Part IA: Mathematics for Natural Sciences B
Examples Sheet 13: The multivariable chain rule, exact differentials, and applications in thermodynamics

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

Questions marked with a ($*$) are difficult and should not be attempted at the expense of the other questions.

The multivariable chain rule for first-order derivatives

1. Let $u \equiv u(x,y), v \equiv v(x,y)$ be functions of x, y, and let $f \equiv f_{xy}(x,y) \equiv f_{uv}(u,v)$ be a function which can be written in terms of x, y or in terms of u, v (so that f_{xy} represents the function f written in terms of x, y, and f_{uv} represents the function f written in terms of u, v).

   (a) Using the limit definition of partial differentiation, show that:

   $$\frac{\partial f_{xy}}{\partial x} = \frac{\partial f_{uv}}{\partial u}\frac{\partial u}{\partial x} + \frac{\partial f_{uv}}{\partial v}\frac{\partial v}{\partial x}, \qquad \text{and} \qquad \frac{\partial f_{xy}}{\partial y} = \frac{\partial f_{uv}}{\partial u}\frac{\partial u}{\partial y} + \frac{\partial f_{uv}}{\partial v}\frac{\partial v}{\partial y}.$$

   These formulae are called the *multivariable chain rules*. Learn them off by heart, and get your supervision partner to test you on them. [*Note: Normally, they are written without the subscripts and the dependence of f on (x,y) or (u,v) is left implicit! From now on, we will drop the coordinates - you can always write them in though, if you feel uncomfortable.*]

   (b) Hence, prove that the differentials satisfy $df_{xy} = df_{uv}$. [*In lectures, you showed that if this is true, the multivariable chain rule follows. Hence, the multivariable chain rule is equivalent to the statement that 'differentials are independent of coordinate choice'.*]

2. Using the multivariable chain rule, show that if $f(u,v) = u^2 + v^2$, and $u(x,y) = x^3 - 2y, v(x,y) = 3y - 2x^2$, we have:

   $$\frac{\partial f}{\partial x} = 2x\left(3x^4 - 6xy - 6y + 4x^2\right), \qquad \frac{\partial f}{\partial y} = 2\left(13y - 6x^2 - 2x^3\right).$$

   Check your results by writing f in terms of x, y first, then taking partial derivatives.

3. Let (x,y) be plane Cartesian coordinates, and let (r,θ) be plane polar coordinates. Let $f \equiv f(x,y)$ be a multivariable function whose expression in terms of Cartesian coordinates is $f(x,y) = e^{-xy}$.

   (a) Compute $\partial f/\partial x$ and $\partial f/\partial y$.

   (b) Compute $\partial f/\partial r$ and $\partial f/\partial \theta$, by: (i) writing f in terms of polar coordinates; (ii) using the multivariable chain rule.

   (c) Using parts (a), (b), show directly in this case that the differential, df, is independent of coordinate choice. [*Hint: express dx and dy in terms of dr and $d\theta$.*]

4. The function $f(x,y)$ satisfies the partial differential equation:

   $$y\frac{\partial f}{\partial x} + x\frac{\partial f}{\partial y} = 0.$$

   By transforming to the coordinates $(u,v) = (x^2 - y^2, 2xy)$, find the general solution of the equation.

The multivariable chain rule for second-order derivatives

5. Let $f(u,v) = u^2 \sinh(v)$, and let $u = x, v = x + y$.
   (a) By differentiating with respect to u, compute $\partial^2 f/\partial u^2$.
   (b) Using the multivariable chain rule, show that:
   $$\frac{\partial^2 f}{\partial u^2} = \frac{\partial^2 f}{\partial x^2} - 2\frac{\partial^2 f}{\partial x \partial y} + \frac{\partial^2 f}{\partial y^2},$$
   Hence compute the derivative in (a) by writing f in terms of x, y, differentiating, and using this relationship.
   (c) Repeat this exercise for the derivatives $\partial^2 f/\partial v^2$ and $\partial^2 f/\partial u \partial v$.

