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Statistical Mechanics
Homework 3

May 8, 2019

H3.1

Maximize the entropy $S = -k \sum_{n=1}^{N} p_n \log p_n$ under the constrains $\sum_{n=1}^{N} p_n A_n = \langle A \rangle$ and $\sum_{n=1}^{N} p_n = 1$ using the method of Lagrange multipliers.

Write down and maximize Λ:

$$\begin{aligned}
\Lambda(p_1, \cdots, p_N; \lambda, \mu) =& -k \sum_{n=1}^{N} p_n \log p_n - \lambda \left(\sum_{n=1}^{N} p_n A_n - \langle A \rangle \right) - \mu \left(\sum_{n=1}^{N} p_n - 1 \right) \\
\frac{\partial \Lambda}{\partial p_n} =& -k \left(\log p_n + 1 \right) - \lambda A_n - \mu \stackrel{!}{=} 0 \\
\iff \; p_n =& \exp\left(-\frac{\lambda A_n}{k} - \frac{\mu}{k} - 1 \right)
\end{aligned}$$

And apply the constrains to find the mutlipliers λ and μ:

$$\begin{aligned}
\sum_{n=1}^{N} p_n =& \exp\left(-\frac{\mu}{k} - 1 \right) \underbrace{\sum_{n=1}^{N} \exp\left(-\frac{\lambda A_n}{k} \right)}_{\equiv Z} = 1 \qquad \text{(i)} \\
\iff \; \frac{1}{Z} =& \exp\left(-\frac{\mu}{k} - 1 \right) \\
\implies & \boxed{p_n = \frac{1}{Z} \exp\left(-\frac{\lambda A_n}{k} \right)}
\end{aligned}$$

$$\langle A \rangle = \sum_{n=1}^{N} p_n A_n = \frac{1}{Z} \sum_{n=1}^{N} A_n \exp\left(-\frac{\lambda A_n}{k} \right) = -\frac{k}{Z} \frac{\partial Z}{\partial \lambda} = -k \frac{\partial \log Z}{\partial \lambda} \qquad \text{(ii)}$$

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H3.2

Consider the pressure in terms of the entropy:

$$\begin{aligned}
\mathrm{d}S &= \left(\frac{\partial S}{\partial V}\right)_E \mathrm{d}V + \left(\frac{\partial S}{\partial E}\right)_V \mathrm{d}E = 0 \\
\implies p &\equiv -\left(\frac{\mathrm{d}E}{\mathrm{d}V}\right)_S = \left(\frac{\partial S}{\partial V}\right)_E \bigg/ \left(\frac{\partial S}{\partial E}\right)_V \\
\implies p &= T\left(\frac{\partial S}{\partial V}\right)_E
\end{aligned}$$

In order to compute this expression, derive first the entropy of the ideal gas confined in a box with $V = L^d$ described by the Hamiltonian $H(p,q) = \sum_{i=1}^N \frac{\vec{p}_i}{2m}$:

$$\begin{aligned}
S &= k \log \Omega \\
\Omega &= \frac{\partial}{\partial E}\int_{H \le E} \mathrm{d}\Gamma, \quad \mathrm{d}\Gamma = \frac{1}{N!}\prod_{i=1}^N \frac{\mathrm{d}^d p\, \mathrm{d}^d q}{(2\pi\hbar)^d} \\
&= \frac{V^N}{N!(2\pi\hbar)^{dN}} \mathrm{S}_{dN}\left(\sqrt{2mE}\right) \\
\implies S &= k\left(N \log V + \log\left(\frac{\mathrm{S}_{dN}\left(\sqrt{2mE}\right)}{N!(2\pi\hbar)^{dN}}\right)\right)
\end{aligned}$$

Then:

$$\begin{aligned}
p &= kT\left(\frac{\partial\left(N \log V + \cdots\right)}{\partial V}\right)_E = \frac{NkT}{V} \\
&\implies \boxed{pV = NkT}
\end{aligned}$$