

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

Lecture - 27
Microcanonical Ultrarelativistic Gas and Quantum Solid

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$$E_i = (n_i + \frac{1}{2}) \hbar \omega \quad \frac{1}{2} m \omega^2 q_i^2$$

$$E = \sum (n_i + \frac{1}{2}) \hbar \omega$$

Consider now 2 particles (n_1, n_2) :

$$\hbar \omega (n_1 + n_2) + \frac{1}{2} \hbar \omega + \frac{1}{2} \hbar \omega = E \quad E = \hbar \omega$$

$$n_1 + n_2 = \frac{E - \hbar \omega}{\hbar \omega} = 0$$

$$n_1 = 0, n_2 = 0$$



Think about it that I have two boxes and I am placing both of them in one of the box, nothing else is allowed; no other freedom.

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$$\hbar\omega (n_1 + n_2) + \frac{1}{2}\hbar\omega + \frac{1}{2}\hbar\omega = E$$

$$n_1 + n_2 = \frac{E - \hbar\omega}{\hbar\omega} = 0$$



$$n_1 = 0, n_2 = 0$$

$$\hbar\omega (n_1 + n_2) + \hbar\omega = 2\hbar\omega$$

$$n_1 + n_2 = \frac{2\hbar\omega - \hbar\omega}{\hbar\omega} = 1$$

$$0, 1$$

$$\hbar\omega (n_1 + n_2) = \frac{3\hbar\omega - \hbar\omega}{1}$$

$E = \hbar\omega$
 2 boxes

 $E = 2\hbar\omega$

 $E = 3\hbar\omega$



If you have $n_1 + n_2 + \hbar\omega$; if you set E is equal to $2\hbar\omega$, then this essentially means that you have twice $\hbar\omega$ and $n_1 + n_2$ is $2\hbar\omega - \hbar\omega$ divided by $\hbar\omega$ that is 1. So, effectively now you have to figure out the combination of n_1 and n_2 which will give you one; this total energy $2\hbar\omega$. So, one possibility is 0 and 1 right.

So, therefore, this is like having 2 boxes in which you place one of the particles in this box and no particles in this box. In this particular case, this is the direct contrast because in this particular case what you had was you were not allowed to put anything in this. So, effectively as if even though you have two boxes even though you have two boxes, you have 0 particles to play with right.

What about the case when E is equal to $3 \hbar \omega$? So, you have $n_1 + n_2$ is going to be $3 \hbar \omega$ minus $\hbar \omega$ and we can bring this $\hbar \omega$ here and you will have 2.

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$0, 1, 1, 0$ $E = 3\hbar\omega$

$$(n_1 + n_2) = \frac{3\hbar\omega - \frac{1}{2}\hbar\omega}{\hbar\omega} = 2 = M$$



$n_1 + n_2 = 2$

$n_1 = 0, n_2 = 2$		<div style="border: 1px solid black; padding: 2px; display: inline-block;">••</div>		$3\hbar\omega - \frac{1}{2}\hbar\omega$
$\frac{1}{2}\hbar\omega$		<div style="border: 1px solid black; padding: 2px; display: inline-block;">••</div>	}	$\frac{5}{2}\hbar\omega$
$n_1 = 1, n_2 = 1$		<div style="border: 1px solid black; padding: 2px; display: inline-block;">••</div>	}	$\frac{3}{2}\hbar\omega$
$\frac{3}{2}\hbar\omega$		<div style="border: 1px solid black; padding: 2px; display: inline-block;">••</div>	}	
$n_1 = 2, n_2 = 0$		<div style="border: 1px solid black; padding: 2px; display: inline-block;">••</div>		

3 possible microstates

$$E = \sum_i \left(n_i + \frac{1}{2} \right) \hbar\omega = \left[\sum_i n_i + \frac{N}{2} \right] \hbar\omega$$

