CE 530 Molecular Simulation

Lecture 20
Phase Equilibria

David A. Kofke
Department of Chemical Engineering
SUNY Buffalo
kofke@eng.buffalo.edu
Thermodynamic Phase Equilibria

- Certain thermodynamic states find that two (or more) phases may be equally stable
  - *thermodynamic phase coexistence*

- Phases are distinguished by an order parameter; e.g.
  - *density*
  - *structural order parameter*
  - *magnetic or electrostatic moment*

- Intensive-variable requirements of phase coexistence
  - \( T^a = T^b \)
  - \( P^a = P^b \)
  - \( \mu_i^a = \mu_i^b, \ i = 1, ..., C \)
Phase Diagrams

Phase behavior is described via phase diagrams

- Gibbs phase rule
  - \( F = 2 + C - P \)
    - \( F \) = number of degrees of freedom
    - independently specified thermodynamic state variables
    - \( C \) = number of components (chemical species) in the system
    - \( P \) = number of phases
  - \emph{Single component,} \( F = 3 - P \)
Approximate Methods for Phase Equilibria by Molecular Simulation 1.

- Adjust field variables until crossing of phase transition is observed
  - *e.g.*, lower temperature until condensation/freezing occurs
- Problem: metastability may obscure location of true transition

- Try it out with the **LJ NPT-MC applet**
Approximate Methods for Phase Equilibria by Molecular Simulation 2.

- Select density variable inside of two-phase region
  - *choose density between liquid and vapor values*
- Problem: finite system size leads to large surface-to-volume ratios for each phase
  - *bulk behavior not modeled*
- Metastability may still be a problem

- Try it out with the **SW NVT MD applet**
Rigorous Methods for Phase Equilibria by Molecular Simulation

- **Search for conditions that satisfy equilibrium criteria**
  - equality of temperature, pressure, chemical potentials

- **Difficulties**
  - evaluation of chemical potential often is not easy
  - tedious search-and-evaluation process

![Diagram showing T constant, Simulation data, Simulation data or equation of state relationship over pressure and chemical potential.](image-url)
Rigorous Methods for Phase Equilibria by Molecular Simulation

- Search for conditions that satisfy equilibrium criteria
  - equality of temperature, pressure, chemical potentials

- Difficulties
  - evaluation of chemical potential often is not easy
  - tedious search-and-evaluation process

![Graph showing chemical potential vs. pressure with T constant and simulation data or equation of state marked]
Rigorous Methods for Phase Equilibria by Molecular Simulation

- Search for conditions that satisfy equilibrium criteria
  - equality of temperature, pressure, chemical potentials

- Difficulties
  - evaluation of chemical potential often is not easy
  - tedious search-and-evaluation process

![Graph showing chemical potential vs. pressure with T constant and simulation data or equation of state annotations.](image)
Rigorous Methods for Phase Equilibria by Molecular Simulation

- Search for conditions that satisfy equilibrium criteria
  - equality of temperature, pressure, chemical potentials

- Difficulties
  - evaluation of chemical potential often is not easy
  - tedious search-and-evaluation process

![Diagram showing chemical potential vs. pressure with T constant and simulation data or equation of state notes]
Rigorous Methods for Phase Equilibria by Molecular Simulation

- Search for conditions that satisfy equilibrium criteria
  - equality of temperature, pressure, chemical potentials

- Difficulties
  - evaluation of chemical potential often is not easy
  - tedious search-and-evaluation process
Rigorous Methods for Phase Equilibria by Molecular Simulation

- Search for conditions that satisfy equilibrium criteria
  - equality of temperature, pressure, chemical potentials

- Difficulties
  - evaluation of chemical potential often is not easy
  - tedious search-and-evaluation process

Many simulations to get one point on phase diagram
Panagiotopoulos in 1987 introduced a clever way to simulate coexisting phases without an interface. Thermodynamic contact without physical contact:

- How?
Gibbs Ensemble 2.

