STATISTICAL MECHANICS: LAST ASSIGNMENT

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Problem 1. Consider a paramagnetic system consisting of four distinguishable, uncoupled, spin-½ magnetic dipoles. The diagram shows all the possible configurations of the system.

- (1) How many microstates does the system have?
- (2) How many macro-states does it have?
- (3) What is the probability of finding the system in the most probable macrostate?

Solution. Let's begin

(1) This is a problem of counting, and because the system can only be in to states, the number os microstates, this is; the number of possible configurations is given by

 2^n

where n is the number of particles in the ensemble, in this case, this number corresponds to n = 4, thus we have

$$\Omega = 2^4$$

thus

$$\Omega = 16$$
.

- (2) Because the dipoles are uncoupled, their spins can be aligned independently, which implies that the possible macro states will correspond to the total spin of the system. The total spin can range from +2 (all spins up) to -2 (all spins down). Therefore, there will be a total of (2 * total spin + 1) macro states, this is $(2 \times 2 + 1) = 5$. We're considering that the spins are distinguishable, then we can form the following combinations:
 - All spins up (+2)
 - Three spins up, one spin down (+1)
 - Two spins up, two spins down (0)
 - Three spins down, one spin up (-1)
 - All spins down (-2)
- (3) The most probable state is the one with the bigger number of microstates, in this case; this macrostate corresponds to having two spins up and two spins down, now, in the following we're going to think that any microstate is equally likely, therefore, the probability will be just the ratio of the number or microstates with the total number of possibilities, and in this case, the number of microstates with tow spins up and two spins down is given by 9, then it follows that

$$P = \frac{9}{16}$$
.

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Problem 2. A system, in thermal contact with a reservoir at temperature T, has four possible states, with the energies shown on the left of the diagram. (**Condition A**) It undergoes a process that raises the energy of each state by $\Delta E > 0$, as shown on the right (**Condition B**).

- (1) When the system changes from **Condition A** to **Condition B**, does the partition function \mathcal{Z} increase, decrease, or stay the same? If \mathcal{Z} changes, by what factor does it change?
- (2) When the system changes from **Condition A** to **Condition B**, does the probability of finding the system in state 2 increase, decrease, or stay the same? If the probability changes, by what factor does it change?
- (3) When the system changes from **Condition A** to **Condition B**, does the ratio of the probability of finding the system in state 1 to the probability of finding the system in state 2, P(1)/P(2), increase, decrease, or stay the same? If the probability ratio changes, by what factor does it change?

Solution. Because the system is in contact with a heat reservoir and there is no particle exchange, we're thinking in a canonical ensemble, and we know that in this ensemble, the partition function is defined as the sum over states of the Boltzmann factors, this is

$$\mathcal{Z} = \sum_{i} \exp\left(-\beta \varepsilon_{i}\right)$$
,

where $\beta = 1/k_BT$, and ε_i corresponds to the energy of that state. Now, with this in mind we can write down the partition function for the system in the Condition A, and Condition B, and then compare them. Let's do that, for A, we have

$$\mathcal{Z}_A = \sum_i \exp(-\beta \varepsilon_i),$$

= $\exp(-\beta \varepsilon_0) + \exp(-\beta \varepsilon_1) + \exp(-\beta \varepsilon_2) + \exp(-\beta \varepsilon_3),$

where $\varepsilon_0 = 0$, $\varepsilon_1 = 1$, $\varepsilon_2 = 2$, $\varepsilon_3 = 3$, we can write the previous expression in a nicer way, of course, but for our purposes that will be enough. Now, let's write the partition function for the B condition, this is

$$\mathcal{Z}_B = \sum_i \exp\left(-\beta \epsilon_i\right)$$
,

where $\epsilon_i = \varepsilon + \Delta E$, then

$$\mathcal{Z}_{B} = \sum_{i} \exp(-\beta (\varepsilon_{i} + \Delta E)),$$

$$= \sum_{i} \exp(-\beta \varepsilon_{i}) \exp(-\beta \Delta E),$$

and in the last expression, the term with the ΔE is independent of the sum, then we can put that term outside the sum symbol, thus

$$\mathcal{Z}_{B} = \exp(-\beta \Delta E) \sum_{i} \exp(-\beta \varepsilon_{i})$$
,

but the expression in the sum is the partition function for the Condition A, this is

$$\mathcal{Z}_B = \exp\left(-\beta\Delta E\right)\mathcal{Z}_A,$$
2

then, as we can see, the partition function increases by a factor of determined by the "excess" of energy in the new configuration, this is $\exp(-\beta\Delta E)$.