$\sum_i n_i = M$

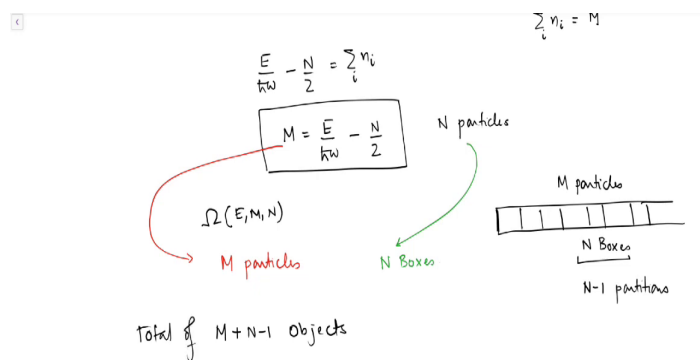
So, $n_1 + n_2$ is going to be 2; that means, I have n_1 is equal to 0 n_2 is going to be n_1 equal to 0 gives me half $\hbar \omega$ and I have to take it to $3 \hbar \omega$ minus half $\hbar \omega$. So, that is going to be $5/2 \hbar \omega$. So, I have to place n_2 in a level where I have the whose energy is going to be $5/2 \hbar \omega$ and that happens when n_2 is equal to 2.

What happens when n_1 is equal to 1? This gives me $3/2 \hbar \omega$ and I need another $3/2 \hbar \omega$ right. So, that n_2 can also be 1 which is obvious because $n_1 + n_2$ has to be 1 and then finally, I have n_1 is equal to 2 and I have n_2 is equal to 0. So, as if I have now

2 boxes, I am placing 0 particles in this box and both of them are over here and here the configuration is this and here the configuration is this.

So, I hope the general idea is clear to you now. So, going back to the general case where I had E is equal to sum over i n_i plus half h bar times ω which gives me sum over i n_i plus n by 2 times h bar of ω .

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So, that this h bar ω minus n by 2 is going to be sum over i n_i and clearly this sum over i which is the sum over the occupation numbers is going to be M an integer. So, I have M is equal to E over h bar ω minus N by 2. Now, the idea is with N particles. So, the entropy for the total number of microstates is ω is going to be a function of E , M and N .

Idea is now the interpretation is as we have seen in the earlier examples if you look over here, then 2 boxes means 2 particles sorry the other way around 2 particles n_1 and n_2 ; two boxes.

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$M \equiv n_1 + n_2 = \frac{kT - kT}{kT} = 0$
 $n_1 = 0, n_2 = 0$
 $E = 2kT$
 $kT(n_1 + n_2) + kT = 2kT$
 $n_1 + n_2 = \frac{2kT - kT}{kT} = 1 = M$
 $0, 1, 1, 0$
 $E = 3kT$
 $(n_1 + n_2) = \frac{3kT - kT}{kT} = 2$
 $n_1 + n_2 = 2$
 $n_1 = 0, n_2 = 2$
 $\frac{1}{2}kT$
 $n_1 = 1, n_2 = 1$
 $\frac{1}{2}kT$
 $m = 1$
 $3kT - \frac{1}{2}kT$
 $\frac{5}{2}kT$
 $\frac{3}{2}kT$
 2 possible microstates

This quantity which is identical to M is 0 means no particle, you have no particles to play with. They have to be there in that box when you have this case. In this case M is equal to 1. This is equal to your M and you have seen that n_1, n_2 either has a combination 0 and 1 or 1 and 0 that is also a valid thing in which you place one of them here, the other one here it is like 2 boxes and you are just putting one particle either in this box; in this box.

So, there are two possible microstates two possible microstates here and in this case, as we have seen in detail where $N = M$ the value of M was 2; there are three possible microstates. So,

the general idea is that this is now interpreted as M particles and this is now interpreted as N boxes.

Therefore, its like you have N boxes and you have M particles. Well you are thinking about particles, you can think about M marbles also which you want to put them in the boxes and this effectively means that N boxes means the end of these things are fixed. So, you have N minus 1 partitions.

