Foundations of Computational Materials Modelling
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Introduction to phase average and time average
Lecture 23

So, let us continue with the class and discuss what we were from where we left off. So, let me do a small recap. We covered a lot of stuff last class but I only want you to understand most of it qualitatively rather than quantitatively okay, because some of these derivations can be a little bit complicated. I will just briefly outline some of the key features of what we did last class which I want you to remember.

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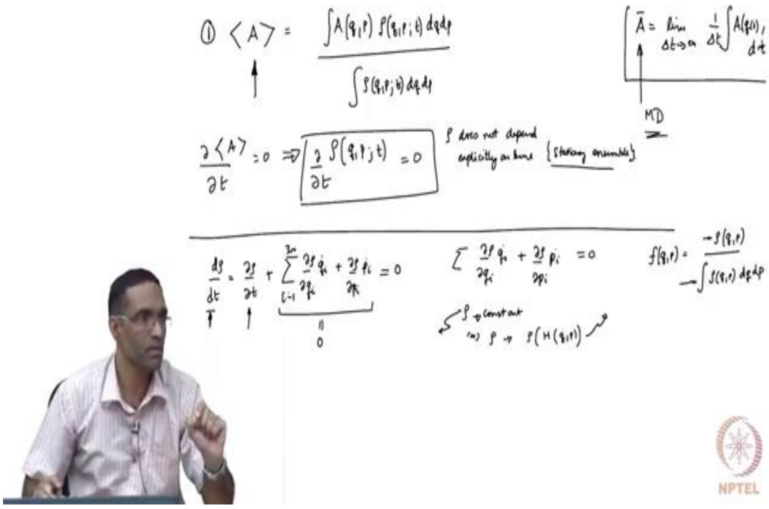


① $\langle A \rangle = \frac{\int A(q,p)\,\rho(q,p;t)\,dq\,dp}{\int \rho(q,p;t)\,dq\,dp}$

$\bar{A} = \lim_{\Delta t \to \infty} \frac{1}{\Delta t} \int A(q(t), \; dt$

MD

$\frac{\partial \langle A \rangle}{\partial t} = 0 \Rightarrow \boxed{\frac{\partial}{\partial t} \rho(q,p;t) = 0}$ ρ does not depend explicitly on time {stationary ensemble}

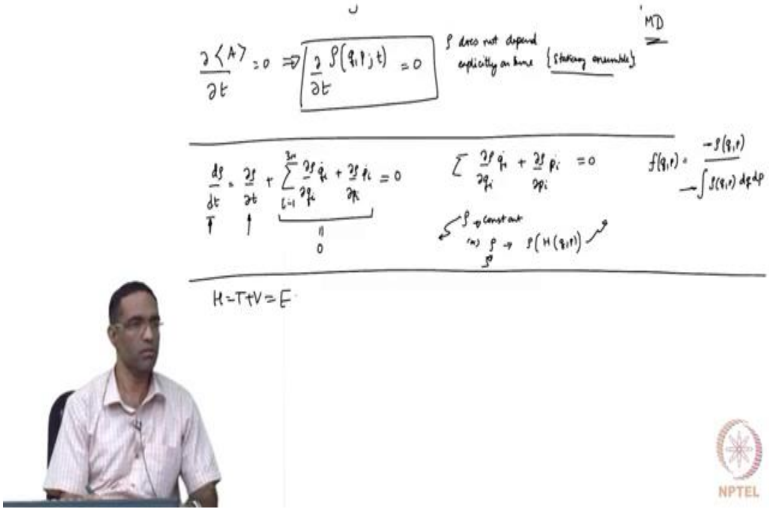
$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \underbrace{\sum_{i=1}^{3N} \frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i}_{0} = 0$

$\sum \frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i = 0$

$f(q,p) = \frac{\rho(q,p)}{\int \rho(q,p)\,dq\,dp}$

ρ → constant

(or) ρ → ρ(H(q,p))



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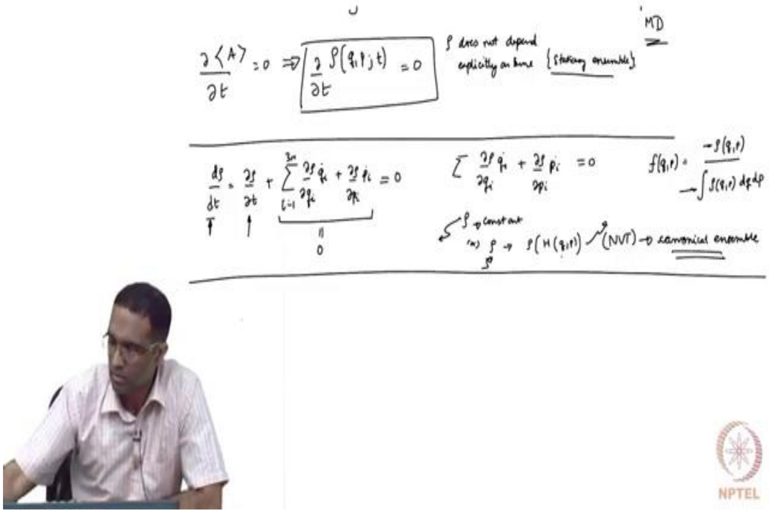
$f(q,p) = \frac{\rho(q,p)}{\int \rho(q,p)\,dq\,dp}$

ρ → constant

(or) ρ → ρ(H(q,p))

$H = T + V = E$



So, firstly what we did was, we talked about the phase average of a quantity and we said that it is equal to if you knew the functional form of that particular physical quantity as a function of q and p, the generalized coordinates and generalized momentum and you knew this function rho which is also a function of q, p and maybe explicitly a function of t than is basically the phase average of this particular quantity.

