I General Theory

Hamiltonian:

$$H\left(p_i, q_i\right) = \sum_i \frac{p_i^2}{2m} + V^{int}\left(q_i, q_j\right) + V^{ext}\left(q_i\right)$$

internal interation is Leonard-Jones Potential:

$$V^{int}\left(q_i, q_j\right) = \sum_{i,j;\quad (i<j)} 4\left[\left(\frac{1}{r_{ij}}\right)^{12} - \left(\frac{1}{r_{ij}}\right)^{6}\right]$$
$$r_{ij} = \left|q_i - q_j\right|$$

external interation is harmonic potential well:

$$V^{ext}\left(q_i\right) = \sum_i \frac{1}{2} q_i^2$$

II Canonical Ensemble

For ideal gas we neglect internal interaction:

$$H\left(p_i, q_i\right) = \sum_i \frac{p_i^2}{2m} + \sum_i \frac{1}{2} q_i^2$$

So the Hamiltonian is quadric form of velocity momentum and position.
Gibbs distribution:

$$\rho = \exp\left[\frac{F}{k_B T}\right] \exp\left(-\frac{1}{k_B T} H\right)$$

$$\rho = \exp\left[\frac{F}{k_B T}\right] \exp\left[-\frac{1}{k_B T}\left(\sum_i \frac{p_i^2}{2m} + \sum_i \frac{1}{2} q_i^2\right)\right]$$

Canonical ensemble is also (N,V,T) ensemble,so
(1) Partition function:

$$Z_c\left(T, V, N\right) = \frac{1}{h^s} \int\int \exp\left[-\frac{1}{k_B T}\left(\sum_i \frac{p_i^2}{2m} + \sum_i \frac{1}{2} q_i^2\right)\right] dp_i dq_i$$

considering the particle is indistinguishable so:

$$
\begin{aligned}
Z_c\left(T,V,N\right) &= \frac{1}{N!h^s}\int \exp\left(-\frac{1}{k_BT}\sum_i \frac{\overrightarrow{p}_i^2}{2m}\right)dp^{3N}\int \exp\left(-\frac{1}{k_BT}\sum_i \frac{1}{2}\overrightarrow{q}_i^2\right)dq^{3N} \\
&= \frac{1}{N!h^s}\left[\int \exp\left(-\frac{1}{k_BT}\frac{p^2}{2m}\right)dp^3\right]^N\int \exp\left(-\frac{1}{k_BT}\sum_i \frac{1}{2}\overrightarrow{q}_i^2\right)dq^{3N} \\
&= \frac{1}{N!h^s}\left[\int \exp\left(-\frac{1}{k_BT}\frac{p_x^2+p_y^2+p_z^2}{2m}\right)dp_xdp_ydp_z\right]^N Q_N\left(N,V,T\right) \\
&= \frac{1}{N!h^s}\left[\int_{-\infty}^{\infty} \exp\left(-\frac{1}{k_BT}\frac{p_x^2}{2m}\right)dp_x\right]^{3N} Q_N\left(N,V,T\right) \\
&= \frac{1}{N!h^s}\left(2\pi m k_BT\right)^{\frac{3}{2}N} Q_N\left(N,V,T\right)
\end{aligned}
$$

Volume term:

$$
\begin{aligned}
Q_N\left(N,V,T\right) &= \int \exp\left(-\frac{1}{k_BT}\sum_i \frac{1}{2}\overrightarrow{q}_i^2\right)dq^{3N} \\
&= \left[\int \exp\left(-\frac{1}{k_BT}\frac{1}{2}\overrightarrow{q}^2\right)dq^3\right]^N \\
&= \left[\iiint \exp\left(-\frac{1}{k_BT}\frac{r^2}{2}\right)r^2\sin\theta dr d\theta d\varphi\right]^N \\
&= \left[\int_0^R \exp\left(-\frac{1}{k_BT}\frac{r^2}{2}\right)4\pi r^2 dr\right]^N \\
&= \left[\int_0^R \exp\left(-\beta\frac{r^2}{2}\right)4\pi r^2 dr\right]^N \\
&= \left\{\begin{array}{c} -4\pi\beta^{-1}\exp\left(-\frac{1}{2}\beta R^2\right)R \\ +2\sqrt{2}\pi^{\frac{3}{2}}\beta^{-\frac{3}{2}}\operatorname{erf}\left(\frac{\sqrt{2}}{2}\sqrt{\beta}R\right) \end{array}\right\}^N
\end{aligned}
$$

