Statistical Mechanics
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Lecture - 23
Examples of Microcanonical Ensemble – Two level System

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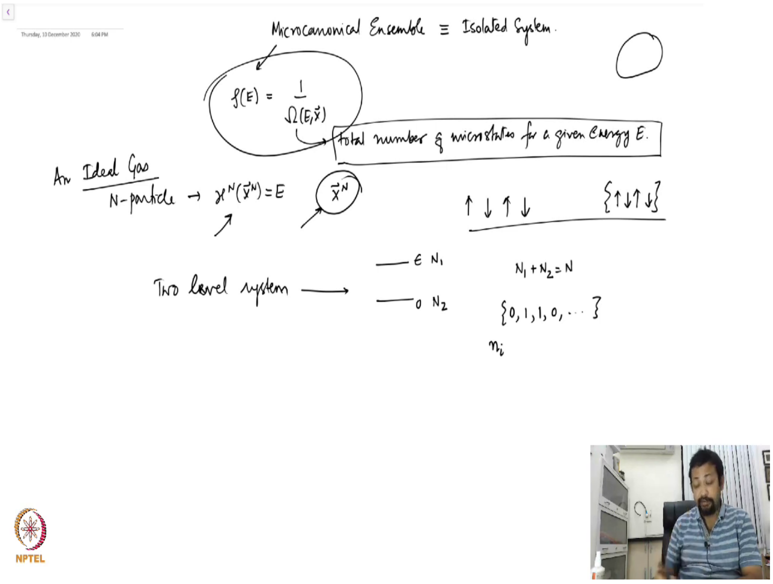

Now, we were looking at Microcanonical Ensemble and this is corresponded to an isolated system the language of thermodynamics. And, here the idea was to determine rho of X n or the probability density rho of E is equal to 1 over E comma X, right. This essentially we have seen that this is the total number of microstates microstates for a given energy E, right.

So, this is what one must keep in mind in doing calculations with micro canonical ensemble. One should always calculate for the total number of microstates for a given energy E. Now, whatever all the derivations and all the calculations that we did in the earlier class, we had considered the system where my phase space variable the microstates could take continuous values, right.

Because for example, not for example, the system that we were particularly interested in was an N – particle system which is similar to a like a gas or a fluid it contained within the box and there was a associated Hamiltonian for this system, right. And, this quantity the state could take real values on the phase space determined by the conservation of the energy.

But, it is also this is not the only type of systems that will encounter. For example, this is clearly the case when we consider an ideal gas right, but there are systems where the states are discrete. For example, one can imagine a spin system on a lattice where the spins can take up or down up and down value.

Here the microstates are clearly the states the configuration of the spins, right. We will do that a little later, but the idea that I want to impress upon you is that there are two possibilities one needs to look at – one, where your microstates can take continuous values is a random variable. Here for example, this X N is a random variable and in the other case where your microstates can take discrete values.

So, we will start off with a very simple system in what is known as a two-level systems. This two-level system has two energy states let us call them 0 and let us call them epsilon, right. Now, I put in n particles in this two-level system some of them are clearly going to occupy the zeroth level. So, we will call them N 2 and some of them is going to occupy the first excited level we will call them N 1. So, that N 1 plus N 2 is equal to N.

Here the microstate is defined by the occupation number. So, first particle 0s; second particle can be epsilon which we denote by 1, 1, 0, so on and so forth. So, the occupation number n i will define the microstate of the system.

