CE 530 Molecular Simulation

Lecture 20

Phase Equilibria

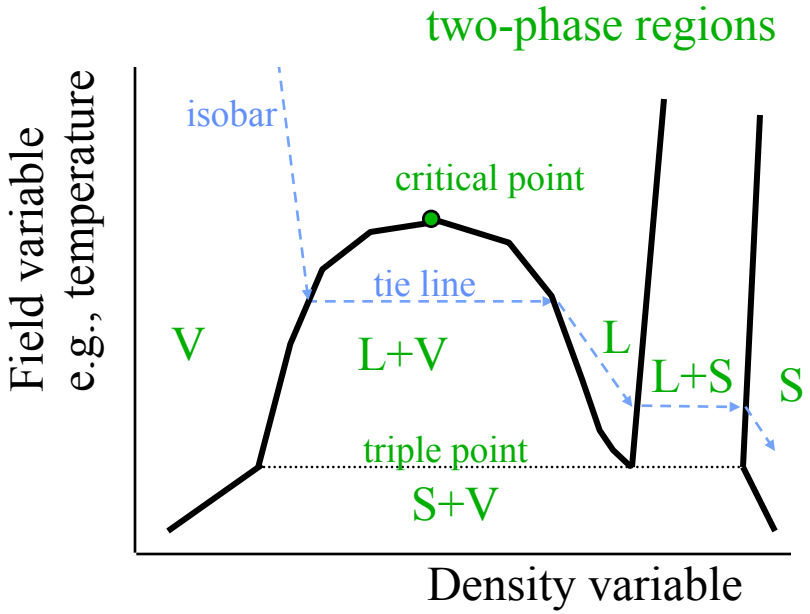
David A. Kofke
Department of Chemical Engineering
SUNY Buffalo
kofke@eng.buffalo.edu

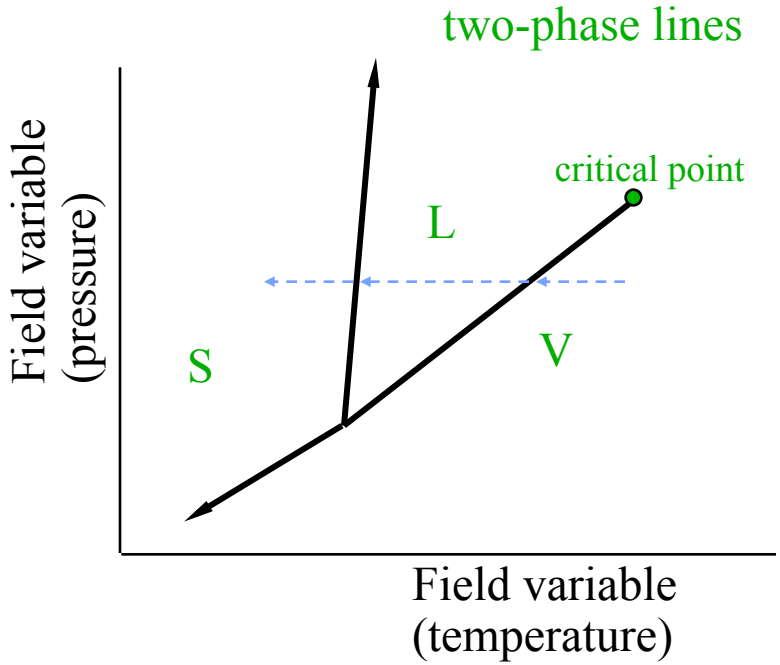
Thermodynamic Phase Equilibria

- 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
  - $T^a = T^b$
  - $P^a = P^b$
  - $\mu_i^a = \mu_i^b,\ i = 1,\ldots,C$

