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Statistical Mechanics

PHYS 5163 Homework Assignment 7

Problems: {1, 2, 3, 4}

Due: April 1, 2022 at 6:00 PM

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Problem 1:

A system is composed of a large number N of one-dimensional quantum harmonic oscillators whose angular frequencies are distributed over the range $\omega_a \leq \omega \leq \omega_b$ with a frequency distribution function $D(\omega) = A\omega^{-1}$, where A is a real constant. Let us assume that the quantum oscillators can be treated as distinguishable quantum particles.

(a) Calculate the specific heat per quantum oscillator at temperature T. Hint: It is convenient to use the canonical ensemble.

To calculate the specific heat per Quantum oscillator we use

$$C_V = \frac{\partial \langle \mathcal{H} \rangle}{\partial T} \qquad (*)$$

Where $\langle \mathcal{H} \rangle$ is the average value of our Hamiltonian. We can find $\langle \mathcal{H} \rangle$ with

$$\langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \log(Q_N) = \int H_n D(\omega)\, d\omega \qquad (**)$$

We of course have to find the partition function to do this. We find Q_N with

$$Q_N(T,V) = \sum_{\{n_{\vec{k}}\}} g\{n_{\vec{k}}\} e^{-\beta E\{n_{\vec{k}}\}} \qquad (***)$$

If we evaluate $(***)$ we have

$$Q_N(T,V) = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta(n+1/2)\hbar\omega} = e^{-\beta\hbar\omega/2} \sum_{n=0} (e^{-\beta\hbar\omega})^n$$

For one particle. This partition function can be re-written as

$$Q(T,V) = e^{-\beta\hbar\omega/2}\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right) = \left(\frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}}\right) = \left(\frac{1}{2}\operatorname{csch}\left(\frac{\beta\hbar\omega}{2}\right)\right)$$

We now normalize the frequency distribution with

$$N = A\int_{\omega_a}^{\omega_b} \frac{1}{\omega}\, d\omega = A \cdot \ln(\omega_b/\omega_a) \Rightarrow A = \frac{N}{\ln(\omega_b/\omega_a)}$$

Our frequency distribution is then

$$D(\omega) = \frac{N}{\ln(\omega_b/\omega_a)} \frac{1}{\omega}$$

We then find the average value of $\mathcal{H}$ with one ω to be

$$\langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \log\left(\left(\frac{1}{2}\sinh^{-1}\left(\frac{\beta\hbar\omega}{2}\right)\right)\right) = \frac{\partial}{\partial \beta} \log\left(2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right) = \frac{\omega\hbar}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right)$$

Problem 1: Continued

we then find our weighted $\langle \tilde{H} \rangle$ with

$$\langle \tilde{H} \rangle = \int \langle H \rangle D(\omega)\, d\omega = \int_{\omega_a}^{\omega_b} \frac{\omega\hbar}{2} \coth\left(\frac{\beta\hbar\omega}{2}\right) \frac{N}{\ln(\omega_b/\omega_a)} \frac{1}{\omega}\, d\omega$$

$$= \frac{N\hbar}{2\ln(\omega_b/\omega_a)} \int_{\omega_a}^{\omega_b} \coth\left(\frac{\beta\hbar\omega}{2}\right) d\omega = \frac{N\hbar}{2\ln(\omega_b/\omega_a)} \cdot \frac{2}{\beta\hbar} \ln\left(\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right)\Bigg|_{\omega_a}^{\omega_b}$$

$$= \frac{N}{\beta\ln(\omega_b/\omega_a)} \ln\left(\sinh\left(\frac{\beta\hbar\omega_b}{2}\right) / \sinh\left(\frac{\beta\hbar\omega_a}{2}\right)\right)$$

we now find C_v with

$$\langle C_v \rangle = \frac{\partial \langle \tilde{H} \rangle}{\partial T} = \frac{\partial \langle \tilde{H} \rangle}{\partial \beta} \frac{\partial \beta}{\partial T}$$

This is then,

$$\frac{\partial \langle \tilde{H} \rangle}{\partial \beta} = -\frac{N}{\beta^2 \ln(\omega_b/\omega_a)} \ln\left(\sinh\left(\frac{\beta\hbar\omega_b}{2}\right) / \sinh\left(\frac{\beta\hbar\omega_a}{2}\right)\right)$$
$$+ \frac{N}{\beta\ln(\omega_b/\omega_a)} \left(\frac{\hbar\omega_b}{\exp(\hbar\omega_b\beta)-1} - \frac{\hbar\omega_a}{\exp(\hbar\omega_a\beta)-1} + \frac{\hbar}{2}(\omega_b - \omega_a) \right)$$

$$\frac{\partial \beta}{\partial T} = -\frac{1}{KT^2}$$

The specific heat is then

$$\boxed{C_v = \frac{NK}{\ln(\omega_b/\omega_a)} \ln\left(\frac{\sinh(\hbar\omega_b/2KT)}{\sinh(\hbar\omega_a/2KT)}\right) - \frac{N\hbar}{T\ln(\omega_b/\omega_a)} \left(\frac{\omega_b}{e^{\hbar\omega_b/KT}-1} - \frac{\omega_a}{e^{\hbar\omega_a/KT}-1} + \frac{1}{2}(\omega_b - \omega_a) \right)}$$

(b) Evaluate your result from part (a) in the high temperature limit (clearly define what "high T" and "low T" mean).

