CE 530 Molecular Simulation

Lecture 21
Histogram Reweighting Methods

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Histogram Reweighting

- Method to combine results taken at different state conditions
- Microcanonical ensemble

\[ \Omega(E,V,N) = \sum_{\text{micro states}} 1 \]

- Canonical ensemble

\[ \pi(r^N, p^N) = \frac{1}{Q} e^{-\beta E} \quad \text{Probability of a microstate} \]

\[ \pi(E; \beta) = \frac{\Omega(E) e^{-\beta E}}{Q(\beta)} \quad \text{Probability of an energy} \]

- The big idea:

  - Combine simulation data at different temperatures to improve quality of all data via their mutual relation to \( \Omega(E) \)
In-class Problem 1.

- Consider three energy levels
  \[ \Omega_0 = 1 \quad E_0 = 0 = \ln 1 \]
  \[ \Omega_1 = 100 \quad E_1 = 2.3 = \ln 10 \]
  \[ \Omega_2 = 1000 \quad E_2 = 6.9 = \ln 1000 \]

- What are Q, distribution of states and <E> at \( \beta = 1 \)?
In-class Problem 1A.

Consider three energy levels

- $\Omega_0 = 1 \quad E_0 = 0 = \ln 1$
- $\Omega_1 = 100 \quad E_1 = 2.3 = \ln 10$
- $\Omega_2 = 1000 \quad E_2 = 6.9 = \ln 1000$

What are $Q$, distribution of states and $\langle E \rangle$ at $\beta = 1$?

$$Q = \Omega_0 e^{-\beta E_0} + \Omega_1 e^{-\beta E_1} + \Omega_2 e^{-\beta E_2}$$
$$= e^{-\ln 1} + 100 e^{-\ln 10} + 1000 e^{-\ln 1000}$$
$$= 1 \times 1 + 100 \times 0.1 + 1000 \times 0.001$$
$$= 12$$

$$\pi_0 = \frac{\Omega_0 e^{-\beta E_0}}{Q} = \frac{1}{12} = 0.083 \quad \langle E \rangle = \sum \pi_i E_i$$
$$= 0.083 \times 0 \quad + 0.833 \times 2.3 \quad + 0.083 \times 6.9$$
$$= 2.49$$

$$\pi_1 = \frac{\Omega_1 e^{-\beta E_1}}{Q} = \frac{10}{12} = 0.833$$

$$\pi_2 = \frac{\Omega_2 e^{-\beta E_2}}{Q} = \frac{1}{12} = 0.083$$
In-class Problem 1A.

Consider three energy levels

\[ \begin{align*}
\Omega_0 &= 1 & E_0 &= 0 = \ln 1 \\
\Omega_1 &= 100 & E_1 &= 2.3 = \ln 10 \\
\Omega_2 &= 1000 & E_2 &= 6.9 = \ln 1000
\end{align*} \]

What are \( Q \), distribution of states and \( \langle E \rangle \) at \( \beta = 1 \)?

\[ Q = \Omega_0 e^{-\beta E_0} + \Omega_1 e^{-\beta E_1} + \Omega_2 e^{-\beta E_2} \]
\[ = e^{-\ln 1} + 100 e^{-\ln 10} + 1000 e^{-\ln 1000} \]
\[ = 1 \times 1 + 100 \times 0.1 + 1000 \times 0.001 \]
\[ = 12 \]

\[ \pi_0 = \frac{\Omega_0 e^{-\beta E_0}}{Q} = \frac{1}{12} = 0.083 \]
\[ \langle E \rangle = \sum \pi_i E_i \]
\[ = 0.083 \times 0 + 0.833 \times 2.3 + 0.083 \times 6.9 \]
\[ = 2.49 \]

And at \( \beta = 3 \)?

\[ Q = e^{-3 \ln 1} + 100 e^{-3 \ln 10} + 1000 e^{-3 \ln 1000} \]
\[ = 1 \times 1 + 100 \times 0.001 + 1000 \times 1000^{-3} \]
\[ = 1.1 \]

\[ \pi_0 = \frac{1}{1.1} = 0.91 \]
\[ \langle E \rangle = 0.91 \times 0 + 0.09 \times 2.3 + 0.00 \times 6.9 \]
\[ = 0.21 \]
Histogram Reweighting Approach

- Knowledge of $\Omega(E)$ can be used to obtain averages at any temperature

- Simulations at different temperatures probe different parts of $\Omega(E)$
- But simulations at each temperature provides information over a range of values of $\Omega(E)$
- Combine simulation data taken at different temperatures to obtain better information for each temperature
In-class Problem 2.