Phase Diagrams

- Phase behavior is described via phase diagrams

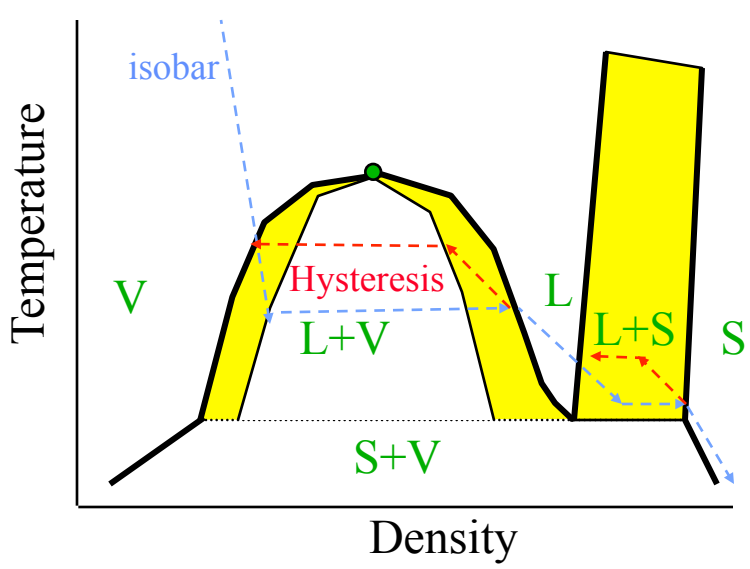


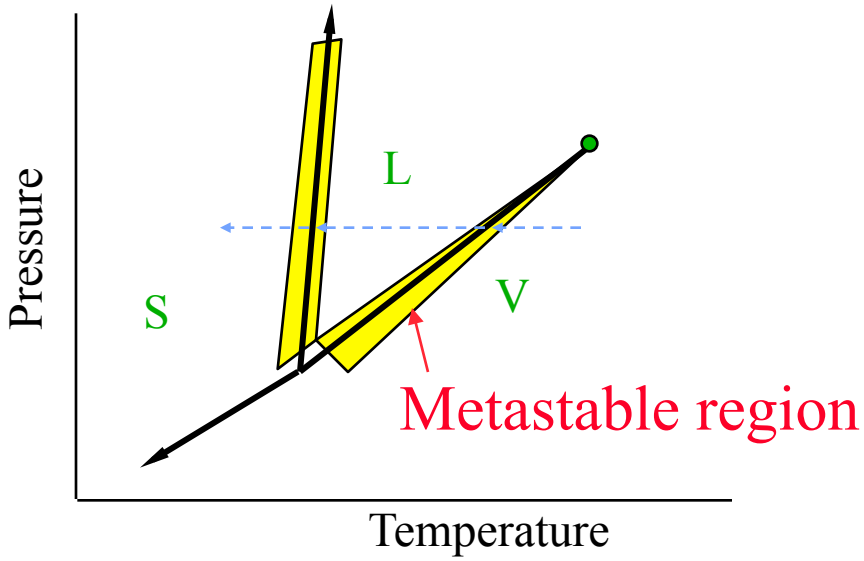


- Gibbs phase rule
  - $F = 2 + C - P$
    - F = number of degrees of freedom
      - independently specified thermodynamic state variables
    - C = number of components (chemical species) in the system
    - P = number of phases
  - *Single component,* $F = 3 - P$

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 obsure location of true transition