High T is interpretted as $T \to \infty$, conversely low T is $T \to 0$. With this in mind we have for $T \to \infty$

$$\lim_{T\to\infty} C_v = \frac{NK}{\ln(\omega_b/\omega_a)} \ln\left(\frac{\cancel{\hbar}\omega_b/\cancel{2K}}{\cancel{\hbar}\omega_a/\cancel{2K}}\right) = \frac{NK}{\cancel{\ln(\omega_b/\omega_a)}} \cancel{\ln(\omega_b/\omega_a)} = NK$$

Problem 1: Continued

If we then look at $T \to 0$ we then have

$$\lim_{T \to 0} C_V = 0$$

Where for $T \to \infty$ we used

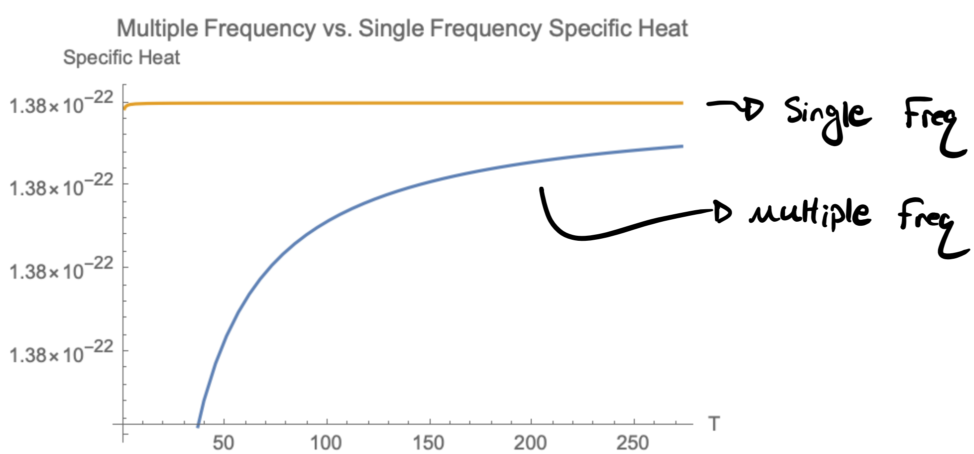
$$\lim_{T \to \infty} \ln\left(\frac{\sinh(a/T)}{\sinh(b/T)}\right) = \ln\left(\frac{a}{b}\right).$$

Packaged up like a present we have

$$\boxed{\begin{array}{l} T \to \infty \, , \; C_V = Nk \\ T \to 0 \, , \; C_V = 0 \end{array}}$$

(c) Make a plot of your result from part (a) and compare with the single-frequency case.

For the following plots, I selected values for ω_a, ω_b, N and then plotted the specific heats against temperature. To simulate a single frequency, I closed the gap between ω_a and ω_b s.t it was small enough to simulate a single frequency



For the multiple frequency case we see that as $T \to \infty$ it will approach a constant value. As $T \to 0$ for the multiple frequency case we see C_V essentially become zero.

We also can see that as T goes to infinity for the multiple frequency case it will approach the same C_V for that of a single frequency

In[400]:=

$$a = \frac{\omega_1}{k\,T};$$

$$b = \frac{\omega_2}{k\,T};$$

$$C_v = \frac{n\,k}{\text{Log}[\omega_2/\omega_1]} * \text{Log}\left[\frac{\text{Sinh}\left[\frac{h}{2} * b\right]}{\text{Sinh}\left[\frac{h}{2} * a\right]}\right] - \frac{n\,h}{T\,\text{Log}[\omega_2/\omega_1]} * \left(\frac{\omega_2}{\text{Exp}[b]-1} - \frac{\omega_1}{\text{Exp}[a]-1} + \frac{1}{2} * (\omega_2 - \omega_1)\right);$$

```
h = 6.626 * 10^(-34);
k = 1.38 * 10^(-23);
n = 10;
```