- Consider simulation data from a system having three energy levels
  - $M = 100$ samples taken at $\beta = 0.5$
  - $m_i$ times observed in level $i$

- What is $\Omega(E)$?


<table>
<thead>
<tr>
<th>$m_0$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$E_0$</th>
<th>$E_1$</th>
<th>$E_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>46</td>
<td>50</td>
<td>0</td>
<td>2.3</td>
<td>9.2</td>
</tr>
</tbody>
</table>

$E_i = \ln(i+1)$
In-class Problem 2.

- Consider simulation data from a system having three energy levels
  - $M = 100$ samples taken at $\beta = 0.5$
  - $m_i$ times observed in level $i$

- What is $\Omega(E)$?

Reminder: $\pi(E) = \Omega(E) \frac{e^{-\beta E}}{Q(\beta)}$

<table>
<thead>
<tr>
<th>$m_0$</th>
<th>$E_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_1$</td>
<td>$E_1$</td>
</tr>
<tr>
<td>$m_2$</td>
<td>$E_2$</td>
</tr>
<tr>
<td>4</td>
<td>$\ln 1$</td>
</tr>
<tr>
<td>46</td>
<td>$\ln 100$</td>
</tr>
<tr>
<td>50</td>
<td>$\ln 10000$</td>
</tr>
</tbody>
</table>
In-class Problem 2.

Consider simulation data from a system having three energy levels

- *M = 100 samples taken at* $\beta = 0.5$
- $m_i$ *times observed in level* $i$

What is $\Omega(E)$?

Hint: $\pi(E) = \left( \frac{\Omega(E)}{Q(\beta)} \right) e^{-\beta E}$

Can get only relative values!

<table>
<thead>
<tr>
<th>$m_0$</th>
<th>$E_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$0 = \ln 1$</td>
</tr>
<tr>
<td>$m_1$</td>
<td>$E_1 = 2.3 = \ln 100$</td>
</tr>
<tr>
<td>46</td>
<td></td>
</tr>
<tr>
<td>$m_2$</td>
<td>$E_2 = 9.2 = \ln 10000$</td>
</tr>
<tr>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>
In-class Problem 2A.

Consider simulation data from a system having three energy levels

- \( M = 100 \) samples taken at \( \beta = 0.5 \)
- \( m_i \) times observed in level \( i \)

What is \( \Omega(E) \)?

\[
\begin{align*}
\Omega_0 &= \frac{m_0}{M} e^{\beta U_0} Q_A = 0.04 \times 1^{0.5} Q = 0.04 Q_A \\
\Omega_1 &= \frac{m_1}{M} e^{\beta U_1} Q_A = 0.46 \times 100^{0.5} Q = 4.6 Q_A \\
\Omega_2 &= \frac{m_2}{M} e^{\beta U_2} Q_A = 0.50 \times 10000^{0.5} Q = 50 Q_A
\end{align*}
\]

\( m_0 = 4 \quad E_0 = 0 = \ln 1 \)
\( m_1 = 46 \quad E_1 = 2.3 = \ln 100 \)
\( m_2 = 50 \quad E_2 = 9.2 = \ln 10000 \)
In-class Problem 3.

Consider simulation data from a system having three energy levels
- \( M = 100 \) samples taken at \( \beta = 0.5 \)
- \( m_i \) times observed in level \( i \)

What is \( \Omega(E) \)?

\[
\begin{align*}
\Omega_0 &= \frac{m_0}{M} e^{\beta U_0} Q_A = 0.04 \times 10^{0.5} Q_A = 0.04 Q_A \\
\Omega_1 &= \frac{m_1}{M} e^{\beta U_1} Q_A = 0.46 \times 100^{0.5} Q_A = 4.6 Q_A \\
\Omega_2 &= \frac{m_2}{M} e^{\beta U_2} Q_A = 0.50 \times 10000^{0.5} Q_A = 50 Q_A
\end{align*}
\]

Here’s some more data, taken at \( \beta = 1 \)
- \( m_0 = 50 \)
- \( m_1 = 48 \)
- \( m_2 = 2 \)

What is \( \Omega(E) \)?
In-class Problem 3.