- MC simulation includes moves that couple the two simulation volumes

  - Particle exchange equilibrates chemical potential
  - Volume exchange equilibrates pressure

  Incidentally, the coupled moves enforce mass and volume balance

- Try it out with the **LJ GEMC applet**
Gibbs Ensemble Formalism

○ Partition function

\[ Q^{GE}(N,V,T) = \sum_{N_1=0}^{N} \int dV_1 Q(N_1,V_1,T)Q(N-N_1,V-V_1,T) \]

○ Limiting distribution

\[ \pi(\mathbf{r}^N,N_1,V_1) dV_1 ds^{N_1} ds^{N_2} = \frac{\Lambda^{3N}}{Q^{GE}} \left[ V_1^{N_1} ds^{N_1} e^{-\beta U(s^{N_1},V_1)} \right] \left[ V_2^{N_2} ds^{N_2} e^{-\beta U(s^{N_2},V_2)} \right] \]

○ General algorithm. For each trial:

• *with some pre-specified probability, select*
  molecules displacement/rotation trial
  volume exchange trial
  molecule exchange exchange trial

• *conduct trial move and decide acceptance*
Molecule-Exchange Trial Move
Analysis of Trial Probabilities

Detailed specification of trial moves and probabilities

<table>
<thead>
<tr>
<th>Event [reverse event]</th>
<th>Probability [reverse probability]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Select box A [select box B]</td>
<td>1/2 [1/2]</td>
</tr>
<tr>
<td>Select molecule k [select molecule k]</td>
<td>1/N_A [1/(N_B+1)]</td>
</tr>
<tr>
<td>Move to r^{new} [move back to r^{old}]</td>
<td>Scaled volume</td>
</tr>
<tr>
<td>Accept move [accept move]</td>
<td>min(1,\chi) [min(1,1/\chi)]</td>
</tr>
</tbody>
</table>

**Forward-step trial probability**
\[
\frac{1}{2} \times \frac{ds}{N_A} \times \min(1, \chi)
\]

**Reverse-step trial probability**
\[
\frac{1}{2} \times \frac{ds}{N_B + 1} \times \min(1, \frac{1}{\chi})
\]

\(\chi\) is formulated to satisfy detailed balance
Molecule-Exchange Trial Move
Analysis of Detailed Balance

Forward-step trial probability
\[ \frac{1}{2} \times \frac{ds}{N_A} \times \min(1, \chi) \]

Reverse-step trial probability
\[ \frac{1}{2} \times \frac{ds}{N_B + 1} \times \min(1, \frac{1}{\chi}) \]

Detailed balance
\[ \pi_i \pi_{ij} = \pi_j \pi_{ji} \]

Limiting distribution
\[ \pi(\mathbf{r}^N, N_A, V_A) dV_A d\mathbf{s}^N_A d\mathbf{s}^N_B = \frac{\Lambda^{3N}}{Q_{GE}} \left[ V_A^{N_A} d\mathbf{s}^N_A e^{-\beta U(\mathbf{s}^N_A, V_A)} \right] \left[ V_B^{N_B} d\mathbf{s}^N_B e^{-\beta U(\mathbf{s}^N_B, V_B)} \right] \]
Molecule-Exchange Trial Move
Analysis of Detailed Balance

Forward-step trial probability
\[
\frac{1}{2} \times \frac{ds}{N_A} \times \min(1, \chi)
\]

Reverse-step trial probability
\[
\frac{1}{2} \times \frac{ds}{N_B + 1} \times \min(1, \frac{1}{\chi})
\]

Detailed balance
\[
\pi_i \pi_{ij} = \pi_j \pi_{ji}
\]

Limiting distribution
\[
\pi(\mathbf{r}^N, N_A, V_A) dV_A d\mathbf{s}^N_A d\mathbf{s}^N_B = \frac{\Lambda^{3N}}{Q^{GE}} \left[ V_A^{N_A} d\mathbf{s}^N_A e^{-\beta U(\mathbf{s}^N_A, V_A)} \right] \left[ V_B^{N_B} d\mathbf{s}^N_B e^{-\beta U(\mathbf{s}^N_B, V_B)} \right]
\]
Molecule-Exchange Trial Move
Analysis of Detailed Balance

Forward-step trial probability
\[ \frac{1}{2} \times \frac{ds}{N_A} \times \min(1, \chi) \]

