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Statistical Mechanics
Homework 5

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H5.1 Systems of identical particles

The entropy is an extensive quantity, i. e. $S(\text{System}_1 + \text{System}_2) = S(\text{System}_1) + S(\text{System}_2)$.

Verify this property, first using the naïve partition function $Z'_N = (\alpha kT)^{\frac{3N}{2}} V^N$ and then taking into account particles being indistinguishable $Z_N = \frac{1}{N!}(\alpha kT)^{\frac{3N}{2}} V^N$, where $\alpha \equiv 2\pi m$ and for simplicity $V_1 = V_2 = V$ and $N_1 = N_2 = N$.

The entropy can be obtained from both partition functions via:

$$\begin{aligned} S &= -\frac{\partial F}{\partial T} = \frac{\partial}{\partial T} kT \log Z_N(T) \\ &= k \log Z_N(T) + \frac{3}{2} kN \end{aligned}$$

(i) Using Z'_N:

$$\begin{aligned} S(V_1, N_1) + S(V_2, N_2) = 2S(V, N) &= 2Nk \log V + 3Nk \log \alpha kT + 3Nk \\ S(V_1 + V_2, N_1 + N_2) = S(2V, 2N) &= 2Nk \log 2V + 3Nk \log \alpha kT + 3Nk \end{aligned}$$

$$\implies 2S(V, N) \neq S(2V, 2N)$$

(ii) On the other hand with Z_N (using Sterling's formula):

$$S = Nk \log V + \frac{3N}{2} k \log \alpha kT - Nk \log N + \frac{5N}{2} k$$

$$\begin{aligned} 2S(V, N) &= 2Nk \log \frac{V}{N} + 3Nk \log \alpha kT + 5Nk \\ S(2V, 2N) &= 2Nk \log \frac{2V}{2N} + 3Nk \log \alpha kT + 5Nk \end{aligned}$$

$$\implies \boxed{2S(V, N) = S(2V, 2N)}$$

H5.2 Relativistic particles

Consider the Hamiltonian $H = \sqrt{p^2c^2 + m^2c^4}$ and compute the partition function:

$$
\begin{aligned}
Z_N &= \frac{1}{N!} \int \prod_{j=1}^{N} \frac{\mathrm{d}^3 p_j \, \mathrm{d}^3 q_j}{(2\pi\hbar)^3} e^{-\beta c \sqrt{p^2 + m^2 c^2}} \\
&= \frac{1}{N!} \left(\frac{4\pi V}{(2\pi\hbar)^3} \int\limits_0^\infty \mathrm{d}p \, p^2 e^{-\beta c^2 m \sqrt{\frac{p^2}{m^2c^2} + 1}} \right)^N
\end{aligned}
$$

Using:

$$
\int\limits_0^\infty \mathrm{d}p \, p^2 e^{-a\sqrt{p^2+1}} = \int\limits_1^\infty \mathrm{d}u \, u\sqrt{u^2-1} e^{-au} = \frac{K_2(a)}{a}
$$

where K_α is the modified Bessel function.

$$
\implies Z_N = \frac{1}{N!} \left(\frac{4\pi V m^2 c}{(2\pi\hbar)^3 \beta} K_2(\beta m c^2) \right)^N
$$

Using the asymptotical expansion:

$$
K_2(x) \sim \sqrt{\frac{\pi}{2x}} e^{-x} \left(1 + \frac{15}{8x} + \cdots \right) \quad \text{as} \quad x \to \infty
$$

which yields:

$$
\implies Z_N^{\mathrm{rel}} = Z_N^{\mathrm{cl}} e^{-N\frac{mc^2}{kT}} \left(1 + \frac{15kT}{8mc^2} \right)^N \quad \text{as} \quad \frac{1}{c} \to 0
$$

$$
\text{with} \quad Z_N^{\mathrm{cl}} = \frac{1}{N!} \left[V \left(\frac{2\pi mkT}{(2\pi\hbar)^2} \right)^{3/2} \right]^N
$$

Onwards to the heat capacity:

$$
C = T\frac{\partial S}{\partial T}, \quad S = -\frac{\partial F}{\partial T} \quad \implies C = -T\frac{\partial^2 F}{\partial T^2}
$$