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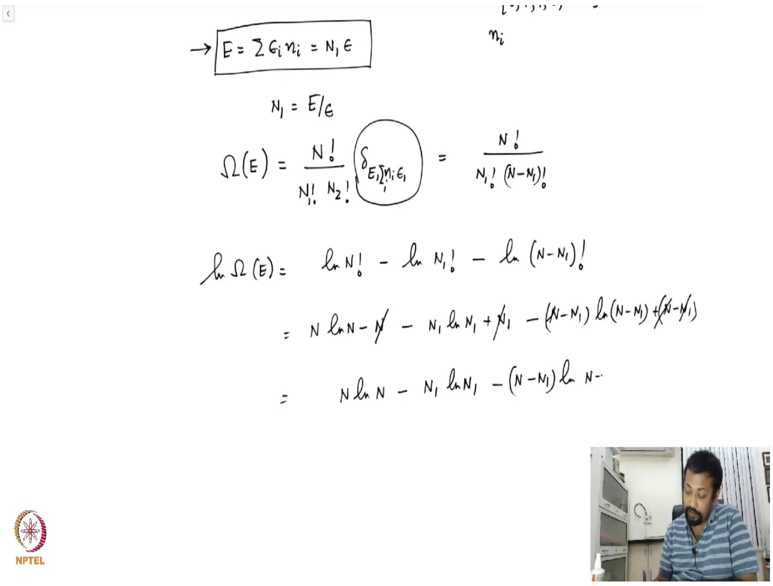

n_i

$$\rightarrow \boxed{E = \sum \epsilon_i n_i = N_1 \epsilon}$$

$$N_1 = E/\epsilon$$

$$\Omega(E) = \frac{N!}{N_1!\, N_2!} \delta_{E, \sum_i n_i \epsilon_i} = \frac{N!}{N_1!\,(N-N_1)!}$$

$$\ln \Omega(E) = \ln N! - \ln N_1! - \ln (N-N_1)!$$

$$= N \ln N - \cancel{N} - N_1 \ln N_1 + \cancel{N_1} - \cancel{(N-N_1)} \ln (N-N_1) + \cancel{(N-N_1)}$$

$$= N \ln N - N_1 \ln N_1 - (N-N_1) \ln N-$$

So, that the total energy we can write down as sum over epsilon i n i which becomes N 1 over epsilon. For all those particles which are occupying the first level excited level sorry. For all those particles which occupy the first excited level contribute to the energy the ground state does not contribute to the energy. So, we have therefore, N 1 as E over epsilon.

Now, I want to find out the total energy total number of microstate. So, this is the case where my microstates are discrete and I want to find out the total number of microstates omega corresponding to this. So, clearly this is a problem in combinatorics I have N 1 factorial N 2 factorial and I have n i epsilon i right sum over i.

This would be N factorial. This guarantees this delta function guarantees that this is obeyed. So, therefore, this becomes N 1 factorial N minus N 1 factorial, right. So, ln of omega E is ln N factorial minus ln N 1 factorial minus ln N minus N 1 factorial which if I use the starlings approximation this becomes N ln N minus N minus N 1 ln N 1 plus N 1 minus N minus N 1 ln N minus N 1 plus N minus N 1.

Let us simplify this you clearly see that this N 1 is going to cancel with this, this plus N is going to cancel with this. You are left out with N ln N minus N 1 ln N 1 minus N minus N 1 ln.

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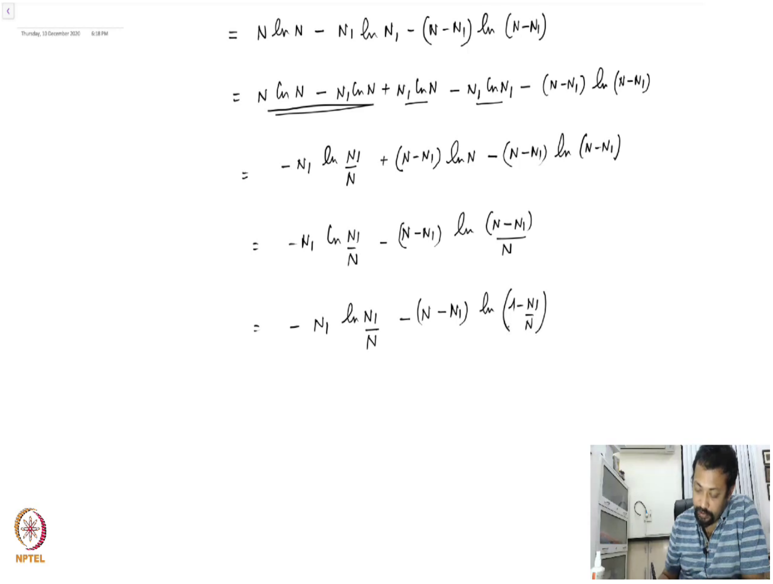

