Statistical Physics
Test 2

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03/06/2026

1. Problem sheet 4. Solve one of the following questions:

   (a) In the presence of an external potential $U\left(\overrightarrow{r}\right)$, the distribution function is inhomogeneous in space:

   $$f\left(\overrightarrow{p},\overrightarrow{r}\right) \propto \exp\left(-\beta\left(\frac{\overrightarrow{p}^2}{2m}+U\left(\overrightarrow{r}\right)\right)\right)$$

   Consider a gas in the harmonic potential $U\left(\overrightarrow{r}\right)=\frac{1}{2}\kappa r^2$. Calculate its density $n\left(\overrightarrow{r}\right)$ (up to multiplicative constant).
   Notice that mean radius is zero $\langle\overrightarrow{r}\rangle=0$, why? Calculate mean-square radius $\langle r^2\rangle$.

   (b) The Maxwell-Boltzmann distribution is given as:

   $$f\left(\overrightarrow{p}\right) \propto e^{-\beta\frac{\overrightarrow{p}^2}{2m}}$$

   Find the distribution function in terms of energy $f_E(E)$ and express the n^{th} energy moment of this distribution $\langle E^n\rangle\,,\ n\in\mathbb{N}$.
   Hint:

   $$\Gamma(x)=\int_0^\infty t^{x-1}e^{-t}\,dt$$

2. Problem sheet 5 - partition function. Solve one of the following questions:

   (a) The one-dimensional quantum harmonic oscillator has its energy spectrum given by:

   $$E_n=\left(n+\frac{1}{2}\right)\hbar\omega$$

   where $\omega>0$ is the angular frequency of the oscillator, $\hbar$ is Dirac constant, $n\in\mathbb{N}_0$. Find the partition function for such an oscillator and then calculate its internal energy and heat capacity.
   Hint:

   $$Z=\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

(b) Consider a system composed of two subsystems $A,\ B$. In general, its energy states can be written as:

$$E_{ij} = E_i^A + E_j^B + V_{ij}$$

where V_{ij} corresponds to interactions - if it vanishes, these subsystems are independent. It is reasonable to conclude then that other properties like **free energy** or **entropy** also can be decomposed into a sum over these subsystems. In statistical mechanics, your task is to prove this.

Hint: start with

$$Z_{AB} = \sum_{i,j} e^{-\beta E_{ij}}$$

Examples of solutions

1. Problem sheet 4

   (a) Of course, since the potential does not depend on the momenta of particles:

$$\begin{aligned} n\left(\overrightarrow{r}\right) &= \int_{\mathbb{R}^3} f\left(\overrightarrow{p}, \overrightarrow{r}\right) d^3p \\ &= C\exp\left(-\beta U\left(\overrightarrow{r}\right)\right)\int_{\mathbb{R}^3}\exp\left(-\frac{\beta\overrightarrow{p}^2}{2m}\right)d^3p \\ &= \tilde{C}\exp\left(-\frac{1}{2}\beta\kappa\overrightarrow{r}^2\right) \end{aligned}$$

Since the integral is a Gaussian one, hence it's finite. One can easily notice that:

$$\tilde{C} = n\left(\overrightarrow{0}\right) \equiv n_0$$

Mean radius of this density function is zero since, by construction, the potential is centred at the beginning of the $\mathbb{R}^3$. In other words:

$$\begin{aligned} \langle x\rangle &= n_0\int_{\mathbb{R}^3} xe^{-\frac{1}{2}\beta\kappa\left(x^2+y^2+z^2\right)}dxdydz \\ &= \int_{\mathbb{R}} e^{-\frac{1}{2}\beta\kappa y^2}dy\cdot\int_{\mathbb{R}} e^{-\frac{1}{2}\beta\kappa z^2}dz\cdot\int_{\mathbb{R}} xe^{-\frac{1}{2}\beta\kappa x^2}dx \end{aligned}$$

and since x is an odd function, the Gaussian is even, the total integral vanishes. The same applies for other components of $\overrightarrow{r} = (x, y, z)$

In order to calculate mean-square radius:

$$\begin{aligned} \left\langle r^2\right\rangle &= \left\langle x^2+y^2+z^2\right\rangle \\ &= n_0\int_{\mathbb{R}^3}\left(x^2+y^2+z^2\right)e^{-\frac{1}{2}\kappa\beta\left(x^2+y^2+z^2\right)}dxdydz \\ &= n_0\int_{\mathbb{R}} x^2e^{-\frac{1}{2}\kappa\beta x^2}dx\cdot\int_{\mathbb{R}} e^{-\frac{1}{2}\kappa\beta y^2}dy\cdot\int_{\mathbb{R}} e^{-\frac{1}{2}\kappa\beta z^2}dz\cdot 3 \end{aligned}$$

where the factor 3 follows from the separation of the original integral into a sum of products of integrals and the indistinguishability of integrals.

