PROFESSOR: OK, let's start. So last time, having dealt with the ideal gas as much as possible, we started with interacting systems. Let's say interacting gas. And the first topic that we did was what I called an approach towards interaction through the Cumulant expansion.

The idea is that we certainly solved the problem where we had particles in a box and it was just a trivial system. Basically, the particles were independent of each other in the canonical ensemble. And things become interesting if you put interactions among all of the particles. Very soon, we will have a specific form of this interaction. But for the beginning, let's maintain it as general as possible.

And the idea was that we are trying to calculate the partition function for a system that has a given temperature. The box has some volume V and there are N particles in it. And to do so, we have to integrate over the entirety of the phase space of N particles. So we have to integrate over all of the momenta and coordinates of e to the minus beta h.

But we said that we are going to first of all, note that for identical particles, we can't tell apart the phase space if you were to make these in [? factorial ?] permutations. And we also made it dimensionless by dividing by h to the 3n.

And then we have e to the minus beta h, which has a part that is e to the minus sum over i pi squared over 2m, that depends on the momenta. And a part that depends on the interaction U.

The integrals over the momenta, we can easily perform. They give us the result of

Gaussians that we can express as lambda to the power of 3n where we introduced this lambda to be h over root 2 pi m k t.

And actually, sort of keeping in mind the result that we had for the case of the ideal gas, let's rewrite this as V over lambda cubed to the power of N. So I essentially divided and multiplied by V to the N so that this part becomes the partition function than I would have had if U was absent. And so then the remainder is the integral over all of the q's, but I divided by V. So basically, with each integration, I'm uniformly sampling all of the points inside the box with probability density 1/V e to the minus beta U.

And we said that this quantity we can regard as sampling e to the minus beta U through 0 to all other probability distribution in which the particles ideal-like are uniformly distributed. And we call this e to the minus beta U. And the index 0 again to indicate that we are dealing with a uniform 0 to order distribution with respect to which this average is taken.

And then, this quantity we can write as Z0. And this exponential we can formally express as a sum over all, let's say, l running from 0 to infinity minus beta to the l divided by l factorial. Then, expanding this, a quantity that depends on the coordinates is U. So I could have U raised to the l power, this kind of average taken with respect to that.

And immediately, my writing something like this suggests that what I'm after eventually is some kind of a perturbation theory. Because I know how to solve the problem where U is absent. That's the ideal gas problem. Maybe we can start to move away from the ideal gas and calculate things perturbatively in some quantity. And exactly what that quantity is will become apparent shortly. At this time, it looks like it's an expansion in beta U having to be a small quantity.

Now, of course, for calculating thermodynamic functions and behaviors, we don't really rely usually on Z, but log Z, which can be related to the free energy, for example. So taking the log of that expression, I have a term that is log of Z0. And a term that is the log of that sum. But we recognize that that sum, in some sense, is a

generator of moments of this quantity U.

And we have experienced that when we take the logarithm of a generator of moments, what we will get is a generator of Cumulants, now starting with l equals to 1 minus beta to the power of l divided by l factorial U to the l0 with a subscript c. Of course, this subscript c sort of captures all of the various subtractions that you have to make in order to go from a moment to a Cumulant. But that's quite general and something that we know essentially is relating log of the expansion to the expansion itself. But that's well-known.

So presumably, I can perturbatively calculate these. And I will have, therefore, progressively better approximations to log Z in the presence of this interaction.

Now at this point, we have to start thinking about a particular expression for U. So let's imagine that our U is a sum over pairwise interactions. So if I think about the particles, there are molecules that are in the gas in this room. Basically, the most important thing is when the two of them approach each other and I have to put a pairwise interaction between them of this form. In principle, I could add three-point and higher-order interactions. But for all intents and purposes, this should be enough.

And then again, what I have here to evaluate, the first term would be minus beta, the average of the first power, and the next one will be beta squared over 2. For the first Cumulant, it is the same thing as the first moment. The second Cumulant is the thing that is the variance. So this would have been U squared 0 minus average of U squared, and then there will be higher orders.

So let's calculate these first two moments explicitly for this potential. So the first term U in this 0 to order average, what is it?

Well, that's my U. So I have to do a sum over i and j of V of qi minus qj. What does the averaging mean?

It means I have to integrate this over all qi divided by V. Let's call this qk divided V and this is [INAUDIBLE]. OK, so let's say we look at the first term in this series which

involves V of q1 minus q2. Let's say we pick that pair, q1 and q2. And explicitly, what I have here is integrals over q1, q2, qn, each one of them coming with a factor of V.

Now, of course, it doesn't matter which pair I pick. Everything is symmetric. The weight that I start with uniformly is symmetric. So clearly, my choice of this pair was arbitrary and the answer when I do the sum is the answer for 1 times the number of pairs, which is N N minus 1 over 2.