$$\omega_1 = 10\,000;$$

$$\omega_2 = 1\,000\,000;$$

$$C_{v'} = \frac{n\,k}{\text{Log}[1.05]} * \text{Log}\left[\frac{\text{Sinh}\left[\frac{h}{2} * \frac{105}{k\,T}\right]}{\text{Sinh}\left[\frac{h}{2} * \frac{100}{k\,T}\right]}\right] - \frac{n\,h}{T\,\text{Log}[1.05]} * \left(\frac{105}{\text{Exp}\left[\frac{105}{k\,T}\right]-1} - \frac{100}{\text{Exp}\left[\frac{100}{k\,T}\right]-1} + \frac{1}{2} * (5)\right);$$

```
Plot[{Cv, Cv'}, {T, 1, 273}, PlotLegends → {"Multiple Frequency Cv",
   "Single Frequency Cv"}, AxesLabel → {"T", "Specific Heat"},
 PlotLabel → "Multiple Frequency vs. Single Frequency Specific Heat"]
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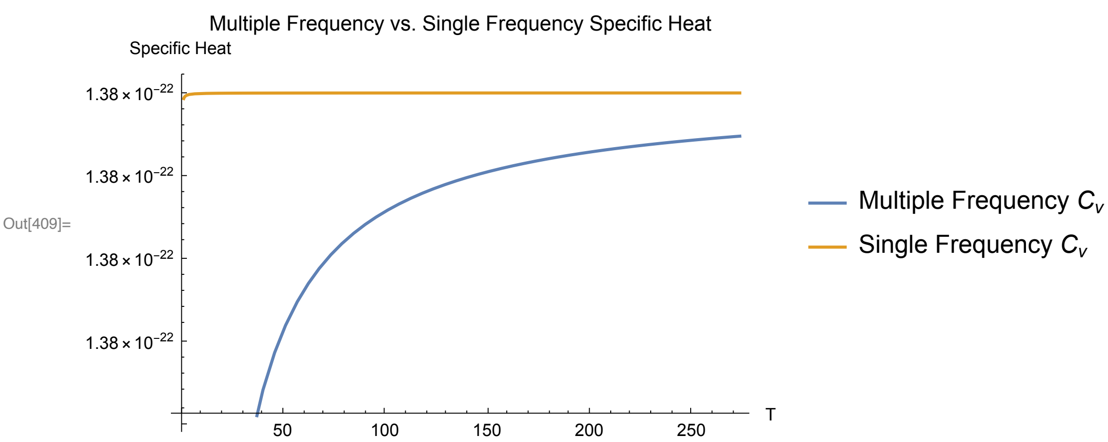
Out[409]=



Problem 1: Review

Procedure:

- – We are going to calculate the specific heat of these quantum oscillators with

$$C_V = \frac{\partial \langle \bar{\mathcal{H}} \rangle}{\partial T}$$

  where $\langle \mathcal{H} \rangle$ is the ensemble average of our Hamiltonian

  – We calculate the ensemble average of our Hamiltonian with

$$\langle \mathcal{H} \rangle = -\frac{\partial}{\partial \beta} \log\left(Q_N\right)$$

  and the Quantum Mechanical Partition function for our ensemble is

$$Q_N(T,V) = \sum_{\{n_{\vec{k}}\}} g\{n_{\vec{k}}\} e^{-\beta E\{n_{\vec{k}}\}}$$

  where n_k are our allowed states and $g\{n_{\vec{k}}\}$ is the degeneracy of our allowed states for a specific value of $\vec{k}$

  – We then have to count the number of particles in our system with N and this is essentially our frequency distribution being normalized

$$N = \int D(\omega)\, d\omega$$

  – After finding a normalized frequency distribution we then move on to calculating a weighted ensemble average of our Hamiltonian with

$$\langle \bar{\mathcal{H}} \rangle = \int \langle \mathcal{H} \rangle\, D(\omega)\, d\omega$$

  where $D(\omega)$ is normalized. We now can calculate C_V from the first equation

- – Simply evaluate C_V for the limits given to us in the problem statement

- – Create a plot of the specific heats for multiple frequencies and single frequencies
    - ∗ To create a plot for a single frequency without completely redoing the entire problem just simply let the difference between $\{\omega_a, \omega_b\} \to 0$

Key Concepts:

- – Because our oscillators have a range of frequencies we must describe these frequencies with a distribution equation. We then normalize this distribution and put it into an equation for the ensemble average of our Hamiltonian to find an average of our average ensemble Hamiltonian. We can then use statistics to extrapolate information that we want

- – In the limit that the temperature goes to infinity we see that the specific heat will go only be dependent upon Boltzmann's constant and

  – In the limit that the temperature goes to zero the specific heat will be zero since any change in energy will result in an increase in temperature

- – We can see that as T goes to infinity, the specific heat of our multiple frequency distribution and our single frequency distribution approach the same limit

Variations:

- – We could be given a different frequency distribution
    - ∗ This would then slightly change the normalization constant of the distribution but the same method and logic would apply

- – For parts (b) and (c), we could be asked to evaluate the specific heat at different limits
    - ∗ This would then change the final answers to our questions but the same method would hold

Problem 2:

The "baloneyon" is an imaginary fermion with spin-1/2 and the relationship $E = B|\vec{p}|^4$ between the energy E and the momentum $\vec{p}$ (as an aside, such dispersion curves can be engineered to a very good approximation using cold atoms),