As this system is actually sampling the phase space, the various points of phase space. This is so one way to basically write down the phase average of this particular quantity. And we the reason why we brought this in the picture was, we had another expression that looks something like this, right limit delta t tends to a very large quantity 1 over delta t integral A of q of t, p of t dt right.

And so this in order to evaluate this particular quantity, it is important for us to know how q and p evolves with time and for complicated system comprising of a very large number of atoms, it will be impossible for us to theoretically solve these solve for these unknowns. solve for the variation of q and p with time.

So, we take a different approach called as the phase space approach where we say that we get this quantity and this quantity we wave our hands and say that this quantity, the phase average and the time average have to be equal, okay. There are proofs or there are arguments that can be made in order to say that these two are equal but it is not too hard for us to intuitively understand that if we take a large number of points in phase space, it is most likely to get all the points, the p and q are traversing even with time, okay.

In molecular dynamics stimulations, we generally use the time average but in statistical mechanics, we generally talk about this face average. Now, this phase average gives additional useful information. Primarily, we said that, if this quantity average of A has to be independent of time, independent of time, then it kind of implicitly implies that this density function should also be not be explicitly should also not be explicitly dependent on time, right.

We make the statement and I would like to know point out such a ensemble for which rho does not depend explicitly on time is called as stationary ensembles, okay. So, if rho is not explicitly depend on time, it is called as stationary ensemble and obviously a stationary ensemble is a good ensemble to have to depict systems which are at equilibrium.

Simply because it is average coded does not vary with time which is what our observation tells us. Now, then we switch gears a little bit be wrote down this equation right here. We wrote down this equation right here. And we said that this has to be 0, correct? We did not prove it, we just told you that this has to be 0, can be kind of compared it with the mass balance equation and talking about incompressible the points in phase space move like an incompressible fluid.

So, if this has, this is anyway 0, this is always 0 and we want dou rho by dou t also to be 0. Then one of the condition that the rho must satisfy is that this quantity must also be 0. This quantity right here and which I have marked. And for this quantity to be 0, for to be equal to 0, what must happen, we said that rho can either be a constant or if rho happens to be an explicit function of p and q only through the Hamiltonian, even then this turns out to be 0, right, remember this? So, these are the two conditions for which this term here turned out to be 0.

Now, this is something that we can derive right now, okay. It so happens that, the probability density, this is nothing but the probability, this is nothing but the density, right, number of points per unit volume and the probability density which we will now represent using f, is nothing but rho of q , p divided by integral rho of q , p dq dp, right integrated over the entire phase space.

This is number of the numerator here, is the number of points per unit volume. This is the total number of points, right? So, number of points per unit volume divided by total number of points is some kind of measure of the probability density, the probability that a certain in a certain given volume dp dq, you find the value p q. That is what it means, right.

What we are going to try to do now is, we are going to see under what conditions or I am going to tell you under what conditions rho happens to be explicitly depended on H okay and for conservative systems, H or the Hamiltonian is nothing but, what is it? What is H? T plus V. So, the kinetic energy plus a potential energy and is nothing but the energy, total energy of the system. For conservative systems, the Hamiltonian is nothing but the energy of the system.

So, what happens is that, you can find out that this rho is apparently dependent explicitly on the energy of the system. That is what we are going to do now. So, this happens to be the case for the NVT ensembles or the Canonical ensembles. So, whether rho is explicitly dependent on H or f is explicitly dependent on H does not matter. It all means the same thing. So, now how do we do this?

So, first I am going to do this derivation where I show you that this rho explicitly depended on H or f explicitly depends on H or the energy through a simple intuitive means and then we will do a slightly more, a slightly different approach giving us exactly the same result.

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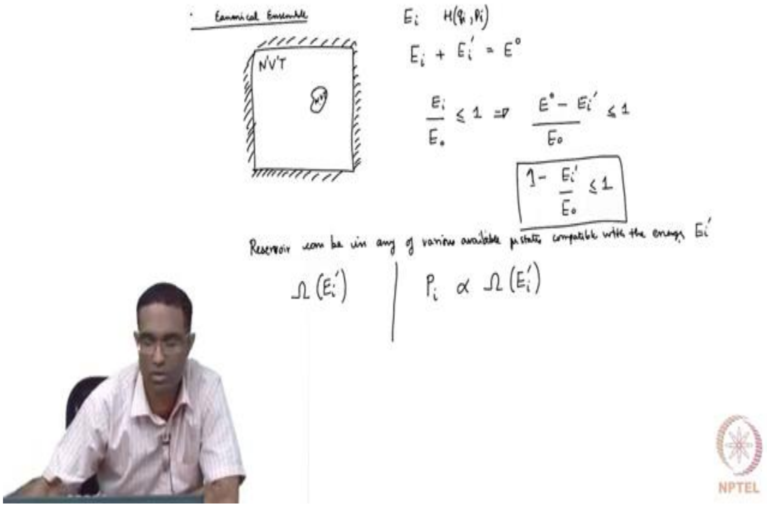