Now, over here I have integrals over q3 or qn, et cetera, that don't appear in the function that I'm integrating. So all of those integrals will give me factors of 1. And really, the only thing that I am going to be left with is these two integrals over q1 and q2. But even then, the function that I'm integrating is only a function of the relative coordinate that I can call q. And then I can, if I want, integrate over q1 and q. The integral over q1 would also give me 1 when I divide by the volume. So the answer is going to be N N minus 1 over 2, which is the number of pairs. The integral over the relative coordinate times the potential-- there is a factor of 1 over V that I can put out here. So you tell me what the first pair potential is and I tell you that this is the first correction that you will get once you multiply by minus beta to log Z from which you can calculate the partition functions. Yes.

AUDIENCE: How did you turn the product of two differentials d q1 times d q2 into just one differential?

PROFESSOR: OK, I have the integral dq q1 dq q2, some function of q1 minus q2. I change variables keeping q1 as one of my variables and q [INAUDIBLE] replace q2 with q minus q2. So then I have the integration over q1. I have the integration over q2. Not q2, but q f of q. And then everything's fine.

All right, so that's the first term. Let's calculate the next term.

Next term becomes somewhat interesting. I have to calculate this quantity as a Cumulant. It's the variance. V itself is a sum over pairs. So to get V squared to U squared, I have to essentially square this expression. So rather than having sum

over one pair ij, I have the sum over two pairs ij and kl. And then what I need to calculate is an average that if I were to square this, I will get v of qi minus qj, v of qk minus ql 0. This will be the average of U squared.

But when I calculate the variance, I have to subtract from it the average of U squared. So I have to subtract V of qi minus qj V of qk minus ql. Fine.

So this is just rewriting of that expression in terms of the sum. Now, each one of these is N N minus 1 over two terms. And so this, when I sum over all possibility, is the square of N N minus 1 over two possible terms that will occur here in the series that I've written.

Now, let's group those terms that can occur in this as follows. One class of terms will be when the pair ij that I pick for the first sum is distinct from the pair kl. So huge number of terms as I go through the pairs will have this possibility. OK, then what happens?

Then when I calculate the average of qi minus qj qk minus ql, which is this part, what I need to do is to do all of these integral of this form over all q's. And then I have this V of qi minus qj V of qk minus ql.

Now, my statement is that I have, let's say here, q1 and q2 and somewhere else q7 and q8. Or, q7 and q974. It doesn't matter. The point is that this integral that involves this pair of variables has nothing to do with the integral that involves the other pair of variables. So this answer is the same thing as the average of qi minus qj average of qk minus ql.

Essentially, in the 0 order probability that we are using, the particles are completely independently exploring this space and these averages will independently rely on one pair and independently rely on another pair. And once this kind of factorization occurs, it's clear that this subtraction that I need to do for the variance will get rid of this term. So these pairs do not contribute. No contribution.

If you like, this is this thing. All right, so let's do the next possible term, ij and ik, with k not equal to this k.

So basically, I make the pairs have one point in common. So previously, I had a pair here, a pair here. Now I joined one of their points. So what do I get here?

I will get for this average q_i minus q_j q_i minus q_l. You can see that essentially, the three integrals that I need to worry about are the integrals that involve these three indices. All the others will give me 0. So this is going to be the integral q_i q_j q_l divided by V. I have V of q_i minus q_j V of q_i minus q_l.

AUDIENCE: You switched [INAUDIBLE].

PROFESSOR: OK. I think that's fine. All right.

Now, I can do the same thing that I did over here. I have three variables. I will pick q_i to stay as one of my variables. I replace q_j with this difference, q j i. I replace q_l with its distance to i. And again, I can independently integrate over these three variables. So this again, becomes the same thing as V of q_i minus q_j average V of q_i minus q_l average. And again, there is no contribution.

Now, the first class it was obvious because this pair and this pair were completely distinct. This class is a little bit more subtle because I joined one of the points together, and then I used this and this as well as this point as independent variables. And I saw that the sum breaks into pieces. And you won't be surprised if no matter how complicated I make various more interactions over here, I can measure all of the coordinates with respect to the single point and same thing would happen.

This class of diagrams are called 1-particle reducible. And the first part had to do with distinct graphs. You didn't have to worry about them. But if I were to sort of convert this expression-- and we will do so shortly-- into graphs, it corresponds to graphs where there is a point from which everything else is hanging. And measuring coordinates with respect to that point will allow the average to break into pieces, and then to be removed through this subtraction. So this is simple example of something that is more general.

So at the level of this second-order theorem, the only type of thing that will survive is if the pairs are identical, ij and other term is also the same pair ij. What do I get then?

I get V of qi minus qj squared minus V of qi minus qj 0 order squared. So it's the variance of a single one of these bond contributions.

If I write that in terms of integrals, this becomes the integral d cubed q1, d cubed q2-- well, qi qj. I will have factors of V. Then, I would have V squared qi minus qj for the first term and then the square of something like this for the second term.