$$= N \ln N - N_1 \ln N_1 - (N - N_1) \ln (N - N_1)$$

$$= \underline{\underline{N \ln N - N_1 \ln N}} + N_1 \underline{\ln N} - N_1 \underline{\ln N_1} - (N - N_1) \ln (N - N_1)$$

$$= -N_1 \ln \frac{N_1}{N} + (N - N_1) \ln N - (N - N_1) \ln (N - N_1)$$

$$= -N_1 \ln \frac{N_1}{N} - (N - N_1) \ln \frac{(N - N_1)}{N}$$

$$= -N_1 \ln \frac{N_1}{N} - (N - N_1) \ln \left(1 - \frac{N_1}{N}\right)$$

So, we have this expression. Now, we let us simplify this expression I want to add ln N minus N 1 ln N plus N 1 and ln N minus N 1 ln N 1 minus N minus N 1 ln of N minus N 1 right. So, then let us combine this one with this one. So, then I have minus N 1 ln of N 1 over N and if I combine these two I have plus N minus N 1 ln of N minus N minus N 1 ln of N minus N 1 which is minus N 1 ln of N 1 over N minus N minus N 1 ln of N minus N 1 divided by N.

So, this reduces to the very simple expression N 1 ln N 1 over N there has to be an N outside here. I can recall now, this is fine N 1 ln N 1 over N minus N minus N 1 ln 1 minus N 1 over N.

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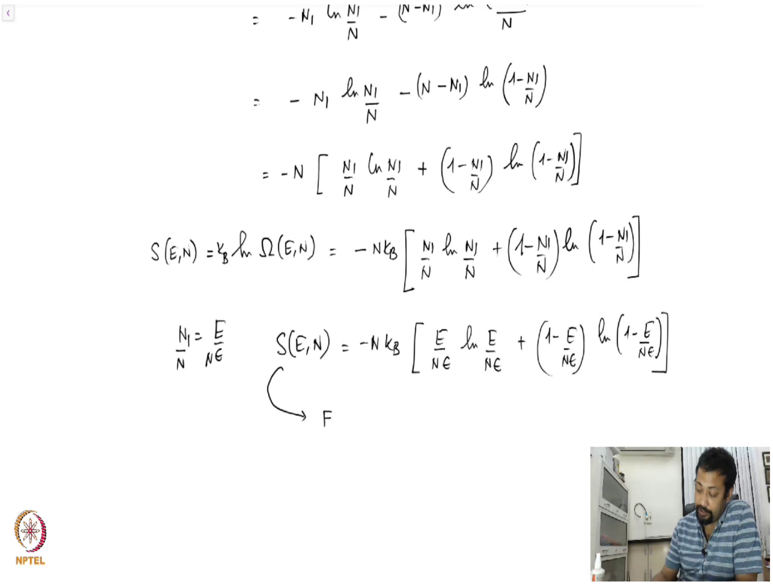

$$= -N_1 \ln \frac{N_1}{N} - (N-N_1) \ln \frac{\quad}{N}$$

$$= -N_1 \ln \frac{N_1}{N} - (N-N_1) \ln \left(1-\frac{N_1}{N}\right)$$

$$= -N \left[\frac{N_1}{N} \ln \frac{N_1}{N} + \left(1-\frac{N_1}{N}\right) \ln \left(1-\frac{N_1}{N}\right)\right]$$

$$S(E,N) = k_B \ln \Omega(E,N) = -N k_B \left[\frac{N_1}{N} \ln \frac{N_1}{N} + \left(1-\frac{N_1}{N}\right) \ln \left(1-\frac{N_1}{N}\right)\right]$$

$$\frac{N_1}{N} = \frac{E}{N\epsilon} \qquad S(E,N) = -N k_B \left[\frac{E}{N\epsilon} \ln \frac{E}{N\epsilon} + \left(1-\frac{E}{N\epsilon}\right) \ln \left(1-\frac{E}{N\epsilon}\right)\right]$$

If I take n outside minus n then this becomes N 1 over N ln N 1 over N plus 1 minus N 1 over N ln 1 minus N 1 over N. Therefore, the entropy which is a function of E comma N is ln omega E comma N with K B sitting outside is minus N K B N 1 over N; N 1 over N plus 1 minus N 1 over N ln 1 minus N 1 over N , but N 1 is E over epsilon.