Consider simulation data from a system having three energy levels

- $M = 100$ samples taken at $\beta = 0.5$
- $m_i$ times observed in level $i$

What is $\Omega(E)$?

$$\Omega_0 = \frac{m_0}{M} e^{+\beta U_0} Q_A = 0.04 \times 10^{0.5} Q_A = 0.4 Q_A \quad Q_A \equiv Q(\beta = 0.5)$$

$$\Omega_1 = \frac{m_1}{M} e^{+\beta U_1} Q_A = 0.46 \times 100^{0.5} Q_A = 4.6 Q_A$$

$$\Omega_2 = \frac{m_2}{M} e^{+\beta U_2} Q_A = 0.50 \times 10000^{0.5} Q_A = 50 Q_A$$

Here’s some more data, taken at $\beta = 1$

- $m_0 = 50 \quad m_1 = 48 \quad m_2 = 2$

What is $\Omega(E)$?

$$\Omega_0 = 0.50 \times 1 Q_B = 0.5 Q_B \quad Q_B \equiv Q(\beta = 1.0)$$

$$\Omega_1 = 0.48 \times 100 Q_B = 48 Q_B$$

$$\Omega_2 = 0.02 \times 10000 Q_B = 200 Q_B$$
Reconciling the Data

- We have two data sets

<table>
<thead>
<tr>
<th></th>
<th>$\Omega_0$</th>
<th>$\Omega_1$</th>
<th>$\Omega_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega_0$</td>
<td>$0.04Q_A$</td>
<td>$0.50Q_B$</td>
<td></td>
</tr>
<tr>
<td>$\Omega_1$</td>
<td>$4.6Q_A$</td>
<td>$48Q_B$</td>
<td></td>
</tr>
<tr>
<td>$\Omega_2$</td>
<td>$50Q_A$</td>
<td>$200Q_B$</td>
<td></td>
</tr>
</tbody>
</table>

- Questions of interest
  - what is the ratio $Q_A/Q_B$? (which then gives us $\Delta A$)
  - what is the best value of $\Omega_1/\Omega_0$, $\Omega_2/\Omega_0$?
  - what is the average energy at $\beta = 2$?

- In-class Problem 4
  - make an attempt to answer these questions
In-class Problem 4A.

- We have two data sets

<table>
<thead>
<tr>
<th>Ω_0</th>
<th>.04Q_A</th>
<th>Ω_0</th>
<th>.50Q_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ω_1</td>
<td>4.6Q_A</td>
<td>Ω_1</td>
<td>48Q_B</td>
</tr>
<tr>
<td>Ω_2</td>
<td>50Q_A</td>
<td>Ω_2</td>
<td>200Q_B</td>
</tr>
</tbody>
</table>

- What is the ratio Q_A/Q_B? (which then gives us ΔA)
  - Consider values from each energy level
    
    \[
    \frac{Ω_0}{Ω_0} = \frac{0.04Q_A}{0.50Q_B} \quad \frac{Ω_1}{Ω_1} = \frac{4.6Q_A}{48Q_B} \quad \frac{Ω_2}{Ω_2} = \frac{50Q_A}{200Q_B}
    \]
    
    \[
    \frac{Q_A}{Q_B} = \frac{0.50}{0.04} = 12.5 \quad \frac{Q_A}{Q_B} = \frac{48}{4.6} = 10.4 \quad \frac{Q_A}{Q_B} = \frac{200}{50} = 4
    \]

- What is the best value of Ω_1/Ω_0, Ω_2/Ω_0?
  - Consider values from each temperature
    
    \[
    \beta = 0.5 \quad Ω_1 \quad Ω_0 = \frac{4.6Q_A}{0.04Q_A} = 115 \quad Ω_2 \quad Ω_0 = \frac{50Q_A}{0.04Q_A} = 1250
    \]
    
    \[
    \beta = 1 \quad Ω_1 \quad Ω_0 = \frac{48Q_B}{0.05Q_B} = 96 \quad Ω_2 \quad Ω_0 = \frac{200Q_B}{0.5Q_B} = 400
    \]