Canonical Ensemble

$E_i \quad H(q_i, p_i)$

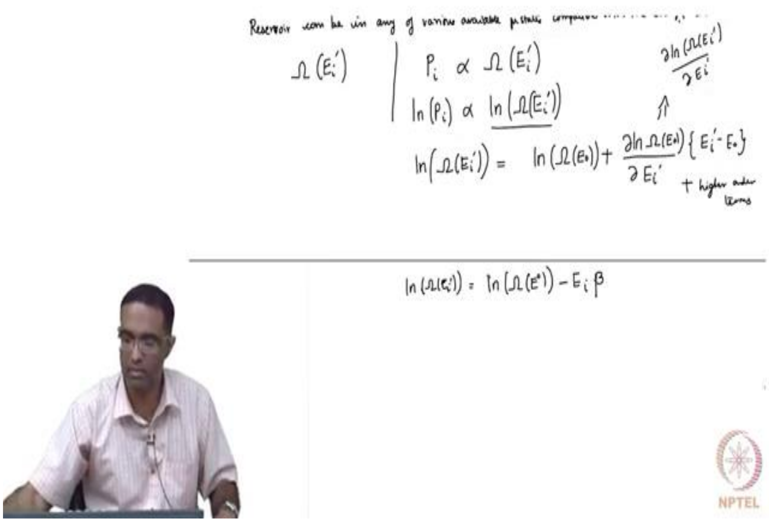
$E_i + E_i' = E^0$

$\frac{E_i}{E_0} \leq 1 \Rightarrow \frac{E^0 - E_i'}{E_0} \leq 1$

$\boxed{1 - \frac{E_i'}{E_0} \leq 1}$

Reservoir can be in any of various available μ-states compatible with the energy E_i'

$\Omega(E_i') \quad \Big| \quad P_i \propto \Omega(E_i')$



Reservoir can be in any of various available μstates [illegible]

$\Omega(E_i')$

$P_i \propto \Omega(E_i')$

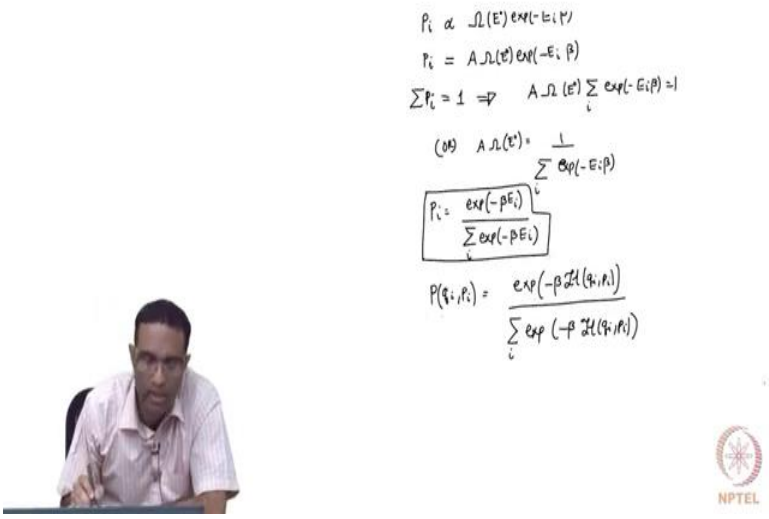
$\ln(P_i) \propto \underline{\ln(\Omega(E_i'))}$

$\frac{\partial \ln(\Omega(E_i'))}{\partial E_i'}$

$\Uparrow$

$\ln(\Omega(E_i')) = \ln(\Omega(E_0)) + \frac{\partial \ln \Omega(E_0)}{\partial E_i'}\{E_i' - E_0\}$ + higher order terms

$\ln(\Omega(E_i')) = \ln(\Omega(E^0)) - E_i\beta$



$P_i \propto \Omega(E^0)\exp(-E_i\beta)$

$P_i = A\Omega(E^0)\exp(-E_i\beta)$

$\sum P_i = 1 \Rightarrow A\Omega(E^0)\sum_i \exp(-E_i\beta) = 1$

(OR) $A\Omega(E^0) = \frac{1}{\sum_i \exp(-E_i\beta)}$

$\boxed{P_i = \frac{\exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}}$

$P(q_i, p_i) = \frac{\exp(-\beta \mathcal{H}(q_i, p_i))}{\sum_i \exp(-\beta \mathcal{H}(q_i, p_i))}$

So, let us consider the micro canonical ensemble, sorry the canonical ensemble, I mean the canonical ensemble. The canonical ensemble represents a system at constant number of atoms, constant volume and constant temperature. So, this is our system here N, V and T. So, it may be at some arbitrary temperature initially, but what we are going to do is, we are going to take this entire system and equilibrate it with a large reservoir.

So this is our N, V, T okay and this is our N prime, V prime and T. So, this is the large reservoir which is also and isolate these two systems. What is that? So, they are both in thermal equilibrium with each other. We are waiting long enough so that, so basically there large reservoir is at temperature T.

So, if we have to bring this smaller system to temperature T, we just put it inside and wait until equilibrium has been reached, okay. This is very large. So, now at any instant of time till the question that we want to ask, okay the question, the actual question that we want to ask is, what is the probability that this system that is there right here has an energy E I, what is the probability the system has an energy E i? Or in other words, has an Hamiltonian corresponding to some q i comma p i.