So, N 1 over N is E over N epsilon and therefore, I have N K B E over N epsilon ln E over N epsilon plus 1 minus E of N epsilon ln 1 minus E over N epsilon. And, this gives me the entropy as a function of E comma N.

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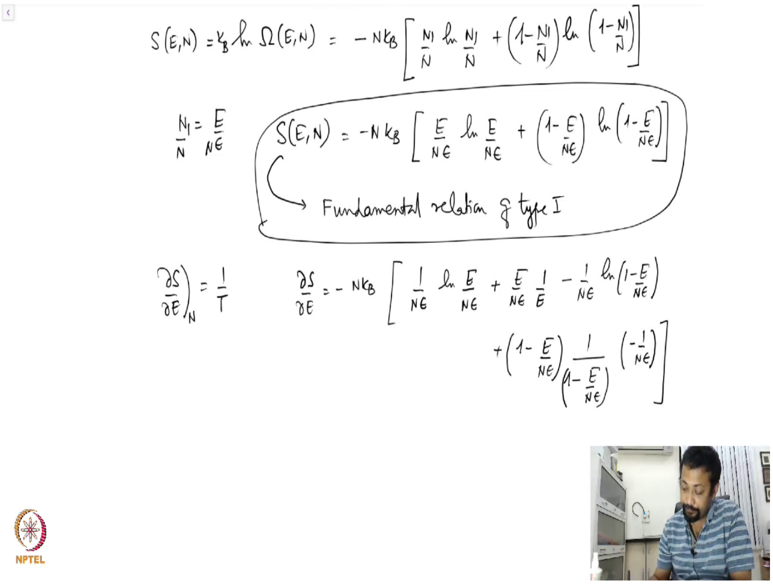

$$S(E,N) = k_B \ln \Omega(E,N) = -Nk_B\left[\frac{N_1}{N}\ln\frac{N_1}{N} + \left(1-\frac{N_1}{N}\right)\ln\left(1-\frac{N_1}{N}\right)\right]$$

$$\frac{N_1}{N} = \frac{E}{N\epsilon} \qquad \boxed{S(E,N) = -Nk_B\left[\frac{E}{N\epsilon}\ln\frac{E}{N\epsilon} + \left(1-\frac{E}{N\epsilon}\right)\ln\left(1-\frac{E}{N\epsilon}\right)\right]}$$

Fundamental relation of type I

$$\left.\frac{\partial S}{\partial E}\right)_N = \frac{1}{T} \qquad \frac{\partial S}{\partial E} = -Nk_B\left[\frac{1}{N\epsilon}\ln\frac{E}{N\epsilon} + \frac{E}{N\epsilon}\frac{1}{E} - \frac{1}{N\epsilon}\ln\left(1-\frac{E}{N\epsilon}\right) + \left(1-\frac{E}{N\epsilon}\right)\frac{1}{\left(1-\frac{E}{N\epsilon}\right)}\left(-\frac{1}{N\epsilon}\right)\right]$$

Recall from thermodynamics this relation is what we called as fundamental relation of type I. And there we said that within the scope of thermodynamics it is not possible to derive this equation or these relations. But given these relations you can exactly derive all the properties of the thermodynamic system.

But, now here from the microscopic picture, we have very nicely derived this fundamental relation of type I. So, how we proceed? Well, we proceed by looking at this this is 1 over T; you know the derivative is going to be inverse of temperature.

So, if we calculate the derivative del S del E is going to be minus N K B 1 over N epsilon ln E over N epsilon plus E over N epsilon 1 over E plus. Sorry, this is going to be a minus 1 over N epsilon ln 1 minus E over N epsilon plus 1 minus E over N epsilon times 1 by 1 minus E over N epsilon minus 1 over N epsilon.