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$\Omega(E, M, N)$
 M particles N Boxes

Total of $M+N-1$ objects
 $\Omega(M, N) = \frac{(M+N-1)!}{M!(N-1)!}$ ← Sterling's approximation
 $\ln N! = N \ln N - N$

$S = k_B \ln \Omega(M, N) = k_B [\ln(M+N-1)! - \ln M! - \ln(N-1)!]$
 $= k_B [(M+N-1) \ln(M+N-1) - (M+N-1) - M \ln M + M]$



So, total of M plus N minus 1 objects and for this all possible arrangements that are possible are M plus N minus 1 factorial, but then you see if you interchange this partition with this one, you are doing nothing nothing changes. Similarly if you have placed a particle over here and if you have placed a particle in this box; if you interchange these particles, you do not get a new microstate.

So, clearly this is an over counting and the over counting is exactly given by M factorial because you can interchange between the particles and that is not going to give you anything else new and you can interchange between the partitions that is also not going to give you anything new. Therefore the total number of microstates $\Omega_{M,N}$ is going to be this.

So, now, when we have this expression for the total number of microstates, we want to write down the entropy of the system as $k_B \ln \Omega_{M,N}$ which essentially means that this is $k_B \ln (M + N - 1)!$ minus $\ln N!$ minus $\ln (N - 1)!$.

So, if I now use a Sterling's approximation if you recall the Sterling approximation, essentially approximates $\ln N!$ for large enough N as $N \ln N - N$. We write down this as $k_B (M + N - 1) \ln (M + N - 1) - (M + N - 1) - M \ln M + M$ do not make the mistakes with the signs.

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$$= k_B \left[(M+N-1) \ln(M+N-1) - \overset{-(M+N-1)}{M} \ln M + \overset{+(M+N-1)}{N} \ln N - (N-1) \ln(N-1) \right]$$

$$S = k_B \left[(M+N-1) \ln(M+N-1) - M \ln M - (N-1) \ln(N-1) \right]$$

$$\left. \frac{\partial S}{\partial E} \right|_N = \frac{1}{T} = \left. \frac{\partial S}{\partial M} \right|_N \frac{\partial M}{\partial E} \quad M = \frac{E}{\hbar \omega} - \frac{N}{2}$$

$$\frac{\partial M}{\partial E} = \frac{1}{\hbar \omega}$$

$$= \frac{1}{\hbar \omega} \left. \frac{\partial S}{\partial M} \right|_N = \frac{1}{\hbar \omega} k_B \left[(M+N-1) \ln(M+N-1) - M \ln M - (N-1) \ln(N-1) \right]$$



And then you have minus N minus 1 ln of N minus 1 plus N minus 1. Look at this expression carefully and you see that this plus and this plus gives you a plus M plus N minus 1. So, this factor now cancels with this factor and you have S is equal to K B M plus N minus 1 ln of M plus N minus 1 minus M ln M minus N minus 1 ln N minus 1.

This is the entropy of the system to proceed further we note the thermodynamic relation del S del E and held fixed is 1 by T. Now this although it looks very complicated, this expression for the entropy looks complicated and taking derivative might be very cumbersome. One can simplify this just writing del S del M N held constant times del M del E N held constant recall that M is going to be E over h bar minus N over 2.

So, that del M del E gives you N held constant gives you just 1 over h bar omega and you have del S del M N held constant 1 over h bar omega. So, that you have 1 over h bar 1 by T is

equal to $\frac{1}{T} = \frac{1}{h\nu} \frac{\partial}{\partial M} \left[k_B \left[(M+N-1) \ln(M+N-1) - M \ln M - (N-1) \ln(N-1) \right] \right]$
 minus $M \ln M$ minus $N \ln(N-1)$.

