Particles in a box

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PROBLEM

Consider a single free particle of mass m confined to a volume V. Let $Z_1(m)$ denote the quantum partition function for this system (where the partition sum is taken over the discrete energy levels of a particle of mass m in a box of volume V).

a) Show that $Z_1(m) \to V/\lambda^3$ with $\lambda = h/\sqrt{2\pi mkT}$ in the classical (or small $\hbar$) limit. Use this result to calculate the classical energy and heat capacity at fixed volume of the single particle system.

b) Identify the temperature at which this approximation breaks down.

c) Now consider a system consisting of two identical, non-interacting particles in the same box. Because of the effects of identical particle statistics, the classical expectation for the two-particle partition function $Z_2(m) = Z_1(m)^2$ is not quite correct. Show that the exact free boson and free fermion two-particle partition sums can in fact be expressed in a simple way in terms of the one-particle functions $Z_1(m)$ and $Z_1(m/2)$.

d) Using the classical approximation $Z_1(m) = V/\lambda^3$ derived in the first part of this problem, calculate the correction to the energy E and the heat capacity C due to Bose or Fermi statistics.

SOLUTION TO PART A

In the classical limit, the single particle partition function is given by

$$Z_1(m) = \frac{1}{h^3}\int d^3q \int d^3p\, e^{-\beta H(p,q)} = \frac{V}{h^3}\left(\int_{-\infty}^{\infty} dp\, e^{-\frac{p^2}{2mkT}}\right)^3 = V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} = \frac{V}{\lambda^3}$$

By equipartition theorem of classical statistical mechanics, the internal energy of a given temperature is

$$U = \frac{3}{2}kT$$

And then the heat capacity is given by

$$c_V = \frac{3}{2}k\,.$$

SOLUTION TO PART B

When the de Broglie wave length of thermal motion is comparable to the size of the box, the classical approximation will break down, and the temperature is given by

$$T \sim \frac{h^2}{mkV^{2/3}}$$

SOLUTION TO PART C

In this part we consider about the quantum partition function for fermions and bosons. We start with the diagonal elements of the density matrix $e^{-\beta H}$:

$$\langle r_1, r_2|e^{-\beta H}|r_1, r_2\rangle = \frac{1}{2!}\sum_{k_1,k_2} e^{-\left(\frac{\hbar^2 k_1^2}{2mkT}+\frac{\hbar^2 k_2^2}{2mKT}\right)}\psi^*_{k_1,k_2}(r_1,r_2)\psi_{k_1,k_2}(r_1,r_2)$$

in which the first 1/2! comes from the permutation redundancy of the two momenta in the term $e^{-\beta(E_1+E_2)}$, and the symmetric/antisymmetric wave function $\psi_{k_1,k_2}(r_1,r_2)$ is

$$\psi_{k_1,k_2}(r_1,r_2) = \frac{1}{\sqrt{2!}}\sum_P \delta_P u_{k_1}(Pr_1)u_{k_2}(Pr_2) = \frac{1}{\sqrt{2!}}\sum_P \delta_P u_{Pk_1}(r_1)u_{Pk_2}(r_2)$$

in which P stands for all the possible permutation for two particles, and $\delta_P = (\pm 1)^P$. For fermions we take -1 and for bosons we take $+1$. We take all these into consideration, then the diagonal elements of the density matrix is

$$\langle r_1, r_2|e^{-\beta H}|r_1, r_2\rangle = \frac{1}{2!2!}\sum_{k_1,k_2} e^{-\left(\frac{\hbar^2 k_1^2}{2mkT}+\frac{\hbar^2 k_2^2}{2mKT}\right)}\sum_P \delta_P u_{k_1}(Pr_1)u_{k_2}(Pr_2)\sum_{P'}\delta_{P'}u^*_{P'k_1}(r_1)u^*_{P'k_2}(r_2)$$