Reverse-step trial probability
\[ \frac{1}{2} \times \frac{ds}{N_B + 1} \times \min(1, \frac{1}{\chi}) \]

Detailed balance
\[ \pi_i \quad \pi_{ij} \quad = \quad \pi_j \quad \pi_{ji} \]
\[ \frac{e^{-\beta U_{old}^{N_A}} V_A^{N_A} ds^N V_B^{N_B} ds^N dV_A}{\Lambda^{-3N} Q^{GE}} \left[ ds \min(1, \chi) \right] = \frac{e^{-\beta U_{new}^{N_A-1}} V_A^{N_A-1} ds^{N_A-1} V_B^{N_B+1} ds^N dV_A}{2 N_A} \left[ ds \min(1, \frac{1}{\chi}) \right] \]

Acceptance probability
\[ \chi = \frac{V_B}{V_A} \frac{N_A}{N_B + 1} e^{-\beta \Delta U_{tot}} \]
**Volume-Exchange Trial Move**

**Analysis of Trial Probabilities**

- Take steps in $\lambda = \ln(V_A/V_B)$
  
  $$d\lambda = \left(\frac{1}{V_A} + \frac{1}{V_B}\right)dV_A = \frac{V}{V_AV_B}dV_A$$

  $$dV_A = \frac{1}{V} V_A V_B d\lambda$$

- Detailed specification of trial moves and probabilities

<table>
<thead>
<tr>
<th>Event</th>
<th>Probability</th>
<th>Forward-step trial probability $\frac{d\lambda}{\Delta} \times \min(1, \chi)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step to $\lambda^{\text{new}}$ [step to $\lambda^{\text{old}}$]</td>
<td>$d\lambda/\Delta$</td>
<td>$\frac{d\lambda}{\Delta} \times \min(1, \chi)$</td>
</tr>
<tr>
<td>Accept move [accept move]</td>
<td>$\min(1, \chi)$ [min(1, $1/\chi$)]</td>
<td>$\frac{d\lambda}{\Delta} \times \min(1, \frac{1}{\chi})$</td>
</tr>
</tbody>
</table>
Volume-Exchange Trial Move
Analysis of Detailed Balance

Forward-step trial probability:
\[ \frac{d\lambda}{\Delta} \times \min(1, \chi) \]

Reverse-step trial probability:
\[ \frac{d\lambda}{\Delta} \times \min(1, \frac{1}{\chi}) \]

Detailed balance:
\[ \pi_i \pi_{ij} = \pi_j \pi_{ji} \]

Limiting distribution:
\[ \pi(\mathbf{r}^N, N_A, V_A) d\lambda ds^{N_A} ds^{N_B} = \frac{d\lambda \Lambda^{3N}}{VQ^{GE}} \left[ V_A^{N_A+1} ds^{N_A} e^{-\beta U(s^{N_A}, V_A)} \right] \left[ V_B^{N_B+1} ds^{N_B} e^{-\beta U(s^{N_B}, V_B)} \right] \]
Volume-Exchange Trial Move
Analysis of Detailed Balance

Forward-step trial probability
\[ \frac{d\lambda}{\Delta} \times \min(1, \chi) \]

Reverse-step trial probability
\[ \frac{d\lambda}{\Delta} \times \min(1, \frac{1}{\chi}) \]

Detailed balance
\[ \begin{align*}
\pi_i & = \pi_j \\
\pi_{ij} & = \pi_{ji}
\end{align*} \]

Limited distribution
\[ \pi(r^N, N_A, V_A) \text{d} \lambda \text{d}s^N_A \text{d}s^N_B = \frac{d\lambda \Lambda^{3N}}{VQ^{GE}} \left[ V_A^{N_A+1} \text{d}s^N_A e^{-\beta U(s^N_A, V_A)} \right] \left[ V_B^{N_B+1} \text{d}s^N_B e^{-\beta U(s^N_B, V_B)} \right] \]
Volume-Exchange Trial Move
Analysis of Detailed Balance

Forward-step trial probability
\[ \frac{d\lambda}{\Delta} \times \min(1, \chi) \]

Reverse-step trial probability
\[ \frac{d\lambda}{\Delta} \times \min(1, \frac{1}{\chi}) \]

