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Practice for Qualifying Exams

Problem Source: **CMU Qualifying Exam August 2004**

(1) (a) Write down the canonical partition function Z_q for a quantum system E_s for the energy of state s, and $\beta = \frac{1}{k_B T}$ (k_B is Boltzmann's constant, T is the absolute temperature). Next write down the classical partition function Z_c appropriate for a monatomic gas of N identical non-relativistic particles of mass m in a volume V as an integral involving the Hamiltonian H.

$$Z_q = \sum_s e^{-\beta E_s}$$

where the N and V dependencies appear in the energy states and analogously,

$$Z_c = \frac{1}{N!h^{3N}} \int\int e^{-\beta H(\vec{p},\vec{q})} d^{3N}p\, d^{3N}q$$

(b) Beginning with appropriate expressions for the averages $\langle E \rangle$ and $\langle E^2 \rangle$, show that the variance of the energy E can be written in the form

$$\left\langle \left(E - \langle E \rangle\right)^2 \right\rangle = -\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{V,N}$$

for both the quantum and classical systems considered in part (a).

First, note that $\left\langle \left(E - \langle E \rangle\right)^2 \right\rangle = \left\langle E^2 - 2E\langle E \rangle + \langle E \rangle^2 \right\rangle = \langle E^2 \rangle - \langle E \rangle^2$.

Further,

$$\langle E \rangle_q = \frac{\sum_s E_s e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}$$

$$\langle E^2 \rangle_q = \frac{\sum_s E^2{}_s e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}$$

and,

$$\langle E \rangle_c = \frac{1}{N!h^{3N}} \int\int H(\vec{p},\vec{q}) e^{-\beta H(\vec{p},\vec{q})} d^{3N}p\, d^{3N}q$$

$$\langle E^2 \rangle_c = \frac{1}{N!h^{3N}} \int\int H(\vec{p},\vec{q})^2 e^{-\beta H(\vec{p},\vec{q})} d^{3N}p\, d^{3N}q$$

Now:

$$\left[\frac{\partial\langle E\rangle_q}{\partial\beta}\right]_{V,N} = -\frac{\sum_s E_s{}^2 e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} + \frac{\sum_s E_s e^{-\beta E_s}}{\left[\sum_s e^{-\beta E_s}\right]^2}\left(\sum_s E_s e^{-\beta E_s}\right)$$

$$= -\langle E^2\rangle + \langle E\rangle^2$$

$$so \quad -\left[\frac{\partial\langle E\rangle_q}{\partial\beta}\right]_{V,N} = \langle E^2\rangle - \langle E\rangle^2$$

It is clear that since $\frac{\partial}{\partial\beta}$ commutes with the classical integral, the same phenomenon will give an analogous result.

(c) Evaluate the result of part (b) for a classical monatomic ideal gas, by first using the partition function you derived in part (a) in order to obtain $\langle E\rangle$. From your result, estimate how many atoms such a gas would have to have in order for its root mean square fluctuation in energy (i.e., standard deviation), divided by the number of particles to be $10^{-4}k_BT$

$$Z_c = \frac{1}{N!h^{3N}}\int\int e^{-\beta H(\vec{p},\vec{q})}d^{3N}pd^{3N}q$$

$$= \frac{V^N}{N!h^{3N}}\int e^{-\beta\frac{p^2}{2m}}d^{3N}p = \frac{V^N}{N!h^{3N}}\int_0^\infty e^{-\beta\frac{p^2}{2m}}4\pi p^2 d^N p$$

evaluating,

$$\int_0^\infty e^{-\beta\frac{p^2}{2m}}4\pi p^2 dp$$

$$u = p \qquad du = pdp$$

$$dv = e^{-\beta\frac{p^2}{2m}}pdp \quad v = -\frac{m}{\beta}e^{-\beta\frac{p^2}{2m}}$$

$$= 4\pi\left[-\frac{m}{\beta}e^{-\beta\frac{p^2}{2m}}p\right]\Bigg|_{p=0}^{\infty} + 4\pi\frac{m}{\beta}\int_0^\infty e^{-\beta\frac{p^2}{2m}}dp$$

$$= 4\pi\frac{m}{\beta}\int_0^\infty e^{-\beta\frac{p^2}{2m}}dp$$

This is a Gaussian integral. I notice that:

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi} = 2\int_{0}^{\infty} e^{-x^2} dx \quad \int_{0}^{\infty} e^{-ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$$

so that

$$Z_c = \frac{1}{N!h^{3N}}\left[V\frac{2\pi m}{\beta}\sqrt{\frac{2m\pi}{\beta}}\right]^N = \frac{1}{N!h^{3N}}\left[V\left(\frac{2m\pi}{\beta}\right)^{\frac{3}{2}}\right]^N$$

Now recall that I actually need $\frac{\partial\langle E\rangle}{\partial\beta}$. In this case, I see that clearly,

$$\langle E\rangle = -\frac{1}{Z_c}\left[\frac{\partial Z_c}{\partial\beta}\right]$$

so that I have

$$\left\langle E^2\right\rangle - \left\langle E\right\rangle^2 = -\frac{\partial}{\partial\beta}\left[-\frac{1}{Z_c}\frac{\partial Z_c}{\partial\beta}\right]$$

$$= -\frac{1}{Z_c{}^2}\left[\frac{\partial Z_c}{\partial\beta}\right]^2 + \frac{1}{Z_c}\left[\frac{\partial^2 Z_c}{\partial\beta^2}\right]$$

so that

$$\frac{\partial Z_c}{\partial\beta} = -\frac{V^N}{N!h^{3N}}\left(\frac{3}{2}N\right)\left(\frac{2m\pi}{\beta}\right)^{\frac{3}{2}N-1}\left(\frac{2m\pi}{\beta^2}\right) = -\frac{V^N}{N!h^{3N}}\left(\frac{3N}{2\beta}\right)\left(\frac{2m\pi}{\beta}\right)^{\frac{3}{2}N}$$

