so in this lecture four i will be discussing a bit of interacting systems before that let me recapitulate at least some aspects of whatever we did in the
third lecture
so this is our lecture number four we shall start by recalling what we talked about specific heat capacity we introduce the notion of c v specific
it measured at a constant volume c p specific heat measured at a
constant pressure and c p minus c v c p minus c v is equal to r for an ideal gas
this i did not prove but we accepted this form three situations we talked about firstly
what is most important is equi partition of energy ok i say it each degrees of freedom contributes
half kt to the energy ok this is called equi partition theorem what is important energy is
equal to p square over two m ok
so this quadratic form of energy is very important in having this
form of half kt
so now we did it for mono atomic mono atomic gases for mono atomic gases we know there is
only translational degrees of freedom so n monoatomic gas molecules will
contribute an energy three by two n k b t ok three because it is three
dimension three components of momenta and each giving me half kt n is the total number of molecules
so i found out cv should be equal to 3 by 2 r and c p is equal to
five by two r ok
so this is the simplest situation where we can have only translational
degrees of freedom if i go to diatomic situation diatomic molecules diatomic molecules we should be careful
because what i did in the last class is a rigid approximation i will take you slightly beyond
that and tell you vibrational modes also
so i can have translational plus rotational and vibrational in the last lecture i focused on these two
parts for diatomic molecules translational and rotational assuming a rigid diatomic
molecules ok
so translational degrees of freedoms are very simple they will give me three by two n k b t because it is three dimension but if you think of rotation and if you assume
that there is a dumbbell like structure this length being fixed this is the rigid
approximation then you can have rotational two rotation axis one you can think of lying on the
board this is the center of mass of let us say one is lying on the board other is coming out
of the board or going into the board and we know rotational kinetic energy rotational kinetic
energy corresponding to these two modes they will be of the form half i omega square two of these
terms will come moment of inertia let us write it of this form corresponding to axis one we have
drawn and there will be another corresponding to axis two once again this quadratic form

is very important with angular velocity will give me half kt so i will be get getting another half kt into two because of two rotational degrees of freedom plus k b t this i did in the last class this gives me five by two and you can immediately find out what is c p if i give you this form five by two k b t if i have n molecules i should be having an n here so c v will be given by five by two r but thats not all there could be vibrational modes now this vibrational mode i wrote as f in the last class but one has to be careful ok i say f by 2 f by 2 you can add but one has to be careful here why it should be careful a vibrational mode corresponds to a situation like a simple harmonic oscillator in a simple harmonic oscillator you know that there is a q and there is a p which i discussed in the last class if we have e of the form p square over 2 m plus half k x square i have 2 degrees of freedom because i told you that my style of counting degrees of freedom will be including p as 1 x as another

so it will give me from equi partition at temperature t if i have a system of harmonic oscillator ok in one dimension say at a temperature t i will be having energy is equal to e n k v t

so each vibrational mode which i wrote f in the last class i write wrote f by two assuming that f is two for each vibrational mode to be precise one can write c v is equal to three by two r some f prime what is difference between f f has two both q and p ok f prime if i add with this

so i will get cv is equal to let me correct this part of it five by two i was getting cv is equal to five by two plus f k prime k b t ok f prime each vibrational mode each vibrational mode has one coordinate one momenta each contributing half kt ok

so if you write f prime its of the order of one kt or you can write it simply i write it as f ok as long as you remember if has both kinetic and potential degrees of freedom each contributing half ready this is what i wanted to clarify

so remember whenever there is a vibrational mode there is a f and that f is actually having a contribution from kinetic energy and having a contribution from potential energy

so it will be f k t ok f counts both x and p here

so if you have one vibrational mode so you will be having one harmonic oscillator one p gives me half k t and other keep gets other half kt comes from this x component ok now generalizing to poly atomic molecules polyatomic which i did also in the last class polyatomic there will be a three