Now, let's calculate the probability for finding the system in the state 2, in the Condition A, this is given by

$$P\left(\varepsilon_{2}\right)_{A}=rac{\exp\left(-eta\varepsilon_{2}
ight)}{\mathcal{Z}_{A}},$$

now, let's compute the same probability using Condition B, this is

$$P(\epsilon_{2})_{B} = \frac{\exp(-\beta\epsilon_{2})}{\mathcal{Z}_{B}},$$

$$= \frac{\exp(-\beta(\epsilon_{2} + \Delta E))}{\exp(-\beta\Delta E) \mathcal{Z}_{A}},$$

$$= \frac{\exp(-\beta\Delta E) \exp(-\beta\epsilon_{2})}{\exp(-\beta\Delta E) \mathcal{Z}_{A}},$$

and as we can see the "excess" in the partition function cancels out, leaving us with

$$P(\epsilon_2)_B = \frac{\exp(-\beta\epsilon_2)}{\mathcal{Z}_A},$$

but this is the same expression for the probability in the Condition A, therefore

$$P(\epsilon_2)_B = P(\epsilon_2)_A$$
,

and from this we can conclude that the probability stays the same.

Problem 3. In class, we worked out many properties of a degenerate Fermi gas in three dimensions. In this problem, you will repeat the process in two dimensions.

- (1) This may appear to be a purely academic exercise after all, we live in a three-dimensional world but it's actually experimentally realizable. In the analysis we did in class, we assumed the particles were confined in a cubical box with equal sides L. But suppose one of the sides, say in the z direction, is much smaller, so instead of in a cube, the particles are in a thin sheet. Then the energy spacings between orbitals associated with motion in the small dimension will be much larger, and if the spacing between the two lowest energy levels is much greater than $k_B T$, only the ground state will be occupied. In that case the electron gas is effectively two-dimensional in its properties and behavior, even though the film has nonzero thickness in the third dimension. Suppose we deposit a metal film (on an insulating substrate) that is 10 atomic layers thick. Estimate how low the temperature would have to be in order for the electron gas to behave as a two-dimensional system.
- (2) For such a two-dimensional Fermi gas, derive appropriate expressions for the Fermi energy and density of states. Also determine how the heat capacity varies with temperature (you don't have to work out an exact expression, but figure out the *T*-dependence). Discuss any similarities or differences from the three-dimensional case.

Solution. 1. We know that the eigen-energies for the "particle in a box" problem are given by

$$E=\frac{n\pi^2\hbar^2}{2mL^2},$$

On the other hand, because the film is much thinner in the one of the spatial dimensions, we have that the size of the box becomes d d in that direction. It follows that, the energy spacing ΔE between the first two energy levels (ground state and first excited state) in the dimension is approximately given by

$$\Delta E = \frac{\pi^2 \hbar^2}{2md^2},$$

and even more, if ΔE is much greater than $k_B T$, then, only the ground state will be occupied, and the system effectively behaves as two-dimensional, which imposes the following condition

$$\Delta E \gg k_B T$$

therefore, it follows that

$$\frac{\pi^2\hbar^2}{2md^2}\gg k_BT,$$

and in this form, we have the following condition for the temperature

$$T \ll \frac{\pi^2 \hbar^2}{2mk_B d^2}.$$

2) For this part we first need to compute the density of states and having that we can derive the partition function, and from this all the other thermodynamical quantities. So, let's begin: we know that the density of states is defined as follows

$$g(k) dk = \frac{\text{volume in } k \text{ -space of a complete speherical shell}}{\text{volume in } k \text{ -space occupied per allowed state}},$$

but that was for the 3D case, and in 2D, we have to make some changes, in particular, we have the following definition

$$g(k) dk = \frac{\text{area in } k \text{ -space of a complete speherical shell}}{\text{area in } k \text{ -space occupied per allowed state}},$$

thus, we have

$$g(k) dk = \frac{2\pi k dk}{\left(\frac{2\pi}{L}\right)^2} \times 2,$$

the factor in the denominator comes from the solution of the solution of the Schrödinger equation for a particle in a box, and the overall two comes from the spin degeneracy of the electrons. And from this we can obtain the following expression