So putting everything together up to this order, what do I get? I will get log Z, which is log of Z0. Let me remind you, log of Z0 was N log of V over lambda cubed N. That's on form such as this.

And then I have these corrections. Note that both of the terms that have survived correspond to looking at one pair. So the corrections will be of the order of N N minus 1 over 2. Because in both cases, I really look at one pair.

The first contribution was minus beta integral d cubed q v of q. There was a factor of 1 over V. Actually, I can take-- well, let's put the factor of 1 over V here for the time being.

The next term will be beta squared over 2 because I am looking at the second-order term. And what do I have?

I have the difference of integral d cubed q over V V squared. And the square of the integral of d cubed q over V V. And presumably, there will be higher-order terms as we will discuss.

Now, I'm interested in the limit of thermodynamics where N and V are large. And in that limit, what do I get?

I will get log Z is log of Z0. And then I can see that these terms I can write as beta. N N minus 1 I will replace will N squared. The factors-- here I have a 1 over V. Here, I have 1 over V squared. So this factor is smaller by an amount that is order of V in

the large V-limit.

I will bring the factor of V outside, so I have something like this. And then, what do I have here?

Actually, let's keep this in this form, minus beta integral d cubed q V plus beta squared over 2 integral d cubed q V squared [INAUDIBLE]. So the kinds of things that we are interested and we can measure are the energy of the system, but let's say we focus on pressure.

And if you look through various things that we derived before, beta times the pressure you can get from taking a derivative of log Z with respect to V. We can express the log Z in terms of the free energy, and then the derivative of free energy with respect to volume will give you the pressure of the various factors of beta [? and signs, ?] we will come up with this.

So from the first term, N long V, we get our ideal gas result. Beta p is the same thing as density. And we see that we get a correction from here when I divide by-- when I take a derivative with respect to V of 1 over V, I will get minus 1 over V squared. So the next term would be the square of the density. And then, there is a series that we will encounter which depends on the interaction potential.

Now, it turns out that so far I have calculated terms that relied on only two points, ij. And hence, they become at the end proportional to density squared. If I go further in my expansion, I will encounter things that I will need triangular points. For example, i j k forming a triangle. And then, that would give me something that would be of the order of the density cubed.

So somehow, I can also see that ultimately this series in perturbation theory, as we shall see, also more precisely can be organized in powers of density. Why is that important?

Because typically, as we discussed right at the beginning, when you look at the pressure of a gas when it is dilute and over V is very small, it is always ideal gas-

like. As you make it more dense, you start to get corrections that you can express in powers of density. And the coefficients of that are called Virial coefficients. So in some sense, we have already started in calculating the second Virial coefficient, and there are higher-order Virial coefficients, which together give you the equation of states relating pressure to density by a power series.

AUDIENCE: Question.

PROFESSOR: Yes.

AUDIENCE: The Virial coefficients, if they have integral over the whole volume, then they will be functions of volume, right?

PROFESSOR: Yes. But imagine that I'm thinking about the gas in this room and the interaction of two oxygen molecules. So what I am saying is you pick an oxygen molecule. There is interaction and I have to integrate over where the other oxygen molecule is. And by the time it is tiny, tiny bit [? away, ?] the interaction is 0. It doesn't really matter.

AUDIENCE: If the characteristic volume of interaction is much smaller than volume--

PROFESSOR: Of the space.

AUDIENCE: [INAUDIBLE], then the integrals just converge to [? constant. ?]

PROFESSOR: That's right. So if you want to be even more precise, you will get corrections when your particles are close to the wall and uniformity, et cetera, is violated. So there will, actually, be corrections to, say, log Z that are not only proportional ultimately to number volume, but the area of the enclosure and other [? subleading ?] factors. But in the thermodynamic limit, we ignore all of that. So a lot of that is resolved by this statement here.

Again, you won't be surprised that if I were to go ahead, then there will be a term in this series that would be beta cubed over 3 factorial integral over q of vq, et cetera. And that's actually very good because as I have written for you currently, this expression is totally useless. Why is it useless?

Because let's think back about these two oxygen molecules in the gas in this room and what the potential of interaction between them would look like. Presumably, it is a function of the relative separation. We can call it r or q, it doesn't matter. And if you bring them closer than the typical size of these molecules, their potential will go to infinity. So basically, they don't want to come close to each other.

If you go very far away, typically you have the van der Waals attraction between the particles. So out here, it is attractive. The potential is negative and falls off, typically, as 1 over r to the 6 related to the polarizabilities of the particles. And these, when you come very short distances, the electronic clouds will overlap and the potential goes to infinity.

And if you want to sort of think about numbers, typical scales that we have here-- let's say here, are presumably of the order of angstroms. And the typical depths of these potentials in units that make sense to statistical physics are of the order of 100 degrees Kelvin. So it's why typical gases liquidy at range of temperatures that is of the order of 100 degrees Kelvin.