$$\beta = \frac{1}{k_BT}$$

We make some approximation

$$Q_N\left(V,T\right) = \left[\frac{4\,\pi}{3}\,R^3 - \frac{2\,\pi\,\beta}{5}\,R^5 + \frac{\pi\,\beta^2}{14}R^7 - \frac{\pi\,\beta^3}{108}R^9 + O\left(R^{10}\right)\right]^N$$

We know that

$$V = \frac{4}{3}\pi R^3$$

$$R = \left(\frac{3}{4\pi}V\right)^{\frac{1}{3}}$$

So we obtain

$$
\begin{aligned}
Q_N(V,T) &= \left[\frac{4\,\pi}{3}\,R^3 - \frac{2\,\pi\,\beta}{5}\,R^5 + \frac{\pi\,\beta^2}{14}R^7 - \frac{\pi\,\beta^3}{108}R^9 + O\left(R^{10}\right)\right]^N \\
&= \left[V - \frac{2\,\pi\,\beta}{5}\,\left(\frac{3}{4\pi}V\right)^{\frac{5}{3}} + \frac{\pi\,\beta^2}{14}\,\left(\frac{3}{4\pi}V\right)^{\frac{7}{3}} - \frac{\pi\,\beta^3}{108}\,\left(\frac{3}{4\pi}V\right)^{\frac{9}{3}} + O\left(V^{\frac{10}{3}}\right)\right]^N \\
&= \left[V - \frac{2\,\pi\,\beta}{5}\,\left(\frac{3}{4\pi}\right)^{\frac{5}{3}}\,V^{\frac{5}{3}} + ...\right]^N \\
&= V^N - N\frac{2\,\pi\,\beta}{5}\,\left(\frac{3}{4\pi}\right)^{\frac{5}{3}}\,V^{N-1}V^{\frac{5}{3}} + ... \\
&\approx V^N - N\frac{2\,\pi\,\beta}{5}\,\left(\frac{3}{4\pi}\right)^{\frac{5}{3}}\,V^{N-1}V^{\frac{5}{3}} \\
&= V^N - N\frac{2\,\pi\,\beta}{5}\,\left(\frac{3}{4\pi}\right)^{\frac{5}{3}}\,V^{N-1}V^{\frac{5}{3}} \\
&= V^N\left[1 - \frac{2\,\pi\,\beta}{5}\,\left(\frac{3}{4\pi}\right)^{\frac{5}{3}}\,NV^{\frac{2}{3}}\right] \\
&= V^N\left[1 - \frac{2}{5}\,(\pi)^{-\frac{2}{3}}\,\left(\frac{3}{4}\right)^{\frac{5}{3}}\,\beta NV^{\frac{2}{3}}\right]
\end{aligned}
$$

So the partition function's final result:

$$
\begin{aligned}
Z_c(N,V,T) &= \frac{1}{N!h^s}\,(2\pi mk_BT)^{\frac{3}{2}N}\,Q_N(N,V,T) \\
&= \frac{1}{N!h^s}\,(2\pi mT)^{\frac{3}{2}N}\,V^N\left[1 - \frac{2}{5}\,(\pi)^{-\frac{2}{3}}\,\left(\frac{3}{4}\right)^{\frac{5}{3}}\,\beta NV^{\frac{2}{3}}\right] \\
&= \frac{1}{N!}\left(\frac{2\pi mT}{h^2}\right)^{\frac{3}{2}N}\,V^N\left[1 - \frac{2}{5}\,(\pi)^{-\frac{2}{3}}\,\left(\frac{3}{4}\right)^{\frac{5}{3}}\,\beta NV^{\frac{2}{3}}\right] \\
&= \frac{1}{N!}\frac{V^N}{\lambda^{3N}}\left[1 - \frac{2}{5}\,(\pi)^{-\frac{2}{3}}\,\left(\frac{3}{4}\right)^{\frac{5}{3}}\,\beta NV^{\frac{2}{3}}\right] \\
&= \frac{1}{N!}\frac{V^N}{\lambda^{3N}}\left[1 - a(T)\,NV^{\frac{2}{3}}\right]
\end{aligned}
$$