Now consider about the summation over different P'. All of these terms have the same contribution because they are just permutation over all the 2! momenta. So we can only choose the identity in all of the P' and then multiply by 2!, and no matter which statistic it satisfies $\delta_{P'} = 1$. Then the equation becomes

$$\langle r_1, r_2|e^{-\beta H}|r_1, r_2\rangle = \frac{1}{2!}\sum_{k_1,k_2} e^{-\left(\frac{\hbar^2 k_1^2}{2mkT}+\frac{\hbar^2 k_2^2}{2mKT}\right)}\sum_P \delta_P u_{k_1}(Pr_1)u^*_{k_1}(r_1)u_{k_2}(Pr_2)u^*_{k_2}(r_2)$$

The single particle wave function is a plane wave in a box:

$$u_k(r) = \frac{1}{\sqrt{V}}e^{ik\cdot r}$$

Then the density matrix diagonal elements are

$$\begin{aligned}\langle r_1, r_2|e^{-\beta H}|r_1, r_2\rangle &= \frac{1}{2!}\frac{1}{V^2}\sum_{k_1,k_2} e^{-\left(\frac{\hbar^2 k_1^2}{2mkT}+\frac{\hbar^2 k_2^2}{2mKT}\right)}\left(1+(-1)^\eta e^{ik_1\cdot(r_2-r_1)}e^{ik_2\cdot(r_1-r_2)}\right)\\ &= \frac{1}{2!}\int\frac{d^3k_1}{(2\pi)^3}\int\frac{d^3k_2}{(2\pi)^3}e^{-\left(\frac{\hbar^2 k_1^2}{2mkT}+\frac{\hbar^2 k_2^2}{2mKT}\right)}\left(1+(-1)^\eta e^{ik_1\cdot(r_2-r_1)}e^{ik_2\cdot(r_1-r_2)}\right)\end{aligned}$$

in which $\eta = 1$ for fermion and $\eta = 0$ for boson. We can use the Gaussian integral, and the result is

$$\langle r_1, r_2|e^{-\beta H}|r_1, r_2\rangle = \frac{1}{2!\lambda^6}\left(1+(-1)^\eta e^{-\frac{2\pi(r_1-r_2)^2}{\lambda^2}}\right)$$

Then it is straightforward to find the partition function $Z_2(m) = \mathrm{tr}(e^{-\beta H})$:

$$\begin{aligned}
Z_2(m) &= \int d^3r_1 \int d^3r_2 \, \langle r_1, r_2 | e^{-\beta H} | r_1, r_2 \rangle \\
&= \int d^3r_1 \int d^3r_2 \, \frac{1}{2!\lambda^6} \left(1 + (-1)^\eta e^{-\frac{2\pi r^2}{\lambda^2}}\right) \\
&= \frac{1}{2} \frac{V^2}{\lambda^6} \left(1 + (-1)^\eta \frac{1}{V} \int d^3r \, e^{-\frac{2\pi r^2}{\lambda^2}}\right) \\
&= \frac{1}{2} \left(\frac{V}{\lambda^3}\right)^2 \left[1 + (-1)^\eta \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{V}\right)\right] \\
&= \frac{1}{2} \left[Z_1^2(m) + (-1)^\eta Z_1(m/2)\right] .
\end{aligned}$$

SOLUTION TO PART D

Energy can be calculated from the partition function

$$U = -\frac{\partial}{\partial \beta} \log Z_2(m) = 3kT \frac{Z_1^2(m) + \frac{1}{2}(-1)^\eta Z_1(m/2)}{Z_1^2(m) + (-1)^\eta Z_1(m/2)} = 3kT \left(1 - \frac{1}{2} \frac{(-1)^\eta Z_1(m/2)}{Z_1^2(m) + (-1)^\eta Z_1(m/2)}\right)$$

and the heat capacity is given by

$$c_V = \frac{\partial U}{\partial T} = 3k + \frac{3k}{2} \frac{\frac{1}{2}(-1)^\eta Z_1^2(m) - Z_1(m/2)}{\left[Z_1^2(m) + (-1)^\eta Z_1(m/2)\right]^2} Z_1(m/2) \, .$$