- What to do?
Accounting for Data Quality

- Remember the number of samples that went into each value
  \[ \Omega_0 = 0.04Q_A \quad m_0 = 4 \quad \Omega_0 = 0.50Q_B \quad m_0 = 50 \]
  \[ \Omega_1 = 4.6Q_A \quad m_1 = 46 \quad \Omega_1 = 48Q_B \quad m_1 = 48 \]
  \[ \Omega_2 = 50Q_A \quad m_2 = 50 \quad \Omega_2 = 200Q_B \quad m_2 = 2 \]

- We expect the A-state data to be good for levels 1 and 2
- ...while the B-state data are good for levels 0 and 1

- Write each \( \Omega \) as an average of all values, weighted by quality of result

\[
\Omega_{0,0}^{est} = w_A \Omega_{0,A}^{est} + w_B \Omega_{0,B}^{est}
\]

\[
= w_A \left( e^{\beta_A U_0 Q_A \frac{m_{0,A}}{M_A}} \right) + w_B \left( e^{\beta_B U_0 Q_B \frac{m_{0,B}}{M_B}} \right)
\]

\[
\pi(E) = \Omega(E) \frac{e^{-\beta E}}{Q(\beta)}
\]
Histogram Variance

- Estimate confidence in each simulation result
  \[ \Omega_0 = 0.04 Q_A \quad m_0 = 4 \quad \Omega_0 = 0.50 Q_B \quad m_0 = 50 \]
  \[ \Omega_1 = 4.6 Q_A \quad m_1 = 46 \quad \Omega_1 = 48 Q_B \quad m_1 = 48 \]
  \[ \Omega_2 = 50 Q_A \quad m_2 = 50 \quad \Omega_2 = 200 Q_B \quad m_2 = 2 \]

- Assume each histogram follows a Poisson distribution
  - probability \( P \) to observe any given instance of distribution
    \[
    P\{m_i\} = M! \prod \frac{\pi_i^{m_i}}{m_i!}
    \]
    \[
    P\{m_1, m_2, m_3\} = M! \frac{\pi_1^{m_1} \pi_2^{m_2} \pi_3^{m_3}}{m_1! m_2! m_3!}
    \]
  - the variance for each bin is
    \[
    \sigma_{m_i}^2 = m_i = M \pi_i
    \]
Variance in Estimate of $\Omega$

○ Formula for estimate of $\Omega$

$$\Omega_{0}^{\text{est}} = w_A e^{\beta_A E_0} Q_A \frac{m_{0,A}}{M_A} + w_B e^{\beta_B E_0} Q_B \frac{m_{0,B}}{M_B}$$

○ Variance

$$\sigma_{\Omega_{0}^{\text{est}}}^2 = w_A^2 e^{2\beta_A E_0} Q_A^2 \frac{1}{M_A^2} \sigma_{m_{0,A}}^2 + w_B^2 e^{2\beta_B E_0} Q_B^2 \frac{1}{M_B^2} \sigma_{m_{0,B}}^2$$

$$= w_A^2 e^{2\beta_A E_0} Q_A^2 \frac{1}{M_A^2} \left(M_A \pi_{0,A}\right) + w_B^2 e^{2\beta_B E_0} Q_B^2 \frac{1}{M_B^2} \left(M_B \pi_{0,B}\right)$$

$$= w_A^2 \Omega_0 e^{\beta_A E_0} Q_A \frac{1}{M_A} + w_B^2 \Omega_0 e^{\beta_B E_0} Q_B \frac{1}{M_B}$$

$$\pi(E) = \Omega(E) \frac{e^{-\beta E}}{Q(\beta)}$$
Optimizing Weights

- Variance
  \[ \sigma_{\Omega_0}^2 = w_Aq_0e^{\beta_A}e_0 \frac{1}{M_A} + w_Bq_0e^{\beta_B}e_0 \frac{1}{M_B} \]

- Minimize with respect to weight, subject to normalization
  - *In-class Problem 5*
  - Do it!
Optimizing Weights

- **Variance**
  \[ \sigma_{\Omega_0}^2 = w_A \Omega_0 e^{\beta_A E_0} Q_A \frac{1}{M_A} + w_B \Omega_0 e^{\beta_B E_0} Q_B \frac{1}{M_B} \]

- **Minimize with respect to weight, subject to normalization**
  - *Lagrange multiplier*
  \[ \text{Min} \left[ \sigma_{\Omega_0}^2 - \lambda \left( \sum w_a - 1 \right) \right] \]

\[ \pi(E) = \Omega(E) \frac{e^{-\beta E}}{Q(\beta)} \approx \frac{m_i}{M} \]

