

Statistical Thermodynamics for Engineers
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Lecture 28
Supplementary Video 9 Problem Solving 1

Welcome everyone to another session of supplementary video and in this video we will be doing some problem solving actually, so let us start.

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$f(x) = C x e^{-x^2/2a^2}$, C is a constant $a > 0$ & $x \geq 0$
Rayleigh distribution
 $C = ?$ $f(x)$ is a probability density function.
 $\int_0^{\infty} f(x) dx = 1 \Rightarrow \int_0^{\infty} C x e^{-x^2/2a^2} dx = 1$ $C \int_0^{\infty} x e^{-x^2/2a^2} dx = 1$
 $C = \frac{1}{a^2}$

Let us say we are given a function f of x equals $C x e$ minus x square over $2a$ square where e is a constant that is given, a is positive and x is greater than equal to 0 , so, those are the given conditions and the question is calculate C , given that f of x is a probability density function. So, this is quite straightforward so we are given the probability distribution actually and this distribution this you have seen lot of other kinds of distribution like the normal distribution, Poisson distribution and let us say the Gaussian distribution, binomial distribution in the main lecture material. So, this is another kind of probability distribution that we encounter quite a lot in probability theory and this distribution is by the way known as the Rayleigh distribution.

So, this is known as the Rayleigh distribution. So, given this Rayleigh probability density function the question is evaluate C , so, this is quite trivial as what we need to do is just impose a condition that the total probability over all possible states is equal to unity, so, that means, what we need to impose is the integral from 0 to infinity f of x dx equals unity.

And since we know f of x in terms of C we can substitute it so, this becomes 0 to infinity $C x e^{-x^2/2a^2}$ minus x square over $2x$ squared equals 1 and from dx equals 1 and from here if you evaluate we can evaluate C by just because C is a constant you can take it out and then compute the integral so this becomes 0 to infinity, $x e^{-x^2/2a^2}$ by $2a^2$ a square dx equals to 1.

So therefore, from here you can calculate given this we can calculate this integral quite easily. So, from here we can find out what C is? So, if you compute the integral C comes out to be 1 over a square, so, that is how we find out the constants that sits in front of let us say any kind of distribution where you impose this important criteria of that the sum of all possible sum of all probabilities actually is unity.

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$C = ?$ $f(x)$ is a probability density function.
 $\int_0^{\infty} f(x) dx = 1 \Rightarrow \int_0^{\infty} C x e^{-x^2/2a^2} dx = 1 \quad C \int_0^{\infty} x e^{-x^2/2a^2} dx = 1$
 $C = \frac{1}{a^2}$
 $\bar{x} = \langle x \rangle = \int_0^{\infty} x f(x) dx = \frac{1}{a^2} \int_0^{\infty} x^2 e^{-x^2/2a^2} dx$
 Standard deviation:
 $\sigma^2 = \bar{x^2} - (\bar{x})^2 \quad \bar{x^2} = \int_0^{\infty} x^2 f(x) dx$
 $\sigma = \sqrt{\bar{x^2} - (\bar{x})^2}$

So, next the question is given the same probability distribution compute the mean. So, that means what they are asking is compute \bar{x} or expectation value of x and this is again quite straightforward given without know C that means we know the probability distribution this is nothing but integral of 0 to infinity x, f of $x dx$. So, this becomes 1 over a square the integral of 0 to infinity x square $e^{-x^2/2a^2}$ dx . So, from here we can directly evaluate the integral we can compute the mean.

Similarly, it can be asked that calculate the standard deviation, compute the standard deviation we know, that the square of the standard deviation also known as the variance is given as x square mean minus the mean whole square. So, you see this quantity can be again easily

evaluated given that this we compute x from this which we show and x square mean is the second moment as you can see this is just integral from 0 to infinity x square f of x dx that is what this term becomes. So, if we substitute this term here this we get the standard deviation can we compute it as the square root of x square bar minus x bar whole square, that is quite straightforward.

So, we will be solving more problems as you can see what we are doing is we are not showing all the steps because the steps that those are quite trivial and based on like if we do each and every step we will not be able to come like cover quite a bit of problems. So, the intention of this problem solving sessions are to cover a variety of problems and so, (what will we do) what will be doing is? Basically provide you the outline of the solution rather than the exactly step by step solution. And if there is any doubt, those doubts could be resolved either in the discussion sessions that we will have live or in the in the NPTEL chat sessions.