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$$\begin{aligned} \frac{1}{T} &= \frac{1}{h\nu} \frac{\partial}{\partial M} \left[k_B \left[(M+N-1) \ln(M+N-1) - M \ln M - (N-1) \ln(N-1) \right] \right] \\ &= \frac{k_B}{h\nu} \left[\ln(M+N-1) + \frac{(M+N-1)}{(M+N-1)} - \ln M - \frac{1}{M} \right] \\ \frac{1}{T} &= \frac{k_B}{h\nu} \left[\ln \left(\frac{M+N-1}{M} \right) \right] \\ \frac{h\nu}{k_B T} &= \ln \left(1 + \frac{N-1}{M} \right) \approx \ln \left(1 + \frac{N}{M} \right) \\ \Rightarrow 1 + \frac{N}{M} &= e^{\frac{h\nu}{k_B T}} \quad \boxed{\frac{N}{M} = e^{\frac{h\nu}{k_B T}} - 1} \end{aligned}$$



k_B comes outside and sits on top of $h\nu$. k_B divided by $h\nu$. And if you take the derivative of the first term, you are going to get $\ln(M+N-1) + M+N-1$ minus 1 derivative of the log is going to give you $1/(M+N-1)$ and similarly you are going to get $\ln M$ minus M divided by M .

So, that you see this expression this term is 1, this term is 1 which cancels with each other because both of them have opposite signs, you have $\ln(M+N-1)$ divided by M . This part I am going to recast by writing $h\nu$ over $k_B T$ is going to be \ln of $1 + N$ minus 1 over M .

Now, since we are in the thermodynamic limit such that N is very large, this is going to be approximated as $\ln 1 + N \text{ over } M$ and this implies that \ln sorry $1 + N \text{ over } M$ is going to be e to the power $\hbar \omega \text{ over } K B T$. So, that $N \text{ over } M$ is going to be e to the power $\hbar \omega \text{ over } K B T$ minus 1.

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$$\Rightarrow 1 + \frac{N}{M} = e^{\frac{\hbar \omega}{k_B T}} \quad \left[\frac{N}{M} = e^{\frac{\hbar \omega}{k_B T}} - 1 \right] \quad \frac{M}{N} = \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1}$$

$$E = \left(M + \frac{N}{2} \right) \hbar \omega = N \hbar \omega \left(\frac{1}{2} + \frac{M}{N} \right)$$

$$E = N \hbar \omega \left[\frac{1}{2} + \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} \right]$$

Classical Limit

$$E = 3 N k_B T$$

$$T \rightarrow \infty$$

$$\beta = \frac{1}{k_B T} \rightarrow 0$$

$$\lim_{T \rightarrow \infty} E = N \hbar \omega \left[\frac{1}{2} + \frac{1}{1 + \frac{\hbar \omega}{k_B T} - 1} \right]$$

$$= N \hbar \omega \left[\frac{1}{2} + \frac{k_B T}{\hbar \omega} \right] \simeq N \hbar \omega \cdot \frac{k_B T}{\hbar \omega} = N k_B T$$



Now, E where did we write that? We take this expression, E is going to be M plus N by 2 times $\hbar \omega$. If we take N constant common and outside, this becomes half plus M by N. So, that the energy is $N \hbar \omega$ half plus M by N follows from this equation is 1 over e to the power $\hbar \omega \text{ over } K B T$ minus 1. So, that I have 1 over e to the power $\hbar \omega \text{ over } K B T$ minus 1 right.

Now, the question is I want to cross check and validate my result. So, the best way to check it first thing that you check is the classical limit. So, in the classical limit, we have seen that this

system is going to have an energy $3 N K_B T$. We have already done this. Hence so, to see whether we go to this limit, what we need to do is to substitute for T to infinity. So, that beta which is equal to $1 / K_B T$ is small. It goes to 0 therefore, you see I can expand the exponential.

So, I have $N \frac{\hbar \omega}{2} \left(1 + \frac{\hbar \omega}{K_B T} \right)^{-1}$ limit of T to infinity which is going to be $N \frac{\hbar \omega}{2} + \frac{K_B T}{\hbar \omega}$. And since my $K_B T$ is very large compared to this $\frac{\hbar \omega}{2}$ factor; this is going to be $N \frac{\hbar \omega}{2} + \frac{K_B T}{\hbar \omega}$ which gives me the result in $K_B T$ which is precisely the result for this because we are looking at a only 1 dimensional system.