Now, if I want to take this potential and calculate this, I have trouble. Because the integral over here will give me infinity. So this expression is, in general, fine. But whenever you have perturbation theory, you start to evaluate things and you have to see whether the correction indeed is sufficiently small. And it seems we can't make it sufficiently small. Yes.

AUDIENCE: If you're modeling interatomic or intermolecular potential as a Lennard-Jones potential, isn't the [INAUDIBLE] term at the-- or near the origin, a phenomenological choice?

PROFESSOR: If you are using as a formula for this the Lennard-Jones potential, people phenomenologically write something like 1 over r to the 12th power, et cetera. But I don't have to assume that.

AUDIENCE: Right. Because I've seen forms of the Lennard-Jones potential which is exponentially decaying at the origin. So it reaches a finite, albeit probably high value

at the origin. Wouldn't that take care of the issue?

PROFESSOR: If you believe in that kind of potential, yes. So what you are saying is that if I make this come to a finite value, I will be able to find the temperature that is sufficiently high compared to this, and then things would be fine.

If we had that, then we would have fusion right here going on, right? So clearly, there is some better truth to a potential that is really very, very high compared to temperatures that we are looking at. So we don't have to worry about that.

Well, we have to worry about this issue. OK? All right.

So you say, well, how about the following-- let's say that I am something like the gas in this room and I am sufficiently dilute. I'm going to forget about these terms. But since this potential becomes essentially large, I can never ignore a particular term in this series. And I keep going adding more and more terms in the series.

If I sort of think back about the picture that I was generating before diagrammatically-- which again, we will clarify later on-- this term corresponds to taking a pair of points and a V that connects them. And this term corresponds to two V's going between the same pair of points. And you say, well, there will be terms that will involve three V's, four V's, and they will contribute in the series in a manner that I can recognize. So why don't I add all of those terms together? And if you like, we can call the resulting object something else. What is that something else?

Well, what I have done is I have minus beta V. Well, all of them-- so what is this?

It is the integral d cubed q. I have minus beta V plus 1/2 beta V squared. The next term is going to be minus 1 over 3 factorial beta V cubed because it will come from the third-order term in the expansion. And I can go on. And you say, well, obviously this whole thing came from the expansion of e to the minus beta V except that I don't have the 0 order term, 1. So this quantity that I will call f of q rather than V of q is obtained as e to the minus beta V of q minus 1.

So if I were to, in fact, add up an infinite number of terms in the series rather than

having to integrate V V squared V cubed, each one of them is divergence. I have to integrate this f of q. So let's see what this f of q-- or correspondingly, f of r looks like as a function of r.

So in the range that I have my hard core and V is large and positive, this is going to give me 0. So the function is minus 1 down here. At exactly whatever point it is that the potential is 0, then f is also 0. So basically, I will come to the same 0.

When the potential is negative, this will be larger than 1. My f will be positive. So presumably, it will have some kind of a peak around where this peak is. And then at large distances, it goes back towards 0. So this is going to go back towards 1 minus 1, which is 0. So actually, this end of the potential is the same thing as minus beta.

And whereas I couldn't integrate any one term in this series, I can certainly integrate the sum over all positions and it will give me a number, which will depend on temperature, the properties of the potential, et cetera. And it is that number that will tell me what the density squared term in the expression for the pressure is and what the second Virial coefficient is. Yes.

AUDIENCE: Is this basically an excluded volume of sorts?

PROFESSOR: Yeah. So this part if I sent it to infinity, corresponds to an excluded volume. So if you want really excluded volume, this would be minus 1 up to some point.

AUDIENCE: [INAUDIBLE].

PROFESSOR: Yeah. But I'm talking about very general, so I would say that excluded volume can be very easily captured within this [INAUDIBLE]. All right.

So we want to sort of follow-up from here. But since you will have a problem set, I will mention one other thing. That this reorganization of the series that I made here is appropriate to the limit of low densities, where I would have a nice expansion in powers of density.

The problem that you will deal with has to do with plasmas, where the interaction range is very large. And you already saw something along those lines when we had

the Vlasov equation as opposed to Boltzmann equation. There was a regime where you had to reorganize the series different ways. In that case, it was the BBGKY hierarchy whether you were looking at the dense limit or a dilute limit. So this is the analog of where the Boltzmann equation would have been inappropriate.

The analog of the regime where you are dense and something like the Vlasov equation would be appropriate. So there is some kind of interaction range, n d cubed if it is much larger than 1. Then it turns out that rather than looking at diagrams that have the fewest number of points-- in this case, 2-- you have to look at diagrams that have the largest number of points. Because each additional point will give you an additional factor of N over V.