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The probability that a monatomic particle will travel a distance x or more between collisions is given by $C e^{-x/\lambda}$; C & λ are constants.

Compute the probability density function? $f(x) = ?$

$$P(a \leq x \leq b) = \int_a^b f(x) dx$$

→

$$\int_a^{\infty} f(x) dx = C e^{-x/\lambda}$$

$f(x) = ?$

Diagram: A horizontal axis with an arrow pointing right, labeled with 0, x , and ∞ . Several horizontal arrows of varying lengths originate from the origin, representing particle travel distances.

Compute the probability density function? $f(x) = ?$

$$P(a \leq x \leq b) = \int_a^b f(x) dx$$

$\int_a^{\infty} f(x) dx = C e^{-x/\lambda}$ $f(x) = ?$

$$\int_0^{\infty} f(x) dx = \int_0^x f(x) dx + \int_x^{\infty} f(x) dx = 1$$

$\int_a^{\infty} f(x) dx = C e^{-x/\lambda}$ $f(x) = ?$

$$\int_0^{\infty} f(x) dx = \int_0^x f(x) dx + \int_x^{\infty} f(x) dx = 1$$

$$\int_x^{\infty} f(x) dx = 1 - \int_0^x f(x) dx$$

$$1 - \int_0^x f(x) dx = C e^{-x/\lambda} \Rightarrow \int_0^x f(x) dx = 1 - C e^{-x/\lambda}$$

$$f(x) dx = -C e^{-x/\lambda} \left(-\frac{1}{\lambda} \right) dx$$

So next, let us see the next question. So, let us say that this is a little bit interesting. So, let us say so, the question is this is the question, next question, the probability that a mono atomic particle will travel a distance x travel or more between collisions is given by $C e^{-x/\lambda}$, where e and λ are constants, so, that is the generic idea.

And the question is that is you see, this is given, so, this is the probability of finding out let us say that a mono atomic particle will cover a distance greater than equal to x basically, it will travel a distance x or more, it is probability of finding the particle at distance greater than equal to x , so that is given as this. So, the question is, compute the probability density function? That means we have to find f of x , so that is the.

So, let us see what we are given is, we are given that probability of finding a particle will say so it is asking that the probability that a mono atomic will travel a distance x or more so that means x has to be greater than equal to like, so, let us put it in a different way. So, let us see the probability where let us say x lies between 2. States a and b let us say given by the integral from a to b , f of x dx , so that is the generic view that we understand, that is the probability of finding let us say, x in the range a to b , given the probability distribution f of x .

Let us say now what we are asking is that x , that the particle will travel a distance x or more or distance x or more so. So, if you translate using this idea, this will give us that integral from x to infinity f of x dx that is equal to $C e$ to the power minus x over λ , so, that needs to be cleared because you see it is greater than equal to x and the maximum x can go is like it is unbounded in the upper state so it can go up to infinity, so, if you think about x , as let us say a some kind of real line it goes, so let us say this is 0 and so this is infinity, what is given is, what we need is that it always lies in this in this range. It is greater than x and it goes till infinity.

So, the probability if you integrate that this is the probability of finding and that is given, so given this we have to find what f of x is, so, that is a mathematical problem that we have. So, let us see, so, we know that total probability, so the total probability can is given by integral 0 to infinity f of x dx equals that we can write as 0 to x f of x dx plus integral x to infinity f of x dx by using the summation rule of integration like you just of the so what we are doing is we are considering the integral from 0 to infinity, and we split the limits from 0 to x first and then from x to infinity, so that is the thing and this is the total probability and this is unity.

So, from here, what we can write is the integral x to infinity f of x dx could be written as 1 minus the integral 0 to x f of x dx , so, if we use this equation and substitute it here, what we get is 1 minus the integral 0 to x f of x dx equals $C e$ minus x over λ or this could be rewritten in a slightly different way.

So, this could be written as the integral 0 to x f of x dx equals to 1 minus $C e$ to the power minus x over λ , see the entire thing of changing the limits of integration from 0 to infinity to x is because now you will see, from this we can compute what f of x ? Because we can write, we can take a derivative of this equation basically and we can write a differential form of this equation and figure out what f of x is. So, that is this will become f of x dx equals take the derivative with

respect to x. So, this will become minus C derivative of exponential is exponential itself minus x over lambda times the derivative of the (())(13:07) which is minus 1 over lambda dx.