6. Let $f(u,v)$ be a multivariable function of $u(x,y) = 1 + x^2 + y^2$, $v(x,y) = 1 + x^2 y^2$, where (x,y) are plane Cartesian coordinates.
   (a) Calculate $\partial f/\partial x, \partial f/\partial y, \partial^2 f/\partial x^2, \partial^2 f/\partial y^2, \partial^2 f/\partial x \partial y$ in terms of the derivatives of f with respect to u, v.
   (b) For $f(u,v) = \log(uv)$, find $\partial^2 f/\partial x \partial y$ by: (i) using the expression derived in part (a); (ii) first expressing f in terms of x, y and then differentiating directly. Verify that your results agree.

7. Let (x,y) be plane Cartesian coordinates, and let (u,v) be plane Cartesian coordinates which are rotated an angle θ anticlockwise about the origin relative to the (x,y) coordinates. Let f be an arbitrary multivariable function of either (x,y) or (u,v). Show that:
   $$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} = \frac{\partial^2 f}{\partial u^2} + \frac{\partial^2 f}{\partial v^2}.$$
   ($*$) Comment on this result in relation to the *Laplacian*, $\nabla^2 = \nabla \cdot \nabla$, where $\cdot$ is the scalar product of vectors.

8. Let (x,y) be plane Cartesian coordinates, and let (r,θ) be plane polar coordinates. Let f be a multivariable function. Show that:
   $$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} = \frac{\partial^2 f}{\partial r^2} + \frac{1}{r}\frac{\partial f}{\partial r} + \frac{1}{r^2}\frac{\partial^2 f}{\partial \theta^2}.$$
   Hence determine all solutions of the partial differential equation:
   $$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} = 0$$
   which are rotationally symmetric about the origin.

9. Consider a function $z(x,y)$ that satisfies $z(\lambda x, \lambda y) = \lambda^n z(x,y)$ for any real λ and a fixed integer n. Show that:
   $$x\frac{\partial z}{\partial x} + y\frac{\partial z}{\partial y} = nz,$$
   and
   $$x^2\frac{\partial^2 z}{\partial x^2} + 2xy\frac{\partial^2 z}{\partial x \partial y} + y^2\frac{\partial^2 z}{\partial y^2} = n(n-1)z.$$

Reciprocity and the cyclic relation

10. Three variables x, y, z are related by the implicit equation $f(x,y,z) = 0$ where f is some multivariable function.
    (a) Derive the reciprocity relation:
    $$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial y}\right)_z = 1,$$
    and the cyclic relation:
    $$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1.$$
    (b) Verify that these relationships hold if: (i) $f(x,y,z) = xyz + x^3 + y^4 + z^5$; (ii) $f(x,y,z) = xyz - \sinh(x+z)$.

Exact differentials, and exact ordinary differential equations

11. 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.
    (c) $(*)$ Is the condition in part (b) sufficient for ω to be exact?

12. 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) $(x + y)dx + (x - y)dy$, (d) $(*)$ $\dfrac{xdy - ydx}{x^2 + y^2}$.

13. 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.

14. 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) $2xy^3z^4dx + 3x^2y^2z^4dy + 4x^2y^3z^3dz$.

15. Consider the first-order differential equation:
$$P(x, y) + Q(x, y)\frac{dy}{dx} = 0. \qquad (\dagger)$$
    Using the multivariable chain rule, show that $f(x, y(x)) = c$, for c and arbitrary constant, is an implicit solution of the equation if and only if $df = \mu \cdot (Pdx + Qdy)$, for some multivariable function $\mu(x, y)$, which is not identically zero. [*Hence, equation (†) can be solved implicitly if the differential $Pdx + Qdy$ is exact ($\mu = 1$), or can be made exact through multiplication by some 'integrating factor' - note this is* not *the same type of integrating factor we dealt with earlier in the course.*]

16. 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) $\sinh(x)\sin(y) + \cosh(x)\cos(y)\dfrac{dy}{dx} = 0$.