You can see that these factors of N N minus 1 over 2 came from the number of points that I had selected. So if I had to select three points, I would have N cubed and the corresponding V. So the more points that I have in my series, I will have more powers of the density. So in that case, it turns out that rather than looking at two points and all lines between them, you organize things in terms of what are called ring diagrams, which are things such as this, this, this.

So basically, for a given number of lines, the most number of points is obtained by creating your ring. And so one of the problems that you have is to sort of sum these ring diagrams and see what happens.

But it seems like what I'm telling you here is while we calculated order of density squared, but maybe I want to calculate order of density cubed. And it makes much more sense rather than when faced with potentials of this form arranging the series in powers of the potential to arrange it in powers of this quantity e to the minus beta V minus 1. So let's go through a route in which I directly expand everything in terms of this quantity. And that's the second type of expansion that I will call the cluster expansion.

So once more, what we want to calculate is the partition function. It depends on temperature, volume, number of particles obtained by integrating over all degrees of freedom. The integration over momenta we saw is very simple. Ultimately, will

give us this N factorial lambda to the 3N. This time, I won't pull out the factor of V to the N at this point.

And then I have the integration over all of these q's. I did not divide by V because I did not multiply by V to the N. OK. And then I have e to the minus beta U, but this is my U. U is the sum of various terms. So e to the minus beta U will be a product over all, let's say-- let's call this k pairs ij. e to the minus beta V of qi minus qj.

So basically, the only thing that I did was e to the minus beta-- this quantity I wrote as a product of contributions from the different pairs.

Now, this quantity I have it in the line above. This is also a relative position. Clearly, I can think of this as 1 plus the f that would correspond to the distance between qi and qj. And again, I can either write it as Vf of qi minus qj, or simplify of i-- my notation-- and write it as f i j. So f i j means-- so let me maybe write it here. f i j I have defined to be e to the minus beta V of qi minus qj minus 1. So what do I expect?

I saw that the first correction to something that was interesting to me had one power of f in it that I had to ultimately integrate. So maybe what I should do is I should start organizing things in terms of how many f's I have. So an expansion in powers of f. So what's going to happen here?

I would have 1 over N factorial lambda to the 3N. I have a product of all of the integrations. And I have all of these factors of 1 plus f1 2 times 1. So basically, this is maybe-- it's really a product of 1 plus f1 2, 1 plus f1 3, 1 plus all of one of these things. So the thing that has least number of f's is when I pick the 1 from all of these brackets that are multiplying each other.

The next term is to pick 1f from one pair and all the others would be 1. The next term would be sum over ij kl f i j f k l, and then there will be diagrams that would progressively have more and more factors of f.

Now, what I will do is to represent the various terms that I generate in this series

diagrammatically. So first of all, I have to integrate over N points. So I put points 1 through N. So I have 1, 2, 3, 4. It doesn't matter how I put them-- N.

And then, this 1 would correspond to just this diagram. The next thing is I put a line for f i j. So let's say that I picked in this series the term that was f 2 3. I will represent that by a line that goes between 2 and 3.

Later on in the picture, maybe I will pick a term that is f 2 3 f 4 5. So some second-order term could be something like this.

Maybe later on in the series, I will pick a term that is connecting f3 and f4. So this would be a third-order term in the series.

Maybe later on the series, I have some other pair over here. So any one of the huge number of terms that I have generated here has one diagram that is appearing over here.

Now, the next step is, of course I have to integrate over all of the q's. I mean, these diagrams, what they represent is essentially some f of q1 minus q3, some f of whatever. And I have to integrate over all of these q's. So the contribution to the partition function that I will get would be some value associated with one of these graphs obtained by doing the integrations over q.

Now, the thing that I want you to notice is that contribution of one of these graphs or diagrams is the product of contributions of its linked clusters.

So here I have one particular diagram that is represented here. Well, let's say 2, 3, 4, 5 are linked together and separate from whatever this is. Let's say this is 7, 9.

So when I do the integrations over q2, q3, q4, q5, I don't really rely on any of the other things. So my integration here, we break off into the integration that involves this, the integration that involves this, as well as integrations over all of these points that are not connected to anybody. All of those will simply give me a factor of v.

So is everybody happy with this simple statement that the contribution-- if I think of these linked clusters as some collection of points that are linked together, the value

that I would get for this diagram would be the contribution-- product of the contributions that I would have for this. So yes?

AUDIENCE: Can you explain [INAUDIBLE]?

PROFESSOR: OK. So let's pick a particular thing. Let's say we do something like this, where this is number 7, 245, 6, 5, 4. This is a particular thing. So what do I have to do?

There's also a whole bunch of points-- 1, 2, 3. What I am instructed to do is to integrate over q_1, q_2, q_3, et cetera.

Now, the integral over q_1 is just the integral of q_1. So this integral by itself will give me V. Any number of points that are by themselves will also give me V. So the first term that becomes nontrivial is when I have to do the integration over q_4, q_5, q_6 of f 4 5, f 5 6, f 6 4.