$$\frac{\partial^2 Z_c}{\partial\beta^2} = \frac{V^N}{N!h^{3N}}\left(\frac{3N}{2\beta^2}\right)\left(\frac{2m\pi}{\beta}\right)^{\frac{3}{2}N} + \frac{V^N}{N!h^{3N}}\left(\frac{3N}{2\beta}\right)^2\left(\frac{2m\pi}{\beta}\right)^{\frac{3}{2}N}$$

$$= \frac{V^N}{N!h^{3N}}\left(\frac{2m\pi}{\beta}\right)^{\frac{3}{2}N}\frac{1}{\beta^2}\left(\frac{3}{2}N + \frac{9}{4}N^2\right)$$

So that:

$$\left\langle E^2\right\rangle - \left\langle E\right\rangle^2 = -\frac{1}{Z_c^{\ 2}}\left[\frac{\partial Z_c}{\partial\beta}\right]^2 + \frac{1}{Z_c}\left[\frac{\partial^2 Z_c}{\partial\beta^2}\right]$$

$$= -\left(\frac{3N}{2\beta}\right)^2 + \frac{1}{\beta^2}\left(\frac{3}{2}N + \frac{9}{4}N^2\right) = \frac{3N}{2\beta^2}$$

Now I want to solve:

$$\frac{\sqrt{\left\langle E^2\right\rangle - \left\langle E\right\rangle^2}}{N} = \frac{10^{-4}}{\beta} = \frac{1}{\beta}\sqrt{\frac{3}{2N}}$$

$$\frac{3}{2N} = 10^{-8} \quad N = 1.5\times 10^8$$

(d) **Now calculate the energy fluctuation (variance) for N independent, three-dimensional quantum harmonic oscillators, each with the same classical angular frequency ω. Compare the result with what you found for an ideal gas of N particles in part (c), both at high and low temperatures, in each case indicating the dominant temperature dependence.**

Dropping the zero-point energy term, I see that this would become a sum which via the prescription whereby one selects the density of states within an octant of space.

$$Z_q = \sum_{x,y,z=0}^{\infty} e^{-\frac{\beta}{\hbar\omega}\left(\varepsilon_x+\varepsilon_y+\varepsilon_z\right)^2} \to V^N\left[1+\int_0^{\infty} e^{-\frac{\beta}{\hbar\omega}\varepsilon^2}\left(\frac{4\pi}{8}\varepsilon^2\right)d\varepsilon\right]^N$$

Thus the result of the integral is exactly the same as before ith $m \to \frac{\hbar\omega}{2}$ and an overall factor of $\left(\frac{1}{8}\right)$, but I had to include the zero-energy term since in this prescription the zero-energy state is not counted due to the zero coefficient in the integral.

Thus,

$$Z_q = V^N\left[1+\left(\frac{\hbar\omega\pi}{8\beta}\right)^{\frac{3}{2}}\right]^N$$

$$\langle E^2 \rangle - \langle E \rangle^2 = -\frac{1}{Z_q^{\ 2}}\left[\frac{\partial Z_q}{\partial \beta}\right]^2 + \frac{1}{Z_c}\left[\frac{\partial^2 Z_q}{\partial \beta^2}\right]$$

$$\frac{\partial Z_q}{\partial \beta} = -V^N N\left(\frac{\hbar\omega\pi}{8\beta^2}\right)\left[1+\left(\frac{\hbar\omega\pi}{8\beta}\right)\right]^{N-1}$$

$$\frac{\partial^2 Z_q}{\partial \beta^2} = V^N N(N-1)\left(\frac{\hbar\omega\pi}{8\beta^2}\right)^2\left[1+\left(\frac{\hbar\omega\pi}{8\beta}\right)\right]^{N-2} + V^N(2N)\left(\frac{\hbar\omega\pi}{8\beta^3}\right)\left[1+\left(\frac{\hbar\omega\pi}{8\beta}\right)\right]^{N-1}$$

$$\langle E^2 \rangle - \langle E \rangle^2 =$$

$$\left[1+\left(\frac{\hbar\omega\pi}{8\beta}\right)\right]^{-2}\left[-N^2\left(\frac{\hbar\omega\pi}{8\beta^2}\right)^2 + N(N-1)\left(\frac{\hbar\omega\pi}{8\beta^2}\right)^2 + (2N)\left(\frac{\hbar\omega\pi}{8\beta^3}\right)\left[1+\left(\frac{\hbar\omega\pi}{8\beta}\right)\right]\right]$$

$$= \left[1+\left(\frac{\hbar\omega\pi}{8\beta}\right)\right]^{-2}\left[-N\left(\frac{\hbar\omega\pi}{8\beta^2}\right)^2 + (2N)\left(\frac{\hbar\omega\pi}{8\beta^3}\right)\left[1+\left(\frac{\hbar\omega\pi}{8\beta}\right)\right]\right]$$

$$= \left[1+\left(\frac{\hbar\omega\pi}{8\beta}\right)\right]^{-2}\left[\left(\frac{\hbar\omega\pi}{8\beta^2}\right)^2 + (2N)\left(\frac{\hbar\omega\pi}{8\beta^3}\right)\right]$$

Essentially, though, this is identical to the classical solution with an additional "condensed" state. The dominant dependence at low temperatures where $\frac{1}{\beta} \to 0$ is then clearly of order $\frac{1}{\beta^3} \propto T^3$ and at high temperatures where $\frac{1}{\beta} \to \infty$ will be of order $\frac{1}{\beta^2} \propto T^2$, just as in the classical case.