$$g(k) dk = \frac{L^2}{\pi} k dk,$$

and now, with this in mind let's write the density of states in terms of the energy, and in order to to that, we're going to consider that

$$E=\frac{\hbar^2 k^2}{m},$$

and from this it follows that

$$dE = \frac{\hbar^2}{m} k dk \implies k dk = \frac{m}{\hbar^2} dE,$$

thus, we can rewrite the density of states as

$$g(k) dk \rightarrow g(E) dE = \frac{mL^2}{\pi \hbar^2} dE$$

and even more, let's call $L^2 = A$, then, we have that the density of states can be written as

$$g(E) dE = \frac{mA}{\pi \hbar^2} dE.$$

Now, for the determination of the Fermi Energy, let's compute

$$N = \int_0^\infty \frac{g(E) dE}{\exp \left[\beta (E - \mu)\right] + 1},$$

at T=0, but in this regime, the fermi statistics takes the form of a step function, and thus, the previous equation transforms into

$$N = \int_{0}^{E_{F}} g(E) dE,$$

$$\implies N = \frac{mA}{\pi \hbar^{2}} \int_{0}^{E_{F}} dE,$$

$$\implies \frac{N}{A} = \frac{m}{\pi \hbar^{2}} E_{F},$$

and making n = N/A, we have

$$n=\frac{m}{\pi\hbar^2}E_F,$$

which implies that

$$E_F = \frac{\pi \hbar^2}{m} n,$$

and now, if $T \neq 0$, then we have to deal with the whole integral, which usually can be recasted in terms of the polylogarithm functions, or we can use the Sommerfeld approximation, and in any case, in order to compute the heat capacity, we first need to compute the internal energy, and then derive with respect to the temperature, but first let's focus on the internal energy, which can be computed via the expectation value

$$U = \langle E \rangle$$
,

which in this kind of statistics is given by

$$U = \int_0^\infty \frac{Eg(E) dE}{\exp[\beta (E - \mu)] + 1},$$

and now, if we put the density of states previously computed we have that

$$U = \frac{mA}{\pi\hbar^2} \int_0^\infty \frac{EdE}{\exp\left[\beta \left(E - \mu\right)\right] + 1},$$

now, I decided to go with Sommerfeld's approximation, which reads

$$U = \int_0^{\mu} Eg(E) dE + \frac{\pi^2}{6} (k_B T)^2 \left[\frac{d}{dE} (Eg(E)) \right]_{u} + \cdots,$$

and from this we have that

$$\int_0^{\mu} Eg(E) dE = \frac{mA}{\pi \hbar^2} \int_0^{\mu} EdE,$$

$$\implies \int_0^{\mu} Eg(E) dE = \frac{mA}{2\pi \hbar^2} \mu^2,$$

and

$$\frac{d}{dE}\left(Eg\left(E\right)\right) = \frac{d}{dE}\left(E\frac{mA}{\pi\hbar^{2}}\right),$$

$$\implies \frac{d}{dE}\left(Eg\left(E\right)\right) = \frac{mA}{\pi\hbar^{2}},$$

therefore, we have that the internal energy is given by

$$U pprox rac{mA}{2\pi\hbar^2}\mu^2 + rac{\pi^2}{6}rac{mA}{\pi\hbar^2}\left(k_BT\right)^2$$
 ,

and from this it follows that the heat capacity, which is defined by

$$C=\frac{\partial U}{\partial T},$$

is given by

$$C = \frac{\pi^2}{3} \frac{mA}{\pi \hbar^2} k_B^2 T,$$

which means that the heat capacity depends linearly with the temperature, which is the same result as the three dimensional case, up to some constants, of course, which come from the differences between the density of states. Now, let me elaborate a little more on this:in both cases, 2D and 3D, the heat capacity shows a linear dependence on temperature (T) at low temperatures which is where the Sommerfeld approximation is good, on the other hand the key difference lies in the density of states, as stated before, in the 2D, the density of states scales linearly with the wave vector k, whereas in 3D, it scales as k^2 , and this leads to a different pre-factor in the final expression for the heat capacity. And finally, while both show a temperature dependence, the pre-factor in the 2D case is smaller than in

3D, which indicates that a 2D electron gas will have a lower heat capacity compared to a 3D gas with the same number of electrons and temperature.