I don't know what this is, but there is something that will come from here. Then, later on I have to integrate over 7 and something else. So then I have the integral over q_7, q-- let's call this 8. f of 7 8. So this is something else.

So the overall value of this term in the perturbation theory is the product of contributions from a huge number of one clusters. Here, I have a two cluster. Here, I have a three cluster. Maybe I will have more things.

Also, notice that if I have more of these two clusters, the result for them would be exactly the same. So if I have lots of these pairs, the same way that I had lots of single points-- and it became V to the number of single points-- it will become whatever that y is to the number of pair points, x, whatever that is, to the number of triplets that I have in triangles. So this is how this object is built up. Yes?

AUDIENCE: How are we deciding how many triplets and how many pairs we actually have?

PROFESSOR: At this point, I haven't told you. So there is a multiplicity that we have to calculate. Yes. So at this point, all I'm saying is given this, the answer is the product of contribution. There is a multiplicity factor-- you're right. We have to calculate that.

OK? Anything else?

All right. So I mean, think of this as taking a number and writing it as the product of its prime factors, factorizing into primes. So you sort of immediately know that somehow prime factors, the prime numbers, are more important. Because everything else you can write as prime numbers. So clearly, what is also buried in heart of calculating this partition function is these clusters. So let me define the analog of prime numbers as follows.

I define bl to be the sum over contributions of all linked clusters of l-points. So let's go term by term. b1 corresponds essentially to the one point by itself in the diagram that I was drawing down here. And corresponds to integrating over the coordinate that goes all over the space. And hence, the volume is the same thing as the volume V.

b2 is a cluster of two points. So it is this. And so it is the integral over q1 and q2, which are two endpoints of this, of f of q1 minus q2. And this we have seen already many times. It's the same thing as volume, the integral over q f of q. It is the thing that was related to our second Virial coefficient.

Now, this is very important for b3. I note that I underlined here "all." And this is for later convenience. It seems that I'm essentially pushing complexity from one place to another. So there are a number of diagrams that have three things linked together. This is one of them. Let's say, think of 1, 2, 3 connected to each other.

But then, I have diagrams. At this stage, I don't really care that this is one particle irreducible. Here, I have no constraints on one particle irreducibility. And in fact, this comes in three varieties because the bond that is missing can be one of three. So once I pick the triplets of three points, sum over all clusters that involve these three points is this, in particular with this one, appearing three times. Yes.

AUDIENCE: Do we still count all the diagrams when particles are identical?

PROFESSOR: Yes. Because here, at this stage, there is an N factorial out here. All I'm really doing is transcribing a mathematical formula. The mathematical formula says you have to

do a bunch of integrations. And I am just following translating that mathematical formula to diagrams. At this stage, we forget. This has nothing to do with this N factorial or identity. It's just a transcription of the mathematics

So at this stage, don't try to correct my conceptual parts but try to make sure that my mathematical steps are correct. OK? Yes.

AUDIENCE: I didn't understand what that missing links represents.

PROFESSOR: OK. So at the end of this story, what I want to write down is that the value of some particular term in this series is related to product of contributions. I described to you how productive contributions comes along. And each contribution is a bunch of points that are connected together. So what I want to do, in order to make my algebra easier later on, is to say that-- let's say these three points are part of a cluster. They are connected together somehow. So they will be giving me some factor.

Now, they are connected, if they are connected like this, like this, like this, like that. So basically, any one of these is a way of connecting these three points so that they will make a contribution together. Yes.

AUDIENCE: So the one with all three bonds comes with a different [INAUDIBLE] in the series than the ones with only two bonds, right?

PROFESSOR: Yes. Now, there is reason, ultimately, why I want to group all of them together. Because there was a question before about multiplicity factors. I can write down a closed form, nice expression for the multiplicity factor if I group them together. Otherwise, I have to also worry that there are three of these and there is one of them, et cetera. There is an additional layer of multiplicity. And I want to separate those two layers of multiplicity.

So here, the thing that I have is I have these endpoints. I want to say that the eventual result for endpoints comes from clusters that involves 1's, clusters that involve pairs, and cluster that involve triplets.

Now, I realize suddenly that if I made the multiplicity count here, then for this triplet, I could have put all of them together like this or like that. And the next order of business when I am thinking about four objects, I can connect them together into a cluster in multiple ways. And there is a separate way of calculating the relative multiplicity of what comes outside and the multiplicity of this quartic with respect to entirety. So you have to think about this a little bit. So I'll proceed with this.

So this mathematically would be the integral q_1, q_2, q_3, f_{12}, f_{23}, f_{31} plus, say, f_{12}, f_{23}, plus f_{13} f_{32} plus f_{23}, f_{31}, something like this.

Well, 1, 2. 2 is repeated. 3 is repeated. I should repeat 1. OK. Of course, the last three are the same thing, but this is the expression for this.