$$E = B|\vec{p}|^4. \tag{1}$$

Consider a non-interacting gas of baloneyons in two spatial dimensions.

(a) What units does B have?

We know that $E = [J]$, also momentum $\vec{p} = [N \cdot s]$, using this we can say

$$J = B(N \cdot s)^4 \Rightarrow \cancel{N} \cdot m = B \cdot N^{\cancel{4}} \cdot s^4 \Rightarrow B = \frac{m}{N^3 s^4} = \frac{m}{kg^3 \cdot m^3/s^2} = \frac{s^2}{m^2 kg^3}$$

Therefore in fundamental units B is

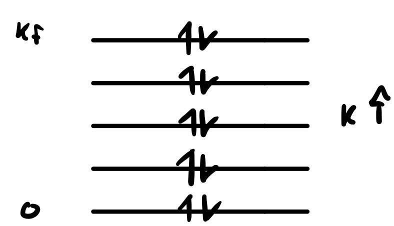
$$\boxed{B = \left[\frac{s^2}{m^2 kg^3}\right]}$$

(b) Determine the Fermi energy of a non-interacting gas of baloneyons as a function of the particle density.

Using the fact that baloneyons are spin-½ particles, we know that

$$\Phi = 2s + 1 = 2(½) + 1 = 2$$

Which means only 2 particles are allowed per energy level. If we are looking at the groundstate (T=0), then every level up to a certain point is filled. This looks like



Where the orientations of the spins above are just examples. If we wanted to count the number of particles we would use

$$N = 2 \cdot \left(\frac{L}{2\pi}\right)^2 \int d^2k .$$

When calculating the area of k-space we are only considering positive values of k. This is because when we solve the Schrödinger equation in 2D

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi = E\psi$$

Problem 2: Continued

The general solution is of the form

$$\Psi(x,y) = X(x)Y(y)$$

Where we have the solutions in each direction to be

$$X(x) = \sqrt{\frac{2}{\ell_x}}\sin(k_x x) \quad , \quad Y(y) = \sqrt{\frac{2}{\ell_y}}\sin(k_y y)$$

Where $\vec{k}$ is of course

$$k_x = \frac{n_x \pi}{\ell_x} \quad , \quad k_y = \frac{n_y \pi}{\ell_y}$$

Where our eigenvalue equation then tells us

$$E_k = \frac{\hbar^2 \vec{k}^2}{2m}$$

Where $\vec{k}$ is as previously defined. The Fermi Energy is defined to be the energy of the highest occupied state. To do this we have to count the number of particles that occupy this ensemble and then the area in which that they occupy.

The value for N is then,

$$N = \frac{L^2}{2\pi^2}\int_0^{2\pi}\int_0^{k_f} k \, dk \, d\varphi = \frac{L^2}{2\pi^2}\cdot 2\pi \cdot \frac{1}{2}k^2\Big|_0^{k_f} = \frac{L^2}{2\pi}k_f^2$$

We then solve for k_f^2

$$k_f^2 = 2\pi\frac{N}{L^2} \Rightarrow k_f^2 = 2\pi n \quad w/ \; n = \frac{N}{L^2}$$

We then can say that our Fermi energy is

$$E = B|\vec{p}|^4 = B(\hbar k_f)^4 = B\hbar^4 k_f^4$$

Therefore our Fermi Energy is

$$\boxed{E_f = B\hbar^4(2\pi n)^2}$$

Problem 2: Continued

(c) Explicitly check the units of your result obtained in part (b).

The Fermi Energy in the previous part in terms of units is

$$E = [B\hbar^4 (\cancel{2\pi}\#)^2] = [B\hbar^4] = [J] \checkmark$$

Where we can see that the units work out

(d) Provide a physical interpretation of the Fermi energy.

The Fermi energy is dependent upon the highest level occupied, which is quantified by k_F. As we are allowed more possible states, (i.e k_F increases) the Fermi energy will increase.

Problem 2: Review

Procedure:

- – Evaluate the units of B by expressing the other units in terms that we already know
- – To calculate the Fermi energy we need to determine how many particles occupy our system up to the highest energy level. This is calculated with
  $$N = 2 \cdot \left(\frac{L}{2\pi}\right)^2 \int d^2k$$
  where the 2 in front comes from the degeneracy of our system
  – Proceed to solve for the normalized wave functions in each direction for a particle in a box
  – Use the eigenvalue equation from the Schrödinger equation to express our energy in terms of $\vec{k}$