Problem 4. In the case of the Fermi gas at T = 0, we found $E_F = \mu$ (T = 0) by setting the integral of the occupancy over all energies, weighted by the density of states, equal to the number of particles, N. We can do a similar calculation for a gas of spinless bosons, at finite nonzero temperature.

(1) Show that such a calculation leads to an implicit relationship for μ given by:

$$\int \frac{\sqrt{x}}{\exp(x - \bar{\mu}) - 1} dx = \frac{\sqrt{\pi}}{2} \frac{n}{n_O}, \quad \bar{\mu} = \frac{\mu}{k_B T}$$

where n_Q is our usual quantum concentration. (Note: This expression is valid provided the temperature is high enough that the population of the ground state is small compared to N – that is, not in the Bose- Einstein condensation regime.)

(2) Show that, in the limit of a classical ideal gas, this expression leads to the result previously derived for the chemical potential of an ideal gas.

Solution. a) In general the density of states is given by the following expression

$$g(k) dk = \frac{(2S+1) 4\pi k^2 dk}{(2\pi/L)^3},$$

where the factor (2S + 1) takes into account the degeneracy in each level. On the other hand, we know that the Bose-Einstein Statistics is given by

$$f(E) = \frac{1}{\exp \left[\beta \left(E - \mu\right)\right] - 1'}$$

and before doing any calculations, let's rewrite the density of states in terms of energy, which is given by

$$g(E) dE = \frac{(2S+1) V E^{1/2} dE}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2},$$

and with that, let's do the following

$$N = \int_0^\infty f(E) g(E) dE,$$

then, it follows that

$$N = \int_0^\infty \frac{1}{\exp\left[\beta (E - \mu)\right] - 1} \frac{(2S + 1) V E^{1/2} dE}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} dE,$$

which can be rewritten as

$$\frac{N}{V} = \frac{(2S+1)}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{E^{1/2} dE}{\exp\left[\beta (E-\mu)\right] - 1},$$

but n = N/V, then it follows that

$$n = \frac{(2S+1)}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{E^{1/2} dE}{\exp\left[\beta (E-\mu)\right] - 1}$$

on the other hand, if we make the following change of variable

$$x = \beta E \implies dE = \frac{dx}{\beta},$$

thus it follows that

$$E^{1/2} = \frac{x^{1/2}}{\beta^{1/2}},$$

then, we have

$$n = \frac{(2S+1)}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{\beta^{3/2}} \int_0^\infty \frac{x^{1/2} dx}{\exp\left[x - \beta\mu\right] - 1},$$

and if we make $\beta \mu = \bar{\mu}$, we have

$$n = \frac{(2S+1)}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{\beta^{3/2}} \int_0^\infty \frac{x^{1/2} dx}{\exp\left[x - \bar{\mu}\right] - 1}$$

and from this we have

$$n\frac{\beta^{3/2}(2\pi)^2}{(2S+1)} \left(\frac{\hbar}{2m}\right)^{3/2} = \int_0^\infty \frac{x^{1/2} dx}{\exp\left[x - \bar{\mu}\right] - 1},$$

and now, let's play a little bit with the math on the left hand side of the previous expression

$$\begin{split} n\frac{\beta^{3/2}2\pi^2}{(2S+1)} \left(\frac{\hbar}{2m}\right)^{3/2} &= n\frac{2\pi^2}{(2S+1)} \left(\frac{\hbar}{2mk_BT}\right)^{3/2},\\ \implies n\frac{2\pi^2}{(2S+1)} \left(\frac{\hbar}{2mk_BT}\right)^{3/2} &= n\frac{2\pi^2}{(2S+1)} \left(\frac{\frac{\hbar}{2\pi}}{\frac{2mk_BT}{2\pi}}\right)^{3/2},\\ \implies n\frac{2\pi^2}{(2S+1)} \left(\frac{\frac{\hbar}{2\pi}}{\frac{2mk_BT}{2\pi}}\right)^{3/2} &= n\frac{2\pi^2}{(2S+1)} \left(\frac{\frac{\hbar}{2\pi}}{\frac{2mk_BT}{2\pi}}\right)^{3/2} \frac{\frac{1}{\hbar^3}}{\frac{1}{\hbar^3}}, \end{split}$$