Both are the same questions, right because the energy and Hamiltonian are the same things for conservative systems. So, what I am going to do now first, at any instant of time, at any instant of time T okay, the system may have energy E i. And the reservoir could be having energy E i fine, right? However, the sum of both these energies can be in any of the various available micro states compatible with the energy E i prime, right.

The reservoir by itself can have various different, it can be with energy E i prime, but have different so many different micro states. So, let omega E i prime be the total number of micro states that is possible for the reservoir. Now, so the larger the number of, the larger the number of micro states, for this particular energy E i prime, the greater is the probability that you will find the reservoir in the energy state E i prime.

Which means, the greater the probability that you will find the system at energy E i, correct? So, P i which is nothing but the probability that the system is at energy E i, is actually propositional to this quantity E i prime, this E i prime remember it is extremely close to E naught because of the sheer size of it. It is a huge reservoir. Which also means, for the purposes of getting specific thermodynamic quantities, I am going to write it as this, okay, which is the same. I have just taken logarithm on both sides.

Now, I can expand this quantity above E naught. Yes.

Student: How Ei prime is related to the probability of the energy of the system?

Professor: Okay, so omega E i prime is a total number of micro states that the reservoir is in okay, the larger the number of micro states available for the reservoir to be in E i prime, the greater the probability that it is actually in E i prime or which essentially means, the greater the probability that the system is in energy E i, because E i prime minus E naught is E i. Isn’t it?

Student: Because E i prime is less probability that is E i

Professor: The system is in E i, because E naught is a constant. If omega, the greater the probability that the reservoir is in the energy E i prime, the greater the probability that the system is in energy what? E i, not anything else. Yes?

Student: How are we making the response of E naught with respect to reservoir?

Professor: So, that we can write a expansion about E not, as you will see. Like I told you this is this is a simpler version of the derivation that I am about to show after this, okay. The reason is, if you expand basically you will get a you get the expression more quickly than through a longer procedure. So, that is it, okay. So, if you take this log of omega E i prime and expand it about E naught, what would you get?

Log of omega evaluated at E naught plus dou log omega E naught with respect to dou E i prime multiplied by E i prime minus E naught plus higher order terms. And I continue here, it becomes log of omega E i prime is equal to log of E not. So, this, what is this E i prime minus E naught is what? E i prime minus E naught is minus of E I, right.

E i prime minus E naught will be minus of E I, minus of E i. And what you think this quantity is, dou log omega E naught by dou log E i prime? No, it is not very legit, it is a thermodynamic quantity. The number of micro states with respect to log of the number of micro states with respect to the energy. We have seen that before. Dou log omega by dou E beta that is the beta quantity or 1 by K t quantity, is not it?

So, however, this is again this is, that is too provided again I approximate this as dou log omega of E i prime with respect to dou log E i prime, right? Because I am saying that I am waving my hands and saying that E naught and E i prime are pretty close to each other. Consequently, this becomes beta. So, what you get here is, the log of P i, the probability that, that the system is at energy E i is propositional to this quantity, right here, log of omega E naught minus E i times beta.

Again which means, P i is proportional to omega E naught times exponential minus E i times beta. Now, again I can include some sort of a constant here, is equal to A omega E naught exp minus E i beta. However, what is this quantity? Summation of probability that is in any energy E i is 1, which implies that A omega E naught summation over all energy states is equal to 1.

Or I can substitute, I can find out what this A omega E naught to be equal to 1 divided by summation over i or the probability that the system is at energy E i is, right? Is this okay? We will do this in a slightly different way also. This can also be written as, probability that I find certain q and p to be equal to exp minus beta. the Hamiltonian at p i q i divided by i exp minus beta. Okay, this is the probability, actual probability. So, this is the probability that you find q i p I, right.

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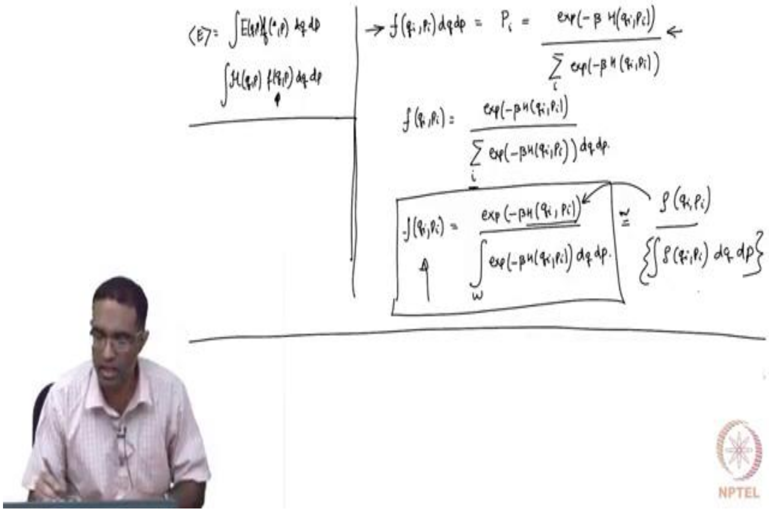

$$\langle E\rangle = \int E(q,p) f(q,p)\, dq\, dp$$

$$\int H(q,p) f(q,p)\, dq\, dp$$

$$\rightarrow f(q_i,p_i)\, dq\, dp = P_i = \frac{\exp(-\beta H(q_i,p_i))}{\sum_i \exp(-\beta H(q_i,p_i))} \leftarrow$$

$$f(q_i,p_i) = \frac{\exp(-\beta H(q_i,p_i))}{\sum_i \exp(-\beta H(q_i,p_i))\, dq\, dp}$$

$$\boxed{f(q_i,p_i) = \frac{\exp(-\beta H(q_i,p_i))}{\int_w \exp(-\beta H(q_i,p_i))\, dq\, dp}} \simeq \frac{\rho(q_i,p_i)}{\left\{\int \rho(q_i,p_i)\, dq\, dp\right\}}$$