  – Proceed to calculate N with the aforementioned integral from above, integrating up to the highest energy level k_f
  – Proceed to solve for k_f^2 and put this into the equation for the energy of Baloneyons
- – Simply evaluate the units of the Fermi Energy. They should of course be Joules
- – Interpret the results found in parts (a) through (c)

Key Concepts:

- – This is simply dimensional analysis and is nothing beyond it
- – We calculate the number of particles that occupy our ensemble up to the highest energy level and then integrate over k-space to find and expression for N
- – This again is just dimensional analysis
- – The Fermi Energy is the energy of the highest occupied state in an ensemble

Variations:

- – The only way this problem changes is if the particle is changed to a different type
  - ∗ We then just calculate the the number of particles again use the same formalism after

Problem 3:

Consider a single electron with mass m, intrinsic spin $\frac{1}{2}\hbar\hat{\vec{\sigma}}$, and spin magnetic moment $\hat{\vec{\mathcal{M}}}_s$, where

$$\hat{\vec{\sigma}} = \begin{pmatrix} \hat{\sigma}_x \\ \hat{\sigma}_y \\ \hat{\sigma}_z \end{pmatrix}. \tag{2}$$

Using the eigen states $|\uparrow\rangle$ and $|\downarrow\rangle$ of $\hat{\sigma}_z$ as basis, we have the following matrix representations:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{3}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \tag{4}$$

and

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{5}$$

The spin of the electron has two possible orientations, up and down, with respect to an applied magnetic field $\vec{B}$. Letting the B-field point along the negative z-direction ($\vec{B} = -B_z\hat{e}_z$ with $B_z = |\vec{B}|$), the quantum mechanical Hamiltonian $\hat{\mathcal{H}}$ takes the form

$$\hat{\mathcal{H}} = -\hat{\vec{M}}_s \cdot \vec{B} = \mu_s \hat{\vec{\sigma}} \cdot \vec{B} = -\mu_B B_z \hat{\sigma}_z, \tag{6}$$

where

$$\mu_B = \frac{e\hbar}{2mc}. \tag{7}$$

Use the canonical ensemble to treat this problem.

Express the density matrix $\hat{\rho}$ in terms of the eigen states $|\uparrow\rangle$ and $|\downarrow\rangle$ of $\hat{\sigma}_z$ and calculate the thermal expectation value $\langle\hat{\sigma}_z\rangle$.

The equation for our density matrix is simply

$$\hat{\rho} = \frac{e^{-\beta\hat{\mathcal{H}}}}{Tr(e^{-\beta\hat{\mathcal{H}}})}$$

Re-writing this for the context of our problem we have

$$\exp(-\beta\mathcal{H}) = \exp(-\beta(-\mu_B B_z\hat{\sigma}_z)) = \exp\left(\frac{e\hbar}{2mc}\cdot\beta B_z\hat{\sigma}_z\right) \doteq \exp(\beta\alpha\hat{\sigma}_z)$$

$\hat{\rho}$ is then

$$\hat{\rho} = \frac{\exp(\beta\alpha\hat{\sigma}_z)}{Tr(\exp(\beta\alpha\hat{\sigma}_z))} \quad w/ \quad \alpha \equiv \frac{e\hbar B_z}{2mc} \tag{*}$$

Now, we then write $\hat{\sigma}_z$ in terms of its eigenstates. This is of course

$$\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = |\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|$$

Putting the above into (*) we have

$$\hat{\rho} = \frac{\exp(\alpha\beta(|\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|))}{Tr(\exp(\alpha\beta(|\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|)))}$$

Problem 3: Continued

Where $\hat{\rho}$ is expressed in terms of the eigenstates of σ_z. This matrix can also be written as

$$\exp(\alpha\beta\hat{\sigma}_z) = \begin{pmatrix} \exp(\alpha\beta) & 0 \\ 0 & \exp(-\alpha\beta) \end{pmatrix} = \begin{pmatrix} \exp(\mu_B B_z \beta) & 0 \\ 0 & \exp(-\mu_B B_z \beta) \end{pmatrix}$$

Where the trace of this matrix is simply

$$\exp(\mu_B B_z \beta) + \exp(-\mu_B B_z \beta) = 2\cosh(\mu_B B_z \beta)$$