Where

$$
\begin{aligned}
a(T) &= \frac{2}{5}(\pi)^{-\frac{2}{3}}\left(\frac{3}{4}\right)^{\frac{5}{3}}\beta \\
&= \frac{2}{5}(\pi)^{-\frac{2}{3}}\left(\frac{3}{4}\right)^{\frac{5}{3}}\frac{1}{k_B T} \\
&= \frac{2}{5}(\pi)^{-\frac{2}{3}}\left(\frac{3}{4}\right)^{\frac{5}{3}}k_B^{-1}T^{-1}
\end{aligned}
$$

The wave length of heat wave.

$$
\lambda = \left(\frac{2\pi m T}{h^2}\right)^{-\frac{1}{2}}
$$

in our problem we know that:

$$
\begin{aligned}
N &= 10 \\
T &= 150 \\
\dim &= 3 \\
DOF: s &= N \times \dim = 30
\end{aligned}
$$

Conclusion:
So finally we obtain the partition function of canonical ensemble:

$$
Z_c(N,V,T) \approx \frac{1}{N!}\frac{V^N}{\lambda(T)^{3N}}\left[1 - a(T)NV^{\frac{2}{3}}\right]
$$

$$
a(T) = \frac{2}{5}(\pi)^{-\frac{2}{3}}\left(\frac{3}{4}\right)^{\frac{5}{3}}\frac{1}{k_B T}
$$

$$
\lambda = \left(\frac{2\pi m T}{h^2}\right)^{-\frac{1}{2}}
$$

for convenient

$$
\beta = \frac{1}{k_B T}
$$

(2) Energy:

$$
U = -\frac{d\ln Z_c}{d\beta}
$$

(3) Entropy:

$$
S = k\beta
$$

(2) Helmholtz free energy:

$$
F(N,V,T) = -k_B T\ln(Z_c)
$$

let

$$\lambda = \left(\frac{2\pi mT}{h^2}\right)^{-\frac{1}{2}}$$

$$a(T) = \frac{2}{5}(\pi)^{-\frac{2}{3}}\left(\frac{3}{4}\right)^{\frac{5}{3}}\frac{1}{k_BT}$$

then

$$\begin{aligned}
F(N,V,T) &= -k_BT\ln\left\{\frac{1}{N!}\frac{V^N}{\lambda^{3N}}\left[1-a(T)NV^{\frac{2}{3}}\right]\right\} \\
&= -k_BT\left\{\ln\frac{1}{N!}+\ln\frac{V^N}{\lambda^{3N}}\left[1-a(T)NV^{\frac{2}{3}}\right]\right\} \\
&= -k_BT\left\{-\ln N!+\ln\left[\frac{V^N}{\lambda^{3N}}\left(1-a(T)NV^{\frac{2}{3}}\right)\right]\right\} \\
&= -k_BT\left\{-\ln N!+\ln\left[\left(\frac{V}{\lambda^3}\right)^N\left(1-a(T)NV^{\frac{2}{3}}\right)\right]\right\} \\
&= -k_BT\left\{-\ln N!+N\ln\left[\frac{V}{\lambda^3}\left(1-a(T)NV^{\frac{2}{3}}\right)\right]\right\}
\end{aligned}$$

