Statistical and Thermal Physics: Homework 3

Due: 6 February 2016

1 Differentiation identities

Consider three variables x, y, z that are not independent. This means that they are related by some function, which could be written $z = z(x, y)$ or $y = y(x, z)$ or $x = x(y, z)$ depending on the choice of independent variables. These functions can all be differentiated with respect to their variables; the derivatives must be related. This exercise will result in general relationships between these derivatives that are always satisfied.

a) To illustrated this let $z = x^2y$. So $z(x, y) = x^2y$. Find expressions for $x = x(y, z)$ and $y = y(x, z)$. Determine expressions for

$$\left(\frac{\partial z}{\partial y}\right)_x, \quad \left(\frac{\partial z}{\partial x}\right)_y, \quad \left(\frac{\partial x}{\partial y}\right)_z, \quad \left(\frac{\partial x}{\partial z}\right)_y, \quad \left(\frac{\partial y}{\partial x}\right)_z, \text{and} \quad \left(\frac{\partial y}{\partial z}\right)_x.$$

According to your results how are $\left(\frac{\partial z}{\partial y}\right)_x$ and $\left(\frac{\partial y}{\partial z}\right)_x$ related to each other? How about $\left(\frac{\partial z}{\partial x}\right)_y$ and $\left(\frac{\partial x}{\partial z}\right)_y$?

b) To prove these relationships *for any function*, first consider x and y as the independent variables. Express $\mathrm{d}z$ in terms of $\mathrm{d}x$ and $\mathrm{d}y$, using appropriate partial derivatives. Note that this must be done for any function $z(x, y)$, not just the special case above. Then express $\mathrm{d}x$ in terms of $\mathrm{d}y$ and $\mathrm{d}z$, using appropriate partial derivatives. Substitute this into the general expression for $\mathrm{d}z$; this will give an expression for $\mathrm{d}z$ in terms of dy and $\mathrm{d}z$. Use the expression to show that

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial z}\right)_y = 1 \quad \text{and} \tag{1}$$

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x. \tag{2}$$

These identities will be important throughout the subject.

c) Check that the identities are valid for the function $z(x, y) = x^2y$.

d) There is nothing special about the order of the variables in Eqs. (1) and (2). You could permute the variables as $x \to y, y \to z$ and $z \to x$ and the identities must still be valid. Do this and check the resulting identities for $z = x^2y$.

e) Check these identities for an ideal gas, with $z \to P, x \to T$ and $y \to V$.

2 Heat capacities for gases

Consider monoatomic gases. For an ideal gas,

$$E = \frac{3}{2} NkT$$

Use this to determine c_V and c_P Extra credit - do both for the Van der Waals gas as well write your answer in terms of P¡ N, and V.

3 Expansion and Compressibility

The isobaric expansion coefficient of any system quantifies how the system expands as its temperature increases and is

$$\alpha := \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P .$$

The isothermal compressibility quantifies how the system expands as its pressure increases and is

$$\kappa_T := -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T .$$

a) Show that, *for any system*

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial P}{\partial T} \right)_V$$

and check this for an ideal gas.

These can be used to check how the pressure must increase when the temperature is raised and while the volume of an object is held constant since

$$\mathrm{d}P = \left(\frac{\partial P}{\partial T} \right)_V \mathrm{d}T$$

if V is constant.

b) In a particular temperature and pressure range the compressibility of water is $4.52 \times 10^{-10}\,\mathrm{Pa}^{-1}$ and the expansion coefficient is $2.1 \times 10^{-4}\,\mathrm{K}^{-1}$. Determine by how much the pressure on the water must increase to increase it temperature by $10^\circ\,\mathrm{C}$ while the volume is kept constant. Express your answer in atmospheres.

c) In a particular temperature and pressure range the compressibility of gold is $4.5 \times 10^{-12}\,\mathrm{Pa}^{-1}$ and the expansion coefficient is $0.42 \times 10^{-4}\,\mathrm{K}^{-1}$. Determine by how much the pressure on the gold must increase to increase it temperature by $10^\circ\,\mathrm{C}$ while the volume is kept constant. Express your answer in atmospheres.

d) Explain why it is easier to heat water and gold at constant pressure rather than constant volume.

4 Differences in heat capacities

Consider an ideal gas initially at temperature T_i. The gas undergoes one of two processes either of which ends in a state at the same temperature T_f. In one process the gas expands at constant pressure. In the other, it's pressure increases while the volume remains constant.

a) Sketch the processes on a PV diagram.

b) How does the change in energy compare for the two processes?

c) Use *only these processes* to decide which of the c_V or c_P is larger. Explain your answer.