Therefore, in all its beauty the density matrix is then

$$\boxed{\hat{\rho} = \frac{1}{2\cosh(\mu_B B_z \beta)} \begin{pmatrix} e^{\mu_B B_z \beta} & 0 \\ 0 & e^{-\mu_B B_z \beta} \end{pmatrix}}$$

We then calculate the thermal expectation value $\langle \sigma_z \rangle$ with

$$\langle \hat{\sigma}_z \rangle = \mathrm{Tr}(\hat{\rho}\hat{\sigma}_z)$$

This is of course simply

$$\hat{\rho}\hat{\sigma}_z = \frac{1}{2\cosh(\mu_B B_z \beta)} \begin{pmatrix} e^{\mu_B B_z \beta} & 0 \\ 0 & e^{-\mu_B B_z \beta} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{1}{2\cosh(\mu_B B_z \beta)} \begin{pmatrix} e^{\mu_B B_z \beta} & 0 \\ 0 & -e^{-\mu_B B_z \beta} \end{pmatrix}$$

Taking the trace of $\hat{\rho}\hat{\sigma}_z$ we have

$$\mathrm{Tr}(\hat{\rho}\hat{\sigma}_z) = \frac{1}{2\cosh(\mu_B B_z \beta)} \left(e^{\mu_B B_z \beta} - e^{-\mu_B B_z \beta} \right) = \frac{2\sinh(\mu_B B_z \beta)}{2\cosh(\mu_B B_z \beta)} = \mathrm{Tanh}(\mu_B B_z \beta)$$

This then means our thermal expectation value is

$$\boxed{\langle \hat{\sigma}_z \rangle = \mathrm{Tanh}(\mu_B B_z \beta)}$$

Problem 3: Review

Procedure:

- – We aim to find the density matrix $\hat{\rho}$ with

  $$\hat{\rho} = \frac{e^{-\beta\hat{\mathcal{H}}}}{\text{Tr}(e^{-\beta\hat{\mathcal{H}}})}$$

  where we can express $e^{-\beta\hat{\mathcal{H}}}$ as

  $$e^{-\beta\hat{\mathcal{H}}} \doteq e^{\alpha\beta\hat{\sigma}_z}$$

  where $\alpha \equiv \mu_B B$ is a constant
  - Expressing the Pauli Spin matrix in terms of its eigenstates we can then write what $e^{-\beta\hat{\mathcal{H}}}$ is in terms of matrix. This of course

  $$e^{-\beta\hat{\mathcal{H}}} = \begin{pmatrix} e^{\mu_B B_z \beta} & 0 \\ 0 & e^{-\mu_B B_z \beta} \end{pmatrix}$$

  - We now have enough to calculate $\hat{\rho}$
  - We then calculate $\langle\hat{\sigma}_z\rangle$ with

  $$\langle\hat{\sigma}_z\rangle = \text{Tr}(\hat{\rho}\hat{\sigma}_z)$$

Key Concepts:

- – We use the eigenvalue relationship

  $$\mathcal{H}\psi = E\psi$$

  to express what $e^{-\beta\hat{\mathcal{H}}}$ will be in the $\hat{\sigma}_z$ basis
  - The thermal expectation value $\langle\hat{\sigma}_z\rangle$ can be calculated with the above trace between the density matrix and spin matrix

Variations:

- – We could be asked to express this matrix in different eigenstates
    - ∗ This would cause our matrices to look slightly different but it would be the same broad procedure

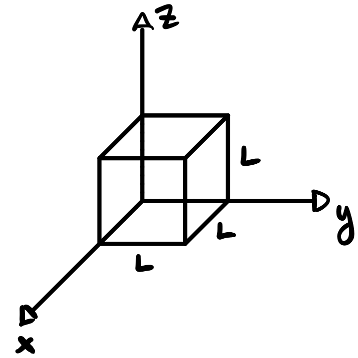
Problem 4:

Consider a three-dimensional free particle in a box of length L. Assume periodic boundary conditions. Use the canonical ensemble to treat this problem.

(a) Find a compact expression for the density matrix $\hat{\rho}$ in the coordinate representation, i.e., find a compact expression for the quantity $\langle \vec{r}|\hat{\rho}|\vec{r}'\rangle$; "compact" means that the ex- pression should not contain any (infinite) sums.

Hint: Consider converting the sum over $\vec{k}$ into an integral.

For a 3D free particle confined to a box it will look like



Where we have a Hamiltonian of the form

$$\tilde{\mathcal{H}} = \frac{\tilde{P}_i^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right).$$

Since we are working with periodic boundary conditions we know

$$\Psi(\alpha) = \Psi(\alpha + L) \quad \text{where} \quad \alpha \doteq \text{any cartesian direction}$$

Where the normalized 3D wave function is

$$\Psi_E(\vec{r}) = \frac{1}{L^{3/2}} e^{i\vec{k}\cdot\vec{r}}$$

Where $\vec{r}$ is our position and $\vec{k}$ can be related with

$$E = \frac{\hbar^2|\vec{k}|^2}{2m} \quad w/ \quad \vec{k} = \frac{2\pi}{L}(n_x\hat{x} + n_y\hat{y} + n_z\hat{z})$$

Now we wish to calculate $\hat{\rho}$ with

