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

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Exact differentials, and exact ordinary differential equations

1. 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.

2. 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) $(x+y)dx + (x-y)dy$.

3. 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.

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

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

6. (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:
$$\frac{dy}{dx} = \frac{\cos(y) - \tanh(x)\sin(y)}{\cos(y) + \tanh(x)\sin(y)}.$$

Algebra of differentials

7. 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:

   $$df = \frac{dx}{x} + \frac{2\,dy}{y}.$$

   Now, verify that your result is correct by computing the partial derivatives of $f(x, y)$.

8. The period T of a simple pendulum can be approximated by the formula:

   $$T = 2\pi\sqrt{\frac{l}{g}},$$

   where l is the length of the pendulum, and g is gravitational acceleration.

   (a) By taking logarithms, show that:
   $$\frac{dT}{T} = \frac{dl}{2l} - \frac{dg}{2g}.$$

   (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%.

9. 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%.

10. 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?

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

    $$dV = 2\pi rhdr + \pi r^2 dh,$$

    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%.

Applications in thermodynamics

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

12. 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:

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

13. 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.

14. (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 $T \to \infty$.

15. (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.