It is useful to remember that:

$$I(\alpha) = \int_{\mathbb{R}} e^{-\alpha x^2}dx = \sqrt{\frac{\pi}{\alpha}}, \qquad \alpha > 0$$

This gives us two integrals from above. We can use this also to calculate remaining one:

$$\begin{aligned} \int_{\mathbb{R}} x^2e^{-\alpha x^2}dx &= -\int_{\mathbb{R}}\frac{\partial}{\partial\alpha}e^{-\alpha x^2}dx = -\frac{d}{d\alpha}\int_{\mathbb{R}} e^{-\alpha x^2}dx \\ &= -\frac{d}{d\alpha}I(\alpha) = -\sqrt{\pi}\frac{d}{d\alpha}\left(\alpha^{-\frac{1}{2}}\right) \\ &= -\sqrt{\pi}\cdot\left(-\frac{1}{2}\right)\alpha^{-\frac{3}{2}} = \frac{\sqrt{\pi}}{2\alpha^{3/2}} \end{aligned}$$

For our purpose: $\alpha = \frac{1}{2}\beta\kappa$. As a result:

$$\begin{aligned} \left\langle r^2\right\rangle &= \ldots. = 3n_0\cdot\frac{\sqrt{\pi}}{2\left(\frac{1}{2}\beta\kappa\right)^{3/2}}\cdot\sqrt{\frac{\pi}{\frac{1}{2}\beta\kappa}}\cdot\sqrt{\frac{\pi}{\frac{1}{2}\beta\kappa}} \\ &= 6\sqrt{2}\; n_0\pi^{3/2}\kappa^{-5/2}\beta^{-5/2} \end{aligned}$$

(b) Since f is a distribution, then:

$$\int f\left(\overrightarrow{p}\right) d^3p = \int f_E(E)dE$$

The energy (kinetic energy) of a gas is:

$$E\left(\overrightarrow{p}\right) = \frac{\overrightarrow{p}^2}{2m} = \frac{p^2}{2m}$$

where $p = |\overrightarrow{p}|$ is the length of momentum vector. From this:

$$p^2 = 2mE, \qquad 2pdp = 2mdE \implies dp = \frac{m}{p(E)}dE = \frac{m}{\sqrt{2mE}}dE = \sqrt{\frac{m}{2E}}dE$$

Let's put everything together:

$$\begin{aligned}\int f_E(E)dE &= \int f\left(\overrightarrow{p}\right) d^3p\\ &= C\int e^{-\beta E\left(\overrightarrow{p}\right)}d^3p\\ &= C\int d\phi \int \sin(\theta)d\theta \int e^{-\beta E(p)}p^2dp\\ &= \tilde{C}\int e^{-\beta E}\cdot 2mE\cdot\sqrt{\frac{m}{2E}}dE\\ &= \overline{C}\int \sqrt{E}e^{-\beta E}dE\end{aligned}$$

and as a result:

$$f_E(E) \propto \sqrt{E}e^{-\beta E}$$

and $\overline{C}$ is just normalisation constant.
To calculate the n^{th} moment of this distribution:

$$\begin{aligned}\langle E^n\rangle &= \int_0^\infty E^n f_E(E)dE\\ &= \overline{C}\int_0^\infty E^n\sqrt{E}e^{-\beta E}dE\\ &= \overline{C}\int_0^\infty E^{n+\frac{1}{2}}e^{-\beta E}dE\end{aligned}$$