$$\hat{\rho} = \frac{\exp(-\beta\hat{\mathcal{H}})}{Tr(\exp(-\beta\hat{\mathcal{H}}))} \qquad (*)$$

Where we can now start to calculate $\langle \vec{r}|\hat{\rho}|\vec{r}'\rangle$. First we calculate the denominator of $(*)$. This is

Problem 4: Continued

$$\langle \vec{r}|\exp(-\beta\hat{\mathcal{H}})|\vec{r}\rangle = \left(\frac{L}{2\pi}\right)^3 \int_T \exp(-\beta\hbar^2 k^2/2m)\, d^3k = \left(\frac{L}{2\pi}\right)^3 \left(\frac{2m\pi}{\beta\hbar^2}\right)^{3/2}$$

$$= \left(\frac{L^2}{4\pi^2}\cdot\frac{2m\pi}{\beta\hbar^2}\right)^{3/2} = \left(\frac{mL^2}{2\pi\beta\hbar^2}\right)^{3/2} = V\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}$$

Where we now focus on finding $\langle \vec{r}|\exp(-\beta\hat{\mathcal{H}})|\vec{r}'\rangle$. We first begin by expanding in a complete set of our Hamiltonian

$$\langle \vec{r}|\exp(-\beta\hat{\mathcal{H}})|\vec{r}'\rangle = \sum_E \langle \vec{r}|\exp(-\beta\hat{\mathcal{H}})|E\rangle\langle E|\vec{r}'\rangle = \exp(-\beta E)\sum_E \langle \vec{r}|E\rangle\langle E|\vec{r}'\rangle$$

$$= \sum_E \exp(-\beta E)\, \psi_E(\vec{r})\psi_E^*(\vec{r}')$$

$$= \sum_E \exp(-\beta E)\left(\frac{1}{L^{3/2}} e^{i\vec{k}\cdot\vec{r}}\right)\left(\frac{1}{L^{3/2}} e^{-i\vec{k}\cdot\vec{r}'}\right)$$

$$= \frac{1}{L^3}\sum_E \exp(-\beta E)\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}$$

Where in order to make our expression compact we convert from a sum to an integral. We do this and the above becomes

$$\langle \vec{r}|\exp(-\beta\hat{\mathcal{H}})|\vec{r}'\rangle = \left(\frac{L}{2\pi}\right)^3\cdot\frac{1}{L^3}\int_T \exp\left(\frac{-\beta\hbar^2k^2}{2m}\right)\exp(i\vec{k}\cdot(\vec{r}-\vec{r}'))\, d^3k$$

To calculate this quantity we first have to write $e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}$ in a usable form. This is

$$e^{i\vec{k}\cdot\vec{r}} = e^{i\cdot k_x\cdot r_x}\, e^{ik_y\cdot r_y}\, e^{ik_z\cdot r_z}$$

We can then write $e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}$ as

$$e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} = e^{ik_x(r_x-r_x')}e^{ik_y(r_y-r_y')}e^{ik_z(r_z-r_z')}$$

Because e^{ix} is hard to integrate, we have to write this as

$$e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} = \prod_{j=x,y,z}\left(\cos(k(r_j-r_j')) + i\sin(k(r_j-r_j'))\right)$$

Using the above we then have

$$\langle \vec{r}|e^{-\beta\hat{\mathcal{H}}}|\vec{r}'\rangle = \frac{1}{V}\left(\frac{\beta\hbar^2}{2\pi m}\right)^{\frac{3}{2}}\int \prod_{j=x,y,z}\left(\cos(k(r_j-r_j')) + i\sin(k(r_j-r_j'))\right)\exp\left(\frac{-\beta\hbar^2k^2}{2m}\right) d^3k$$

Problem 4: Continued

We will examine this by calculating for one direction and then apply it to the other directions. This is then

$$= \int_{-\infty}^{+\infty} \exp\left(\frac{-\beta\hbar^2 k^2}{2m}\right)\cos(k(r_x - r_x')) + i\exp\left(\frac{-\beta\hbar^2 k^2}{2m}\right)\sin(k(r_x - r_x'))\, dk$$

$$= \int_{-\infty}^{+\infty} \exp\left(\frac{-\beta\hbar^2 k^2}{2m}\right)\cos(k(r_x - r_x'))\, dk + i\cancelto{0}{\int_{-\infty}^{+\infty} \exp\left(\frac{-\beta\hbar^2 k^2}{2m}\right)\sin(k(r_x - r_x'))\, dk}$$

↳ odd Fxn, even integral

$$= \int_{-\infty}^{+\infty} \exp\left(\frac{-\beta\hbar^2 k^2}{2m}\right)\cos(k(r_x - r_x'))\, dk = \sqrt{\frac{2m\pi}{\beta\hbar^2}}\exp\left(\frac{-m(r_x - r_x')^2}{2\beta\hbar^2}\right)$$

We can then generalize this for the other directions and we then have

$$\langle \vec{r}|e^{-\beta\hat{H}}|\vec{r}\,'\rangle = \frac{1}{V}\cancel{\left(\frac{\beta\hbar^2}{2\pi m}\right)^{\frac{3}{2}}}\cancel{\left(\frac{2m\pi}{\beta\hbar^2}\right)^{3/2}}\left[\exp\left(\frac{-m(r_x - r_x')^2}{2\beta\hbar^2}\right)\exp\left(\frac{-m(r_y - r_y')^2}{2\beta\hbar^2}\right)\exp\left(\frac{-m(r_z - r_z')^2}{2\beta\hbar^2}\right)\right]$$

