Department of Physics, The Chinese University of Hong Kong
PHYS 5130 Principles of Thermal and Statistical Physics (M.Sc. in Physics)

Problem Set 1

Due: 19 September 2020 (Saturday); "T+2" = 21 September 2020 (Monday) (20% discount)

You should **submit your work in one PDF file via Blackboard** to the appropriate folder no later than 23:59 on the due date. Late submission before the T+2 due date will be marked with a 20% discount on the score. Follow Blackboard → Course Contents → Problem Set → **Problem Set 1 Submission Folder**.

Please work out the steps of the calculations in detail. Discussions among students are highly encouraged, yet it is expected that we do your homework independently.

1.0 **Reading Assignment.** It is a guide to our progress and supplementary reading. **No need to hand in anything**. We started out with a discussion on partial differentiation. The idea is that if you spend 5 hours at the beginning to review/refresh/relearn the topic, you will find it much easier to do many other courses, including PHYS 5130. It is particularly true in thermodynamics and statistical mechanics. We have a **few state variables** and they are related through the **equation of state**. Therefore, typically we have $\mathcal{F}(x, y, z) = 0$ or $\mathcal{F}(P, V, T) = 0$. In addition, these state variables take on specific values for a **thermodynamic equilibrium state**. So the standard question is given that the system is in some initial state (P_1, T_1), what is the change in pressure when the temperature becomes T_2 given some constraint (e.g. volume is kept constant)? Partial differentiation and its properties (nice function and nice surfaces) become the (only) tool to approach such questions. In addition, knowing single-variable differentiation is very different from knowing two-variable (multi-variable) differentiation. For $f(x)$, there is only one tangent and one slope df/dx, and not much one can say about constraint (fixing what?). For for 2-variable $f(x, y)$, there are more derivatives and a much richer physical picture.

About Books:

Mathematical Methods. You don't need to read very mathematical books. Let's be practical. For those who want a short and good introduction, see Martin and Shaw, *Mathematics for Physicists*, which puts all the essential mathematics for a physics B.Sc. degree in less than 500 pages. Math books written for chemistry students are more down-to-earth. Steiner's *The Chemistry Maths Book* is the chemistry analogy of Martin and Shaw. The author collected all the mathematics (actually more than that) for a chemistry B.Sc. degree in one book. The standard texts for physics students such as Boas' *Mathematical Methods in the Physical Sciences* and Riley *et al.*'s *Mathematics Methods for Physics and Engineering* are very good, but I find them too thick to learn something quick.

Thermodynamics. Our course will do Thermodynamics before Statistical Mechanics. Thermodynamics is an old and mature subject with many classics (Planck, Fermi, Pauli, Schrödinger,... all wrote on the subject). For traditional approach to thermodynamics, Finn's "*Thermal Physics*" and C.J. Adkins' "*Equilibrium Thermodynamics*" are excellent. Both books followed the classic *The Elements of Classical Thermodynamics* by A.B. Pippard closely. If you haven't read anything by Fermi, his *Thermodynamics* is a good place to appreciate his deep understanding and clear presentation. Thermodynamics is not only about its laws, it has wide applications across all systems consisting of many stuff (atoms, particles, etc.). If you are chemically inclined (e.g. materials science with a chemistry flavor), thermodynamics treated in physical chemistry books will provide you with many examples in real-world situations. I would recommend McQuarrie's *Physical Chemistry: A Molecular Approach* for which the chapters on thermodynamics and statistical thermodynamics are useful here. Levine's *Physical Chemistry* has a complete discussion with many applications (the first 18 chapters of the book will make you an expert). For the newer physics books, I prefer *Concepts in Thermal Physics* by Blundell and Blundell.

1.1 (15 points) **Partial Differentiation - Warming Up**

(a) Consider $z(x,y) = \cos(x^2 + 2y^2)$, where $x(t) = t$ and $y(t) = t^2$.

   (i) Substituting $x(t)$ and $y(t)$ to obtain $z(t)$ explicitly and then **obtain** dz/dt directly.

   (ii) Without obtaining $z(t)$ as in (i), apply the chain rule to **obtain** dz/dt.

(b) Consider $z(x,y) = x^2 - xy + y^2$. Now x and y are parameterized by $x = r\cos\theta$ and $y = r\sin\theta$. **Find** $(\partial z/\partial\theta)_r$ and $(\partial z/\partial r)_\theta$.

1.2 (18 points) **Partial Differentiation - Changing variables**

Partial derivatives are key to transforming an equation from one system of coordinates (variables) to another.