Compute the Free Energy:

$$
F = -kT \log Z_N = -kT \left\{ \log \left[\frac{1}{N!} \left(\frac{V}{(2\pi\hbar)^3} \right)^N \right] + \frac{3N}{2} \log(2\pi mkT) - N\frac{mc^2}{kT} + N \log\left(1 + \frac{15kT}{8mc^2} \right) \right\}
$$

and its second derivative (with $a = 2\pi mkT$ and $b = \frac{15k}{8mc^2}$):

$$
\frac{\partial^2 F}{\partial T^2} = -Nk \frac{\partial^2}{\partial T^2} \left\{ \frac{3}{2} T \log(aT) + T \log(1 + bT) \right\} = -Nk \left\{ \frac{3}{2T} + \frac{2b}{1+bT} - \frac{b^2 T}{(1+bT)^2} \right\}
$$

Finally:

$$
\implies \boxed{C = Nk \left(\frac{3}{2} + \frac{2bT}{1+bT} - \frac{b^2T^2}{(1+bT)^2} \right)}
$$

H5.3 Quantum corrections

Compute the canonical partition function for the Hamiltonian $\hat{H} = c\,|\hat{\vec{p}}|$ using properly symmetrized basis states:

$$
\begin{aligned}
Z_N &= \operatorname{tr} e^{-\beta \hat{H}} \\
&= \int_V \mathrm{d}^{3N} r \, \langle \vec{r}_1 \cdots \vec{r}_N | e^{-\beta \hat{H}} | \vec{r}_1 \cdots \vec{r}_N \rangle \\
&= \int_V \mathrm{d}^{3N} r \int_{\mathbb{R}} \mathrm{d}^{3N} p \int_{\mathbb{R}} \mathrm{d}^{3N} p' \, \langle \vec{r}_1 \cdots \vec{r}_N | \vec{p}_1 \cdots \vec{p}_N \rangle \left\langle \vec{p}_1 \cdots \vec{p}_N \middle| e^{-\beta \hat{H}} \middle| \vec{p'}_1 \cdots \vec{p'}_N \right\rangle \left\langle \vec{p'}_1 \cdots \vec{p'}_N \middle| \vec{r}_1 \cdots \vec{r}_N \right\rangle \\
&= \frac{1}{N!} \sum_{\hat{P} \in \mathrm{Perms}} (\pm 1)^{\eta_{\hat{P}}} \int_V \mathrm{d}^{3N} r \int_{\mathbb{R}} \mathrm{d}^{3N} p \, e^{-\beta E(\vec{p}_1, \cdots, \vec{p}_N)} \, \langle \vec{r}_1 \cdots \vec{r}_N | \vec{p}_1 \cdots \vec{p}_N \rangle \, \langle \vec{p}_1 \cdots \vec{p}_N | \vec{r}_{\hat{P}1} \cdots \vec{r}_{\hat{P}N} \rangle \\
&= \frac{1}{N!\,(2\pi\hbar)^{3N}} \sum_{\hat{P} \in \mathrm{Perms}} (\pm 1)^{\eta_{\hat{P}}} \prod_{j=1}^{N} \int_V \mathrm{d}^3 r_j \int_{\mathbb{R}} \mathrm{d}^3 p_j \exp\left\{ -\beta\, c\, |\vec{p}_j| + \frac{i}{\hbar} \vec{p}_j \cdot \left(\vec{r}_j - \vec{r}_{\hat{P}j} \right) \right\}
\end{aligned}
$$

Evaluate the p-integral, using $\vec{p} \cdot \vec{r} = p\, r\, \cos\measuredangle(\vec{p}, \vec{r})$, letting $a = \beta\, c$ and $b = \frac{|\vec{r}_j - \vec{r}_{\hat{P}j}|}{\hbar}$ and rotating the coordinate system in such a way that $\theta = \measuredangle(\vec{p}, \vec{r}_j - \vec{r}_{\hat{P}j})$ holds:

$$
\begin{aligned}
&\int_{\mathbb{R}} \mathrm{d}^3 p \exp\left\{ -\beta\, c\, |\vec{p}| + \frac{i}{\hbar} \vec{p} \cdot \left(\vec{r}_j - \vec{r}_{\hat{P}j} \right) \right\} = \\
&= \int_0^\infty \int_{-1}^{1} \int_0^{2\pi} \mathrm{d}p \, \mathrm{d}\cos\theta \, \mathrm{d}\varphi \, p^2 \, e^{-p(a - i\, b \cos\theta)} \\
&= \frac{4\pi}{b} \int_0^\infty \mathrm{d}p \, p \, e^{-ap} \, \sin b\, p
\end{aligned}
$$

