PHYS 351 #6

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1 1

Suppose we have four state variables: W, X, Y , and Z. Physical states lie on a two dimensional surface in the four-dimensional space, so that e.g. we can regard any pair of variables as independent, and the other two as dependent. Define $g_Y \equiv \frac{\partial X}{\partial W}\Big|_Y$ and $g_Z \equiv \frac{\partial X}{\partial W}\Big|_Z$.

1.1 a

Show that in general $g_Y - g_Z = \frac{\partial X}{\partial Z}\Big|_W \frac{\partial Z}{\partial W}\Big|_Y$.

First let us consider X(W,Y), this can be written since X can be uniquely determined by only two of the other 3 variables. We can immediately see that

$$dX = \frac{\partial X}{\partial W}\Big|_Y dW + \frac{\partial X}{\partial Y}\Big|_W dY$$

. Repeating the same process with X(W,Z) we see that dX can also be written as

$$dX = \frac{\partial X}{\partial W}\Big|_Z dW + \frac{\partial X}{\partial Z}\Big|_W dZ$$

. Now let us consider Z(W,Y) we see that a small change in Z is proportional to changes in W and Y

$$dZ = \frac{\partial Z}{\partial W}\Big|_Y dW + \frac{\partial Z}{\partial Y}\Big|_W dY$$

. Plugging in for dZ we see:

$$dX = \frac{\partial X}{\partial W}\Big|_Z dW + \frac{\partial X}{\partial Z}\Big|_W \left(\frac{\partial Z}{\partial W}\Big|_Y dW + \frac{\partial Z}{\partial Y}\Big|_W dY\right)$$

$$dX = \left(\frac{\partial X}{\partial W}\Big|_Z + \frac{\partial X}{\partial Z}\Big|_W \frac{\partial Z}{\partial W}\Big|_Y\right) dW + \frac{\partial X}{\partial Z}\Big|_W \frac{\partial Z}{\partial Y}\Big|_W dY$$

We may select any two variables as independent and ask how the others vary for example select Y and W as our two parameter, do not allow Y to very but do very W i.e.. dY=0. How does dX change?

$$dX = \frac{\partial X}{\partial W}\Big|_Y dW$$

However we now also have another answer:

$$dX = \left(\frac{\partial X}{\partial W}\Big|_Z + \frac{\partial X}{\partial Z}\Big|_W \frac{\partial Z}{\partial W}\Big|_Y\right) dW$$

Since the answer to "how does X very when dY is 0?" must be unique we know that the two solutions we obtain must be equal.

$$\left(\frac{\partial X}{\partial W}\Big|_Z + \frac{\partial X}{\partial Z}\Big|_W \frac{\partial Z}{\partial W}\Big|_Y\right) dW = \frac{\partial X}{\partial W}\Big|_Y dW$$

$$\left.\frac{\partial X}{\partial W}\right|_Z + \left.\frac{\partial X}{\partial Z}\right|_W \left.\frac{\partial Z}{\partial W}\right|_Y = \left.\frac{\partial X}{\partial W}\right|_Y$$

$$\left.\frac{\partial X}{\partial W}\right|_Y - \left.\frac{\partial X}{\partial W}\right|_Z = \left.\frac{\partial X}{\partial Z}\right|_W \left.\frac{\partial Z}{\partial W}\right|_Y$$

$$g_Y - g_Z = \left.\frac{\partial X}{\partial Z}\right|_W \left.\frac{\partial Z}{\partial W}\right|_Y$$

1.2 b

Suppose we also have the following definitions: $K \equiv -\frac{1}{Z}\frac{\partial Z}{\partial Y}\Big|_W$ and $B \equiv \frac{1}{Z}\frac{\partial Z}{\partial W}\Big|_Y$. Further, it is given that $\frac{\partial X}{\partial Z}\Big|_W = \frac{\partial Y}{\partial W}\Big|_Z$. Show in general that $g_Y - g_Z = B^2 Z/K$.

$$B^2 Z/K = -\left(\left.\frac{\partial Z}{\partial W}\right|_Y\right)^2 \left.\frac{\partial Y}{\partial Z}\right|_W$$

Recall that:

$$-1 = \left.\frac{\partial Y}{\partial Z}\right|_W \left.\frac{\partial W}{\partial Y}\right|_Z \left.\frac{\partial Z}{\partial W}\right|_Y$$

$$\left.\frac{\partial Y}{\partial W}\right|_Z = -\left.\frac{\partial Y}{\partial Z}\right|_W \left.\frac{\partial Z}{\partial W}\right|_Y$$

$$\left.\frac{\partial X}{\partial Z}\right|_W = -\left.\frac{\partial Y}{\partial Z}\right|_W \left.\frac{\partial Z}{\partial W}\right|_Y$$

Plugging this in above:

$$B^2 Z/K = \left.\frac{\partial X}{\partial Z}\right|_W \left.\frac{\partial Z}{\partial W}\right|_Y$$

Witch from above will in general be $g_Y - g_Z$.