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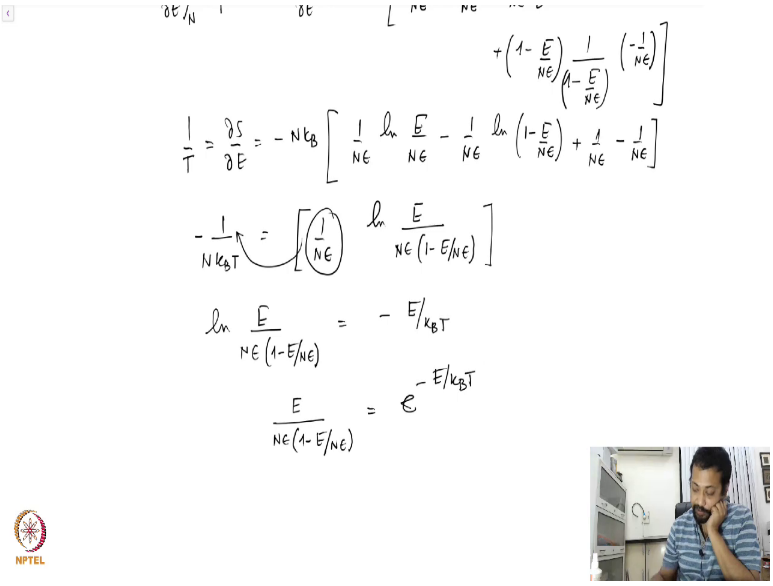

$$+\left(1-\frac{E}{N\epsilon}\right)\frac{1}{\left(1-\frac{E}{N\epsilon}\right)}\left(-\frac{1}{N\epsilon}\right)\Bigg]$$

$$\frac{1}{T}=\frac{\partial S}{\partial E}=-Nk_B\left[\frac{1}{N\epsilon}\ln\frac{E}{N\epsilon}-\frac{1}{N\epsilon}\ln\left(1-\frac{E}{N\epsilon}\right)+\frac{1}{N\epsilon}-\frac{1}{N\epsilon}\right]$$

$$-\frac{1}{Nk_BT}=\left[\frac{1}{N\epsilon}\ln\frac{E}{N\epsilon(1-E/N\epsilon)}\right]$$

$$\ln\frac{E}{N\epsilon(1-E/N\epsilon)}=-E/k_BT$$

$$\frac{E}{N\epsilon(1-E/N\epsilon)}=e^{-E/k_BT}$$

Now, this is a lot of algebra that one has to do, but that is nothing very difficult and is absolutely doable the left hand side is 1 over T. So, that means, I have 1 over N epsilon ln E over N epsilon minus 1 over N epsilon ln 1 minus E over N epsilon plus 1 over N epsilon and this is going to be minus 1 over N epsilon.

So, I have 1 over N K B T with a minus sign is 1 over N epsilon ln E divided by N epsilon 1 minus E over N epsilon, right. So, therefore, if you take the N epsilon to this side, you have ln E over N epsilon 1 minus E over N epsilon is equal to minus E over K B T. So, that E over N epsilon 1 minus E over N epsilon is equal to E to the power minus E over K B T. Good.

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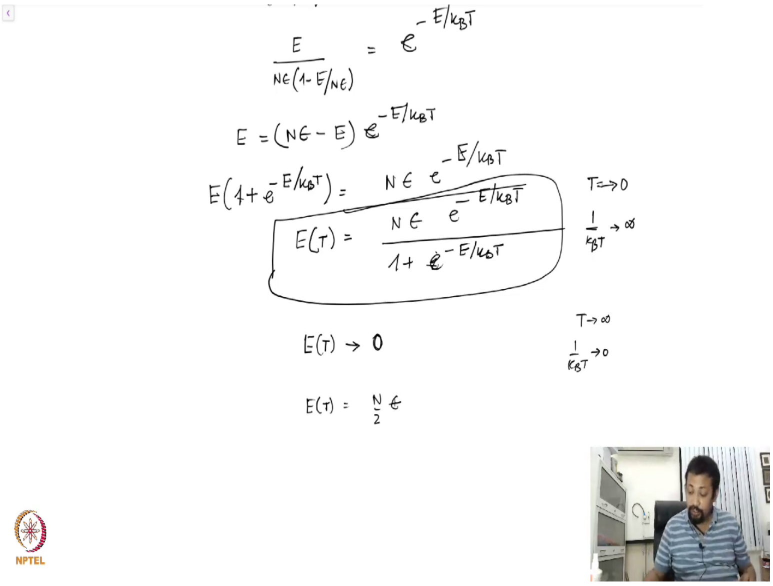