- **Equation for each weight is**
  \[ 2w_a \Omega_0 e^{\beta_a E_0} \frac{Q_a}{M_a} = \lambda \]

- **Rearrange**
  \[ w_a = \lambda \frac{1}{2 \Omega_0} e^{-\beta_a E_0} M_a \]

- **Normalize**
  \[ w_a = \frac{e^{-\beta_a E_0} M_a / Q_a}{e^{-\beta_A E_0} M_A / Q_A + e^{-\beta_B E_0} M_B / Q_B} \]
Optimal Estimate

Collect results

\[ \Omega_{0}^{est} = w_{A}e^{\beta_{A}E_{0}}Q_{A}\frac{m_{0,A}}{M_{A}} + w_{B}e^{\beta_{B}E_{0}}Q_{B}\frac{m_{0,B}}{M_{B}} \]

\[ w_{a} = \frac{e^{-\beta_{a}E_{0}M_{a}/Q_{a}}}{e^{-\beta_{a}E_{0}M_{a}/Q_{A}} + e^{-\beta_{B}E_{0}M_{B}/Q_{B}}} \]

Combine

\[ \Omega_{0}^{est} = \left[ \frac{e^{-\beta_{A}E_{0}M_{A}}}{Q_{A}} + \frac{e^{-\beta_{B}E_{0}M_{B}}}{Q_{B}} \right]^{-1} \left[ \left( \frac{e^{-\beta_{A}E_{0}M_{A}}}{Q_{A}} \right)e^{\beta_{A}E_{0}}Q_{A}\frac{m_{0,A}}{M_{A}} + \left( \frac{e^{-\beta_{B}E_{0}M_{B}}}{Q_{B}} \right)e^{\beta_{B}E_{0}}Q_{B}\frac{m_{0,B}}{M_{B}} \right] \]

\[ = \left[ \frac{e^{-\beta_{A}E_{0}M_{A}}}{Q_{A}} + \frac{e^{-\beta_{B}E_{0}M_{B}}}{Q_{B}} \right]^{-1} \left[ m_{0,A} + m_{0,B} \right] \]
Calculating $\Omega$

- **Formula for $\Omega$**
  \[
  \Omega_0^{\text{est}} = \left[ \frac{e^{-\beta A E_0 M_A}}{Q_A} + \frac{e^{-\beta B E_0 M_B}}{Q_B} \right]^{-1} \left[ m_{0,A} + m_{0,B} \right]
  \]

- **In-class Problem 6**
  - *explain why this formula cannot yet be used*
Calculating $\Omega$

- **Formula for $\Omega$**
  \[
  \Omega_0^{est} = \left[ \frac{e^{-\beta A E_0} M_A}{Q_A} + \frac{e^{-\beta B E_0} M_B}{Q_B} \right]^{-1} \left[ m_{0,A} + m_{0,B} \right]
  \]

- **We do not know the Q partition functions**
  \[
  Q_a = \Omega_0 e^{-\beta_a E_0} + \Omega_1 e^{-\beta_1 E_1} + \Omega_2 e^{-\beta_2 E_2}
  \]
  \[
  \Omega_0^{est} = \left[ \frac{e^{-\beta A E_0} M_A}{\Omega_0 e^{-\beta A E_0} + \Omega_1 e^{-\beta A E_1} + \Omega_2 e^{-\beta A E_2}} + \frac{e^{-\beta B E_0} M_B}{\Omega_0 e^{-\beta B E_0} + \Omega_1 e^{-\beta B E_1} + \Omega_2 e^{-\beta B E_2}} \right]^{-1} \left[ m_{0,A} + m_{0,B} \right]
  \]

- **One equation for each $\Omega$**
- **Each equation depends on all $\Omega$**
- **Requires iterative solution**
In-class Problem 7

○ Write the equations for each $\Omega$ using the example values

$$\Omega_0^{est} = \left[ \frac{e^{-\beta A E_0} M_A}{\Omega_0 e^{-\beta A E_0} + \Omega_1 e^{-\beta A E_1} + \Omega_2 e^{-\beta A E_2}} + \frac{e^{-\beta B E_0} M_B}{\Omega_0 e^{-\beta B E_0} + \Omega_1 e^{-\beta B E_1} + \Omega_2 e^{-\beta B E_2}} \right]^{-1} \left[ m_{0,A} + m_{0,B} \right]$$