Now, we can write the following, we can say, f probability density times some infinite decimal volume element in the phase space d q, d p is actually equal to P i. Probability per unit volume times the unit volume is going to give you the probability, correct? Now this is equal to this quantity right here which means f of q i comma p i is equal to, okay.

So, this summation, is this okay? This sentence, this particular expression is alright. Probability per unit volume times the unit volume give you the probability, right? So, that is what is P i, which is basically the right hand side. This exp minus beta H divided by summation over all the other states.

Therefore, this f probability density is supposed to be this quantity right here. I just brought this d p, d q here. You might, if you are very rigorous in your mathematics you may script okay but we have to do this in order to make the expression appear correct in a simpler manner, okay.

So now this f q i p i is equal to, now this summation is assuming that this p i's, qp i's and qi's are discrete quantities. However, in phase space they are all, they can all be treated as continuous quantities, in phase space, right. You have p's and q's so close to each other they are always like a continuous, continuous set of points, right? They are all moving from one point to the other through time. So, we can replace this expression by the following.

So, this is the probability density, means the probability per unit volume that you can actually find a point q I, p i and is depends on what? The Hamiltonian or the energy of the system which is the same as which is the same as rho q i comma p i divided by integral row q i comma p i dq, dp. Which means, the row is proportional to exp minus beta H q i p i. Or in other words, rho is proportional or a function of is proportional to a function explicitly of the Hamiltonian of the system, okay.

So, this is one way of showing that the most important quantity here is this, the probability that you find a system at energy E i is given by this. So if the system is at NVT, you are maintaining the number of atoms or the number of atoms, the volume and the temperature of system then, if you ask a question, What is the energy, what is the probability that the energy is something j joule some k joules. Then this expression is giving you that the probability, okay.

So, what would be the, what is the average energy of the system? So, the average energy of the system or any quantity is nothing but integral, the energy E r times f or the average energy is nothing but the Hamiltonian the probability that, that particular p and q occur. And this is nothing but this. So you have to substitute this here and perform the integration to find the average energy of the system.

Which is what the systems energy will at, at what? Equilibrium, right? But we are not going to do this this calculation, okay. It is enough you know that this is how it would appears. Now we did something that I sure you have questions about why we did this!? Do you have questions? Or I am going too fast, okay. E is the, E f q comma p. The energy of the system that q comma p and f gives you the probability per unit volume that a q comma p can be found integrated over the entire phase space is going to give you the average energy of the system, okay.

So, E, E of q comma p or H of q comma p is nothing but half M V square plus the potential energy of the system. So, you can in principle now if you want to find out the average energy of a gas at a particular temperature T, you can find it out by just substituting for H, the kinetic energy of the system.

Rho and f, rho is number of points per unit volume that is rho. F is number of points per unit volume divided by total number of points. Therefore, it is a probability, probability density. Rho is number density, number per unit volume that is the difference.

Correct? Yes or No? A second thing that you can look at is again what is this? This denominator here is what? Integral of rho q i p i dq dp must be must be proportional to the total number of points, need not be equal to the total number of points. right? Is proportional to the total number of points because the common factor in the numerator and denominator may have cancelled out when we calculating the probability density, right?

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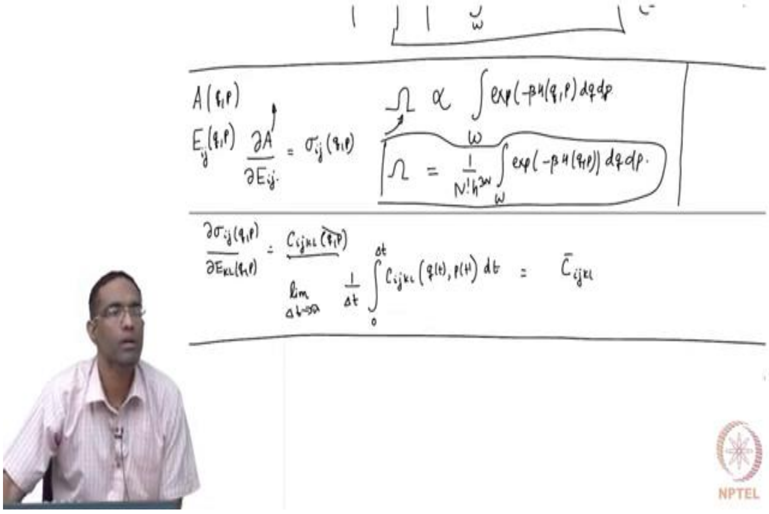