but we know that

$$n_Q = \frac{1}{\hbar^3} \left(\frac{m k_B T}{2\pi} \right)^{3/2},$$

thus if follows that

$$n\frac{2\pi^2}{(2S+1)} \left(\frac{\frac{\hbar}{2\pi}}{\frac{2mk_BT}{2\pi}}\right)^{3/2} \frac{\frac{1}{\hbar^3}}{\frac{1}{\hbar^3}} = \frac{n}{n_Q} \frac{2\pi^{1/2}\hbar^{-3/2}}{(2S+1)}$$

and from this it follows that

$$\int_0^\infty \frac{\sqrt{x}}{\exp(x-\bar{\mu})-1} dx = \frac{\sqrt{\pi}}{2} \frac{n}{n_O},$$

just as we wanted. b) Now for this part we have remember that in the case in which β ($E - \mu$) \gg 1, Bose statistics tend to the Boltzmann distribution, then, using that limit we also have that

$$\beta(E-u) \gg 1 \implies \exp(x-\bar{u}) \gg 1$$

thus it follows that

$$\int_0^\infty \frac{\sqrt{x}}{\exp\left(x - \bar{\mu}\right) - 1} dx \approx \int_0^\infty \frac{\sqrt{x}}{\exp\left(x - \bar{\mu}\right)} dx,$$

but the previous integral is given by

$$\int_0^\infty \frac{\sqrt{x}}{\exp\left(x - \bar{\mu}\right)} dx = \frac{\exp\left(\mu\right)\sqrt{2}}{2},$$

thus we have that

$$\frac{\exp\left(\bar{\mu}\right)\sqrt{\pi}}{2} = \frac{\sqrt{\pi}}{2} \frac{n}{n_{Q}},$$

and from this

$$\bar{\mu} = \ln\left(\frac{n}{n_Q}\right),$$
 $\implies \mu = k_B T \ln\left(\frac{n}{n_Q}\right),$

but we know that

$$\frac{1}{n_Q} = \lambda_{\text{th}}^3,$$

thus we have

$$\mu = k_B T \ln \left(n \lambda_{\text{th}}^3 \right),$$

which corresponds to the chemical potential for an ideal gas.

Problem 5. In class, we discussed the Debye model of the heat capacity of a solid due to lattice vibrations, using the blackbody radiation model with three significant modifications:

- Three polarizations rather than two, because both longitudinal and transverse vibrations are possible;
- A maximum possible frequency ω_D , owing to the fact that there is a minimum wavelength related to the spacing between atoms;
- A wave speed of v_s , the speed of sound in the solid, rather than c.

From this model, we found that at low temperatures, the heat capacity is proportional to T^3 . We still assumed, however, that the wave speed is independent of frequency. Suppose, instead, that the wave speed is related to frequency by:

$$v = v_0 \left(\frac{\omega}{\omega_D}\right)^{\alpha},$$

where the exponent α is a constant greater than or equal to zero. Repeat the Debye calculation for this case, and determine the temperature dependence of the heat capacity. Check that your result is consistent with the Debye result in the appropriate limit.

Solution. As stated in the problem, for the Debye model we used the following dispersion relationship

$$\omega = v_s k$$
,

where k is the wave vector, and v_s the velocity of sound. Here, however, we're going to change that dispersion relationship, and we're going to rewrite the density of states of lattice vibrations. But before doing any calculations, I think that the dispersion relationship is wrong, and here I plan to prove why I state that, in particular, I think the dispersion relationship should be written as

$$v = v_0 \left(\frac{\omega_D}{\omega}\right)^{\alpha}$$
,

and with this in mind I plan to prove that by computing

$$\int_{0}^{\omega_{D}}g\left(\omega\right) d\omega=3N,$$

I can recover the Debye frequency. Now, we know that

$$g(k) dk = \frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3} \times 3,$$

on the other hand we have that $k = \omega/v$, which implies that

$$k = \frac{\omega}{v_0} \left(\frac{\omega}{\omega_D}\right)^{\alpha} \implies k = \frac{1}{v_0} \frac{\omega^{\alpha+1}}{\omega_D^{\alpha}}, \implies k^2 = \frac{1}{v_0^2} \frac{\omega^{2\alpha+2}}{\omega_D^{2\alpha}}$$

and from this it follows that

$$dk = \frac{\alpha + 1}{v_0} \frac{\omega^{\alpha}}{\omega_D^{\alpha}} d\omega,$$