$\beta = 0.5 \quad \beta = 1$

$m_0 = 4 \quad m_0 = 50 \quad E_0 = 0 = \ln 1 \quad M_A = M_B = 100$

$m_1 = 46 \quad m_1 = 48 \quad E_1 = 2.3 = \ln 100$

$m_2 = 50 \quad m_2 = 2 \quad E_2 = 9.2 = \ln 10000$
In-class Problem 7

○ Write the equations for each $\Omega$ using the example values

$$\Omega_{0}^{est} = \left[ \frac{e^{-\beta A E_0} M_A}{\Omega_0 e^{-\beta A E_0} + \Omega_1 e^{-\beta A E_1} + \Omega_2 e^{-\beta A E_2}} + \frac{e^{-\beta B E_0} M_B}{\Omega_0 e^{-\beta B E_0} + \Omega_1 e^{-\beta B E_1} + \Omega_2 e^{-\beta B E_2}} \right]^{-1} \left[ m_{0,A} + m_{0,B} \right]$$

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>$m_0$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$E_0$</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$M_A$</th>
<th>$M_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4</td>
<td>46</td>
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<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>48</td>
<td>2</td>
<td>0</td>
<td>2.3</td>
<td>9.2</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

$$\Omega_{0}^{est} = \left[ \frac{1 \times 100}{1 \Omega_0 + 0.1 \Omega_1 + 0.01 \Omega_2} + \frac{1 \times 100}{1 \Omega_0 + 0.01 \Omega_1 + 0.0001 \Omega_2} \right]^{-1} \left[ 4 + 50 \right]$$

$$\Omega_{1}^{est} = \left[ \frac{0.1 \times 100}{1 \Omega_0 + 0.1 \Omega_1 + 0.01 \Omega_2} + \frac{0.01 \times 100}{1 \Omega_0 + 0.01 \Omega_1 + 0.0001 \Omega_2} \right]^{-1} \left[ 46 + 48 \right]$$

$$\Omega_{2}^{est} = \left[ \frac{0.01 \times 100}{1 \Omega_0 + 0.1 \Omega_1 + 0.01 \Omega_2} + \frac{0.0001 \times 100}{1 \Omega_0 + 0.01 \Omega_1 + 0.0001 \Omega_2} \right]^{-1} \left[ 50 + 2 \right]$$

○ Solution

$$\frac{\Omega_1}{\Omega_0} = 94.7 \quad \frac{\Omega_2}{\Omega_0} = 943.2$$
In-class Problem 7A.

○ Solution

\[
\frac{\Omega_1}{\Omega_0} = 94.7 \quad \frac{\Omega_2}{\Omega_0} = 943.2
\]

○ Compare

\[
\beta = 0.5 \quad \frac{\Omega_1}{\Omega_0} = \frac{4.6Q_A}{0.04Q_A} = 115 \quad \frac{\Omega_2}{\Omega_0} = \frac{50Q_A}{0.04Q_A} = 1250
\]

\[
\beta = 1 \quad \frac{\Omega_1}{\Omega_0} = \frac{48Q_B}{0.05Q_B} = 96 \quad \frac{\Omega_2}{\Omega_0} = \frac{200Q_B}{0.5Q_B} = 400
\]

○ “Exact” solution

\[
\frac{\Omega_1}{\Omega_0} = 100 \quad \frac{\Omega_2}{\Omega_0} = 1000
\]

○ Free energy difference

\[
\frac{Q_A}{Q_B} = \frac{1\Omega_0 + 0.1\Omega_1 + 0.01\Omega_2}{1\Omega_0 + 0.01\Omega_1 + 0.0001\Omega_2} = 9.74
\]

“Design value” = 10
Extensions of Technique

- Method is usually used in multidimensional form
- Useful to apply to grand-canonical ensemble

\[ \Xi = \sum_{N} e^{\beta \mu N} \frac{1}{h^{3N} N!} \int d\mathbf{r}^N d\mathbf{p}^N e^{-\beta E} \]

\[ = \sum_{N} \sum_{U} \Omega(U, V, N) e^{\beta \mu N} e^{-\beta E} \]

- Can then be used to relate simulation data at different temperature and chemical potential
- Many other variations are possible