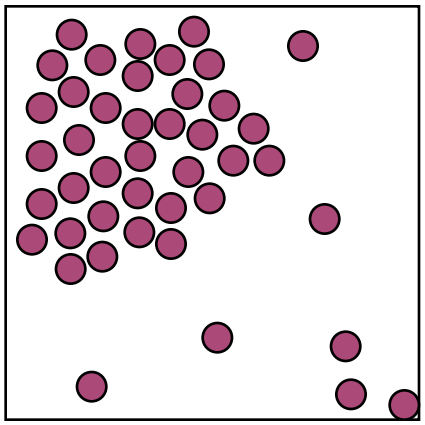


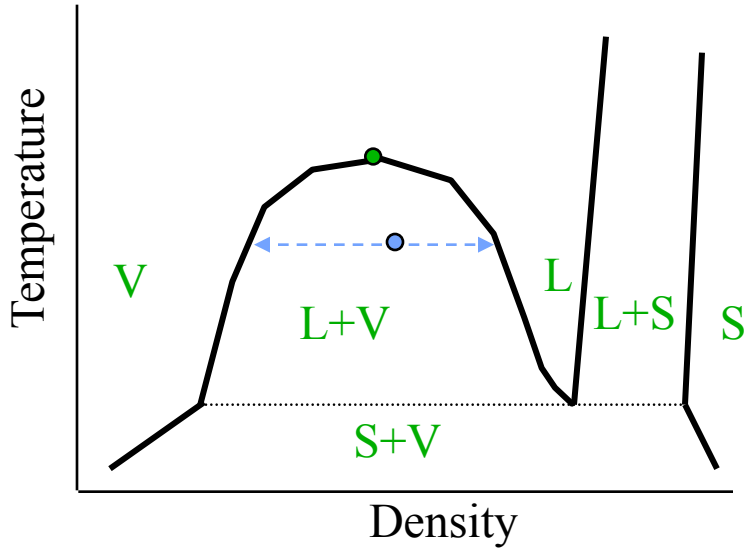


- Try it out with the LJ NPT-MC applet

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

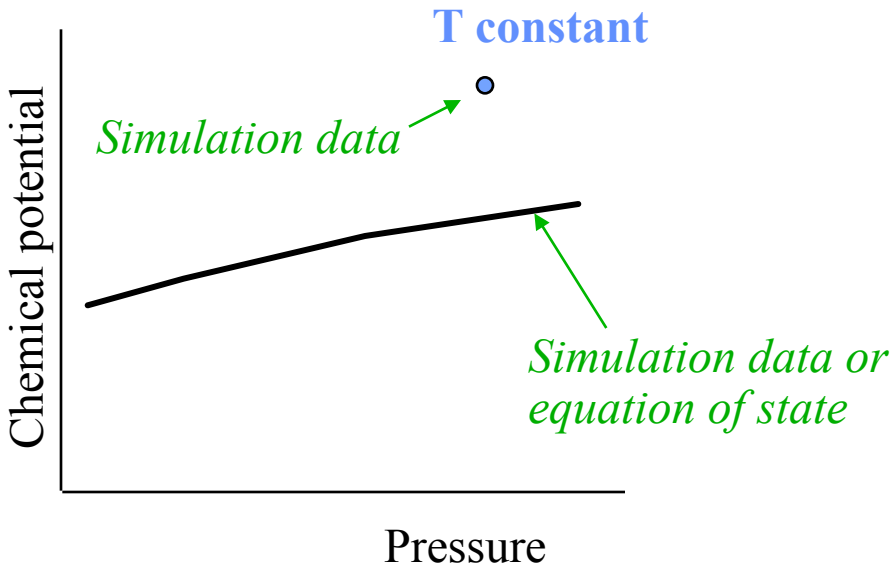




- Try it out with the SW NVT MD applet

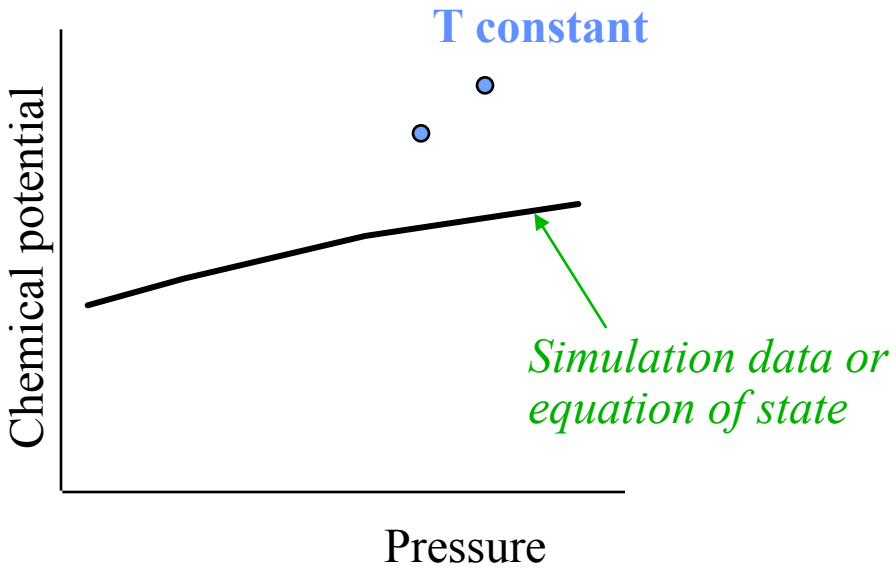
Rigorous Methods for Phase Equilibria by Molecular Simulation