which then, implies that

$$g(\omega) d\omega = \frac{12\pi}{\left(\frac{2\pi}{L}\right)^3} \left(\frac{1}{v_0^2} \frac{\omega^{2\alpha+2}}{\omega_D^{2\alpha}}\right) \left(\left(\frac{\alpha+1}{v_0}\right) \frac{\omega^{\alpha}}{\omega_D^{\alpha}}\right) d\omega,$$

$$\implies g\left(\omega\right)d\omega = \frac{12\pi}{\left(\frac{2\pi}{T}\right)^3} \left(\frac{\alpha+1}{v_0^3} \frac{\omega^{3\alpha+2}}{\omega_D^{3\alpha}}\right) d\omega,$$

now, let's use the condition

$$\begin{split} &\int_{0}^{\omega_{D}}g\left(\omega\right)d\omega=3N,\\ &\frac{12\pi L^{3}}{8\pi^{3}}\frac{\alpha+1}{v_{0}^{3}\omega_{D}^{3\alpha}}\int_{0}^{\omega_{D}}\omega^{3\alpha+2}d\omega=3N, \end{split}$$

but for the integral we simply have

$$\int_0^{\omega_D} \omega^{3\alpha+2} d\omega = \frac{1}{3(\alpha+1)} \omega_D^{3\alpha+3},$$

then it follows that

$$\left(\frac{12\pi L^3}{8\pi^3}\right)\left(\frac{\alpha+1}{v_0^3\omega_D^{3\alpha}}\right)\frac{1}{3\left(\alpha+1\right)}\omega_D^{3\alpha+3}=3N,$$

and from this

$$egin{aligned} rac{4L^3}{8\pi^2v_0^3\omega_D^{3lpha}}\omega_D^{3lpha+3}&=3N,\ &\Longrightarrowrac{L^3}{2\pi^2v_0^3}\omega_D^3&=3N, \end{aligned}$$

and from the last expression we arrive at the following relation for ω_D

$$\omega_D = \left(\frac{6N\pi^2 v_0^3}{L^3}\right)^{1/3},$$

which corresponds to the well known Debye frequency.

Now with this at hand let's move on with the calculation of the heat capacity. By definition, we have that

$$C_X = \left(\frac{\partial U}{\partial T}\right)_X,$$

thus, first we need to compute the expectation value of the internal energy, and for that we're going to make use of the following

$$U = \int_0^{\omega_D} g(\omega) d\omega \left[\hbar \omega \left(\frac{1}{2} + \frac{1}{\exp(\beta \hbar \omega) - 1} \right) \right],$$

but first, let's write $g(\omega) d\omega$ as follows

$$g\left(\omega\right)d\omega=\gamma\omega^{3\alpha+2}d\omega,$$

where

$$\gamma = \frac{3L^3}{2\pi^2} \frac{\alpha + 1}{v_0^3 \omega_D^{3\alpha}},$$

then, it follows that

$$U = \gamma \hbar \int_0^{\omega_D} d\omega \left[\left(\omega^{\alpha+1} \right)^3 \left(\frac{1}{2} + \frac{1}{\exp\left(\beta \hbar \omega \right) - 1} \right) \right],$$

and from this is follows that

$$U = \frac{\gamma \hbar}{2(3\alpha + 4)} \omega^{3\alpha + 4} + \gamma \hbar \int_0^{\omega_D} d\omega \frac{\left(\omega^{\alpha + 1}\right)^3}{\exp\left(\beta \hbar \omega\right) - 1},$$

and it's important to remember that $\beta = 1/k_BT$, thus, taking the derivative with respect to time of the previous expression we have that

$$\frac{\partial U}{\partial T} = \gamma \hbar \int_0^{\omega_D} d\omega \frac{\partial}{\partial T} \left(\frac{\omega^{3\alpha+3}}{\exp(\beta \hbar \omega) - 1} \right),$$

and taking the partial derivative we obtain

$$\frac{\partial U}{\partial T} = \gamma \hbar \int_0^{\omega_D} d\omega \frac{\left(\omega^{\alpha+1}\right)^3}{\left(\exp\left(\beta\hbar\omega\right) - 1\right)^2} \exp\left(\beta\hbar\omega\right) \left(-\frac{\hbar\omega}{k_B T^2}\right),$$

and now, let's play a little bit with the equation, just to find a nicer expression for the integral