17. (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:
$$\frac{dy}{dx} = \frac{\cos(y) - \tanh(x)\sin(y)}{\cos(y) + \tanh(x)\sin(y)}.$$

Applications in thermodynamics

[*This section applies everything we have learned about partial derivatives to a topic that is important in both chemistry and physics.*]

18. 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:

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

19. 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.

20. (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 $T \to \infty$.

21. (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.

Part IA: Mathematics for Natural Sciences B
Lent Review Test 1

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

Complete this test without your notes. You should spend a total of **one and a half hours** on this test. Each question is worth 20 marks.

2024, Paper 2, Question 15: Second-order ordinary differential equations

(a) Consider the second order differential equation:

$$\frac{d^2y}{dx^2} + \beta\frac{dy}{dx} + \gamma y = 0$$

where β and γ are real constants.

(i) When $\beta = 4$, find γ such that the general solution is $y(x) = Axe^{-2x} + Be^{-2x}$ where A and B are arbitrary constants. [3]

(ii) Find all the solutions for $y(x)$ when $\beta = 6$ and $\gamma = 5$. [4]

(iii) Find all the solutions for $y(x)$ when $\beta = 3$ and $\gamma = 4$. [5]

(b) Consider the second order differential equation:

$$\frac{d^2y}{dx^2} - 4\frac{dy}{dx} + 5y = 125x^2.$$

Find the particular solution subject to boundary conditions $y(0) = 1$ and: [8]

$$y\left(\frac{\pi}{2}\right) = \frac{25\pi^2}{4} + 20\pi + 22.$$

2024, Paper 1, Question 14: Partial derivatives, differentials and the multivariable chain rule

(a) A right-angled triangle of area A has sides of length a, b and c, where c is the hypotenuse. Small changes da and db are made to the sides a and b, respectively. Find expressions for the fractional change of the hypotenuse dc/c and the fractional change in the area of the triangle dA/A in terms of a, b and their changes. Find the fractional change in area if a increases by 1% and b decreases by 2%. [6]

(b) Consider a function $z(x, y)$ defined implicitly by the equation:

$$x - \alpha z = \phi(y - \beta z)$$

where α and β are real constants and ϕ is an arbitrary differentiable function. Show that $z(x, y)$ satisfies: [6]

$$\alpha\frac{\partial z}{\partial x} + \beta\frac{\partial z}{\partial y} = 1.$$

(c) Consider a function $z(x, y)$ that satisfies $z(\lambda x, \lambda y) = \lambda^n z(x, y)$ for an arbitrary real positive λ and an integer n. Show that:

$$x\frac{\partial z}{\partial x} + y\frac{\partial z}{\partial y} = nz$$

and [8]

$$x^2\frac{\partial^2 z}{\partial x^2} + 2xy\frac{\partial^2 z}{\partial x \partial y} + y^2\frac{\partial^2 z}{\partial y^2} = n(n-1)z.$$

2024, Paper 1, Question 13: First-order differential equations and exact differentials

(a) Find the general solution of the differential equation: [6]

$$\frac{dy}{dx} = \frac{4y^2}{x^2} - x^2y^2.$$

Determine the solution in each of the following cases:

(i) $y(1) = 1$, [1]

(ii) $y(2) = 0$, [1]

(b) Consider the following differential form,

$$\mu(x)(xy - 16x - x^3)dx + \mu(x)(16 + x^2)dy,$$

where $\mu(x)$ is an unknown real-valued differentiable function.

(i) Find a function $\mu(x)$ for which this differential form is exact. [6]

(ii) Hence or otherwise, find in explicit form the general solution of the equation: [6]

$$(xy - 16x - x^3) + (16 + x^2)\frac{dy}{dx} = 0.$$