three
factor which will come because of the rigid body approximation and with this three you should have this f ok and here i should correct myself this should be n
this should be five by two three plus f into r ok this is specific heat capacity for the poly
atomic molecules
so idea is count appropriately the degrees of freedom and vibrational mode if i
mean f each f one translation one potential giving me a kt ok having said this now i will introduce
mean free path in far more details ok i introduce the notion of mean free path but i will do it in a
more detailed manner in the coming few minutes ok ok lets define what is mean free
path i have been
so far assuming that my gas molecules if not otherwise mentioned
this gas molecules are mono atomic molecules and i am assuming that they suffer no other
collision except for the elastic collisions with the wall that is how i arrived at the expression
p average pressure p is one third m n c square but this is true idealized situation which
is valid only in the dilute limit
so there is a mean free path and the
mean free path is the main free path which i also defined in the last
class is the average distance traversed by a cache molecule between two
successive collisions this is what i defined as mean free path ok important is average i told
you everything we derive in this set of kinetic theory lectures are average in average
frames
so i define again the average speed of a molecule let me call it v bar ok now what is
the distance travelled by this molecule in time delta t that is v bar into delta t ok
and let us now assume that this molecule has a diameter d identical molecules i am telling you it in a sense
i can assume all the molecules have a diameter d now this is the deviation from ideal gas situation
where we initially we made the approximation that molecules are point particles in comparison to
the intermolecular separation but now i am making an approximation that molecules are
hard spheres this very important molecules are heard spheres
of diameter d now how do i calculate mean field free path from these approximation
so lets draw a cylinder okay this is v delta t that is the average distance traversed by the molecule over a time delta t and now let us assume that this area is pi d square
ok
so this area is pi d square this radius is d but i have already defined molecular diameter
is d

