5500 Problem Set 5

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Question I.

In the limit of high energy or low atom density, the number of energy eigenstates with energy $\leq E$ for a monatomic ideal gas with $N >> 1$ atoms in a volume V is

$$\Sigma(E) = \frac{(2\pi m E)^{\frac{3N}{2}} V^N}{(2\pi\hbar)^{3N} N!(3N/2)!}$$

At this point do not ask exact where $\Sigma(E)$came from; and if $(3N/2)!$ gives you pause, assume that N is even. Show that in the thermodynamic limit the entropy is

$$S = kN\left[\ln\frac{n_Q(T)}{n} + \frac{5}{2}\right]$$

Here $n = N/V$ is the density of the gas, and the quantum unit of density and the corresponding thermal de Broglie wavelength are

$$n_q(T) = \frac{1}{\lambda^3}; \quad \lambda = \left(\frac{2\pi\hbar^2}{mkT}\right)^{1/2}$$

Even the additive constant turns out to be correct for entropy such that $S \to 0$ as $T \to 0$!

We know that $S = k\ln\Sigma$, so we begin by taking the natural log of the number of energy eigenstates:

$$\begin{aligned}
\Sigma(E) &= \frac{(2\pi m E)^{\frac{3N}{2}} V^N}{(2\pi\hbar)^{3N} N!(3N/2)!} \\
\ln\Sigma &= \ln\left[\frac{(2\pi m E)^{\frac{3N}{2}} V^N}{(2\pi\hbar)^{3N} N!(3N/2)!}\right] \\
&= \frac{3N}{2}\ln(2mE) + N\ln V - 3N\ln(2\pi\hbar) - \ln(N!) - \ln\left[\left(\frac{3N}{2}\right)!\right]
\end{aligned}$$

Applying the Stirling approximation gives us

$$\begin{aligned}
\ln\Sigma &= \frac{3N}{2}\ln(2mE) + N\ln V - 3N\ln(2\pi\hbar) - N\ln(N) + N - \frac{3N}{2}\ln\left(\frac{3N}{2}\right) + \frac{3N}{2} \\
&= \frac{3N}{2}\ln(3mNkT) + N\ln V - 3N\ln(2\pi\hbar) - N\ln(N) + N - \frac{3N}{2}\ln\left(\frac{3N}{2}\right) + \frac{3N}{2}
\end{aligned}$$

Contracting this we get

$$\begin{aligned}
\ln\Sigma &= N\left[\frac{(3mkT)^{3/2}V}{(2\pi\hbar)^3(3/2)^{3/2}N} + 5/2\right] \\
&= N\left[\ln\frac{n_Q(T)}{n} + \frac{5}{2}\right]
\end{aligned}$$

and from here $S = k \ln \Sigma$ gives the desired result.

Question II.

Suppose we have two independent quantum systems 1 and 2, noninteracting and acting on different degrees of freedom. Show, and forever memorize, that the partition function factorizes:

$$Z_{1+2} = Z_1 Z_2$$

The same obviously applies to an arbitrary number of systems.

At a temperature T with energies ϵ_i, ϵ_j we have

$$\begin{aligned} Z_{1+2} &= \sum_i \sum_j e^{-(\epsilon_i+\epsilon_j)/T} \\ &= \sum_i e^{-\epsilon_i/T} \sum_j e^{-\epsilon_j/T} \\ &= Z_1 Z_2 \end{aligned}$$

Question III.

The canonical partition function for a classical ideal gas, N atoms in a volume V at temperature T in the limit of high temperature or low density, equals

$$Z_N = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N, \quad \lambda = \left(\frac{2\pi\hbar^2}{mkT}\right)^{1/2}$$

where λ is the same thermal de Broglie wavelength as in P1; don't ask .../ Find the chemical potential.

We can use the Helmholtz free energy where

$$\begin{aligned} \mu &= \left(\frac{\partial F}{\partial N}\right)_{TV} \\ F &= -T[N \ln Z_1 - \ln N!] \\ \mu &= -T\left[\ln Z_1 - \frac{\mathrm{d}}{\mathrm{d}N} \ln N!\right] \end{aligned}$$

We can finish this using Stirling where

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}N} \ln N! &= \ln N + \frac{1}{2N} \\ \mu &= T \ln \frac{N}{Z_1} \end{aligned}$$

where $Z_1 = V/\lambda^3$

Question IV.

Given the grand partition function $\mathcal{Z}$, show that the expectation value of particle number and the root-mean square fluctuations of the particle number satisfy

$$N = z\frac{\partial}{\partial z}\ln\mathcal{Z}, \quad (\Delta N)^2 = z\frac{\partial}{\partial z}z\frac{\partial}{\partial z}\ln\mathcal{Z}$$

How do the relative fluctuations, $\Delta N/N$, scale in the thermodynamic limit?

We can take the expectation value of the number operator such that $\left\langle \hat{N} \right\rangle = N$

$$\begin{aligned}
N &= \frac{1}{\mathcal{Z}}\operatorname{Tr}\left\{z^N e^{-\beta\hat{H}}\hat{N}\right\} \\
&= \frac{1}{\mathcal{Z}}\sum_N z^N N e^{-\beta E_N} \\
z\frac{\partial}{\partial z}\ln\mathcal{Z} &= z\frac{\partial}{\partial z}\ln\sum_N z^N e^{-\beta E_N} \\
&= \frac{z}{\mathcal{Z}}\sum_N z^{N-1} N e^{-\beta E_N} \\
&= \frac{1}{\mathcal{Z}}\sum_N z^N N e^{-\beta E_N} \\
&= N
\end{aligned}$$

We then have

$$\begin{aligned}
(\Delta N)^2 &= z\frac{\partial}{\partial z}z\frac{\partial}{\partial z}\ln\mathcal{Z} \\
&= z\frac{\partial}{\partial z}N \\
&= z\frac{\partial}{\partial z}\left(\frac{1}{\mathcal{Z}}\sum_N z^N N e^{-\beta E_N}\right) \\
&= z\left(-\frac{1}{\mathcal{Z}^2}\sum_N z^{N-1}Ne^{-\beta E_N}\sum_N z^N N e^{-\beta E_N} + \frac{1}{\mathcal{Z}}\sum_N z^{N-1}N^2 e^{-\beta E_N}\right) \\
&= \left\langle N^2 \right\rangle - \left\langle N \right\rangle^2
\end{aligned}$$

is the variance of N. We know that in the thermodynamic limit the relative fluctuations $\Delta/N \rightarrow 1/\sqrt{N} \rightarrow 0$.