Solutions to Assignment #05 – MATH 3511

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(I) Look at p. 211.

The text tells us that we can write $dH$ as a total differential:

$$dH = T \, dS + V \, dp.$$ 

(a) If this is a total differential, then $H$ must be a function of which TWO variables? $S$ and $p$.

(b) According the formula, find these values:

$$\left( \frac{\partial H}{\partial S} \right)_p = ???, \quad \left( \frac{\partial H}{\partial p} \right)_S = ???$$

The total differential formula is

$$dH = \left( \frac{\partial H}{\partial S} \right)_p \, dS + \left( \frac{\partial H}{\partial p} \right)_S \, dp.$$ 

Thus, we must have

$$\left( \frac{\partial H}{\partial S} \right)_p = T \quad \text{and} \quad \left( \frac{\partial H}{\partial p} \right)_S = V.$$ 

(c) Explain why this must be true:

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

[Do NOT say, “Because Maxwell said it was true...”!]

From the text (Equation 9.40, p. 209), we have the total differential

$$dU = T \, dS - p \, dV.$$ 

Thus, we must have

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

From the equality of mixed partials (Clairaut), we have

$$\frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right) = \frac{\partial^2 H}{\partial V \partial S} = \frac{\partial T}{\partial V}_S$$

$$\frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right) = \frac{\partial^2 U}{\partial S \partial V} = - \left( \frac{\partial p}{\partial S} \right)_V$$

$$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial p}{\partial S} \right)_V \checkmark$$
(d) Use the same argument and justify the relationship which stems from the Gibbs free energy exact differential.

We know that
\[ dG = -S \, dT + V \, dp. \]

Show that
\[ \left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p. \]

Since it is exact, we must have
\[ \left( \frac{\partial G}{\partial T} \right)_p = -S \quad \text{and} \quad \left( \frac{\partial G}{\partial p} \right)_T = V. \]

By the equality of mixed partials, we have
\[ \frac{\partial}{\partial p} \left( \frac{\partial G}{\partial T} \right) = \frac{\partial^2 G}{\partial p \partial T} = \left( \frac{\partial S}{\partial p} \right)_T \]
\[ \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial p} \right) = \frac{\partial^2 G}{\partial T \partial p} = \left( \frac{\partial V}{\partial T} \right)_p. \]
\[ - \left( \frac{\partial S}{\partial p} \right)_T = \left( \frac{\partial V}{\partial T} \right)_p. \]

(II) Suppose that \( p \) is a function of \( T \) and \( V \):
\[ p(T, V) = \frac{T}{V} \]

(a) Find the total differential \( dp \).
\[ dp = (???) \, dT + (???) \, dV \]

We have
\[ \frac{\partial p}{\partial T} = \frac{1}{V} \quad \text{and} \quad \frac{\partial p}{\partial V} = -\frac{T}{V^2}. \]

Total differential is
\[ dp = \left( \frac{1}{V} \right) dT - \left( \frac{T}{V^2} \right) dV. \]

(b) Use the Test for Exactness and show that this must be an exact differential.

The mixed partials should be equal.

Show that
\[ \frac{\partial}{\partial T} \left[ \frac{\partial p}{\partial V} \right] = \frac{\partial}{\partial V} \left[ \frac{\partial p}{\partial T} \right] \]
\[ - \frac{\partial}{\partial T} \left[ \frac{T}{V^2} \right] = \frac{\partial}{\partial V} \left[ \frac{1}{V} \right] (??). \]

The left side is equal to \( -\frac{1}{V^2} \). The right side is also equal to \( -\frac{1}{V^2} \).
Use the Test for Exactness to evaluate the following (line) integrals:

(a) [Product Rule]
\[
\int (p \, dV + V \, dp) = ???
\]
when we start from \( p = 2 \) and \( V = 5 \) and end at \( p = 4 \) and \( V = 3 \).
This is the exact differential for the product. Here it is:
\[
d[pV] = p \, dV + V \, dp
\]
Thus, the potential function must be \( \varphi(p, V) = pV \).
This integral is independent of path. We need only know the value of \( \varphi \) at the beginning and at the end.
\[
\int (p \, dV + V \, dp) = [pV]_{p=4, \, V=3}^{p=2, \, V=5} = (4) (3) - (2) (5) = 2 \text{ work units.}
\]
According to Physics, what should be the units of this integral?
Either joules or kcals. They must be work or energy units.

(b) Complete p. 226: #47.

If it is, in fact, exact, then the path does not matter.
Integrate \( F \) with respect to \( dx \).
\[
\int (9x^2 + 4y^2 + 4xy) \, dx = 3x^3 + 4xy^2 + 2x^2y + \alpha(y)
\]
Integrate \( G \) with respect to \( dy \).
\[
\int (8xy + 2x^2 + 3y^2) \, dy = 4xy^2 + 2x^2y + y^3 + \beta(x)
\]
Any terms with both \( x \) and \( y \) must agree in both integrations.
The “constants” of integrations are now functions.
We must have \( \alpha(y) = y^3 \) and \( \beta(x) = 3x^3 \). Now both answers are identical.
\[
\varphi(x, y) = 4xy^2 + 2x^2y + 3x^3 + y^3 + C.
\]
[The additional \( C \) will be discarded when we evaluate the definite integral.]
The value of the line integral is
\[
[4xy^2 + 2x^2y + 3x^3 + y^3]_{x=0, \, y=0}^{x=1, \, y=2} = 31.
\]
We have
\[
\varphi(1, \, 2) = 4(1) (2^2) + 2 (1^2) (2) + 3 (1^3) + 2^3 = 31.
\]
It’s clear that \( \varphi(0, \, 0) = 0 \).
(IV) On p. 207, we have the set of equations denoted as (9.35).