$$\left|\begin{array}{l}\beta E = t \implies \beta dE = dt \implies dE = \frac{1}{\beta}dt\\ E^{n+\frac{1}{2}} = (\beta E)^{n+\frac{1}{2}}\cdot\frac{1}{\beta^{n+\frac{1}{2}}} = \frac{t^{n+\frac{1}{2}}}{\beta^{n+\frac{1}{2}}}\\ E = 0 \implies t = 0\\ E \to \infty \implies t \to \infty\end{array}\right.$$

$$\begin{aligned}&= \overline{C}\int_0^\infty \frac{1}{\beta^{n+\frac{3}{2}}}t^{n+\frac{1}{2}}e^{-t}dt\\ &= \frac{\overline{C}}{\beta^{n+\frac{3}{2}}}\Gamma\left(n+\frac{3}{2}\right)\end{aligned}$$

$$\boxed{\langle E^n\rangle = \frac{\overline{C}}{\beta^{n+\frac{3}{2}}}\Gamma\left(n+\frac{3}{2}\right)}$$

2. Problem sheet 5.

   (a) First, let us calculate the partition function:

$$\begin{aligned} Z &= \sum_{n\in\mathbb{N}_0} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega} \\ &= \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} e^{-\frac{1}{2}\beta\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n \\ &= e^{-\frac{1}{2}\beta\hbar\omega} \cdot \frac{1}{1-e^{-\beta\hbar\omega}} \end{aligned}$$

where we used the sum for an infinite geometric series with ratio $|q| < 1$. In order to calculate the internal energy:

$$\begin{aligned} \ln(Z) &= \ln\left(e^{-\frac{1}{2}\beta\hbar\omega} \cdot \frac{1}{1-e^{-\beta\hbar\omega}}\right) \\ &= \ln\left(e^{-\frac{1}{2}\beta\hbar\omega}\right) - \ln\left(1-e^{-\beta\hbar\omega}\right) \\ &= -\frac{1}{2}\beta\hbar\omega - \ln\left(1-e^{-\beta\hbar\omega}\right) \end{aligned}$$

$$\begin{aligned} U &= -\frac{\partial \ln(Z)}{\partial\beta} \\ &= -\frac{\partial}{\partial\beta}\left(-\frac{1}{2}\beta\hbar\omega - \ln\left(1-e^{-\beta\hbar\omega}\right)\right) \\ &= \frac{1}{2}\hbar\omega + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \end{aligned}$$

To calculate heat capacity, we know that:

$$\beta = \frac{1}{k_B T} \implies \frac{d\beta}{dT} = -\frac{1}{k_B T^2} = -k_B\beta^2$$

Therefore:

$$\begin{aligned} C_v &= \frac{\partial U}{\partial T} = \frac{\partial U}{\partial\beta}\frac{d\beta}{dT} \\ &= -k_B\beta^2\frac{\partial U}{\partial\beta} \\ &= -k_B\beta^2\frac{\partial}{\partial\beta}\left(\frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right) \\ &= -k_B\beta^2\left(\frac{-\hbar^2\omega^2 e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} + \frac{\hbar\omega e^{-\beta\hbar\omega}\cdot(-1)\cdot(-1)\cdot(-\hbar\omega)e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}\right) \\ &= k_B\beta^2\hbar^2\omega^2 e^{-\beta\hbar\omega}\frac{1}{(1-e^{-\beta\hbar\omega})^2}\left(1-e^{-\beta\hbar\omega}+e^{-\beta\hbar\omega}\right) \\ &= k_B\beta^2\hbar^2\omega^2\frac{e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2} \end{aligned}$$

(b) We start with:

$$\begin{aligned} Z_{AB} &= \sum_{i,j} e^{-\beta E_{ij}} = \sum_{i,j} e^{-\beta E_i^a - \beta E_j^B} = \sum_i \sum_j e^{-\beta E_i^a} e^{-\beta E_j^B} \\ &= \sum_i e^{-\beta E_i^a} \sum_j e^{-\beta E_j^B} = \sum_i e^{-\beta E_i^a} Z_B \\ &= Z_A Z_B \end{aligned}$$

And therefore free energy:

$$F_{AB} = -kT \ln\left(Z_{AB}\right) = -kT \ln\left(Z_A\right) - kT \ln\left(Z_B\right) = F_A + F_B$$

Next, entropy is given as a derivative[1] of F with respect to T - derivatives are linear operations, hence $S_{AB} = S_A + S_B$.

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[1] with some multiplicative constant