Detailed balance
\[ \pi_i e^{-\beta U_{\text{old}}^{N_A+1} V_{A,i} \hat{d}s_{N_B}^{N_{\text{GE}}}} \pi_{ij} e^{-\beta \min(1, \chi) \frac{d\lambda}{\Delta}} = \pi_j e^{-\beta U_{\text{new}}^{N_A+1} V_{A,j} \hat{d}s_{N_B}^{N_{\text{GE}}}} \pi_{ji} e^{-\beta \min(1, \frac{1}{\chi}) \frac{d\lambda}{\Delta}} \]

Acceptance probability
\[ \chi = \left( \frac{V_A^{\text{new}}}{V_A^{\text{old}}} \right)^{N_A+1} \left( \frac{V_B^{\text{new}}}{V_B^{\text{old}}} \right)^{N_B+1} e^{-\beta \Delta U_{\text{tot}}} \]
Gibbs Ensemble Limitations

- Limitations arise from particle-exchange requirement
  - Molecular dynamics (polarizable models)
  - Dense phases, or complex molecular models

- Solid phases
  \[ N = 4n^3 \text{ (fcc)} \]
Approaching the Critical Point

- Critical phenomena are difficult to capture by molecular simulation
- Density fluctuations are related to compressibility
- Correlations between fluctuations important to behavior
  - *in thermodynamic limit correlations have infinite range*
  - *in simulation correlations limited by system size*
  - *surface tension vanishes*

\[ \frac{\partial P}{\partial \rho} = 0 \]

\[ \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial P} \right) \rightarrow \infty \]

\[ \sigma^2_\rho \propto \kappa \rightarrow \infty \]
Critical Phenomena and the Gibbs Ensemble

- Phase identities break down as critical point is approached
  - *Boxes swap “identities” (liquid vs. vapor)*
  - *Both phases begin to appear in each box*
    - surface free energy goes to zero
Gibbs-Duhem Integration

- **GD equation can be used to derive Clapeyron equation**
  \[
  \left( \frac{\partial \ln p}{\partial \beta} \right)_\sigma = -\frac{\Delta h}{\Delta Z}
  \]
  - *equation for coexistence line*
- **Treat as a nonlinear first-order ODE**
  - *use simulation to evaluate right-hand side*
- **Trace an integration path that coincides with the coexistence line**
GDI Predictor-Corrector Implementation

- Given initial condition and slope \((= -\Delta h/\Delta Z)\), predict new \((p, T)\) pair.

- Evaluate slope at new state condition…

- …and use to correct estimate of new \((p, T)\) pair
GDI Simulation Algorithm

- Estimate pressure and temperature from predictor
- Begin simultaneous NpT simulation of both phases at the estimated conditions
- As simulation progresses, estimate new slope from ongoing simulation data and use with corrector to adjust p and T
- Continue simulation until the iterations and the simulation averages converge
- Repeat for the next state point

Each simulation yields a coexistence point. Particle insertions are never attempted.
GDI Sources of Error

○ Three primary sources of error in GDI method

- Stochastic error
  - Uncertainty in slopes due to uncertainty in simulation averages
  - Quantify via propagation of error using confidence limits of simulation averages

- Finite step of integrator
  - Smaller step
  - Integrate series with every-other datum
  - Compare predictor and corrector values

- Stability
  - Stability can be quantified
  - Error initial condition can be corrected even after series is complete

Incorrect initial condition

True curve
GDI Applications and Extensions

- Applied to a pressure-temperature phase equilibria in a wide variety of model systems
  - emphasis on applications to solid-fluid coexistence
- Can be extended to describe coexistence in other planes
  - variation of potential parameters
    - inverse-power softness
    - stiffness of polymers
    - range of attraction in square-well and triangle-well
    - variation of electrostatic polarizability
  - as with free energy methods, need to identify and measure variation of free energy with potential parameter
    \[
    \frac{\partial \beta A}{\partial \lambda} = \langle \frac{\partial \beta U}{\partial \lambda} \rangle
    \]
  - mixtures
Semigrand Ensemble