Consider the standard form of wave equations in physics

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 u}{\partial t^2}\,, \tag{1}$$

where c is a constant. [Do you know the meaning of the constant c in this context? No bonus point though, sorry!] In this form, the wave u is taken as $u = u(x,t)$. We can transform x and t to two other variables, i.e., $x = x(\xi,\eta)$ and $y = y(\xi,\eta)$. Explicitly, we have $\xi = x - ct$ and $\eta = x + ct$. Therefore, the wave $u(x,y)$ can be transformed into $U(\xi,\eta)$. [Many authors will simply use $u(\xi,\eta)$.] The question is to find the corresponding wave equation for $U(\xi,\eta)$. **Show that** $U(\xi,\eta)$ obeys

$$\frac{\partial^2}{\partial\xi\partial\eta}U(\xi,\eta) = 0\,. \tag{2}$$

[Remarks: Quite neat! When you see Eq. (1), you can think about Eq. (2). In the same way, when you see Eq. (2), you can think about Eq. (1).]

1.3 (12 points) **Checking something an Exact Differential or not**

A student was asked to start with the van der Waals gas law (an equation of state) and write down an expression for dP, where P is the pressure. The student's answer is

$$\frac{RT}{V-b}\,dT + \left(\frac{RT}{(V-b)^2} - \frac{a}{TV^2}\right)dV \tag{3}$$

where T and V are the temperature and (molar) volume, respectively. The other parameters are constants.

The teacher (not me!) forgot the form of the van der Waals gas law when marking the student's work. But the teacher knows of a way at least to check whether it is a possible answer. **Check** where the expression above is a possible answer that comes out from a known equation of state. **Explain the reason of your approach before working out the answer.**

1.4 (20 points) **After checking whether an expression is an exact differential...**

Checking an expression is an exact differential or not is an easy task. There are follow-up questions. If yes, we would like to find the underlying function. If no, we would like to see if there is a way to make some slight changes in the given expression to turn it into an exact differential. Here are the examples.

(a) Is the expression

$$C_V(T)dT + \frac{nRT}{V}dV \tag{4}$$

where $C_V(T)$ is a function of T, an **exact differential?** [Note: You don't need to know the physical meaning of the symbols, although they are rather apparent.]

(b) Following part (a), let's slightly modify the expression to

$$\frac{C_V(T)}{T}\, dT + \frac{nR}{V}dV\,. \tag{5}$$

Is this expression an **exact differential?**

(c) Is the expression

$$(2xy + y^2)dx + (x^2 + 2xy)dy \tag{6}$$

an **exact differential?** It yes, **determine** the underlying function $f(x, y)$ and df is given by the above expression up to an additive constant that cannot be determined unless more information is given. [Hint: You need to do some integration.]

1.5 (20 points) **The cyclic or "−1" rule**

Let's do a silly exercise to practice how to apply the cyclic rule. The van der Waals equation of state is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \tag{7}$$

Here, P is the pressure, V is the molar volume, T is the temperature and n is the number of moles. Of course, we could obtain $(\partial P/\partial T)_{V,n}$ in one step. Let's do something silly. **Obtain** $(\partial V/\partial T)_{P,n}$ and $(\partial V/\partial P)_{T,n}$ and **apply the cyclic rule** to **find** $(\partial P/\partial T)_{V,n}$. Next, **obtain** $(\partial P/\partial T)_{V,n}$ in one step and compare the answers.

[Remarks: It's silly, but it works! Sometimes, the partial derivatives in this winding approach are easier to do than taking the partial derivative directly. In addition, the two intermediate partial derivatives may carry clearer physical meanings (measurable quantities) and have values tabulated in materials handbooks.]

1.6 (15 points) **An extended application of the chain rule**

We discussed this situation in class notes. There are two functions: $z = f(x, y)$ and $u = u(x, y)$. [For example, we have $U(S, V)$ and $T(S, V)$. Another example is that $z = f(x, y)$ is a hill and $u(x, y)$ (a separate function) is a way that a hiker would like to choose the path to walk on the hill.]

Here, consider $z = xy$ (so it is a function of x and y) and $u = x^2 + y^2$. **Find** $(\partial z/\partial x)_u$ and $(\partial z/\partial y)_u$.

[Remarks: For those who want to have a physical picture in mind before doing the math, it will be easier to consider only the quadrant of $x > 0$ and $y > 0$ (although it is not necessary). You may want to use a software to plot $z(x, y)$ and $u(x, y)$ out. For example, the function $u(x, y)$ is to take a parabola on the u-x plane and rotate it along the u-axis. It is like the surface of 1/4 of a watermelon with the tip of the watermelon standing at $(0, 0)$. Now a certain value of u gives a quarter of a circle on the x-y plane. Then go back to $z(x, y)$, but considering the particular circular arc of x and y constrained by u, and map out a particular path in z that will take on different heights along the path. It is on this path (constant u) that we ask the questions above. I hope that you follow the picture. Of course, it is perfectly OK to consider the whole x-y plane and then $z(x, y)$ will take on some negative values. Fine! Instead of hiking, we go underground to explore a cave.]