Statistical Mechanics Prof. Dipanjan Chakraborty Department of Physical Sciences Indian Institute of Science Education and Research, Mohali

Lecture – 13 Joule Expansion and Joule Thomson Effect

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So, today we are going to discuss something very interesting. We are going to discuss what is called the free expansion of a gas. Now we have learnt how to use partial derivatives in dealing with thermodynamic systems and in this setup we are going to use that knowledge. First; so what is this free expansion of this gas? So, consider that I have a chamber which I have partitioned into two halfs. And here in this half I have the gas particles which are contained over here.

The other side this part is vacuum; there is no heat exchange that is allowed. And what you do is you break this partition. What happens is that the gas then expands into this vacuum. And the final state is where the gas has occupied the whole of the volume. So, initially the volume of this particular chamber was V i and the total volume of this chamber is V f right.

Now, this is also this phenomenon is also what is called a Joule expansion. It was first devised by Joule to figure out whether the internal energy depends on the volume of the gas. So, the question now comes in that I want to see if there is a change in temperature.

Please note that there is no heat no work done in the system and this implies. So, there is no heat or work done.

So, that I have TdS is equal to du plus PdV for a hydrostatic system and there is no work done there is no heat; so this implies du is 0. So, the internal energy remains constant. Now with this constraint I want to see if the there is a change in the temperature.

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For that I write dT and infinite decimal change as del T del V the volume is being changed over here because the gas initially occupied a volume V i and then it occupies the volume V f; so this is the information that is given to me. But then this is U is being held constant n is also being held constant, but we will not we will suppress that and I have dV. This del T del V U constant is the quantity which we have to figure out.

So, let us see let us apply all our knowledge on our partial derivatives; how we can manipulate the Maxwell's relations will also be used. So, del T del V times del V del U. So, this is U constant this is T constant and then you have del U del T volume constant is going to be minus of 1. And this implies that I have del T del V U constant is minus del U del V temperature constant divided by del U del T volume constant. Now let us go back to the first law to which we write down as du plus PdV.

You immediately see that if volume is being held constant volume held constant this implies dV is equal to 0 and one has T del S del T volume held constant is del U del T volume held constant. So, you know what this derivative is it follows from this and if you recall this is the definition of C v.

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So, that we write down this as minus 1 over C v del U del V temperature held constant. Now del U del V temperature held constant we use the first law again T del S del V temperature held constant is equal to del U del V temperature held constant plus the pressure.

So, that del U del V temperature held constant is going to be T del S del V temperature held constant minus the pressure. Now here when we have started of this calculation we have

assumed that we do not know the fundamental relation which essentially means that S is a function of U, V, N right.

So, we are handicapped in that respect and we have to figure out this derivative by manipulating this derivative over here. So, we have del U finally, we have del U del V as this. So, now, I have to figure out what is del S del V T held constant. So, this one if I now use let us say F as U minus TS. So, that dF is going to be du minus TdS minus SdT and du minus TdS is minus of PdV. So, that del S del V temperature held constant is del P del T volume held constant.

This is a very familiar derivative for us because I know that del P del T volume held constant del T del V pressure held constant del V del P temperature held constant is minus 1.

So, that del P del T volume held constant is going to be del V del T pressure held constant by del V del P temperature held constant with a minus sign in front. I multiply by 1 by V I divide by 1 by V the ratio remains the same and this I immediately identify as alpha P the expansion coefficient of the gas divided by the isothermal compressibility. So, that this answer gives me alpha P over kappa T.

Hence I have del U del V temperature held constant is alpha P over kappa T minus the pressure. So, that del T del V internal energy held constant is going to be pressure minus there is a minus sign overall over here which means; if I use this relation this becomes minus of del U del V temperature held constant which is minus and this is plus so pressure minus alpha P over kappa T 1 over C v.

And this is the relation that you are looking for. And there has to be a T over here because you are looking at T del S del T. So, this is T del S del T T and there is a T over here. For an ideal gas alpha P which is 1 over V del V del T pressure held constant. And I know the equation of state is N k B T. So, which means del V del T pressure held constant is N k B divided by P. N k B over P is going to be; so let us just write down 1 by V and then I have P V over here and N k B over P V is 1 by T. So, your alpha P for an ideal gas goes as 1 by T.

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$$\frac{\partial T}{\partial V_{U}} = \begin{pmatrix} P - T\frac{d}{d}p \\ \overline{k}T \end{pmatrix} \frac{1}{c_{V}}$$

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$$\frac{1}{2} \frac{\partial V}{\partial T} \frac{1}{p} \frac{1}{V} \frac{\partial V}{\partial T} \frac{1}{p} \frac{\partial V}{\partial V} \frac{1}{p} \frac{1}{p} \frac{1}{p} \frac{\partial V}{\partial V} \frac{1}{p} \frac{1}$$

The compressibility; the isothermal compressibility is minus 1 by V del V del P temperature held constant. And this means that del V del P temperature held constant is minus N k B T over P square I will have a minus 1 by V that makes it plus. Then I am going to write down this as N k B T over P V times 1 by P. And from the equation of state it follows N k B T over P V is 1; so that I have the ratio 1 by P.

