{\partial S}{\partial T}\bigg|_V dT + \left(T\left(\frac{\partial S}{\partial V}\right)\bigg|_T - p\right)dV. \end{aligned}$$

This implies that:

$$\left(\frac{\partial U}{\partial V}\right)\bigg|_T = T\left(\frac{\partial S}{\partial V}\right)\bigg|_T - p.$$

By the second Maxwell relation, the result in the question follows.

(b) The van der Waal's equation of state expresses p as a function of V, T which is exactly what we need for the first part to be applied. We have:

$$\left(\frac{\partial U}{\partial V}\right)\bigg|_T = \frac{RT}{V-b} - \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) = \frac{a}{V^2}.$$

Integrating both sides, we see that:

$$U(V,T) = -\frac{a}{V} + g(T),$$

where $g(T)$ is a function of temperature only. We are given that as $V \to \infty$, $U(V,T) \to cT$; this implies that $g(T) = cT$. Hence the internal energy of a van der Waal's gas is:

$$U(V,T) = cT - \frac{a}{V}.$$

16.

(a) Find an expression for $\left(\frac{\partial p}{\partial V}\right)_T - \left(\frac{\partial p}{\partial V}\right)_S$ in terms of $\left(\frac{\partial S}{\partial V}\right)_T$ and $\left(\frac{\partial S}{\partial p}\right)_V$.

(b) Hence, using the fundamental thermodynamic relation, show that:

$$\left(\frac{\partial \log(p)}{\partial \log(V)}\right)_T - \left(\frac{\partial \log(p)}{\partial \log(V)}\right)_S = \left(\frac{\partial (pV)}{\partial T}\right)_V \left[\frac{p^{-1}(\partial U/\partial V)_T + 1}{(\partial U/\partial T)_V}\right].$$

(c) Show that for a fixed amount of a classical monatomic ideal gas, $pV^{5/3}$ is a function of S. Hence, verify that the relation in part (b) holds for a classical monatomic ideal gas.

Solution:

(a) Regarding p as a function of V, T, we have:

$$dp = \left(\frac{\partial p}{\partial V}\right)\bigg|_T dV + \left(\frac{\partial p}{\partial T}\right)\bigg|_V dT.$$

Similarly regarding p as a function of V, S, we have:

$$dp = \left(\frac{\partial p}{\partial V}\right)\bigg|_S dV + \left(\frac{\partial p}{\partial S}\right)\bigg|_V dS.$$

Subtracting these equations we deduce that:

$$\left[\left(\frac{\partial p}{\partial V}\right)\bigg|_T - \left(\frac{\partial p}{\partial V}\right)\bigg|_S\right] dV = -\left(\frac{\partial p}{\partial T}\right)\bigg|_V dT + \left(\frac{\partial p}{\partial S}\right)\bigg|_V dS.$$

Expanding the differential dV, we have:

$$\left[\left(\frac{\partial p}{\partial V}\right)\bigg|_T - \left(\frac{\partial p}{\partial V}\right)\bigg|_S\right]\left[\left(\frac{\partial V}{\partial S}\right)\bigg|_T dS + \left(\frac{\partial V}{\partial T}\right)\bigg|_S dT\right] = -\left(\frac{\partial p}{\partial T}\right)\bigg|_V dT + \left(\frac{\partial p}{\partial S}\right)\bigg|_V dS.$$

Comparing coefficients of dS, we have:

$$\left(\frac{\partial p}{\partial V}\right)\bigg|_T - \left(\frac{\partial p}{\partial V}\right)\bigg|_S = \left(\frac{\partial p}{\partial S}\right)\bigg|_V \cdot \left(\frac{\partial S}{\partial V}\right)\bigg|_T = \frac{(\partial S/\partial V)|_T}{(\partial S/\partial p)|_V},$$

using reciprocity freely in the last step.