$A(q,p)$

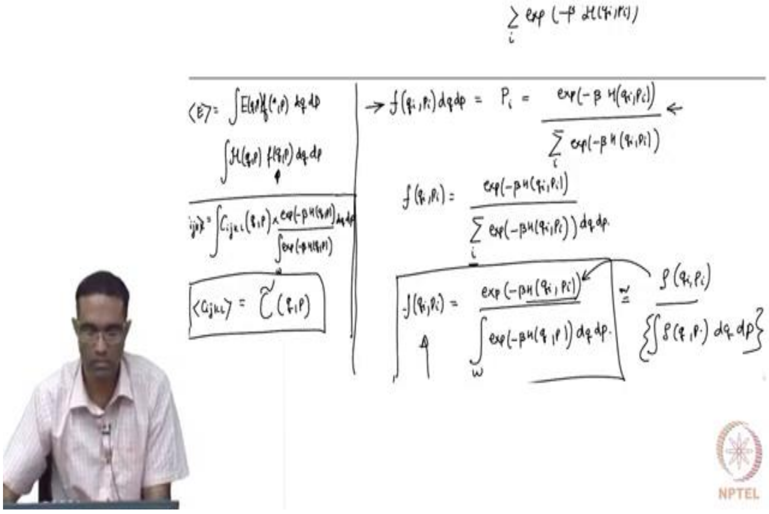
$E_{ij}(q,p) \quad \frac{\partial A}{\partial E_{ij}} = \sigma_{ij}(q,p)$

$\Omega \propto \int_{\omega} \exp(-\beta H(q,p)\, dq\, dp$

$\boxed{\Omega = \frac{1}{N!\,h^{3N}} \int_{\omega} \exp(-\beta H(q,p))\, dq\, dp.}$

$\frac{\partial \sigma_{ij}(q,p)}{\partial E_{kl}(q,p)} = C_{ijkl}(q,p)$

$\lim_{\Delta t \to \infty} \frac{1}{\Delta t} \int_0^{\Delta t} C_{ijkl}(q(t),p(t))\, dt = \bar{C}_{ijkl}$



$\sum_i \exp(-\beta H(q_i,p_i))$

$\langle E \rangle = \int E(q,p) f(q,p)\, dq\, dp$

$\int H(q,p) f(q,p)\, dq\, dp$

$ijkl\rangle = \int C_{ijkl}(q,p) \times \frac{\exp(-\beta H(q,p))}{\int \exp(-\beta H(q,p))}\, dq\, dp$

$\boxed{\langle C_{ijkl} \rangle = \tilde{C}(q,p)}$

$\rightarrow f(q_i,p_i)\, dq\, dp = P_i = \frac{\exp(-\beta H(q_i,p_i))}{\sum_i \exp(-\beta H(q_i,p_i))} \leftarrow$

$f(q_i,p_i) = \frac{\exp(-\beta H(q_i,p_i))}{\sum_i \exp(-\beta H(q_i,p_i))\, dq\, dp}$

$\boxed{f(q_i,p_i) = \frac{\exp(-\beta H(q_i,p_i))}{\int_{\omega} \exp(-\beta H(q,p))\, dq\, dp}} \simeq \frac{\rho(q_i,p_i)}{\left\{\int \rho(q,p)\, dq\, dp\right\}}$

So, this omega is proportional to this quantity right here. So, once I put this thing I should not write, right? Is just rho of p comma q not p i comma q i, right? So, now what is the proportionality constant? I think we already did this, right?

This omega has to be commensurate with the omega that we find using quantum mechanics so, which is essentially means that N factorial you have to divided by N factorial and H power 3 N in order to get the correct enumeration of the micros states. We solve this in the last, at least we mention this in the last class, right.

So, you are going to keep remembering these expressions. This expression is integral exp exponent minus beta H will occur several times when you are working with statistical mechanics, but because every time you want to find out the average property of anything say for example, you want to find the average C i j k l, I do not know what that expression is but just to illustrate.

If you knew explicitly what the expression for C i j k l or the elastic constant of the system as a function of q and p then, this has to be multiplied with this quantity right here exp minus beta the Hamiltonian divided by or f okay, this. And this entire thing would tell you what is the average of the system, okay.

So, to if you are able to perform the integration explicitly, if you are able to perform the integration explicitly, then you would get an explicit say, some function, right? Some function of q and p. we will get some portion of q and p. Now, let us try another way of deriving the same thing. Yes, you had some questions?

Suppose we have the Helmholtz free energy as a function of q and p, and the strain as a function of q and p, then we may theoretically differentiate these Helmholtz free energy with respect to the strain and get the stress as the function of q and p.

Now, if you differentiate this, we basically get as a function of q and p (explicit) expressions for q and p. I substitute this C I j k l q and p here in this expression right here and perform this integration, you would get the average elastic constant that system will have at equilibrium.

But for molecular dynamic stimulation, the beauty is, it is enough if you have this. For molecular dynamic stimulations, it is sufficient if you have this. Because, you are only going to perform a time average but we need, we definitely need at least an expression for A and E in terms of q and p to be able to find out sigma and hence find out the C I j k l in terms of q and p.

Once you find expression for q and p, you can do time averaging. In molecular dynamic stimulations, what you can do is, you can do this. So, limit over log time integral over 0 to delta t C I j k l q as a function of time, p as a function of time dt, can be done in order to calculate the time average. So, for time long enough, we say that the time average or the phase average are both equal. This and this are both equal.

So, it is a good idea to look at we will spend some time in actually re-deriving this expression, the probability that a system is at energy E I through a slightly different means, slightly probably a little bit more intuitive than the derivation that we just did now. And then we will derive how the Helmholtz free energy can be written as a function of q and p.

