Notes on statistical Mechanics*

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Classical Ideal gas: canonical ensemble

Let us consider ideal monatomic gas where there is no interaction between any two atoms and no internal degrees of freedom.

We have

$$p(E)dE = \frac{\exp(-\beta E)\, g(E)\, dE}{\int\limits_0^\infty \exp(-\beta E)\, g(E)\, dE} \tag{1}$$

and

$$Q_N(V,T) = \int\limits_0^\infty \exp(-\beta E)\, g(E)\, dE. \tag{2}$$

Here $Q_N(V,T)$ is the partition function. Now $g(E)\, dE = \rho d\Gamma$, no. of microstates in the volume element $d\Gamma$. The average or expectation value of a physical quantity f is given by

$$\langle f \rangle = \int f(q,p)\, \rho(q,p)\; d^{3N}q\, d^{3N}p \tag{3}$$

where $\rho(q,p)$ represents the density of representative points of the system in phase space. Here $\rho(q,p) \neq \rho(t)$, because the states are equilibrium states. In fact

$$\rho(q,p) \propto \exp(-\beta H(q,p))$$

where $H(q,p)$ is the Hamiltonian of the system. Therefore

$$\langle f \rangle = \frac{\int f(q,p) \exp(-\beta H)\, d\omega}{\int \exp(-\beta H)\, d\omega} \tag{4}$$

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and

$$Q_N(V,T) = \frac{1}{N!h^{3N}} \int e^{-\beta H} d\omega \tag{5}$$

For ideal monatomic gas, no internal degrees of motion is considered. This is confined in volume V and is in equilibrium at temperature T. Because of no intermolecular interaction, the energy is wholely kinetic, and the Hamiltonian is

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} \tag{6}$$

p_is are the momenta of the gas molecules. Therefore

$$\begin{aligned}
Q_N(V,T) &= \frac{1}{N!h^{3N}} \int e^{-\beta \sum\limits_{i=1}^{N} \frac{p_i^2}{2m}} d^{3N}q\, d^{3N}p \\
&= \frac{1}{N!h^{3N}} \int \prod_{i-1}^{N} e^{-\frac{p_i^2}{2mkT}} d^{3N}q\, d^{3N}p \\
&= \frac{V^N}{N!h^{3N}} \left[\int_0^\infty e^{-\frac{p^2}{2mkT}} d^3p \right]^N \\
&= \frac{V^N}{N!h^{3N}} \left[\int_0^\infty e^{-\frac{p^2}{2mkT}} 4\pi p^2 dp \right]^N \\
&= \frac{1}{N!} \left[\frac{V}{h^3} \int_0^\infty e^{-\frac{p^2}{2mkT}} 4\pi p^2 dp \right]^N \\
&= \frac{[Q_1(V,T)]^N}{N!}
\end{aligned} \tag{7}$$

$Q_1(V,T)$ in eqn. (7) may be looked upon as the single particle partition function.

Now

$$Q_1(V,T) = V \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \tag{8}$$

using standard formula

$$\int_0^\infty e^{-Rr^2} r^{2n} dr = \frac{\Gamma\left(n+\frac{1}{2}\right)}{2R^{n+\frac{1}{2}}} \tag{9}$$

Therefore,

$$Q_N\left(V,T\right) \;=\; \frac{1}{N!}\left\{V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right\}^N \tag{10}$$

and the Helmholtz's free energy

$$\begin{aligned} A &= -kT\,\ln Q_N\left(V,T\right) \\ &= -NkT\,\ln\left\{\left(\frac{V}{N}\right)\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} + 1\right\} \end{aligned} \tag{11}$$

The average energy of the system is

$$\begin{aligned} E\left(\text{or}\,U\right) &= -\frac{\partial}{\partial\beta}\left[\ln Q_N\left(V,T\right)\right] \\ &= \frac{3}{2}NkT \end{aligned} \tag{12}$$

The pressure exerted by an ideal classical gas is

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = \frac{NkT}{V} = nkT \tag{13}$$

Now the entropy of the system,

$$\begin{aligned} S &= -\left(\frac{\partial A}{\partial T}\right)_{V,N} \\ &= Nk\left[\ln\left\{\left(\frac{V}{N}\right)\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}\right\} + \frac{5}{2}\right] \end{aligned} \tag{14}$$

Eqn. (14) is just the **Seckur-Tetrode** equation as already obtained from micro-canonical ensemble.

References

[1] Statistical Mechanics: R. K. Pathria