We said in the very beginning that 3 dimensions can be independent can be treated independent of each other. So, if you just do it for 1 dimension you can just adding the results. So, for a 3 dimension, you are going to have two more factors of $N K_B T$ coming in and you will have this.

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1

$$= N \hbar \omega \left[\frac{1}{2} + \frac{k_B T}{\hbar \omega} \right] \approx N \hbar \omega \cdot \frac{k_B T}{\hbar \omega} = N k_B T$$

$$E = N \hbar \omega \left[\frac{1}{2} + e^{-\hbar \omega / k_B T} \right] \quad \left(\beta = \frac{1}{k_B T} \rightarrow \infty \right)$$

$$\begin{aligned} \frac{dE}{dT} &= N \hbar \omega e^{-\hbar \omega / k_B T} \cdot \frac{d}{dT} \left(-\frac{\hbar \omega}{k_B T} \right) \\ &= N \hbar \omega e^{-\hbar \omega / k_B T} \cdot \left(-\frac{\hbar \omega}{k_B} \right) \frac{d}{dT} \left(\frac{1}{T} \right) \\ &= N \hbar \omega e^{-\hbar \omega / k_B T} \cdot \frac{\hbar \omega}{k_B T^2} \end{aligned}$$



Limit of T to 0 is when this factor the exponential factor dominates because 1 over K B T beta goes to infinity and you have N h bar omega half plus e to the power minus h bar omega over K B T.

Once again the specific heat now becomes dE dT at constant N which is N h bar omega e to the power minus h bar omega over K B T times d dT of minus h bar omega over K B T which is going to be N h bar omega e to the power minus h bar omega over K B T. I have a minus h bar omega over K B and the derivative d dT of 1 over T which is going to give me minus 1 over T square. So, this is minus 1 over T square.

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$$\begin{aligned}
 \frac{dE}{dT} &= N \hbar \omega e^{-\hbar \omega / k_B T} \cdot \frac{d}{dT} \left(-\frac{\hbar \omega}{k_B T} \right) \\
 &= N \hbar \omega e^{-\hbar \omega / k_B T} \cdot \frac{-\hbar \omega}{k_B} \frac{d}{dT} \left(\frac{1}{T} \right) \\
 &= N \hbar \omega e^{-\hbar \omega / k_B T} \frac{\hbar \omega}{k_B T^2} \\
 &= N k_B \left(\frac{\hbar \omega}{k_B T} \right)^2
 \end{aligned}$$



So, I have $N \hbar \omega$ minus $\hbar \omega$ over $K_B T$. I am going to have $\hbar \omega$ over $K_B T$ square. Let us recast this a little bit rearrange multiply by K_B and divide by K_B . So, that this K_B , now I plug it over here to give me $\hbar \omega$ divided by $K_B T$ whole square.

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$$\begin{aligned} \frac{dE}{dT} &= N \hbar \omega e^{-\hbar \omega / k_B T} \cdot \frac{d}{dT} \left(-\frac{\hbar \omega}{k_B T} \right) \\ &= N \hbar \omega e^{-\hbar \omega / k_B T} \cdot \left(-\frac{\hbar \omega}{k_B} \right) \frac{d}{dT} \left(\frac{1}{T} \right) \\ &= N \frac{\hbar \omega}{k_B} e^{-\hbar \omega / k_B T} \frac{\hbar \omega}{k_B T^2} \\ \boxed{C} &= N k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 e^{-\hbar \omega / k_B T} \end{aligned}$$



So, there is one factor of $\hbar \omega$ one factor of $\hbar \omega$ that gives me this and I have multiplied with k_B divided by k_B . So, I have multiplied by k_B and divided by k_B and this and this gives me $k_B T^2$ $e^{-\hbar \omega / k_B T}$. So, this is going to be your specific heat.