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$$f'(x) dx = -C e^{-x/\lambda} dx$$

$$f(x) = \frac{C}{\lambda} e^{-x/\lambda}$$

$$\int_0^{\infty} f(x) dx = 1 \quad C \leftarrow$$

$$\bar{x} = \langle x \rangle = \int_0^{\infty} x f(x) dx$$

$$\bar{x}^2 = \int_0^{\infty} x^2 f(x) dx$$

$$\sigma^2 = \bar{x}^2 - (\bar{x})^2$$

So, if you see what we get from here is f of x equals C over lambda e minus x by lambda. So, we found out what is the probability density function and how it looks, as if we now know the probability density function, now it is quite trivial, as we did before to imply the condition 0 to infinity of f x dx equal to 1 to figure out what C is, we know so we use this function (())(13:50) here to do the integral and figure out what C is, put it back so we then get to the total function f of x, so that gives us the probability distribution and similarly if it is asked to find out the mean, x bar or the expectation value of x, that is even straightforward.

Given that we now know f of x properly, so this is 0 to infinity x f x dx, and if it is asked to calculate the variance of the standard deviations, we know the variance is the mean square which is this minus the square mean. So, these all quantities can be computed. So, this is computed from here and x square we know from before 0 to infinity, the second moment is x square f of x dx so that is the crux.

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$$\bar{x} = \langle x \rangle = \int_0^{\infty} x f(x) dx$$

$$\bar{x}^2 = \int_0^{\infty} x^2 f(x) dx$$

$$\sigma^2 = \bar{x}^2 - (\bar{x})^2$$

Find the fraction of molecules having $x \geq 2\lambda$

$$P(x \geq 2\lambda) = \int_{2\lambda}^{\infty} f(x) dx$$

$$P(a \leq x \leq b) = \int_a^b f(x) dx$$

So, let us see there is given f of x now we know the question is find the fraction of molecules having x greater than equal to 2λ , so that what they are asking is P is P what we want to find the probability of finding a particle at x greater than equal to 2λ that is what we need to find out and that is given by integral from 2λ because x is greater than 2λ , 2λ to infinity f of x this is based on the fact that we discussed before that probability of x lying in between a and b is given by the integral from a to b f of x . So, that is how we solve these kinds of problems of probability densities involving probability density functions and other things, where we go. So, it is quite simple as you saw out of the standard procedure is C .

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The Entropy for Bose-Einstein and Fermi-Dirac statistics is given by

$$S(E, V, N) = R(\beta E + \alpha N) - R \sum_j g_j \ln(1 \mp e^{-\alpha} e^{-\beta \epsilon_j})$$

$\alpha, \beta \rightarrow$ Lagrange multipliers

$$N = \sum_j N_j \quad \text{and} \quad E = \sum_j N_j \epsilon_j$$

$$S(E, V, N) = R \left(\beta E + \alpha N \right) - R \sum_j g_j \ln \left(1 + e^{-\alpha} e^{-\beta \epsilon_j} \right)$$

$\alpha, \beta \rightarrow$ Lagrange multipliers

$$N = \sum_j N_j \quad \text{and} \quad E = \sum_j N_j \epsilon_j$$

Find out the Lagrange multipliers??

Recall classical Thermodynamics

$$dS(E, V, N) = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\left(\frac{\partial S}{\partial E} \right)_{V, N} = \left(\frac{1}{T} \right)$$

α, β are functions of E, V, N

$$dS(E, V, N) = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\left(\frac{\partial S}{\partial E} \right)_{V, N} = \left(\frac{1}{T} \right) \quad \alpha, \beta(E)$$

$$S(E, V, N) = R \left(\beta E + \alpha N \right) - R \sum_j g_j \ln \left(1 + e^{-\alpha} e^{-\beta \epsilon_j} \right)$$

$$\left(\frac{\partial S}{\partial E} \right)_{V, N} = R \beta + R E \left(\frac{\partial \beta}{\partial E} \right)_{V, N} + R N \left(\frac{\partial \alpha}{\partial E} \right)_{V, N} - R \sum_j \left[\frac{g_j e^{-\alpha} e^{-\beta \epsilon_j}}{1 + e^{-\alpha} e^{-\beta \epsilon_j}} \right] \left[\left(\frac{\partial \alpha}{\partial E} \right)_{V, N} + \epsilon_j \left(\frac{\partial \beta}{\partial E} \right)_{V, N} \right]$$

Now, let us consider a little bit interesting problem and see this is a bit different kind of a problem and here we will be basically be diving straight into statistical thermodynamics. So, the question is entropy for Bose-Einstein and Fermi-Dirac statistics is given by S that is a function of the total energy volume and the number of particles that is given by is equal to k which is the Boltzmann constant, times βE plus αN minus plus $K \dots$

Let me write it like this $K \sum_j g_j \log \left(1 + e^{-\alpha} e^{-\beta \epsilon_j} \right)$, where α and β are the Lagrange multipliers and N is sum over j of N_j and total energy E is sum over j of $N_j \epsilon_j$, so, those are the things that is given. The question is, find out the Lagrange multipliers?