so molecular radius will be d by two ok so i am constructing a cylinder which has this length height v delta t diameter d where molecular diameter is here which is i have defined d by two if i take this only this area and draw it this is my d and this is my d by two ok now we will make an assumption assume all other molecules all other molecules are static ok this is an approximation but basic result doesn't change alter much if i do not make this approximation now you can see very nice situation what i assumed molecules are hard sphere ok of diameter d now any molecule if i can think of all the molecules are static my target molecule which i have talked about here is moving and this covers this cylinder this inside cylinder over a time delta t now you see if any molecule hits collides with this its center must lie within this cylinder ok if its center lies inside or optimally centralized on this cylinder there will be a collision ok that tells me the number of collisions that the molecule will have which molecule the target molecule that is moving other molecules are static whenever any one centers lie here or inside there will be a collision so how do we know the number of collisions total number of collisions in that case i can easily calculate total number of collisions if i assume n is the number density this is the cylinder area pi d square v average delta t this is the total number of collisions that it will have again i am making an approximation here i am assuming homogeneity that density is same everywhere it does not matter where this target molecule is moving that means i am assuming i am far away from the wall ok so if that be the case now i can find out the rate of collision how many collisions it will suffer per unit time so this is the number of collisions over a time delta t and then time between two successive collisions is n pi d square v average what is the average distance between two successive collisions that i can easily calculate so average distance which i defined as mean free path is v into tau ok v average into tau that takes care of v here and i get n pi d square you can easily check that dimensionally its actually dimension of length ok because this has one by l cube this is l square so you get l so this is typical mean fifa which as it takes into consideration of the fact that dilute gas but if it is too dilute then you see n is in the denominator so number this number of mean free path becomes very very high so for practical purposes that these length is very very large and one can for mathematical purposes one can assume there is no collision inside the container but for realistic situations there is a mean free path given in terms of n and d but thats not the end of the story i made an approximation that all other molecules are static which is not true obviously we know we do not have any specialized molecule or specific molecule that is moving all the molecules are moving so one should actually have here the v relative which is relative velocity between two molecules ok but that does not alter this result much all that you can have a number and more sophisticated calculations will give this number probably of the order of root two but essentially the functional form or the mathematical form we have found out holds true so this completes more or less all i wanted to say about ideal gases now it is time to go beyond ideal gases and do little bit of interacting systems again i recall why interacting systems are important interacting systems are important because in nature we always see phase transitions ok we boil water even to make a cup of tea we see eyes in our refrigerators these phase transitions are never possible as i also emphasized in the last class are never possible without interaction and what type of interaction okay let us take very very simplistic interaction i said deriving the mean free path expression i assume that they are hot sphere molecules they cannot penetrate into each other this is a good approximation to some limit but in fact molecules are soft so they can penetrate in some sense but let us not go into this so first i will consider interaction which is hard sphere interaction okay hard sphere interaction that means they cannot penetrate into each other this is a strong repulsion ok and then there is a weak attractive interaction but very short range ok so very short range weak attractive interaction when the molecules are away from each other if they are close by there would be a hardcore repulsion ok which is very strong which is mostly dominating in the short ranges they are far away there is a weak attractive interaction which is very very small small in magnitude and short ranged ok this has origin from electros statics but i will not explain why and how but since you know potential energy i can draw a curve of potential energy and as a function of r lets say you see what happens there is a strong repulsive potential up to a distance this is the nearest distance molecule can approach and then there will be a weak attractive potential i have simplifying it to this very simple form actual form if you are interested you can find out its name after two famous scientists is called lennar jones potential but this is the simplest form one can think of that there is a strong repulsion potential as a function of r you see there is a strong repulsive force there is a weak attractive force and this when taken into consideration you have already seen that i have a mean free path secondly i will have change in my ideal gas equation of state ok this was my equation of state boltz law charles law everything we found out from here but what we will get simplest correction to ideal gas scenario is van der waals equation of state ok i will spend just half an hour on this van der waal equation of state let me write it in this form p plus a v square v minus b is equal to rt i am assuming one mole of van der waal gash let me call it a real gas so you see the two correction one correction arising due to this so correction to pressure arising due to this attractive force in the beginning we said that our ideal gas molecules will be molecules which do not have any other interaction except for elastic collisions i make a departure from that i said there is an attractive force very weak short range these attractive force average attractive force leads to a correction to pressure ok and second thing a correction to volume you can already guess why this correction to the volume ok correction to the volume is coming because of the second issue i assumed molecules to be point particles we have already seen in the beginning of this lecture they should be taken as hard sphere that is also an approximation but it is a better approximation than point particles so there will be a correction why this correction the entire volume of the container is no longer available to a molecule some volume is excluded v measures the volume that has been excluded now clean this part of the board but what you have to bear in mind that there is a correction to pressure arising due to the attractive weak force and here there is total correction to the volume which takes care of total volume of the container that is excluded it must be excluded because in van der waals approximation we are considering molecules to be hard spheres now let us try to do this in the following way first lets assume identical particles many times i have repeated their heart spheres these herd spheres are of diameter d ok now lets take two of them two of them consider one of them which is static or more scientific way or more physical way of saying this i am moving in the frame of this molecules i am moving with this molecule so that to me it is static ok so this is one having diameter

d this is diameter d once i have of this form now i draw a bigger sphere as i did
while i was deriving the mean free path sphere a concentric sphere which
has a diameter two d or has a radius d ok now again recall the argument i gave while
introducing mean free paths what is that that if i have any other molecule whose center comes here
then there it will be a hard core repulsion ok there will be just deflected there will
be a collision because molecules cannot penetrate into each other their heart spheres so
if that be the case then i can say each molecule has an excluded volume what does it mean this molecule moves but her sphere condition
also gives me a sphere which has a radius d this volume is entire volume excluded ok
for other molecules i am considering a second molecule this volume will be excluded for
the second molecule ok
so every molecule then carries with itself a volume that is excluded
and what is the volume of the sphere ok volume of this sphere ok will simply be four third
pi but here the sphere this bigger sphere has a radius which is double the radius of the
molecule itself ok
so i can write it as d q ok this is the volume that it
excludes i again repeat the argument volume excluded i repeat the argument that is the
sphere ok center of any other molecule i consider can lie maximally here it cannot come closer
because in that case it will have to penetrate the first molecule here
so this is the volume
of excluded by this molecule i am considering
so i can write it in the following form
which is like this eight four third pi d by two q well immediately i know what is four third pi
d by two cube this is the volume of my molecule if you remember initially i started
by saying that b is proportional to the volume of a molecule is that clear if that
is clear you see it is eight times v molecule its not the velocity it is rather the volume of a
molecule assuming the molecule to be a hard sphere of diameter d now i am taking two molecules
into consideration i am asking the question one molecule is there and how much
volume it excludes for the other molecule
so two in the picture
so on an average this
is van der waals original way of argument ok i can say if i considering two molecules
average excluded volume average excluded volume will be half of this quantity eight times volume
of the molecule which tells me that on an average the quantity b will be proportional to four times will be