$$\ln(N!) \approx N\ln(N)-N$$

$$\begin{aligned}
F(N,V,T) &= -k_BT\left\{\ln\frac{1}{N!}+\ln\frac{V^N}{\lambda(T)^{3N}}\left[1-a(T)NV^{\frac{2}{3}}\right]\right\} \\
&\approx -k_BT\left\{-(N\ln(N)-N)+N\ln\left[\frac{V}{\lambda^3}\left(1-a(T)NV^{\frac{2}{3}}\right)\right]\right\} \\
&= -k_BT\left\{-N\ln(N)+N+N\ln\left[\frac{V}{\lambda^3}\left(1-a(T)NV^{\frac{2}{3}}\right)\right]\right\} \\
&= -k_BT\left\{N-N\ln(N)+N\ln\left[\frac{V}{\lambda^3}\left(1-a(T)NV^{\frac{2}{3}}\right)\right]\right\} \\
&= -Nk_BT\left\{1-\ln(N)+\ln\left[\frac{V}{\lambda^3}\left(1-a(T)NV^{\frac{2}{3}}\right)\right]\right\} \\
&= -Nk_BT\left\{1+\ln\left[\frac{V}{N\lambda^3}\left(1-a(T)NV^{\frac{2}{3}}\right)\right]\right\}
\end{aligned}$$

finally we obtain that

$$F(N,V,T) = -Nk_BT\left\{1+\ln\left[\frac{V}{N\lambda^3}\left(1-a(T)NV^{\frac{2}{3}}\right)\right]\right\}$$

where

$$\lambda = \left(\frac{2\pi mT}{h^2}\right)^{-\frac{1}{2}}$$

and

$$a(T) = \frac{2}{5}(\pi)^{-\frac{2}{3}}\left(\frac{3}{4}\right)^{\frac{5}{3}}\frac{1}{k_B T}$$

(3) Gibbs free energy:

$$G = F + PV$$

$$G = -Nk_BT\left\{1 + \ln\left[\frac{V}{N\lambda^3}\left(1 - a(T)NV^{\frac{2}{3}}\right)\right]\right\} + PV$$

(4) Chemical potential:

$$U = TS - PV + \mu N$$

$$\begin{aligned}
\mu &= \frac{1}{N}(U - TS + PV) \\
&= \frac{1}{N}(F + PV) \\
&= \frac{1}{N}G \\
&= -k_BT\left\{1 + \ln\left[\frac{V}{N\lambda^3}\left(1 - a(T)NV^{\frac{2}{3}}\right)\right]\right\} + \frac{PV}{N}
\end{aligned}$$

(5) Internal chemical potential:

$$\mu = \mu_{ini} + \varphi(q_i)$$

$$\varphi(q_i) = \sum_i \frac{1}{2}q_i^2$$

$$\begin{aligned}
\mu_{ini} &= \mu - \varphi(q_i) \\
&= -k_BT\left\{1 + \ln\left[\frac{V}{N\lambda^3}\left(1 - a(T)NV^{\frac{2}{3}}\right)\right]\right\} + \frac{PV}{N} - \varphi(q_i)
\end{aligned}$$

(7) PDF of system:

$$\rho_c = \frac{\exp\left[-\frac{1}{k_BT}\left(\sum_i \frac{p_i^2}{2m} + \sum_i \frac{1}{2}q_i^2\right)\right]}{Z_c}$$

(6) PDF of momentum:

$$\rho_{q_i} = (2\pi m k_B T)^{-\frac{3}{2}}\exp\left(-\frac{1}{k_BT}\frac{p_i^2}{2m}\right)$$

(8) PDF of position:

$$\rho_{p_i} = (2\pi k_B T)^{-\frac{3}{2}} \exp\left(-\frac{1}{k_B T}\frac{1}{2}q_i^2\right)$$

