Topics in Computational Science Report
Derivation of Gibbs Energy in Isothermal-Isobaric Ensemble

Alifian Mahardhika Maulana

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1. Derive the following equation,

$$\begin{aligned}\triangle G(r) &\equiv G(r) - G(r_0) \\ &= -\int_{r_0}^{r} \langle F(r) \rangle_{r=r'} dr'\end{aligned} \tag{1}$$

Answer:

Suppose that,

$$G = -k_B T \ln Y_N(P,T) \quad (2) \qquad Y_N(P,T) = \frac{1}{h^{3N} N!} \iiint \exp\left(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T} \right) d\mathbf{r}^N d\mathbf{p}^N dV \quad (3)$$

We call (2) Gibbs free energy and (3) *configurational integral.* Because (3) is an indefinite integral, we can rewrite it as follow,

$$\begin{aligned} Y_N(P,T) &= \frac{1}{h^{3N} N!} \iiint \exp\left(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T} \right) dV d\mathbf{r}^N d\mathbf{p}^N \\ &= -\frac{1}{h^{3N} N!} \frac{P}{k_B T} \iint \exp\left(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T} \right) d\mathbf{r}^N d\mathbf{p}^N \end{aligned} \tag{4}$$

By using **Thermodynamic Integration**, if the Gibbs free energy, G is a continuous function of r, then we can write,

$$\triangle G(r) = \int_{r_0}^{r} \frac{dG(r)}{dr} dr \tag{5}$$

Substitute (2) to (5) we get,

$$\triangle G(r) = \int_{r_0}^{r} -k_B T \frac{\partial \ln Y_N(P,T)}{\partial Y_N} \frac{\partial Y_N}{\partial r} = \int_{r_0}^{r} -k_B T \frac{1}{Y_N} \frac{\partial Y_N}{\partial r} \tag{6}$$

From definition of Y_N in (4), we can write the following for $\partial Y_N / \partial r$,

$$\frac{\partial Y_N}{\partial r} = -\frac{1}{h^{3N} N!} \frac{P}{k_B T} \iint \frac{\partial}{\partial r} \exp\left(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T} \right) d\mathbf{r}^N d\mathbf{p}^N \tag{7}$$

Applying chain rule to (7), thus

$$\frac{\partial Y_N}{\partial r} = \frac{1}{h^{3N} N!} \frac{P}{k_B T} \frac{1}{k_B T} \iint \frac{\partial H(\mathbf{r}^N, \mathbf{p}^N)}{\partial r} \exp\left(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T} \right) d\mathbf{r}^N d\mathbf{p}^N \tag{8}$$

Substitute (8), (4) into (6) gives:

$$\begin{aligned} \triangle G(r) &= \int_{r_0}^{r} k_B T \frac{k_B T h^{3N} N!}{P \iint \exp\left(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T} \right) d\mathbf{r}^N d\mathbf{p}^N} \frac{P \iint \frac{\partial H(\mathbf{r}^N, \mathbf{p}^N)}{\partial r} \exp\left(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T} \right) d\mathbf{r}^N d\mathbf{p}^N}{k_B^2 T^2 h^{3N} N!} dr \\ &= \int_{r_0}^{r} \frac{\iint \frac{\partial H(\mathbf{r}^N, \mathbf{p}^N)}{\partial r} \exp\left(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T} \right) d\mathbf{r}^N d\mathbf{p}^N}{\iint \exp\left(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T} \right) d\mathbf{r}^N d\mathbf{p}^N} dr \end{aligned} \tag{9}$$

for simplicity, define

$$Z := \iint \exp\Big(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T}\Big) d\mathbf{r}^N d\mathbf{p}^N \tag{10}$$

Then we can rewrite (9) as follow,

$$\triangle G(r) = \int_{r_0}^{r} \Big(\frac{1}{Z} \iint \frac{\partial H(\mathbf{r}^N, \mathbf{p}^N)}{\partial r} \exp\Big(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T}\Big) d\mathbf{r}^N d\mathbf{p}^N \Big) dr \tag{11}$$

By **Ergodic Hypothesis** for expectation value of X,

$$\langle X \rangle = \frac{1}{Z} \iint X \exp\Big(- \frac{H(\mathbf{r}^N, \mathbf{p}^N) + PV}{k_B T}\Big) d\mathbf{r}^N d\mathbf{p}^N \tag{12}$$

Thus (11) become,

$$\triangle G(r) = \int_{r_0}^{r} \Big\langle \frac{\partial H(\mathbf{r}^N, \mathbf{p}^N)}{\partial r} \Big\rangle_{r=r'} dr' \tag{13}$$

Recalling **Hamiltonian** for Free Energy,

$$H(\mathbf{r}^N, \mathbf{p}^N) := K(\mathbf{p}^N) + V(\mathbf{r}^N) \tag{14}$$

We consider our system as **Isothermal-Isobaric** system, the term with *pressure* $\mathbf{p}^N$ are constant, therefore we can rewrite (13) as follow,

$$\triangle G(r) = \int_{r_0}^{r} \Big\langle \frac{\partial V(r)}{\partial r} \Big\rangle_{r=r'} dr' \tag{15}$$

Driving Force in Molecular Dynamics is defined by,

$$F(r) := -\frac{\partial V(r)}{\partial r} \tag{16}$$

Therefore,

$$\triangle G(r) = -\int_{r_0}^{r} \langle F(r) \rangle_{r=r'} dr'$$