proportional to four times the volume of a molecule
so b i would rather write b will
be proportional to four times v molecule of course proportionality constant will have
number of molecules in the container more molecules i have more will be excluded volume more
and more volume will be excluded ok and will have serious correction to this term
so this somehow
gives you a feeling i am again telling i am not deriving anything ok phenomenological
argument y there should be v minus beta next comes the question how do you get this
a by v square term ok a by v square term can be appreciated recalling there is a weak
attractive force but this weak attractive force is very short ranged
so we can assume
whenever my molecule any molecule i target is moving within the container okay let us
assume this room as a container
so whenever molecules are moving inside the this container
so i know this weak force can be neglected but two approximation which ideal gas makes one
is there is no interaction fine let me drop it but when it goes to the wall some molecules are
in the wall and some molecules are inside consider one molecule that hits the wall what will
happen to other molecules they have attractive force they will collectively pull this fellow
the fellow molecule that is hitting the wall that is at the edge you can think in
the following way if i have a molecule inside the container it will have an attractive
force of all the other molecules surrounding it roughly speaking i can say that net average force
acting on it is zero but when it is on the wall okay then other molecules which are inside will
collectively pull it inside ok and this will change the pressure pressure when we derived
we assumed no interaction from other molecules but if other molecules attract them molecules
on the wall i mean then there will be a net attractive force ok that is going to reduce the
pressure there could be one more situation which i never considered in my derivation ok that is
the wall wall i always assumed the world to be a fixed body and heat has no interaction with
the molecules which are going and hitting them ok this is also a very idealized situation we
all know there is adhesion there are phenomena in which liquid molecules ah interact with
the wall
so two approximations there is one attractive force inside the container i can forget

about it but whenever a molecule hits the wall it must fill a net attractive force inside due to the other molecules of the container and wall also should have a repulsive force okay these two taken together must give a correction to the pressure i have been talking about

so two contributions that i will take into consideration to interpret or to appreciate the origin of the term a by b square ok

so one weak attractive force to repulsion from the wall ok repulsive force now here i bring in the concept of homogeneity ok homogeneity will tell me that what is this interaction are proportional to ok you can say at any instant of time number of molecules that hit the wall will be proportional to the density that we have already seen

so first number of molecules at any instant hitting the wall will be proportional to the density n over v okay secondly how many molecules are attracting it inside ok number of molecules on the wall is n by v and whatever is attracting them will be also proportional to n

so two things number of molecules at any instant hitting the wall would be proportional to small l which is density and again the number of molecules which are pulling them is should also be proportional to n

so correction if i write my pressure equation

so this four pressure will be proportional to n square ok just n on the wall n on this this correction is incorporated in the form n is i remind you capital n over v more sophisticated language i can call it a density density interaction ok

so this is proportional to n square or 1 by v square now taken this two into consideration my pressure form will be r t v minus p i try to emphasize how does b come and there will be a correction coming because of this interaction i talked about number of molecules hitting the world and number of molecules which are pulling them both being proportional to small n or one over v i will have a correction of the form a over v square and then immediately putting thing together i will get a v square v minus p is equal to rt

so this gives me the van der waal equation for one mole of real gas ok now having said this in last 10 minutes of my last lecture on kinetic theory i will try to tell you why van der waals equation is

so important ok we always talk about liquid gas transition ok what is the liquid gas transition you have a liquid and you heat it up ok and you get a gaseous state kinetic theory tells us has to happen because kinetic energy of