Now, before would be a huge complex of things. It would have a diagram that is of this form. It would have a number of diagrams that are of this form. It would have diagrams that are of this form, diagrams that are like this, and so forth.

Basically, even within the choice of things that have four clusters, there is a huge number when you go to further and further [? down. ?]

OK, so maybe this statement will now clarify things. So what I have is that the partition function is 1 over N factorial lambda to the 3N. And then it is all of the terms that are obtained by summing this series. And so I have to look at all possible ways that I can break N-points into these clusters.

Suppose I created a situation where I have clusters of size l and then I have nl of them. So I saw that the contribution that I would get from the 1 clusters was essentially the product of the number of 1 clusters. It was V to the number of points that are not connected together. So I have to take b_1, raise it to the power of N_1, which is the number of 1 cluster. Then, I have to do the same thing for b_2, b_3, et cetera.

And then I have to make sure that I have looked at all ways of partitioning N the numbers into these clusters. So I have a sum over nl l has to add up to n. And I have to sum over all nl's that are consistent with this constraint. But then there is

this issue of the multiplicity.

Given that I chose some articular set of these, if I were to reorganize the numbers, I would get the same contribution. So let's say we pick this diagram that has precisely a contribution that is V, which is b1 to the number of these one points. This to the number of b2 to the power of the number of these, this, et cetera.

But then I can take these labels-- 1, 2, 3, 4, 5, 6-- that I assigned to these things and permute them. If I permute them, I will get exactly the same contribution. So there is a large number of diagrams that have exactly this same contribution because of this permutation. There was a question back there.

AUDIENCE: You've already answered it.

PROFESSOR: All right. Actually, this is an interesting thing-- I don't know how many of you recognize this. So essentially, I have to take a huge number, N, and break it into a number of 1 clusters, 2 clusters, et cetera. The number of ways of doing that is called a partition of an integer. And last century, the [INAUDIBLE] calculated what that number is. So there is a [INAUDIBLE] theorem associated with that. And actually, later in the course I will give you a problem to calculate the asymptotic version of the [INAUDIBLE]. But this is different story.

So given that you had made one of these partitions of this integer, what is this degeneracy factor? So let me tell you what this degeneracy factor is.

So given this choice of nl's, you say-- well, the first thing is what I told you. For a particular graph, the value is independent of how these numbers were assigned. So I will permute those numbers in all possible ways and I will get the same thing. So that will give me N factorial. It's the number of permutations.

But then, I have over-counted things because within, let's say, a 2 cluster-- if I count 7, 8, 8, 7 they are the same thing. And by multiplying by this N factorial, I have over-counted that. So I have to divide by 2 for every one of my 2 clusters. So I have to divide by 2 to the power of N2.

For the 3 clusters, I have the permutation of everything that is inside. So it is 3 factor here. So what I have here is I have to divide by the over-counting, which is l factorial-- labels within a cluster-- to the number of clusters that I have that are subject to this.

There is another thing that this pair is 100, 101 and this pair is 7, 8. Exchanging that pair of numbers with that pair of numbers is also part of the symmetries that I have now over-counted. So that has to be taken into account because the number of these 2 clusters here is 2. Here is actually 3. I have to divide by 3 factorial. In general, I have to divide by nl factorial.

OK. Again, this is one of those things that the best advice that I can give you is to draw five or six points so your n is small. And draw some diagrams. And convince yourself that what I told you here rapidly is correct. And it is correct. Yes.

AUDIENCE: Can you just clarify which is in the [INAUDIBLE]?

PROFESSOR: OK. So the N factorial is outside. And then-- so maybe write it better. For each l, I have to multiply nl factorial and l factorial to the power of nl. So this is my partition function in terms of these clusters.

Even with all of these definitions that I have up there, maybe not so obvious an answer. And one of the reason it is kind of an obscure answer is because here I have to do a constrained sum. That is, I have all of these variables. Let's call them n1, n2, n3, et cetera. Each one of them can go from 0, 1, 2, 3. But they are all linked to each other because their sum is kind of restricted by some total value l, by this constraint.

And constrained sums are hard to do. But in statistical physics, we know how to gets rid of constrained sums. The way that we do that is we essentially allow this N to go all the way.

So if I say, let's make-- it's very hard for me to do this n1 from 0 to something, n2 from 0 to something with all of this constrained. My life would be very easier if I could independently have n1 go take any value, n2 take any value, n3 take any

value. But if I do that essentially for each choice of n1, n2, n3, I have shifted the value of big N.

But there is an ensemble that I know which has possibly any value of N, and that's the grand canonical. So rather than looking at the partition function, I say I will look at the grand partition function Q that is obtained by summing over all N. Can take any value from 0 to infinity. I have e to the beta mu N times the partition function that is for N particles. So that's the definition of how you would go from the canonical where you have fixed N to grand canonical where you have fixed the chemical potential mu. So let's apply this sum over there.