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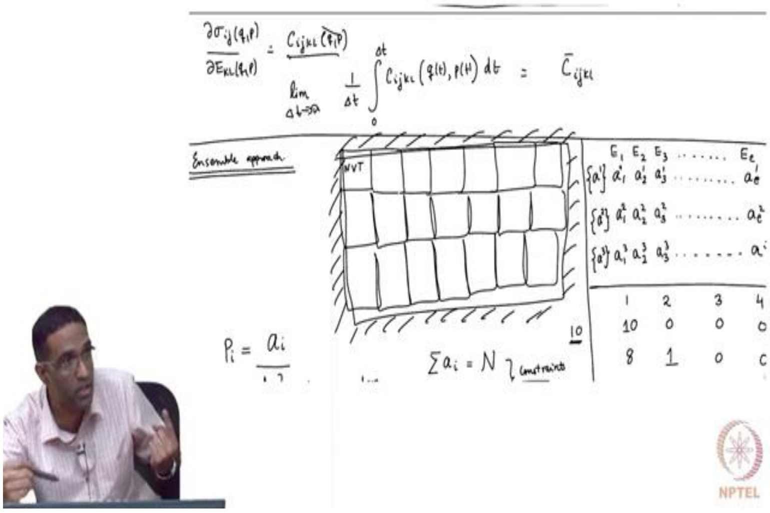


$$\frac{\partial\sigma_{ij}(q,p)}{\partial E_{kl}(q,p)} = \underline{C_{ijkl}(\overline{q,p})}$$

$$\lim_{\Delta t\to\infty}\frac{1}{\Delta t}\int_0^{\Delta t} C_{ijkl}(q(t),p(t))\,dt = \bar{C}_{ijkl}$$

Ensemble approach

NVT

$E_1 \; E_2 \; E_3 \; \ldots\ldots \; E_e$

$\{a^1\} \; a_1^1 \; a_2^1 \; a_3^1 \; \ldots\ldots \; a_e^1$

$\{a^2\} \; a_1^2 \; a_2^2 \; a_3^2 \; \ldots\ldots \; a_e^2$

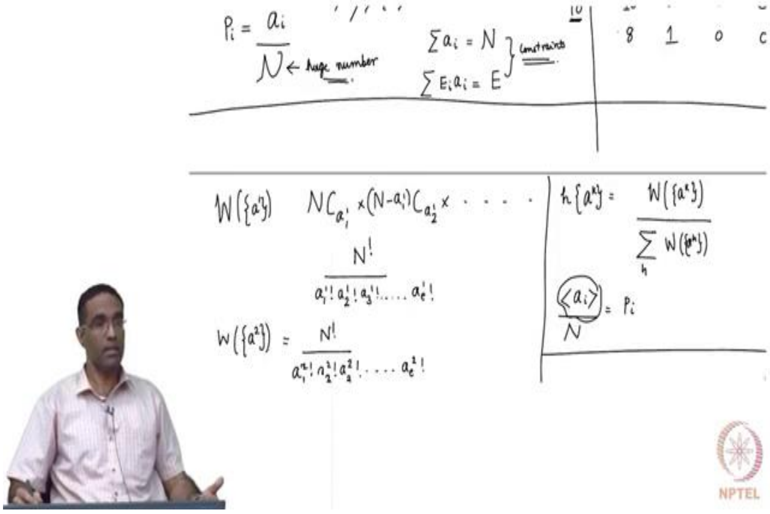
$\{a^3\} \; a_1^3 \; a_2^3 \; a_3^3 \; \ldots\ldots \; a$

1	2	3	4
10	0	0	0
8	1	0	c

10

$P_i = \frac{a_i}{\ }$

$\sum a_i = N$ } constraints



$P_i = \frac{a_i}{N} \leftarrow$ huge number

$\sum a_i = N$

$\sum E_i a_i = E$ } constraints

10

8 1 0 c

$$W(\{a^1\}) \quad {}^{N}C_{a_1^1} \times {}^{(N-a_1^1)}C_{a_2^1} \times \ldots\ldots$$

$$\frac{N!}{a_1^1!\,a_2^1!\,a_3^1!\ldots\ldots a_e^1!}$$

$$W(\{a^2\}) = \frac{N!}{a_1^2!\,a_2^2!\,a_3^2!\ldots\ldots a_e^2!}$$

$$h\{a^k\} = \frac{W(\{a^k\})}{\sum_h W(\{a^h\})}$$

$$\frac{\boxed{\langle a_i\rangle}}{N} = P_i$$

So, the ensemble approach, so let us consider the system having N, V and T. Now, let us assume that, a large number of these systems, each of which is a in a slightly different micro state however, in the same macro state they are all put together, exchanging energy with each other and the entire thing is put inside a bathe and isolated from the surroundings.

Each is the same system, is having the same number of atoms, same volume, same temperature, but it is in a different micro state. It is in a different micro state. It means the p’s and q’s are arranged such that N V T is the same but E and all could be different. Once again, the question that we are going to ask is, what is the probability that a system can be at energy E i?

Same question we ask, what is the probability that the system is having an energy E i? Okay so, if you want to find, if you want to find this, what you need to do actually, what is the expression you know from basic thing, is nothing but the number of systems, okay let me use a as a number of systems with energy E i divided by the total number of systems that is present here.