(6) Fluctuation of energy:

$$\begin{aligned}
\sigma^2 &= \left\langle (\Delta E)^2 \right\rangle \\
&= \left\langle E^2 \right\rangle - \langle E \rangle^2 \\
&= -\frac{\partial U}{\partial \beta} \\
&= k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{V,N} \\
&= k_B T^2 C_V
\end{aligned}$$

$$\begin{aligned}
C_V(N,V,T) &= \left(\frac{\partial U}{\partial T}\right)_{V,N} \\
&= k_B T \left[2\left(\frac{\partial \ln Z}{\partial T}\right)_V + T\left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_V\right] \\
&= k_B T \left[2\left(\frac{\partial}{\partial T}\ln Z\right)_V + T\left(\frac{\partial^2}{\partial T^2}\ln Z\right)_V\right]
\end{aligned}$$

$$\ln Z(N,V,T) = -N\left\{1 + \ln\left[\frac{V}{N\lambda(T)^3}\left(1 - a(T) N V^{\frac{2}{3}}\right)\right]\right\}$$

where

$$\lambda = \left(\frac{2\pi m T}{h^2}\right)^{-\frac{1}{2}}$$

and

$$a(T) = \frac{2}{5}(\pi)^{-\frac{2}{3}}\left(\frac{3}{4}\right)^{\frac{5}{3}}\frac{1}{k_B T}$$

So we obtian

$$\begin{aligned}
C_V &= \left(\frac{\partial U}{\partial T}\right)_{V,N} \\
&= k_B T \left[2\left(\frac{\partial \ln Z}{\partial T}\right)_V + T\left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_V\right] \\
&= k_B T \left[2\left(\frac{\partial}{\partial T}\ln Z\right)_V + T\left(\frac{\partial^2}{\partial T^2}\ln Z\right)_V\right]
\end{aligned}$$

and

$$
\begin{aligned}
\sigma^2 &= \left\langle (\Delta E)^2 \right\rangle \\
&= \langle E^2 \rangle - \langle E \rangle^2 \\
&= -\frac{\partial U}{\partial \beta} \\
&= k_B T^2 \left(\frac{\partial U}{\partial T} \right)_{V,N} \\
&= k_B T^2 C_V
\end{aligned}
$$

III. Macrocanonical Ensemble

For ideal gas we neglect internal interaction:

$$H(p_i, q_i) = \sum_i \frac{p_i^2}{2m} + \sum_i \frac{1}{2} q_i^2$$

(1) The Grand Partition function:

$$Z_{mc}(\mu, V, T) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int dq^{3N} \int dp^{3N} \exp\left\{-\beta \left[H(p,q) - \mu N\right]\right\}$$

we seperate varibles, so we obtained that:

$$Z_{mc}(\mu, V, T) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \exp\left[\frac{\mu N}{k_B T}\right] \int dq^{3N} \int dp^{3N} \exp\left\{-\beta H(p,q)\right\}$$

$$Z_{mc}(\mu, V, T) = \sum_{N=0}^{\infty} \left[\exp\left(\frac{\mu}{k_B T}\right)\right]^N Z_c(T, V, N)$$

We already know that partition function of canonical ensemble is:

$$Z_c(N, V, T) \approx \frac{1}{N!} \frac{V^N}{\lambda(T)^{3N}} \left[1 - a(T) N V^{\frac{2}{3}}\right]$$

$$a(T) = \frac{2}{5} (\pi)^{-\frac{2}{3}} \left(\frac{3}{4}\right)^{\frac{5}{3}} \frac{1}{k_B T}$$

$$\lambda = \left(\frac{2\pi m T}{h^2}\right)^{-\frac{1}{2}}$$

So the partision function of Macrocanonical ensemble is

$$
\begin{aligned}
Z_{mc}(T,V,\mu) &= \sum_{N=0}^{\infty} \frac{1}{N!} \left[\exp\left(\frac{\mu}{k_B T}\right) \right]^N \frac{V^N}{\lambda(T)^{3N}} \left[1 - a(T) N V^{\frac{2}{3}} \right] \\
&= \sum_{N=0}^{\infty} \frac{1}{N!} \left[\exp\left(\frac{\mu}{k_B T}\right) \right]^N \frac{V^N}{\lambda(T)^{3N}} \left[1 - a(T) N V^{\frac{2}{3}} \right]
\end{aligned}
$$