- 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*



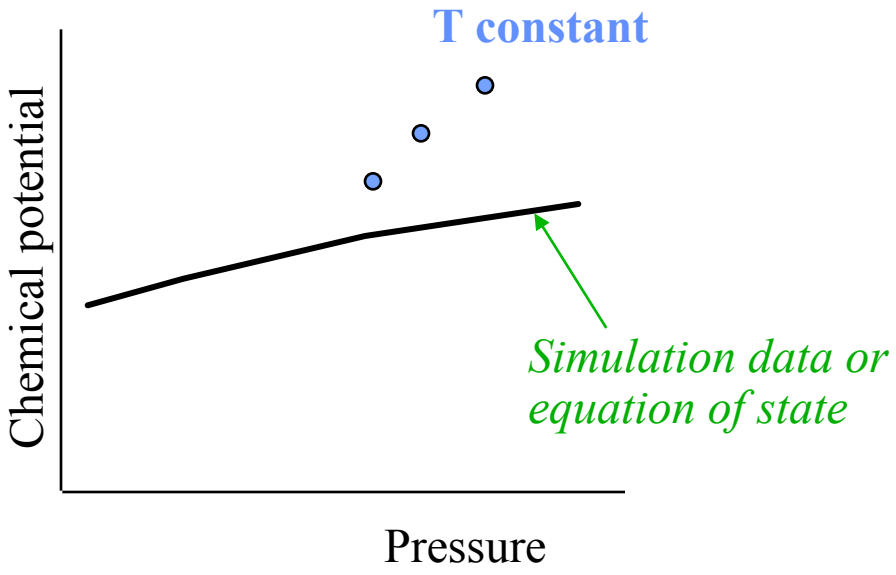
Rigorous Methods for Phase Equilibria by Molecular Simulation

- 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*



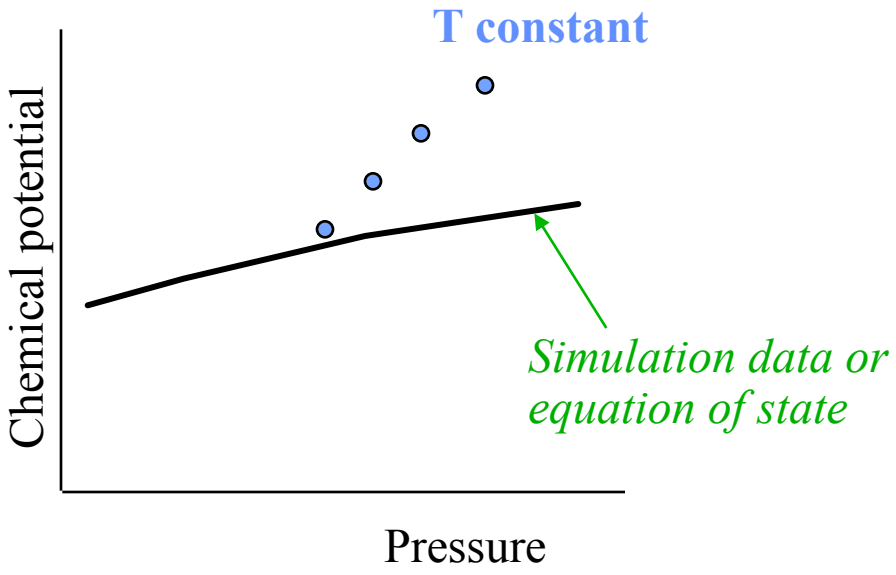
Rigorous Methods for Phase Equilibria by Molecular Simulation