2 2

Suppose that we are given the following general relation between the heat capacities:

$$C_P = C_V + \left.\frac{\partial Q}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P$$

By the First Law of Thermodynamics, $dU = dQ - dW$; for a hydrostatic system, this becomes $dU = dQ - PdV$, and it directly follows that $\frac{\partial Q}{\partial V}\Big|_T = \frac{\partial U}{\partial V}\Big|_T + P$. As a result, for a hydrostatic system we have

$$C_P = C_V + \left[P + \left.\frac{\partial U}{\partial V}\right|_T\right] \left.\frac{\partial V}{\partial T}\right|_P$$

2.1 a

Show that $\frac{\partial U}{\partial V}\Big|_T = \frac{C_P - C_V}{\beta V} - P$, where the coefficient of volume expansion $\beta = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_P$.

This is purely algebra from:

$$C_P = C_V + \left[P + \left.\frac{\partial U}{\partial V}\right|_T\right] \left.\frac{\partial V}{\partial T}\right|_P$$

$$C_P = C_V + \left[P + \left.\frac{\partial U}{\partial V}\right|_T\right] V\beta$$

$$C_P - C_V = \left[P + \frac{\partial U}{\partial V}\bigg|_T\right] V\beta$$
$$\frac{C_P - C_V}{V\beta} = P + \frac{\partial U}{\partial V}\bigg|_T$$
$$\frac{C_P - C_V}{V\beta} - P = \frac{\partial U}{\partial V}\bigg|_T$$

2.2 b

Use the identity $\frac{\partial Q}{\partial V}\Big|_T = T\frac{\partial P}{\partial T}\Big|_V$ (which we will subsequently derive in class), to show that for an ideal gas $\frac{\partial U}{\partial V}\Big|_T = 0$.

We are here discussing a ideal gas thus $P = \frac{nRT}{V}$. Note that:

$$\frac{\partial Q}{\partial V}\bigg|_T = T\frac{\partial P}{\partial T}\bigg|_V = T\frac{nR}{V} = P$$

Using the equation $\frac{\partial Q}{\partial V}\Big|_T = \frac{\partial U}{\partial V}\Big|_T + P$ we see:

$$\frac{\partial Q}{\partial V}\bigg|_T = \frac{\partial U}{\partial V}\bigg|_T + P = P \Rightarrow 0 = \frac{\partial U}{\partial V}\bigg|_T$$

2.3 c

Now show that $\frac{\partial U}{\partial P}\Big|_T = 0$ as well. Thus, show that the internal energy of an ideal gas is a function only of temperature: U = U(T). (This is purely an exercise in shifting to a different pair of independent variables, and thus no further magical identities are needed in fact you will be penalized for using any as-yet underived identities.)

Lets first write dU in two different forms (first U(T,V) then U(T,P)):

$$dU = \frac{\partial U}{\partial V}\bigg|_T dV + \frac{\partial U}{\partial T}\bigg|_V dT$$

$$dU = \frac{\partial U}{\partial P}\bigg|_T dP + \frac{\partial U}{\partial T}\bigg|_P dT$$

Now find dP assuming P(T,V):

$$dP = \frac{\partial P}{\partial V}\bigg|_T dV + \frac{\partial P}{\partial T}\bigg|_V dT$$

Consider the situation where we hold T fixed and allow V to very. How does U change?

$$dU = \frac{\partial U}{\partial V}\bigg|_T dV$$

$$dU = \frac{\partial U}{\partial P}\bigg|_T dP$$

Note:

$$dP = \frac{\partial P}{\partial V}\bigg|_T dV$$

so:

$$dU = \frac{\partial U}{\partial V}\bigg|_T dV$$

$$dU = \frac{\partial U}{\partial P}\bigg|_T \frac{\partial P}{\partial V}\bigg|_T dV$$

$$\frac{\partial U}{\partial V}\bigg|_T = \frac{\partial U}{\partial P}\bigg|_T \frac{\partial P}{\partial V}\bigg|_T$$

$$0 = \frac{\partial U}{\partial P}\bigg|_T \frac{\partial P}{\partial V}\bigg|_T$$

Note that (assuming that we actually have a real situation i.e.. $P, V, n, T \neq 0$):

$$\frac{\partial P}{\partial V}\bigg|_T = -\frac{nRT}{V^2} \neq 0$$

We must conclude:

$$0 = \frac{\partial U}{\partial P}\bigg|_T$$

Since U does not change when ether P or V change while temperature is held fixed the internal energy cannot depend on ether P or V.

2.4 d

From part (b), we know that for an ideal gas, $\frac{\partial U}{\partial V}\Big|_T = 0$. Use this to show that for an ideal gas, $C_P - C_V = nR$.

We know that:

$$C_P = C_V + \left[P + \frac{\partial U}{\partial V}\bigg|_T\right] \frac{\partial V}{\partial T}\bigg|_P$$

$$C_P = C_V + P\frac{\partial V}{\partial T}\bigg|_P$$

Note:

$$V = \frac{nRT}{P}$$

So:

$$P\frac{\partial V}{\partial T}\bigg|_P = nR$$

$$C_P = C_V + nR$$

$$C_P - C_V = nR$$