$$\frac{E}{N\epsilon(1-E/N\epsilon)} = e^{-E/k_BT}$$

$$E = (N\epsilon - E)\, e^{-E/k_BT}$$

$$E(1+e^{-E/k_BT}) = N\epsilon\, e^{-E/k_BT}$$

$$\boxed{E(T) = \frac{N\epsilon\, e^{-E/k_BT}}{1+e^{-E/k_BT}}}$$

$T \to 0$

$\frac{1}{k_BT} \to \infty$

$T \to \infty$

$\frac{1}{k_BT} \to 0$

$$E(T) \to 0$$

$$E(T) = \frac{N}{2}\epsilon$$

So, now one proceeds to simplify this expression. So, I can write down N epsilon minus E e to the power minus K B T. So, that E if I bring it to this side 1 plus e to the power minus E over K B T is equal to N epsilon e to the power E over K B T. Therefore, the energy as a function of temperature becomes N epsilon e to the power E over K B T divided by 1 plus E over K B T right.

Now, the question is ok whether we are correct in all our calculations let us see. So, let us take the limit of T to 0. If I take the limit of T to 0 then 1 over K B T tends to infinity, right and the total energy would tend to 0, correct. Why? Because as you lower and lower the temperature there is not much of an excite energy available to go to the first excited level. So, correspondingly all the particles are in the ground state.

What happens to T to infinity? T to infinity would mean that K B T goes to 0 and you see E of T goes as N by 2 epsilon. So, you have so much of energy available that half of the particles populate the first excited level, half of them populate the ground level, so that the total energy is N by 2 epsilon.

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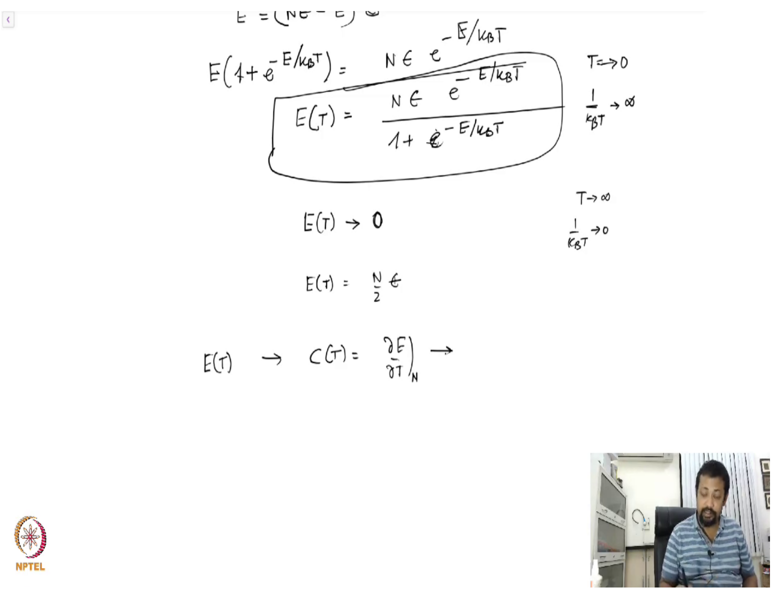

$$E = (N\epsilon - E)\,e$$

$$E\left(1+e^{-\epsilon/k_BT}\right) = N\epsilon\, e^{-\epsilon/k_BT}$$

$$\boxed{E(T) = \frac{N\epsilon\, e^{-\epsilon/k_BT}}{1+e^{-\epsilon/k_BT}}}$$

$T \to 0$, $\frac{1}{k_BT} \to \infty$

$E(T) \to 0$

$T \to \infty$, $\frac{1}{k_BT} \to 0$

$E(T) = \frac{N}{2}\epsilon$

$$E(T) \to C(T) = \left.\frac{\partial E}{\partial T}\right)_N \to$$

From this of course, given E of T, one can calculate the specific heat as a function of temperature which is del E del T and constant. This I leave it as an exercise.