the molecules average kinetic energy of the molecules is proportional to the temperature
ok if you increase the temperature kinetic energy will be very very high and it will go
to a gaseous state freely moving ok now also there is a liquid gas transition and you
may have noted sometimes we call gas sometimes we call vapor the ideal gas equation will never
be able to tell me about this transition or about the liquid and vapor what is their
difference van der waal equation tells you that and though its a very phenomenological derivation
almost guessing the corrections ok still experimental plots if you look for if you just
google van der waal equation experimental plots you will see similar plots were experimentally
observed more than hundred years back
so what i am going to plot is called isotherms ok
isotherms these terms you will see many times these isothermal adiabatic in thermodynamics
part of this set of lectures what is an isotherm you keep temperature constant this is very
important ok you keep temperature t constant ok and then plot pressure as a function of volume ok these are called isotherms you
plot it for different constant temperatures ok now let me plot van der waal isotherms and lets
see how can it talk about liquid gas transition ok and secondly how does it talk about the
critical temperature which i am going to tell you now
so first let me plot pressure as
a function of volume this is my first curve ok for a temperature t 1 this is for a temperature let us say t 2
pressure as a function of volume this is t 1 t 2 let me plot some particular temperature i
am calling it t c or the critical temperature and above this this is my curve now see let
me make this curve slightly more realistic you see there is a region which is almost
horizontal this region is called the coexistence region okay and i demarcate by this region by this
dotted curve ok and this region is coexistence of liquid of liquid and vapor ok
so you increase the temperature
ok you go from the one phase to the other temperature is increasing in this direction
this is t greater than t c
so t one t two is higher than t one t c is higher than t
two and what you see this dotted region tells you the coexistence region shrinks to a point
at that critical temperature
so what is the importance of critical temperature firstly if
you change pressure ok if you change the pressure this is your high pressure low volume this is
low pressure high volume region

so liquid and gas   they coexist here in this region okay but as you
increase the temperature this coexistence region   shrinks to a point and for
temperature
greater than the critical temperature   there is no such coexistence region ok
this is
the first meaning of the critical temperature
so if you change pressure there is a
coexistence region between liquid and gas okay   or rather liquid and vapor why
i change the
terminology you will soon see because below the   critical temperature tc you
can change pressure
and go from one phase to the other ok this   is second implication or related
implication
i will call a gas a vapor below the critical   temperature above the critical
temperature
what would happen no amount of pressure no amount of pressure can liquify can
liquefy a gas this is the
implication of
so called critical temperature   if you want to plot p t diagram p as a
function of t this is also very useful   ok keeping volume fixed you will see
that this p t
diagram ends at the critical point ok this is your this is your gas and they
coexist up to
critical temperature and beyond that there is   no coexistence
so van der waals equation which i
explained for you leads us to following things it   explains liquid gas
transition which we
observe in nature this liquid gas transition   can be achieved by changing
temperature ok
will boil water all the time or by application   of pressure ok but if i am
sufficiently high in
temperature which is the critical temperature ok   we cannot liquefy a gas by
application of any
amount of pressure if i am below testing critical   temperature there will be
always a coexistence
region in which vapor and liquid will coexist   either it is entirely liquid
phase or it is gas
phase or it will coexist ok
so this is the summary   ok of implication of van der waal equation
so i
corrected ideal gas equation to the van der waals   equation taking into
consideration finite size of
the molecules that give a correction term to the   volume weak attractive force
between the molecules
which was otherwise completely neglected and that   resulted in some interaction
which is proportional
to the density of the molecules and hence there   was a correction to the
pressure which was not
there in the ideal gas case fine that leads us   phenomenologically to the van
der waals equation
which i have written here for one mole of real gas   if i plot van der waals
isotherms this tells us
nicely that there could be phase transition either   by changing temperature or
changing pressure

but there is a critical temperature above which   no amount of pressure can liquefy a gas if i am at
temperature t greater than t c for t less than t c   i can achieve that through a coexistence region in
which liquid and vapor coexist for t less than t c   i will call it a vapor t greater than t c it
is a gash kinetic energy dominates pressure   cannot liquefy it with this i will end my set
of lectures on kinetic theory and next set of   lectures will start discussions of
thermodynamics thank you for today's class you