5 Speed of sound in a material

A detailed analysis of vibrations in a material give that the speed of sound in a material is

$$v_{\text{sound}} = \sqrt{\frac{\partial P}{\partial \rho}}$$

where P is the pressure of the material and ρ the mass per unit volume.

a) Show that for sound in any gas

$$v_{\text{sound}} = \sqrt{\frac{B}{\rho}}$$

where the bulk modulus is

$$B = -V\,\frac{\partial P}{\partial V}$$

b) Determine the bulk modulus for an ideal gas that undergoes an isothermal process and use the result to determine an expression for the speed of sound if the sound propagation occurs via an isothermal process.

c) Show that for an adiabatic process

$$B = \gamma P$$

where $\gamma = c_P/c_V$. Use the result to determine an expression for the speed of sound if the sound propagation occurs via an adiabatic process.

d) How do the two speeds compare? Which process is more likely to occur for sound propagation in air?

e) Assume that air is an ideal gas determine a value for the speed of sound in air as predicted by the above analysis. Use $\gamma = \frac{7}{5}$ and assume sea level.

f) Recalling homework 1, does sound travel at a different speed as your elevation increases?

6 Enthalpy and specific heat

a) Determine an expression for the enthalpy in terms of $T, P,$ and V for a monoatomic ideal gas (this will require using the known expressions for internal energy). Use this to determine expressions for c_V and c_P. Use f for a monoatomic gas.

b) Determine an expression for the enthalpy in terms of T, P, and V for a diatomic ideal gas. Use this to determine expressions for c_V and c_P. *For an ideal gas* $E = \frac{5}{2}\, PV$.

c) For carbon monoxide, measurements give that, provided that the temperatures are between 298.15 K and 1200 K, the enthalpy per mole is

$$H = H_0 + AT + \frac{B}{2}\, T^2 + \frac{C}{3} T^3$$

where $A = 25.57\,\text{J/mol K}, B = 6.096 \times 10^{-3}\,\text{J/mol K}^2, C = 4.055 \times 10^{-6}\,\text{J/mol K}^3$ and T is the temperature in Kelvin (source: NIST Chemistry webbook). Determine an expression for the heat capacity at constant pressure per mole for carbon monoxide. Determine the heat capacities at 300 K and 400 K?. How do these compare to the heat capacity for a diatomic ideal gas?

d) For any gas

$$c_P = \left(\frac{\partial H}{\partial T}\right)_P$$

allows one to determine one partial derivative of $H(T, P)$ from experimental measurements. By following a similar scheme as was done for energy, show how one can relate the other partial derivative

$$\left(\frac{\partial H}{\partial P}\right)_T$$

to c_V and c_P.

7 Gould and Tobochnik, *Statistical and Thermal Physics*, 2.56, page 104.

8 Deflated footballs

In the 2014 AFC Championship game, footballs were apparently deflated. NFL regulations require that the pressure of the football be between 12.5 psi and 13.5 psi. It is possible that the footballs could have been deflated during play as a result of the temperature drop between room where they were inflated and the outside. Suppose that the balls were inflated to 13 psi in a room at 75° F and then taken outside where the temperature was 51° F. Assume that the air inside the ball was an ideal gas. Note that the stated pressures are gauge pressures, i.e. pressure above atmospheric pressure. Note, 1 psi = 6894 pascals. Also need total pressure = atmospheric pressure plus gauge pressure. Return the final gauge pressure in psi.

a) Suppose that the volume of the ball remained constant. Determine the pressure of the air inside the ball once it is in equilibrium outside. In this process is any work done on the ball? Does heat enter or leave the ball?

b) Suppose that the ball were inflated from 0 psi to 13 psi. Assume that the air was initially at room temperature before it was pumped into the ball and that the pumping process was adiabtaic. Determine the temperature of the ball (in the room) immediately after it had been pumped up. This ball is then taken outside. Determine the pressure in the ball once it reaches equilibrium outside. Use $TP^{\frac{1-\gamma}{\gamma}} = \textit{constant}$ with $\gamma = \frac{7}{5}$.

c) Would either of these explain a reduction in pressure to 11.5 psi?

9 Free expansion of a gas

If a free expansion a gas that is not in thermal contact with its surroundings is allowed to expand into a vacuum region.

a) Is any work done on this gas during a free expansion? Explain your answer.

b) Noting that the gas is thermally isolated, what is that change in energy during a free expansion?

c) Suppose that the gas is an ideal gas. During a free expansion does its temperature increase or decrease? Explain your answer.

d) Suppose that the gas is a van der Waals gas. During a free expansion does its temperature increase or decrease? Explain your answer.