Integrating partially two times, one finds:

$$
\int_0^\infty \mathrm{d}p \, e^{-ap} \, \sin b\, p = -\frac{e^{-ap} \left(a\, \sin b\, p + b\, \cos b\, p \right)}{a^2 + b^2}
$$

And integrating partially another time yields:

$$
\frac{4\pi}{b} \int_0^\infty \mathrm{d}p \, p \, e^{-ap} \, \sin b\, p = \frac{4\pi}{b} \frac{2ab}{\left(a^2 + b^2 \right)^2} = \frac{8\pi a}{\left(a^2 + b^2 \right)^2}
$$

Now one has the expression:

$$
\sum_{\hat{P} \in \mathrm{Perms}} (\pm 1)^{\eta_{\hat{P}}} \prod_{j=1}^{N} \int_V \mathrm{d}^3 r_j \, f(\vec{r}_j - \vec{r}_{\hat{P}j}), \quad f(\vec{r}) = \frac{8\pi \hbar^4 \beta c}{\left((\hbar \beta c)^2 + \vec{r}^2 \right)^2}
$$

When expanding this device, the 0th order term is given by the identity permutation $\hat{P} \equiv \mathrm{Id}$, which yields:

$$
\prod_{j=1}^{N} \int_V \mathrm{d}^3 r_j \, f(0) = \left(\frac{8\pi V}{(\beta c)^3} \right)^N
$$

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For the 1st order term consider the permutation, which only switches one pair $\hat{P}i = \begin{cases} a & \text{if} \quad i = b \\ b & \text{if} \quad i = a \\ i & \text{otherwise} \end{cases}$:

$$\prod_{i=1}^{N} \int_V \mathrm{d}^3 r_j \, f(\vec{r}_i - \vec{r}_{\hat{P}i}) = \left(\frac{8\pi V}{(\beta c)^3} \right)^{N-2} \int_V \mathrm{d}^3 r_a \int_V \mathrm{d}^3 r_b \, f^2(\vec{r}_a - \vec{r}_b)$$

$$\int_V \mathrm{d}^3 r_a \int_V \mathrm{d}^3 r_b \, f^2(\vec{r}_a - \vec{r}_b) \approx 4\pi V \int\limits_0^\infty \mathrm{d}u \, \frac{\left(8\pi\hbar^4 \beta c\right)^2}{\left((\hbar\beta c)^2 + u^2\right)^4}$$

using partial fraction decomposition and $\displaystyle\int \frac{\mathrm{d}x}{1+x^2} = \operatorname{atan} x$: $\displaystyle\int\limits_0^\infty \frac{\mathrm{d}x}{(1+x^2)^4} = \frac{5\pi}{32}$

$$\implies \int_V \mathrm{d}^3 r_a \int_V \mathrm{d}^3 r_b \, f^2(\vec{r}_a - \vec{r}_b) \approx \frac{40\pi^4 \hbar V}{(\beta c)^5}$$

Since there are $\binom{N}{2} = \frac{N(N-1)}{2} \approx \frac{N^2}{2}$ such permutations (with $\rho = \frac{N}{V}$):

$$\binom{N}{2} \prod_{i=1}^{N} \int_V \mathrm{d}^3 r_j \, f(\vec{r}_i - \vec{r}_{\hat{P}i}) = \frac{N^2}{2} \left(\frac{8\pi V}{(\beta c)^3} \right)^{N-2} \frac{40\pi^4 \hbar V}{(\beta c)^5} = \left(\frac{8\pi V}{(\beta c)^3} \right)^{N} \frac{5\pi^2 \hbar \beta c N \rho}{16}$$

Finally, one can write down the partition function with first order quantum corrections:

$$\implies \boxed{Z_N^{\mathrm{qm}} = Z_N^{\mathrm{cl}} \left(1 \pm \frac{5\pi^2 \hbar c N \rho}{16 kT} \right)}$$

$$\text{with} \quad Z_N^{\mathrm{cl}} = \frac{1}{N!} \left(8\pi V \left(\frac{kT}{2\pi\hbar c} \right)^3 \right)^N$$

Furthermore, the gas can be treated classically for small densities, i. e.:

$$\frac{\hbar c N \rho}{kT} \ll 1 \iff \rho \ll \frac{kT}{\hbar c N} \sim 1 \times 10^{-18}\,\mathrm{m}^{-3} \quad \text{with} \quad T = 300\,\mathrm{K}, \quad N = 1 \times 10^{23}$$