- 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*



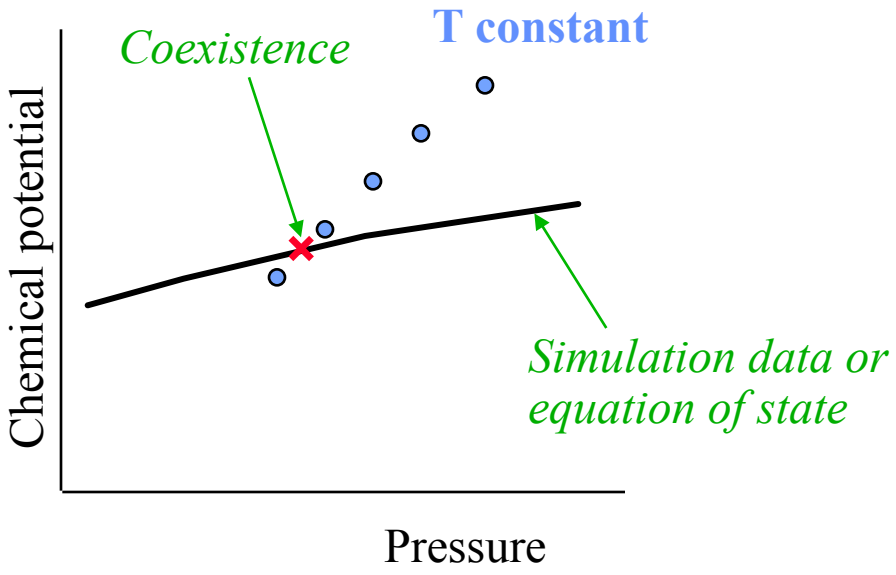
Rigorous Methods for Phase Equilibria by Molecular Simulation

- 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*



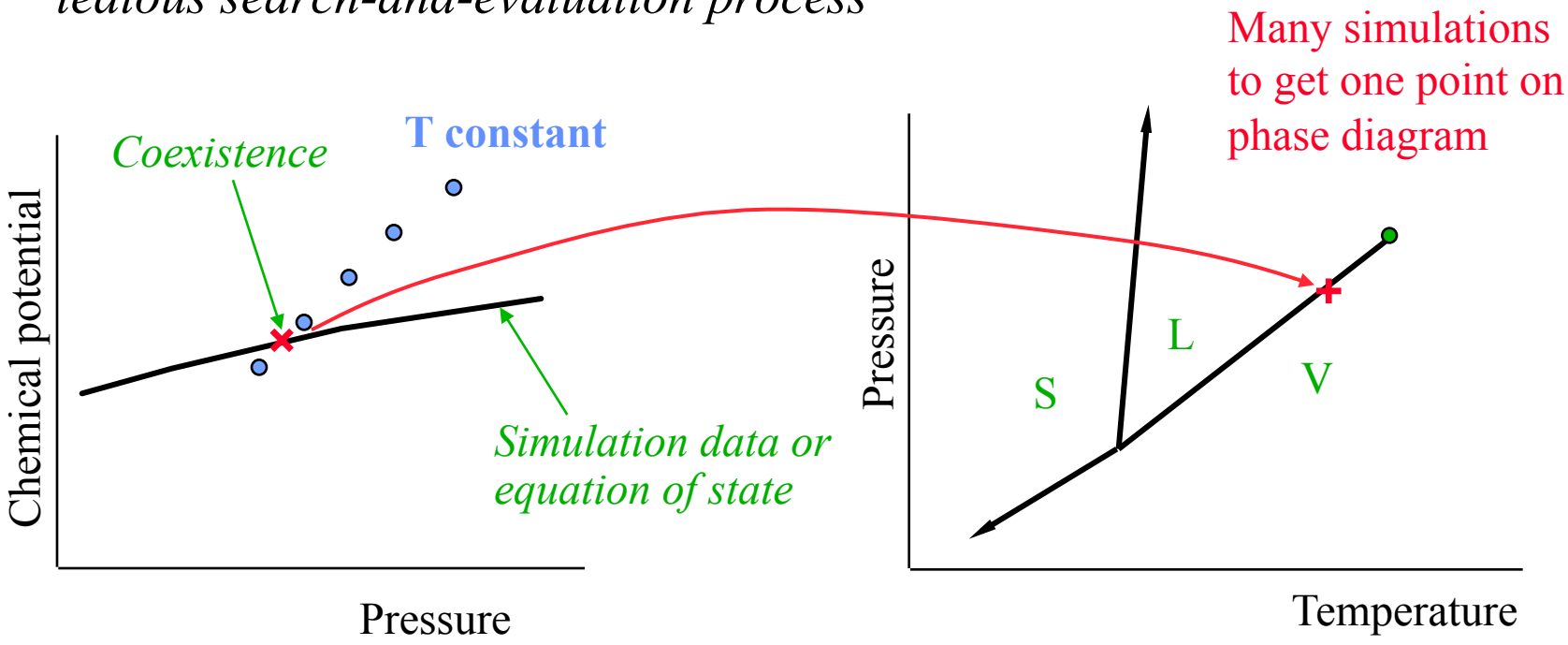
Rigorous Methods for Phase Equilibria by Molecular Simulation

