Constant pressure

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1 Isobatic phase space distribution and partition function

Assume two system coupled to a common thermal reservoir so that each system is described by a canonical distribution at temperature T. System 2 act as a barostat whose number of particles and volume is much larger than system 1, respectively.
If the volume of each system were fixed, the total canonical partition function would be

$$\begin{aligned} Q(N,V,T) &= C_N \int dx_1 dx_2 e^{-\beta\mathscr{H}_1(x_1)+\mathscr{H}_2(x_2)} \\ &= g(N,N_1,N_2) C_{N_1} \int dx_1 d e^{-\beta\mathscr{H}_1(x_1)} C_{N_2} int dx_2 d e^{-\beta\mathscr{H}_2(x_2)} \end{aligned} \tag{1}$$

The canonical phase space distribution function $f(x)$ of combined system 1 and 2 is

$$f(x) = \frac{C_N e^{-\beta\mathscr{H}}}{Q(N,V,T)} \tag{2}$$

To determine the distribution function of system 1, we need to integrate over the phase space of system 2

$$\begin{aligned} f_1(x_1,V_1) &= \frac{g(N,N_1,N_2)}{Q(N,V,T)} C_{N_1} d e^{-\beta\mathscr{H}_1(x_1)} C_{N_2} \int dx_2 d e^{-\beta\mathscr{H}_2(x_2)} \\ &= \frac{Q_2(N-N_1,V-V_1,T)}{Q(N,V,T)} C_{N_1} d e^{-\beta\mathscr{H}_1(x_1)} \end{aligned} \tag{3}$$

Express the patition function in terms of Helmholtz free energies according to $Q(N,V,T) = e^{\beta A(N,V,T)}$,

$$\frac{Q_2(N_2,V-V_1,T)}{Q(N,V,T)} = e^{\beta[A(N-N_1,V-V_1,T)-A(N,V,T)]} \tag{4}$$

Expand $A(N-N_1, V-V_1, T)$ to first order

$$A(N-N_1, V-V_1, T) \approx A(N,V,T) - N_1\Big(\frac{\partial A}{\partial N}\Big)\Big|_{N_1=0,V_1=0} - V_1\Big(\frac{\partial A}{\partial V}\Big)\Big|_{N_1=0,V_1=0}$$
$$= A(N,V,T) - \mu N_1 + PV_1 \tag{5}$$

So

$$f_1(x_1, V_1) = g(N, N_1, N_2)e^{\beta\mu N_1}e^{-\beta PV_1}e^{-\beta\mathscr{H}_1} \tag{6}$$

2 Nosé-Hoover From canonical ensemble to isothermal-isobaric

Nosé introduced a Hamiltonian

$$H_{\text{Nosé}} = \Phi(q) + \sum\frac{p^2}{2ms^2} + (X+1)kT\ln s + \frac{p_s^2}{2Q} \tag{7}$$

and the equations of motion from it is

$$\begin{aligned}\dot{q} &= \frac{p}{ms^2}\\ \dot{p} &= F(q)\\ \dot{s} &= \frac{p}{Q}\\ \dot{p}_s &= \sum\frac{p^2}{ms^3} - \frac{(X+1)kT}{s}\end{aligned} \tag{8}$$

The partition function of the ensemble is

$$Q_{\text{Nosé}} = (N!)^{-1}\int dsdqdpdp_s\delta(H_{\text{Nosé}} - E) \tag{9}$$

The equations can be simplified by take $dt_{old} \equiv sdt'$

$$\begin{aligned}\dot{q} &= \frac{p'}{ms}\\ \dot{p'} &= sF(q)\\ \dot{s} &= \frac{sp'_s}{Q}\\ \dot{p'}_s &= \sum\frac{p'^2}{ms^2} - (X+1)kT\end{aligned} \tag{10}$$

The partition function of the ensemble becomes

$$Q_{\text{Nosé}} = (N!)^{-1}\int dsdqdp'dp'_s\delta[\Phi(q) + \sum\frac{p^2}{2ms^2} + (X+1)kT\ln s + \frac{p_s^2}{2Q} - E] \tag{11}$$