(a) Sketch an appropriate tree and show that these equalities makes sense. [Shown in class.]

(b) Now show the algebra which allows us to solve for \( \frac{\partial z}{\partial x} \) and \( \frac{\partial z}{\partial y} \).

(c) From the previous page, we have the Chain Rules:

\[
\left( \frac{\partial z}{\partial r} \right)_\theta = \left( \frac{\partial z}{\partial x} \right)_y \left( \frac{\partial x}{\partial r} \right)_\theta + \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial r} \right)_\theta
\]

\[
= \left( \frac{\partial z}{\partial x} \right)_y \cos(\theta) + \left( \frac{\partial z}{\partial y} \right)_x \sin(\theta)
\]

and

\[
\left( \frac{\partial z}{\partial \theta} \right)_r = \left( \frac{\partial z}{\partial x} \right)_y \left( \frac{\partial x}{\partial \theta} \right)_r + \left( \frac{\partial z}{\partial y} \right)_x \left( \frac{\partial y}{\partial \theta} \right)_r
\]

\[
= \left( \frac{\partial z}{\partial x} \right)_y (-r \sin(\theta)) + \left( \frac{\partial z}{\partial y} \right)_x (r \cos(\theta)).
\]

Multiply the first equation by \( r \sin(\theta) \).

\[
\left( \frac{\partial z}{\partial r} \right)_\theta r \sin(\theta) = \left( \frac{\partial z}{\partial x} \right)_y r \sin(\theta) \cos(\theta) + \left( \frac{\partial z}{\partial y} \right)_x r \sin^2(\theta)
\]

Multiply the second equation by \( \cos(\theta) \).

\[
\left( \frac{\partial z}{\partial \theta} \right)_r \cos(\theta) = \left( \frac{\partial z}{\partial x} \right)_y (-r \sin(\theta) \cos(\theta)) + \left( \frac{\partial z}{\partial y} \right)_x (r \cos^2(\theta))
\]

If we add the equations, the middle terms cancel and...

\[
\left( \frac{\partial z}{\partial r} \right)_\theta \sin(\theta) + \left( \frac{\partial z}{\partial \theta} \right)_r \cos(\theta) = \left( \frac{\partial z}{\partial y} \right)_x (r \cos^2(\theta) + \sin^2(\theta))
\]

\[
r \left( \frac{\partial z}{\partial y} \right)_x = \left( \frac{\partial z}{\partial r} \right)_\theta \sin(\theta) + \left( \frac{\partial z}{\partial \theta} \right)_r \cos(\theta)
\]

\[
\left( \frac{\partial z}{\partial y} \right)_x = \sin(\theta) \left( \frac{\partial z}{\partial r} \right)_\theta + \frac{\cos(\theta)}{r} \left( \frac{\partial z}{\partial \theta} \right)_r
\]

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Similarly, if we multiply the first equation by $r \cos(\theta)$ and the second by $\sin(\theta)$, then we subtract the second from the first.

\[
\left(\frac{\partial z}{\partial r}\right)_r r \cos(\theta) = \left(\frac{\partial z}{\partial x}\right)_y r \cos^2(\theta) + \left(\frac{\partial z}{\partial y}\right)_x r \cos(\theta) \sin(\theta)
\]

\[
\left(\frac{\partial z}{\partial \theta}\right)_r \sin(\theta) = \left(\frac{\partial z}{\partial x}\right)_y (-r \sin^2(\theta)) + \left(\frac{\partial z}{\partial y}\right)_x r \cos(\theta) \sin(\theta)
\]

\[
\left(\frac{\partial z}{\partial r}\right)_r r \cos(\theta) - \left(\frac{\partial z}{\partial \theta}\right)_r \sin(\theta) = \left(\frac{\partial z}{\partial x}\right)_y r \cos(\theta) + \sin^2(\theta)
\]

\[
r \times \left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial r}\right)_r r \cos(\theta) - \left(\frac{\partial z}{\partial \theta}\right)_r \sin(\theta)
\]

\[
\left(\frac{\partial z}{\partial x}\right)_y = \cos(\theta) \times \left(\frac{\partial z}{\partial r}\right)_r - \sin(\theta) \times \left(\frac{\partial z}{\partial \theta}\right)_r
\]

(d) Find the value of those two partials (previous part) if

\[
z = \frac{\cos(\theta)}{r^2}.
\]

So now we can find the rectangular first partials when the function is given in polar. We note that we could convert to rectangular first, but it’s always more convenient to do the algebra in polar and keep everything in polar through to the end.

\[
z = \frac{x}{\sqrt{x^2+y^2}} = \frac{x}{(x^2+y^2)^{3/2}}.
\]

Clearly, we could use the Quotient Rule and find $z_x$ and $z_y$, but the we would probably need to convert the answer back into polar.

Our formula short-cuts that process.

\[
\left(\frac{\partial z}{\partial y}\right)_x = \sin(\theta) \times \left(\frac{-2 \cos(\theta)}{r^3}\right) + \left(\frac{\cos(\theta)}{r}\right) \times \left(\frac{-\sin(\theta)}{r^2}\right)
\]

\[
= \frac{-3 \sin(\theta) \cos(\theta)}{r^3}.
\]

Here’s the other one.

\[
\left(\frac{\partial z}{\partial x}\right)_y = \cos(\theta) \times \left(\frac{-2 \cos(\theta)}{r^3}\right) - \frac{\sin(\theta)}{r} \times \left(\frac{-\sin(\theta)}{r^2}\right)
\]

\[
= \frac{-2 \cos^2(\theta) + \sin^2(\theta)}{r^3}.
\]

So if we have any particular polar point on the surface $z = \frac{\cos(\theta)}{r^2}$, we can find the rectangular first partials easily.