That will give me the average number of systems. What is the probability that the system is at energy E i? So, these (number) N is actually large, huge number. So, in order to get this probability, in order to find out this probability, we have to first enumerate how different ensembles can be put in different energy level? So, let us say that, there is, there are energy levels E1, E2, E3, and so on till some energy level Ee.

Okay and one possible distribution is that, there could be say, a 1 1 number of ensembles in energy E1, a 2 1 at with energy E2, a 3 1 with energy E3 and so on and a e 1 with energy Ee, okay. We also before I proceed further I need to (under) I need to make sure that, the total number of is N so, if you count them, they have to be N because we have taken N different ensembles. So, there is a constraint there.

The second constraints is that, the energy of each system, so if E i is the total number of is the energy and a i is the total number of systems with energy E i, then this entire thing has to be some constant energy E right, because I have just put everything together, right? So, these are the two constraints that the system has to satisfy.

So, one way this is one way the system can have some energy distribution, right? So, there can be certain number of systems at energy E1, some number of systems at energy E2, and so on. So, we will call this distribution as say a1 distribution. There could be another distribution which I am going to call as a2 distribution where, a 1 2 is the total number of systems with energy E1, a 2 2, a 3 2 and so on.

Similarly, I can have many-many-many-many distributions and all of these are expected to satisfy the constraints that summation of Ei ai is equal to E, okay. This is the third distribution. I will tell you. Subscript is, a suffix i means, number of systems with energy E1 in the first distribution, okay. So, I can have 5 systems at energy E1, so in one distribution.

In another distribution, I can have only 4, I have only 4 systems at energy E1, so that is the second distribution. Then I can have some arbitrary number of some other number of systems at energy E1 that is another distribution. There are so many different distributions possible, is not it? So, the suffix represents the energy that is energy represents the energy and the super fix represents the specific distribution.

If I, is that okay? No? Specific distribution. So, I have to give an example, so, let us say, the energy levels are 1, 2, 3 and 4 and the total energy of the system is may be say, maybe 10. Then I can have 10 systems in energy E1, 0 here, 0 here, 0 here. This is one distribution. In another distribution, I can have maybe 8 with this and one system with this energy and still energy is 10.

This is the second distribution. So, so in this case, a 1 2 is 8, a 2 2 is 1, a 3 2 is 0 and so on. And a 1 1 is 10, a 2 1 is 2 and so on. I can keep writing and if I increase this number to a large value, you can imagine how many different distributions I can basically have right, huge number. Yeah. Any finite energy, actually see, actually I am writing it in a discrete manner. So, it basically will depend upon the total number of the Eigen’s states, the quantum system has, okay. So, it is basically depends on that.

All possible energies that you can have. So, you can have many-many distributions. So, how many ways can this distribution can a particular distribution be realised? So, number of ways a particular distribution number of ways this particular distribution can be write, a 1, super fix 1 distribution can be realised, is nothing but NC taken a 1 1 at a time multiplied by N minus a 1 1 C taken a 2 1 at a time, right?

This is the combination, right? And you can keep writing and this basically becomes, N factorial divided by a 1 1 factorial a 2 1 factorial times a 3 1 factorial and so on till a e 1 factorial. This is the total number of ways a particular distribution can be realised. In the similar manner, I have I am going to write this as this because this is the distribution, I am putting it in flower brackets just to emphasize the fact that it is a distribution.

So, total number of ways a second distribution can be realised will be again N factorial divided by a 2 1 factorial, a 2 2 factorial, a 3 2 factorial so on till a e 2 factorial also, okay. So, what is the probability that you are able to find a specific distribution? Probability that we are able to find a specific distribution, is nothing but, number of ways that particular distribution occurs divided by all possible total number of ways all possible distributions can occur.

Summation over H, H a k is nothing but the probability that a specific distribution can be realised. Because it is nothing but total number of ways a particular distribution can be realised divided by total number of ways all possible distributions can be realised.

We want to find out again, reminding you we want to find out what is the total number of ways a particular system can have an energy E i? Or what is the probability that a particular the systems takes an energy E i? So, that would nothing but be the average number of systems that have energy E I, right average, on an average how many systems have energy E i divided by total number of systems will actually be E i.

Or, if you want to find out this is, how will you, now if you want to elaborate a little bit on this, what is the average number of systems with energy E1? If I find out, let us see, what is a suffix i? A suffix i is the average number of systems with energy E i, right? If I divide it by the total number of systems present, then I find out the probability that the system has energy E i.

Now, my task is to find out what is the average number of ways a system has, what is the average number of systems in the energy E i? How will I find that out? How will I find out? For example, the average number of systems with energy E1, not E1, not probability E1, so listen to the question carefully. I want to find out the average number of systems with energy E1? So, basically a 1 1 plus a 1 2 plus a 1 3 plus so on, so on, so on, so on, so on divided by total number, that is going to be the average number of systems with energy E1.

That can also be written using probability in the following manner, a 1 1 times the probability that a 1 1 occurs plus a 1 2 times the probability that a 1 2 occurs, a 1 3 times the probability that a 1 3 occurs. But, the probability that a 1 1 systems are in energy E1 is nothing but, the probability that the distribution occurs, is not it? The probability that there are a 1 1 systems in energy E1, is nothing but the probability that the a 1 distribution occurs.