○ Thermodynamic formalism for mixtures
\[
d(\beta A) = Ud \beta - \beta P dV + \beta \mu_1 dN_1 + \beta \mu_2 dN_2 + \beta \mu_1 dN_2 - \beta \mu_1 dN_2
\]

○ Rearrange
\[
d(\beta A) = Ud \beta - \beta P dV + \beta \mu_1 d(N_1 + N_2) + \beta (\mu_2 - \mu_1) dN_2
\]
\[
= Ud \beta - \beta P dV + \beta \mu_1 dN + \beta \Delta \mu_2 dN_2
\]

○ Legendre transform
\[
d(\beta Y) \equiv d(\beta A - \beta \Delta \mu_2 N_2)
\]
\[
= Ud \beta - \beta P dV + \beta \mu_1 dN - N_2 d(\beta \Delta \mu_2)
\]

• Independent variables include \(N\) and \(\Delta \mu_2\)
• Dependent variables include \(N_2\)
  
  must determine this by ensemble average
  
  ensemble includes elements differing in composition at same total \(N\)

○ Ensemble distribution
\[
\pi(r^N, p^N, N_2) = \frac{1}{Y \hbar^{3N} N!} e^{-\beta E(p^N, r^N, N_2)} e^{+N_2 \beta \Delta \mu_2}
\]
GDI/GE with the Semigrand Ensemble

- Governing differential equation (pressure-composition plane)

\[
\left(\frac{\partial \ln p}{\partial \beta \Delta \mu_2}\right)_{T,\sigma} = \frac{\Delta x_2}{\Delta Z}
\]

Simple LJ Binary

- \(\sigma_{11} = 1\)  \(\epsilon_{11} = 1\)
- \(\sigma_{12} = 1\)  \(\epsilon_{12} = 0.75\)
- \(\sigma_{22} = 1\)  \(\epsilon_{22} = 1\)
GDI with the Semigrand Ensemble

- Freezing of polydisperse hard spheres
  - *appropriate model for colloids*
- Integrate in pressure-polydispersity plane

Findings
- *upper polydispersity bound to freezing*
- *re-entrant melting*

\[
\left( \frac{dp}{dv} \right)_{\text{sat}} = \frac{\Delta m_2 / 2\nu^2}{\Delta(V / N)}
\]
Other Views of Coexistence Surface

- Dew and bubble lines
- Residue curves
- Azeotropes
  - *semigrand ensemble*
  - *formulate appropriate differential equation*

\[
\left( \frac{dP_{\text{sat}}}{d\beta} \right)_{\text{azeo}} = -\frac{h_L - h_V}{\beta (v_L - v_V)}
\]

\[
\left( \frac{d(\beta\Delta\mu)}{d\beta} \right)_{\text{azeo}} = \left\{ \left( \frac{\partial X_1}{\partial \beta} \right)_{P,\beta\Delta\mu} - \left( \frac{\partial Y_1}{\partial \beta} \right)_{P,\beta\Delta\mu} \right\} + \left\{ \left( \frac{\partial X_1}{\partial P} \right)_{\beta,\beta\Delta\mu} - \left( \frac{\partial Y_1}{\partial P} \right)_{\beta,\beta\Delta\mu} \right\} \left( \frac{dP_{\text{sat}}}{d\beta} \right)_{\text{azeo}}
\]

- *integrate as in standard GDI method*
  
  right-hand side involves partial molar properties
Tracing of Azeotropes

- Lennard-Jones binary, variation with intermolecular potential
  - $\sigma_{11} = 1.0; \sigma_{12} = 1.05; \sigma_{22} = \text{variable}$
  - $\varepsilon_{11} = 1.0; \varepsilon_{12} = 0.90; \varepsilon_{22} = 1.0$
  - $T = 1.10$
Summary

- Thermodynamic phase behavior is interesting and useful
- Obvious methods for evaluating phase behavior by simulation are too approximate
- Rigorous thermodynamic method is tedious
- Gibbs ensemble revolutionized methodology
  - two coexisting phases without an interface
- Gibbs-Duhem integration provides an alternative to use in situations where GE fails
  - dense and complex fluids
  - solids
- Semigrand ensemble is useful formalism for mixtures
- GDI can be extended in many ways