So, you see for an ideal gas it follows that del T del V is going to be; pressure minus temperature times alpha P is 1 by T and the kappa T is 1 by T P. So, that this becomes this and you have this 0. Hence you conclude; there is no cooling in Joule expansion for an ideal

gas; dT we come back to our original starting point dT del V U times dV which is 1 over C v and then you have P minus T alpha P over kappa T times dV.



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So, if the quantity in the bracket is positive then there is heating. So, the temperature of the gas increases; increases if this is negative then temperature of the gas decreases right. So, this is how you deal with this system if you do not know the fundamental relation. If you know the fundamental relation; which is S as a function of U, V, N. What you can do here is; you can determine take the derivative del S del U to give you 1 over T.

So, that you can know T as a function of U, V and N in which case your delta T is going to be T of U remains fixed T f, V f, N minus T i, U, V i, N; this is how you will determine the change in the temperature; if you know this fundamental relation S.

What is interesting to note here is if I take this approach; that I do not know I do not know the fundamental relation, but I want to calculate the change in the entropy. And the change in the entropy follows from the same way as we have calculated the change in the temperature del S del V; U is being held constant.

So, I have; the change in the entropy we follow the same procedure as we have determined the change in the temperature. We write dS as del S del V U is being held constant times dV. And if you look at the first law which was TdS was du plus PdV then you see that del S del V; U held constant is actually P by T. So, that you have PdV over T. But P by T from the equation of state is NkB divided by the volume. And you have Nk B divided by the volume. So, that you have dV by V.

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Hence the change in entropy delta S in going from the initial state to the final state is given by N k B dV over V V i to V f which is N k B ln of V f over V i. Surprisingly; there is a change in entropy. Even though you do not have any change in this is for an ideal gas; for a real gas one has to substitute the equation of state over here. So, this is for an ideal gas we are looking at this expression is valid for an ideal gas.

But this is the general expression that is valid for any gas or any hydrostatic system except that you have to now to proceed further with this relation one has to replace P by T by the from the appropriate equation of state. Now, this tells you that delta S is positive; so that there is a change in entropy. And the reason this happens is because this is an irreversible process. Your entropy is only defined in the initial and the final not in the intermediate states.

So, you get an irreversible process where the initial and the final states are equilibrium states, but not the intermediate states and therefore, you cannot define an entropy. Now recall for an ideal gas the entropy had this expression 5. So, we had N k B 5 by 2 plus log of V over N alpha U raised to the power N alpha U by N raised to the power 3 by 2.

This was the expression that we had where alpha was a constant which is still not yet known to us and we promise that we will determine this constant when we use statistical mechanics, but right now it suffices to have this expression.

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If you look at this let us just first calculate delta S which is the easiest thing to do. Then delta S is 5 by 2 plus ln V f over N alpha U and raised to the power 3 half minus N k B 5 by 2 plus ln V i over N alpha U over N raised to the power 3 half.

Since, essentially the no heat and no work has been done the internal energy for both the states remain the same. And you immediately see that this answer matches with the answer which you had obtained earlier that this is going to be delta S is going to be ln V f over V i for an ideal gas.

Since, I know S if this is my starting point if this equation is my starting point then I want to determine dT; the change in the temperature delta T for this particular system which is essentially the ideal gas. And I know that del S del U is going to be 1 by T and we have done this exercise this essentially tells you that U is going to be 3 half N k B T.

So, that T is 2 3rd U over N k B and therefore, you have T as a function of U, V, N from this relation surprisingly for a real gas for an ideal gas it does not depend on the volume. So, that delta T it clearly follows since it does not depend on the volume delta T is going to be 0.

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A similar so essentially this Joule expansion tells you that for an ideal gas internal energy u does not depend on volume. A similar experiment is what is called a Joule Thompson effect which is also called the Throttling process. And what the setup I mean what you have over here is you have two chambers which is divided by a porous media which allows for the gas to pass through. On this side of it you have a piston and on this side of it you have another piston.

The purpose of this pistons are to maintain the gas in the two chambers at two different pressures. So, this one maintains it at low pressure and this one maintains it at a high

pressure. So, let us call this P i and let us call this P f. If I take one mole of the gas let us call the molar volume V f and then the molar volume here on the left hand side is V i. Now, essentially you push the piston so all the gas has gone from the left to the right so it goes from left to the right.

Now when all of the gas has moved to the right chamber then there has some work has been done by the piston which is this one which is given by P i times V i. Now, when all of the gas has moved to the right chamber some amount of work has to be done by this piston which maintains the low pressure and that is P f times v f; where v i and V f are the molar volume.

So, the net difference in the work is going to be the conservation of energy tells me the change in the internal energy u f minus u i must be the worked network time. I can rearrange this equation so that I can write down this as P i v i plus u i is going to be P f v f plus u f where the small u's are the internal energy the molar internal energy. Just to as the small v is where the molar volume.