We can go on to further say

$$(r_x - r_x')^2 + (r_y - r_y')^2 + (r_z - r_z')^2 = |\vec{r} - \vec{r}\,'|^2$$

Where we can finally say

$$\boxed{\langle \vec{r}|e^{-\beta\hat{H}}|\vec{r}\,'\rangle = \frac{1}{V}\exp\left(\frac{-m|\vec{r} - \vec{r}\,'|^2}{2\beta\hbar^2}\right)} \quad (*)$$

(b) Evaluate and interpret the quantity $\langle\vec{r}|\hat{\rho}|\vec{r}\rangle$.

We actually inadevertently found this quantiy

$$\langle\vec{r}|\hat{\rho}|\vec{r}\rangle$$

Earlier. This quantity is just our density and is then

$$\boxed{\langle\vec{r}|\hat{\rho}|\vec{r}\rangle = \frac{1}{V}}$$

Since $\langle\vec{r}|\hat{\rho}|\vec{r}\,'\rangle = \langle\vec{r}|\hat{\rho}|\vec{r}\rangle$ if $\vec{r} = \vec{r}\,'$

Problem 4: Continued

(c) Calculate $\langle \hat{\mathcal{H}} \rangle$.

We can calculate the mean value of our Hamiltonian with

$$\langle \hat{\mathcal{H}} \rangle = -\frac{\partial}{\partial \beta} \log(Q_N) = -\frac{\partial}{\partial \beta} \log(\mathrm{Tr}(\exp(-\beta \hat{\mathcal{H}})))$$

We have previously calculated $\mathrm{Tr}(\exp(-\beta\hat{\mathcal{H}}))$. We will recycle this result and we then have

$$\langle \hat{\mathcal{H}} \rangle = -\frac{\partial}{\partial \beta} \log\left(V\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}\right) = -\frac{\partial}{\partial \beta}\left(\cancelto{0}{\log(V)} + \cancelto{0}{\frac{3}{2}\log(m)} - \frac{3}{2}\log(2\pi\beta\hbar^2)\right)$$

$$= \frac{\partial}{\partial \beta}\left(\frac{3}{2}\log(2\pi\beta\hbar^2)\right) = \frac{3}{2}\frac{1}{\beta} = \frac{3}{2}kT \rightarrow \text{oh wow, what a shock}$$

Our ensemble average of our Hamiltonian is

$$\boxed{\langle \hat{\mathcal{H}} \rangle = \frac{3}{2}kT}$$

Problem 4: Review

Procedure:

- – Starting with the normalized wave function for this problem

  $$\psi(\vec{r}) = \frac{1}{L^{3/2}} e^{i\vec{k}\cdot\vec{r}}$$

  we use the eigenvalue relationship of a particle in a box to decimate how we can express $\hat{\rho}$ in terms of our problem
  – We proceed to find this desired quantity by expanding in a complete set and converting our infinite sum to an integral
- – Proceed to calculate this matrix element with the mathematical formalism found in Quantum Mechanics
- – Calculate the expectation value of our Hamiltonian with

  $$\langle\tilde{\mathcal{H}}\rangle = -\frac{\partial}{\partial\beta}\log\left(Q_N\right) = -\frac{\partial}{\partial\beta}\log\left(\mathrm{Tr}(e^{-\beta\tilde{\mathcal{H}}})\right)$$

  where the partition function was found with

  $$\langle\vec{r}|e^{-\beta\hat{\mathcal{H}}}|\vec{r}\rangle$$

  – Knowing the above we can then calculate $\langle\tilde{\mathcal{H}}\rangle$

Key Concepts:

- – Using the formalism in Quantum Mechanics we can determine what the matrix element

  $$\langle\vec{r}|e^{-\beta\hat{\mathcal{H}}}|\vec{r'}\rangle$$

  is in terms of an integral that can be evaluated
- – This quantity is essentially our density and this specific result can be obtained quickly by setting $\vec{r} = \vec{r'}$ in the final result of (a)
- – The quantity $3/2kT$ shows up again because that was Boltzmann's favorite number

Variations:

- – With a different set up of the problem that has a different total energy this problem can change drastically
  * This means we would have a different Hamiltonian and everything that involves the Hamiltonian and after would have to incorporate this change
- – We could be asked to find something different
  * This of course is contingent upon what is given to us but we would find it in the same way
- – Same as parts (a) and (b)