$$\frac{\partial U}{\partial T} = -\gamma \hbar^2 \int_0^{\omega_D} d\omega \frac{k_B \omega^{3\alpha+4} \exp{(\beta \hbar \omega)}}{k_B^2 T^2 \left(\exp{(\beta \hbar \omega)} - 1\right)^2} = -\gamma \hbar^2 k_B \int_0^{\omega_D} d\omega \frac{\beta^2 \omega^{3\alpha+4} \exp{(\beta \hbar \omega)}}{\left(\exp{(\beta \hbar \omega)} - 1\right)^2},$$

and now, if we make the following change of variable

$$x = \beta \hbar \omega \implies x_D = \beta \hbar \omega_D$$

then we have

$$\frac{\partial U}{\partial T} = \frac{\gamma k_B \beta^2 \hbar^2}{(\beta \hbar)^{3\alpha + 4}} \int_0^{x_D} \frac{dx}{\beta \hbar} \frac{x^{3\alpha + 4} \exp(x)}{(\exp(x) - 1)^2},$$

$$\implies \frac{\partial U}{\partial T} = \frac{\gamma k_B}{(\beta \hbar)^{3\alpha + 3}} \int_0^{x_D} dx \frac{x^{3\alpha + 4} \exp(x)}{(\exp(x) - 1)^2},$$

$$\implies \frac{\partial U}{\partial T} = \gamma k_B \left[\left(\frac{\omega_D}{x_D} \right)^{\alpha + 1} \right]^3 \int_0^{x_D} dx \frac{x^{3\alpha + 4} \exp(x)}{(\exp(x) - 1)^2},$$

therefore, we have that

$$C = \gamma k_B \left[\left(\frac{\omega_D}{x_D} \right)^{\alpha + 1} \right]^3 \int_0^{x_D} dx \frac{x^{3\alpha + 4} \exp(x)}{\left(\exp(x) - 1 \right)^2},$$

and from the previous expression we can investigate the high/low temperature limits as follows:

• For the high *T* limit we have $x \to 0$, which implies that $(\exp(x) - 1) \to x$, and from this we have

$$C \to \gamma k_B \left[\left(\frac{\omega_D}{x_D} \right)^{\alpha+1} \right]^3 \int_0^{x_D} dx \frac{x^{3\alpha+4}}{x^2},$$

and now, if we consider $\alpha = 0$, we have

$$C \to \gamma k_B \left(\frac{\omega_D}{x_D}\right)^3 \int_0^{x_D} dx \frac{x^4}{x^2},$$

$$\implies C \rightarrow \gamma k_B \left(\frac{\omega_D}{x_D}\right)^3 \frac{x_D^3}{3},$$

and if now we put the definition of γ with $\alpha = 0$ too, we have

$$C \rightarrow \left(\frac{3L^3}{2\pi^2}\frac{k_B}{v_0^3}\right)\frac{\omega_D^3}{3},$$

but we can also use the definition of the Debye frequency, and that implies that

$$C
ightarrow \left(rac{L^3}{2\pi^2} rac{k_B}{v_0^3}
ight) \left(rac{6N\pi^2 v_0^3}{L^3}
ight) = 3Nk_B,$$
 $C
ightarrow 3Nk_B,$

which is expected from the equipartition theorem.

• For low *T* limit, we have $\exp(x) \gg 1$, thus, it follows that

$$C \to \gamma k_B \left[\left(\frac{\omega_D}{x_D} \right)^{\alpha+1} \right]^3 \int_0^\infty dx \frac{x^{3\alpha+4} \exp(x)}{\left(\exp(x) - 1 \right)^2},$$

and again, making $\alpha = 0$, we have that

$$C \to \gamma k_B \left(\frac{\omega_D}{x_D}\right)^3 \int_0^\infty dx \frac{x^4 \exp(x)}{(\exp(x) - 1)^2},$$

but we know the value of the integral, which is given by

$$\int_0^\infty dx \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} = \frac{4\pi^4}{15},$$

thus, we have

$$C \to \gamma k_B \left(\frac{\omega_D}{x_D}\right)^3 \frac{4\pi^4}{15}$$

but $x_D = \beta \hbar \omega_D$, thus

$$C o \gamma k_B \left(rac{\omega_D}{eta\hbar\omega_D}
ight)^3 rac{4\pi^4}{15} = rac{4\pi^4\gamma k_B^4}{15\hbar^3} T^3,$$

and if we make

$$\delta = \frac{4\pi^4 \gamma k_B^4}{15\hbar^3},$$

we have that

$$C \rightarrow \delta T^3$$
,

which agrees with the Debye model.