Now, you immediately see that this means that for a 1 mole of a gas the molar enthalpy in the initial state the left hand side is going to be the molar enthalpy in the final state. So, that the enthalpy the molar enthalpy remains constant; not sorry the molar enthalpy in the not remains constant, but the molar enthalpy in the initial state is equal to the molar enthalpy in the final state.

Please note that this is only a statement of the fact that the initial enthalpy and the final enthalpy remains the same. In the intermediate states this is a once again a non equilibrium as an irreversible process as we have seen in the Joule expansion the enthalpy is not defined.

So, this relation does not talk about the enthalpies in the intermediate states and this equality is not valid there. So, now, what I want to figure out is if there is a temperature change because of this process. And again we do it del T del P motivated by our earlier work enthalpy constant times dP.

This is a derivative which is very curious and which is not a standard derivative which we can evaluate very easily. So, one has to manipulate this derivative of course, we still do not we do not know the fundamental relation.

 $\frac{\langle I_{i}, V_{i} \rangle}{J_{0} L_{i} L_{i} - T_{i} J_{0} J_{i} J_{i} V_{i}} + \frac{J_{i} J_{i} L_{i} J_{i} J_{i} V_{i}}{J_{i} J_{i} J_{i}$

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So, then we start off by writing del T del P, but even before that.

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We first write down we have to look at the enthalpy which is U plus PV and dH is going to be d u plus PdV plus VdP this is TdS from the first law TdS is going to be d u plus PdV; so that you have TdS plus VdP. Now let us write down del T del H sorry del T del P enthalpy held constant times del P del H temperature held constant times del T del H pressure held constant is going to be minus 1. This is a cyclic relation which you have used several times.

So, del T del P enthalpy held constant is minus del H del P temperature held constant and then I have del H del T pressure held constant. If I look this look at this expression for dH pressure held constant means dP is going to be 0. And you see del H del T pressure held constant is T del S del T pressure held constant and this you immediately know is the specific heat at constant pressure. So, I write down this as 1 over C p del H del P temperature held constant.

Del H del P from this equation itself follows that del H del P temperature held constant is going to be T del S del P temperature held constant plus V. So, therefore, evaluation of this partial derivative is equivalent to evaluation of this.

And once again this is the problematic derivative partial derivative that I have because it is not in a any it does not relate to a standard derivative that we know of any of like a response function. So, we have to figure it out. Now, you see I have del S del P. So, let us try to figure out if there is a Maxwell relation. If there is a Maxwell relation that would give me what this derivative is.

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Then you see this must be the differential of that free energy must have SdT and VdP. Whenever you see VdP you know that you have to look at the Gibbs and G is equal to U minus TS plus PV and a dG is going to be du minus TdS minus SdT plus Pd V plus VdP. So, that du minus TdS plus PdV is 0 from the first law and one has minus SdT plus VdP.

You immediately see the Maxwell's relation is del S del P temperature held constant is minus del V del T pressure held constant. And del V del T pressure held constant is a derivative we are familiar with because it relates to the expansion coefficient of the gas. So, that del H del T sorry del H del P temperature held constant is T del S del P temperature held constant I have minus T del V del T pressure constant plus v and this I write down as minus T by V times V del V del T pressure constant.

And I immediately see that this quantity there is a plus V this quantity is equivalent to your expansion coefficient alpha p. So, I have V common 1 minus alpha p times T; very nice. So, therefore, this ratio which we started of with is del T del P H held constant is going to be 1 over C p V over C p this factor comes in over here. This is where you substitute this so that this becomes V over C p alpha P T minus 1.

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So, that dT is going to be V over C p alpha P times T minus 1 times dP. For an ideal gas alpha P goes as 1 over T is equal to 1 over T we have just seen in our earlier calculation. And therefore, this implies that dT is equal to 0. So, this means that for an ideal gas there is no cooling no heating no change in temperature as the gas goes from the left chamber to the right chamber in the (Refer Time: 28:56)

However, depending on the sign of this quantity one can expect whether the gas can either cool down or heat up. So, for example, let us take it very simply this is this just pertain to any system let us say if I have C p going as a times volume and I take alpha P T minus 1 is equal to a constant which is equal to let us say B and this is greater than 0. Then very trivially you see that dT is going to be B over times d P.

And therefore, in under these conditions dT if I know integrate you see depending on the sign of B it depends on the sign of B. If B is positive B is greater than 0 which means alpha P T is greater than 1 and provided this ratio V over C p does not depend on pressure. It is just a constant number then you see dT is less than 0. Why because if you integrate this you are going to come up with a relation which is going to be P f minus P i.

Initial pressure was high final pressure was low so this delta P is negative and therefore, your temperature is negative so the gas cools down. In contrast when B is less than 0 your change in temperature is going to be positive so that your gas heats up.

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So, this means essentially the conclusion that we draw is that for an ideal gas; for an ideal gas the internal energy U does not depend on pressure. In earlier exercise we have seen that it does not depend on volume therefore, U is only a function of temperature. Of course we know

this result, but nevertheless if we did not had not known any of these things that U was 3 by 2 N k B T which followed from S of U, V, N for an ideal gas. We could have deduced all of this using these two experiments.