And with $\dot{q}$ we can get

$$\begin{aligned}\ddot{q} &= \frac{\dot{p}}{ms} - \frac{p\dot{s}}{ms^2} \\ &= \frac{F(q)}{m} - \frac{pp_s}{Qms} \\ &= \frac{F(q)}{m} - \zeta\dot{q}\end{aligned} \tag{12}$$

where the thermodynamics fiction coefficient is defined as

$$\zeta \equiv \frac{p_s}{Q} \tag{13}$$

thus

$$\dot{\zeta} = \frac{1}{Q}\big[\sum \frac{p^2}{ms^2} - (X+1)kT\big] \tag{14}$$

In order to get the equations of motion with ζ instead of s, we redefine $p \equiv m\dot{q}$ and obtain

$$\begin{aligned}\dot{q} &= \frac{p}{m} \\ \dot{p} &= \frac{d}{dt}(m\dot{q}) = F(q) - \zeta p \\ \dot{\zeta} &= \frac{1}{Q}\big[\sum \frac{p^2}{ms^2} - (X+1)kT\big]\end{aligned} \tag{15}$$

If we introduce $x \equiv q/V^{1/D}$, the equations of motion become

$$\begin{aligned}\dot{x} &= \frac{d}{dp}\big(\frac{q}{V^{1/D}}\big) = \frac{p}{mV^{1/D}} - \frac{\dot{\epsilon}}{D}x \\ \dot{p} &= F - \zeta p + \frac{\dot{\epsilon}}{D}p \\ \dot{\epsilon} &= \frac{\dot{V}}{DV} \\ \ddot{\epsilon} &= \frac{d}{dt}\frac{\dot{V}}{DV} = \frac{\ddot{V}}{DV} - \frac{\dot{V}^2}{DV^2} = \frac{P-P_0}{DVM} - D\dot{\epsilon} \\ \dot{\zeta} &= \frac{1}{Q}\big[\sum \frac{p^2}{ms^2} - (X+1)kT\big]\end{aligned} \tag{16}$$

The microcanonical ensemble average of the function F is denoted F_{NVE}, which is defined as

$$F_{NVE}(N,V,E) \equiv [N!\Omega(N,V,E)]^{-1}\int_V d\mathbf{r}^N \int d\mathbf{p}^N \delta[\mathscr{H}(\mathbf{r}^N,\mathbf{p}^N;V) - E]F(\mathbf{r}^N,\mathbf{p}^N;V) \tag{17}$$

where

$$\Omega(N,V,E) = (N!)^{-1} \int_V d\mathbf{r}^N \int d\mathbf{p}^N \delta[\mathscr{H}(\mathbf{r}^N, \mathbf{p}^N; V) - E] \tag{18}$$

is the microcanonical ensemble partition function.
The canonical ensemble partition function is

$$Q(N,V,T) = (N!)^{-1} \int_V d\mathbf{r}^N \int d\mathbf{p}^N \exp\big[- \frac{\mathscr{H}(\mathbf{r}^N, \mathbf{p}^N; V)}{kT} \big] \tag{19}$$

The isothermal-isobaric ensemble partition function is

$$\Delta(N,P,T) = (N!)^{-1} \int_0^\infty dV \int_V d\mathbf{r}^N \int d\mathbf{p}^N \exp\big[- \frac{PV + \mathscr{H}(\mathbf{r}^N, \mathbf{p}^N; V)}{kT} \big] \tag{20}$$

The isoenthalpic-isobaric ensemble partition function is

$$\Gamma(N,P,H) = (N!)^{-1} \int_0^\infty dV \int_V d\mathbf{r}^N \int d\mathbf{p}^N \delta[\mathscr{H}(\mathbf{r}^N, \mathbf{p}^N; V) + PV - H] \tag{21}$$

For any function $F(\mathbf{r}^N, \mathbf{p}^N; V)$