(b) Performing the differentiation on the left hand side, we have:

$$\left(\frac{\partial \log(p)}{\partial \log(V)}\right)_T - \left(\frac{\partial \log(p)}{\partial \log(V)}\right)_S = \frac{V}{p}\left(\frac{\partial p}{\partial V}\bigg|_T - \frac{\partial p}{\partial V}\bigg|_S\right) = \frac{V}{p}\frac{(\partial S/\partial V)|_T}{(\partial S/\partial p)|_V}. \quad (*)$$

From the fundamental thermodynamic relation $dU = TdS - pdV$, we have:

$$dS = \frac{dU}{T} + \frac{pdV}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\bigg|_V dT + \frac{\partial U}{\partial V}\bigg|_T dV\right) + \frac{pdV}{T}.$$

This gives:

$$\left(\frac{\partial S}{\partial V}\right)\bigg|_T = \frac{1}{T}\frac{\partial U}{\partial V}\bigg|_T + \frac{p}{T},$$

allowing us to simplify the numerator.

For the denominator, note from the fundamental thermodynamic relation $dU = TdS - pdV$, we have:

$$dU = T\left(\frac{\partial S}{\partial T}\right)\bigg|_V dT + T\left(\frac{\partial S}{\partial V}\right)\bigg|_T dV - pdV,$$

giving $(\partial U/\partial T)|_V = T(\partial S/\partial T)|_V$. Regarding S as a function of both T, V and alternatively p, V gives both:

$$dS = \left(\frac{\partial S}{\partial T}\right)\bigg|_V dT + \left(\frac{\partial S}{\partial V}\right)\bigg|_T dV = \left(\frac{\partial S}{\partial p}\right)\bigg|_V dp + \left(\frac{\partial S}{\partial V}\right)\bigg|_p dV.$$

Expanding dp on the left hand side, we have:

$$\left(\frac{\partial S}{\partial T}\right)\bigg|_V dT + \left(\frac{\partial S}{\partial V}\right)\bigg|_T dV = \left(\frac{\partial S}{\partial p}\right)\bigg|_V \left[\left(\frac{\partial p}{\partial T}\right)\bigg|_V dT + \left(\frac{\partial p}{\partial V}\right)\bigg|_T dV\right] + \left(\frac{\partial S}{\partial V}\right)\bigg|_p dV.$$

Comparing coefficients of dT, we see that:

$$\left(\frac{\partial S}{\partial T}\right)\bigg|_V = \left(\frac{\partial S}{\partial p}\right)\bigg|_V \left(\frac{\partial p}{\partial T}\right)\bigg|_V.$$

This reveals that $(\partial S/\partial p)|_V = T^{-1}(\partial T/\partial p)|_V(\partial U/\partial T)|_V$, which on putting everything together gives in $(*)$:

$$\begin{aligned}\left(\frac{\partial \log(p)}{\partial \log(V)}\right)_T - \left(\frac{\partial \log(p)}{\partial \log(V)}\right)_S &= \frac{V}{p}\frac{p}{T}\frac{p^{-1}(\partial U/\partial V)|_T + 1}{T^{-1}(\partial T/\partial p)|_V(\partial U/\partial T)|_V} \\ &= \left(\frac{\partial (pV)}{\partial T}\right)\bigg|_V \frac{p^{-1}(\partial U/\partial V)_T + 1}{(\partial U/\partial T)_V},\end{aligned}$$

as required, phew!

(c) Using the results of Question 14, we have:

$$pV^{5/3} = nR\Phi_0^{2/3}\exp\left(\frac{2S}{3nR}\right),$$

which is indeed purely a function of S, i.e. $pV^{5/3} = f(S)$ for some f (which we have explicitly from Question 14). Taking logarithms, we have:

$$\log(p) = -\frac{5}{3}\log(V) + \log(f(S)).$$

Also regarding p as a function of V, T we have $pV = nRT$, which gives $\log(p) = -\log(V) + \log(nR) + \log(T)$. Thus the derivatives required in part (b) are:

$$\frac{\partial \log(p)}{\partial \log(V)}\bigg|_T = -1, \qquad \frac{\partial \log(p)}{\partial \log(V)}\bigg|_S = -\frac{5}{3},$$

so the left-hand side is $-1 + 5/3 = 2/3$.

Recall also that $U = \frac{3}{2}nRT$. Hence, on the right hand side, we have:

$$\frac{\partial U}{\partial V}\bigg|_T = 0, \qquad \frac{\partial U}{\partial T}\bigg|_V = \frac{3}{2}nR.$$

We also have:

$$\frac{\partial (pV)}{\partial T}\bigg|_V = nR.$$

Putting everything together then, we see that the right-hand side is $2/3$, in perfect agreement.