

Topics in Computational Science Report

Gibbs Energy in Isothermal-Isobaric Ensemble

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1. Derive the following equation,

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

Answer:

Suppose that,

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

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

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

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

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

Substitute (2) to (5) we get,

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

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

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

Applying chain rule to (7), thus

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

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

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

for simplicity, define

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

Then we can rewrite (9) as follow,

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

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

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

Thus (11) become,

$$\Delta G(r) = \int_{r_0}^r \left\langle \frac{\partial H(\mathbf{r}^N, \mathbf{p}^N)}{\partial r} \right\rangle_{r=r'} dr' \quad (13)$$

Recalling **Hamiltonian** for Free Energy,

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

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

$$\Delta G(r) = \int_{r_0}^r \left\langle \frac{\partial V(r)}{\partial r} \right\rangle_{r=r'} dr' \quad (15)$$

Driving Force in Molecular Dynamics is defined by,

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

Therefore,

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