So, in order to do that we need to recall from our classical let us recall from classical thermodynamics, recall classical thermodynamics, that we can write this expression dS of here using the same independent variables E , V and N here so dS of E , V , N is given $1/T$, dE plus p/T dV minus μ/T dN . So, that is coming from classical thermodynamics.

So, given the form of entropy for Bose-Einstein and Fermi-Dirac statistics and we know the definition of the differential of entropy from classical thermodynamics what we need to do is? We need to calculate this Lagrange multipliers and you know that Lagrange multipliers are quite important because those directly feed into the equilibrium particle distribution and which are used to calculate the final statistics the above Bose-Einstein(19:49) or the Fermi-Dirac.

So, let us see how this to be done, so, if you see from this expression what you see is? The partial S with respect to E is a partial S partial E at constant V and N that is given by $1/T$, so, that is 1 over the temperature. So, this is coming from classical thermodynamics, but this right hand side is coming from classical thermodynamics, so what we will do is? This left hand side we will compute from statistical thermodynamics and that (because) how can we calculate? Because we are given so this is given, so, the entropy for Bose-Einstein Fermi-Dirac statistics is given by that expression.

And how this expression is coming? That is derived in the main lectures; so, refer to the main lectures where talk about the partition functions and how entropy is related to the partition function and how this expression was derived for Bose-Einstein and Fermi-Dirac statistics. So, given this entropy distribution S of E , V , N what we can do is we can compute the partial derivative of the entropy with respect to the total energy at constant V and N .

And if we do that what it will become as partial S partial E at constant V constant N is equal to k times β plus k E partial β partial E , V , N . One very important thing to keep in mind is Lagrange multipliers α and β they themselves are functions of these variables E , V , N . So, α , β are functions of E , V , N , so that is why when we are differentiated with respect to let us say e we need to differentiate the Lagrange multipliers themselves with respect to E keeping V , N and constants.

So, if you see this expression, so, the first term is quite simple because we are differentiating with respect to E , so, the first term is just k , but the second term if you see, α can also be a

function of K is the Boltzmann constant, so that is a constant, but then so α can be a function of e and n , where we have this $k N$, (22:22) so this becomes $k \beta$ becomes $k e$.

Actually, let me rewrite the entropy equation once more here, just to that I can have some reference here before we do because otherwise it is difficult to keep the bookkeeping let me rewrite the entropy is $S(E, V, N)$ which is $k \beta E + \alpha n - k \sum_j g_j \log(1 - e^{-\beta \epsilon_j})$, that is given.

And let us now do the partial derivative, the partial derivative of S with respect to E at constant V and N , constant V and N realizing that α and β are also functions as V so they are also functions of E , so this become $k \beta$, so, that is the first term plus k , if you see this as a product of two terms we have B and E . So, first what we did was we took this constant and we differentiated E with respect to V that is why we have $k \beta$ plus we have now $k E$.

And now we need to differentiate B β itself so partial B with respect to E V, N , plus $k N$ partial α partial E at constant V and constant N and you see one thing here k and N is constant that is why just we have a derivative of α with respect to E and then we have minus plus the Boltzmann constant sum over j and now we have to take the derivative of this inside term.

So, but now you see this is the derivative of a product, so it is the product of the g_j times the log function, we do it one step at a time, so, this will become if we do. So, if we take the derivative of the log that will become 1 over let me write the denominator first, $1 - e^{-\beta \epsilon_j}$ that is the derivative of the log in which we kept g_j constant, so g_j goes in the numerator and then we need to differentiate.