if we neglect external potneital field we obtain:

$$
\begin{aligned}
Z_{mc}(T,V,\mu) &= \sum_{N=0}^{\infty} \left[\exp\left(\frac{\mu}{k_B T}\right) \right]^N \frac{1}{N!} \frac{V^N}{\lambda(T)^{3N}} \\
&= \sum_{N=0}^{\infty} \left[\exp\left(\frac{\mu}{k_B T}\right) \right]^N Z_{mc}(T,V,N) \\
&= \sum_{N=0}^{\infty} \left[\exp\left(\frac{\mu}{k_B T}\right) \right]^N \frac{1}{N!} \left[Z_{mc}(T,V,1) \right]^N \\
&= \sum_{N=0}^{\infty} \frac{1}{N!} \left[Z_{mc}(T,V,1) \exp\left(\frac{\mu}{k_B T}\right) \right]^N \\
&= \exp\left[\exp\left(\frac{\mu}{k_B T}\right) Z_{mc}(T,V,1) \right]
\end{aligned}
$$

(2) Grand potential:

$$
\begin{aligned}
\phi(T,V,\mu) &= -k_B T \ln Z(T,V,\mu) \\
&= -k_B T \exp\left(\frac{\mu}{k_B T}\right) \frac{V}{\lambda(T)^3}
\end{aligned}
$$

(3) Chemical potential:

$$
d\phi = -p dV
$$

$$
-\left(\frac{\partial \phi}{\partial V}\right)_{T,\mu} = p(T,V,\mu) = k_B T \exp\left(\frac{\mu}{k_B T}\right) \frac{1}{\lambda(T)^3}
$$

$$
p = k_B T \exp\left(\frac{\mu}{k_B T}\right) \frac{1}{\lambda(T)^3}
$$

So we obtain the expression of chemical potential:

$$
\frac{p\lambda^3}{k_B T} = \exp\left(\frac{\mu}{k_B T}\right)
$$

$$
\mu = k_B T \ln\left(\frac{p\lambda^3}{k_B T}\right)
$$

$$\lambda = \left(\frac{2\pi mT}{h^2}\right)^{-\frac{1}{2}}$$

and the detail scheme:

$$\mu = k_B T \ln\left[\frac{p}{k_B T}\left(\frac{2\pi mT}{h^2}\right)^{-\frac{3}{2}}\right]$$

(3) Fluctuation of energy:

$$\begin{aligned}
\sigma^2 &= \left\langle (\Delta E)^2 \right\rangle \\
&= \left(\frac{\partial^2 \ln Z_{mc}}{\partial \beta^2}\right)_{z,V} \\
&=
\end{aligned}$$

3. System Pressure

System pressure:finally we obtain that

$$F(N,V,T) = -Nk_B T\left\{1 + \ln\left[\frac{V}{N\lambda(T)^3}\left(1 - a(T)NV^{\frac{2}{3}}\right)\right]\right\}$$

where

$$\lambda = \left(\frac{2\pi mT}{h^2}\right)^{-\frac{1}{2}}$$

and

$$a(T) = \frac{2}{5}(\pi)^{-\frac{2}{3}}\left(\frac{3}{4}\right)^{\frac{5}{3}}\frac{1}{k_B T}$$

Gas State Equation:

$$dF = -SdT - pdV$$

$$\begin{aligned}
P &= \left(\frac{\partial F}{\partial V}\right)_T \\
&= \frac{\partial}{\partial V}\left\{-Nk_B T\left\{1 + \ln\left[\frac{V}{N\lambda(T)^3}\left(1 - a(T)NV^{\frac{2}{3}}\right)\right]\right\}\right\} \\
&= -1/3\,\frac{Nk_B T\left(5\,aNV^{2/3} - 3\right)}{V\left(aNV^{2/3} - 1\right)} \\
&= \frac{Nk_B T}{V}\frac{\left(3 - 5\,aNV^{2/3}\right)}{3\left(aNV^{2/3} - 1\right)}
\end{aligned}$$