I have a sum over N, but I said that if I allowed the nl's to vary independently, it is equivalent to varying that N, recognizing that this n is sum over l l nl. That's the constraint. So that's just the first term. I have rewritten this sum that was constrained and this sum over the total number as independent sums over the nl's. Got rid of the constraint.

Now, I write W. Oh, OK. The partition function. Now, write the partition function.

I have 1 over N factorial. I have lambda cubed raised to this power. So actually, let me put this in this fashion. So both e to the beta mu over lambda cubed that is raised to that power. OK, so that's that part.

The sum I have gotten rid of. I notice that my W has an N factorial. So this is the N factorial that came from here. But then there is an N factorial that is up here from the W. So the two of them will cancel each other, N factorial.

And then I have a product over all clusters. Part of it is this bl to the power of nl, and then I have the contribution that is nl factorial l factorial to the power of nl. So this part cancels. For each l, I can now independently sum over the values of nl can be anything, 0 to infinity. And what do I have?

I have bl to the power of nl. I have division by nl factorial. I have l factorial to the power of nl. And then I have e to the beta mu over lambda cubed raised to the power of l nl.

I recognize that each one of these terms in the sum is 1 over nl factorial something raised to the power of nl, which is the definition of the exponential. So my q is a product over all l's. Once I exponentiate, I have e to the beta mu over lambda cubed raised to the power of l. And then I have bl divided by l factorial.

Or, log of Q, which is the quantity that I'm interested, is obtained by summing over all clusters 1 to infinity e to the beta mu over lambda cubed raised to the power of l bl divided by l factorial. So what does this tell us, which is kind of nice and fundamentally important?

You see, we started at the beginning over here with a huge number of graphs. These graphs could be organizing all kinds of clusters. And they would give us either the partition function or summing over N, the grand partition function. But when we take the log, I get only single connect objects.

And this is something that you had already seen as the connection that we have between moments and Cumulants. So the way that we got Cumulants was to look at the expansion of the log. So the function itself was the generator of all moments and we took the log. And graphically, we presented that as getting the moments by putting together all kinds of clusters of points that corresponded to Cumulants. And this is again, a representation of the same thing. That is, in the log you have essentially individual contributions. Once you exponentiated, you get multiple contributions.

Now, the other thing is, that if I am thinking about the gas, then log of Q is e to the minus beta g. And g is E minus TS minus mu N. Bur for a gas that has extensive properties, E is TS mu N minus PV. So this is the same thing as beta PV. So this quantity that we have calculated here is, in fact, related to the pressure directly through this formula.

And the important part or the important observation is that it says that it should be proportional to volume. You can see that each one of my b's that I calculated here will have one free integral. If you like, its center of mass. You can go over the entire

volume. So all of my b's are indeed proportionality to volume. And you can see what disaster it would have been if there was a term here that was not just a linked cluster but product of two linked clusters. Then I would have something that would go like V squared. It's not allowed. So essentially, this linked cluster nature is also related to extensivity in this sense.

So in some sense, what I have established here-- again, related to that-- is that clearly all of my bl's are proportional to volume. And I can define something that I will call bl bar, which is divide the thing by the volume. And then what we have established is that the pressure of this interacting gas as an expansion beta p, which takes this nice, simple form, sum over l e to the beta mu divided by lambda cubed bl bar-- the intensive part of the contribution of these cluster-- divided by l factorial. This, of course, runs from 1 to [INAUDIBLE]. Yes.

AUDIENCE: [INAUDIBLE] is raised to the l?

PROFESSOR: Who's asking the question?

AUDIENCE: The term in the parentheses is raised to the l?

PROFESSOR: Exactly. Thank you very much. Yes.

AUDIENCE: [INAUDIBLE]. But they don't, actually. Could that be true, for example [INAUDIBLE]?

PROFESSOR: OK. So the triangle, I have it here. Integral d q1, d q2, d Q3, f 1 2, f 2 3, f 3. Let's write it explicitly. It is f of q1 minus q2, f of q2 minus q3, f of q3 minus q1. I call this vector x. I call that vector y. This vector is x plus y. Yes.

AUDIENCE: Does the contribution from [INAUDIBLE]?

PROFESSOR: OK. So you say that I have here an expansion for the pressure. I had given you previously an expansion for pressure that I said is sensible, which is this Virial expansion, which is powers of density. This is not an expansion in powers of density.

So whether or not the terms in this expansion becomes smaller or larger will depend

on density in some indirect way. So my next task, which I will do next lecture, is within this ensemble I have told you what the chemical potential is. Once I know what the chemical potential is, I can calculate the number of particles as d log Q by d beta mu. And hence, I can calculate what the density is. And so the answer for this will also be a series in powers of e to the beta mu. And what then I will do is I will combine these two series to get an expansion for pressure in powers of density, and then identify the convergence of this series and all of that via that procedure.