So, then you need to differentiate this entire term which is $e^{-\beta \epsilon_j}$ times $e^{-\beta \epsilon_j}$ which is self that is same thing that will become $e^{-\beta \epsilon_j}$ times $e^{-\beta \epsilon_j}$. Times now, we need to differentiate the powers of E which is $\alpha \beta$ that will become this is multiplied by, so that I will write down partial α partial E at constant V, N plus ϵ_j that is this thing partial β partial E at constant V, N plus ϵ_j that is this thing partial β partial E at constant V, N

bracket close. You see that see whether that term is clear or not? So, if you see now this term is the massive term if you see this term, but if you realize this term we know actually from before.

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$$N_j = \frac{g_j}{e^\alpha e^{\epsilon_j} + 1} = \frac{g_j e^{-\alpha} e^{-\epsilon_j}}{1 + e^{-\alpha} e^{-\epsilon_j}}$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = R\beta + RE \left(\frac{\partial \beta}{\partial E}\right)_{V,N} + RN \left(\frac{\partial \alpha}{\partial E}\right)_{V,N} - R \sum_j N_j \left[\left(\frac{\partial \alpha}{\partial E}\right)_{V,N} + \epsilon_j \left(\frac{\partial \beta}{\partial E}\right)_{V,N} \right]$$

$$\sum_j N_j = N, \quad \sum_j N_j \epsilon_j = E$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = R\beta + RE \left(\frac{\partial \beta}{\partial E}\right)_{V,N} + RN \left(\frac{\partial \alpha}{\partial E}\right)_{V,N} - R \sum_j N_j \left[\left(\frac{\partial \alpha}{\partial E}\right)_{V,N} + \epsilon_j \left(\frac{\partial \beta}{\partial E}\right)_{V,N} \right]$$

$$\sum_j N_j = N, \quad \sum_j N_j \epsilon_j = E$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = R\beta + RE \left(\frac{\partial \beta}{\partial E}\right)_{V,N} + \cancel{RN \left(\frac{\partial \alpha}{\partial E}\right)_{V,N}} - \cancel{RN \left(\frac{\partial \alpha}{\partial E}\right)_{V,N}} - RE \left(\frac{\partial \beta}{\partial E}\right)_{V,N}$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = R\beta$$

$$\sum_j N_j = N, \quad \sum_j N_j \epsilon_j = E$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = k\beta + kE \left(\frac{\partial \beta}{\partial E}\right)_{V,N} + kN \left(\frac{\partial \alpha}{\partial E}\right)_{V,N} - kN \left(\frac{\partial \alpha}{\partial E}\right)_{V,N} - kE \left(\frac{\partial \beta}{\partial E}\right)_{V,N}$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = k\beta = \frac{1}{T} \Rightarrow \beta = \frac{1}{kT}$$

$$\alpha = ?$$

If you recall or B E and F D statistics equilibrium particle distribution is given by N_j is g_j by e to the power α e to the power β ϵ_j minus plus 1, so, that is the equilibrium partition distribution and this could be written as $g_j e$ to the power minus α e to the power minus β ϵ_j all divided by 1 minus plus e to the power minus α e to the power minus β ϵ_j , if you see that this complicated term is nothing but that is N_j itself.

So, therefore partial S partial E with respect to V comma N is given by k times β plus k times E , partial β partial E V comma N plus kN partial α partial E, V comma N minus k , now, we are at this term start and minus k and then we have let us say sum over j N_j where we just taking the one of the sign which is the negative sign which we are taking now, minus k sum over j N_j and then we have partial α partial E V comma N plus ϵ_j partial β partial E V comma N. If you see and this is the final expression for partial S partial E but we realized that sum over j N_j is N and sum over j $N_j \epsilon_j$ is E .

So, if you realize that we will see what this become is partial S partial E is V comma N and so that becomes k times β plus kE partial β partial E, V comma N plus kN partial α partial E V comma N minus and now, if you see this is N basically this because minus kN partial α partial E V comma N so that is the first term sum over j , but here the second term, the second term is sum over $N_j \epsilon_j$ sum over j that is E so this becomes minus kE partial β partial E V comma N.

And if you see this term cancels this term, this and this gets cancelled and similar did this term gets canceled by this term so what we are left is partial S partial E is V comma or V comma N at constant V and N k times beta. And recall, from classical thermodynamics we showed what the derivative was? That partial derivative was 1 over T, so, that was 1 over T.

From here we conclude that one we found out one of the Lagrange multipliers which is beta. So, beta is 1 over Boltzmann constants times temperature, that is how we find the Lagrange multipliers. So, next is but remember we have two Lagrange multipliers we also have to find out alpha and that will we will do in the next segment. So, thank you.