- 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*



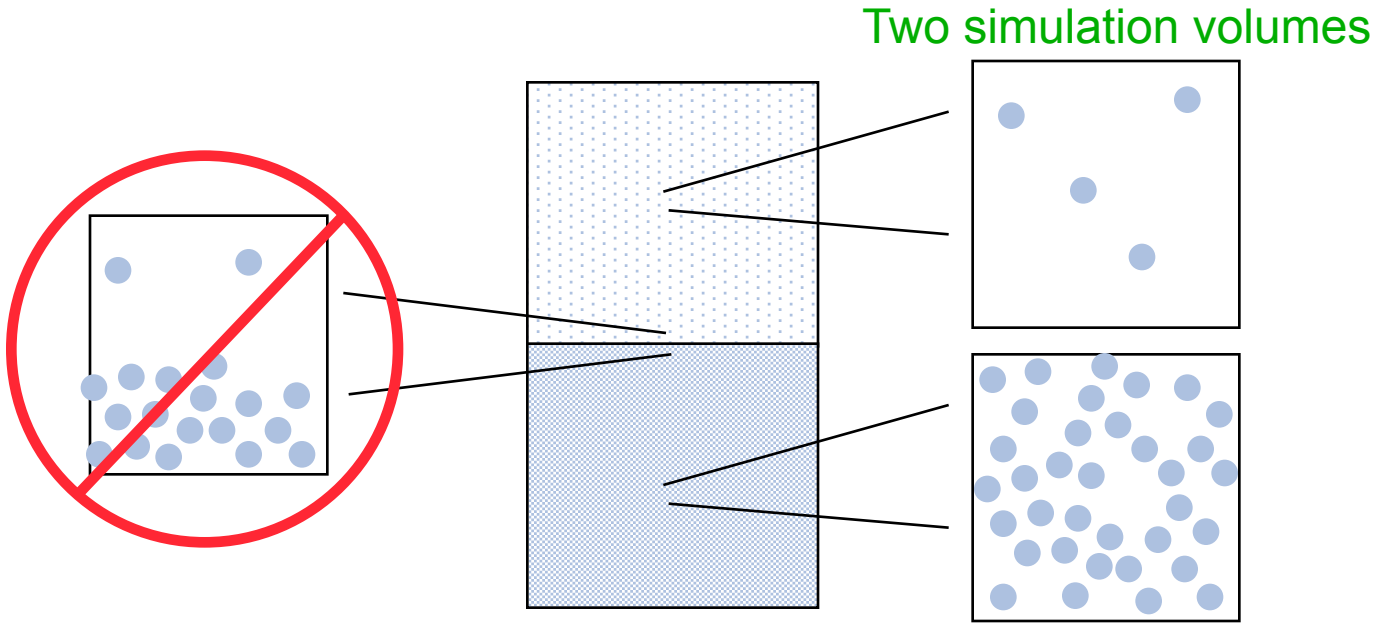
Rigorous Methods for Phase Equilibria by Molecular Simulation

- 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*



Gibbs Ensemble 1.

- Panagiotopoulos in 1987 introduced a clever way to simulate coexisting phases without an interface

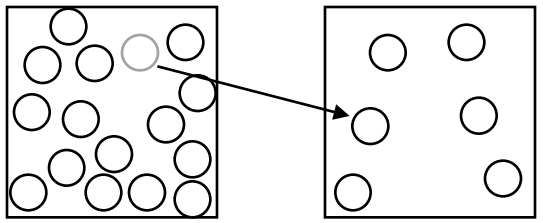


- Thermodynamic contact without physical contact
  - *How?*

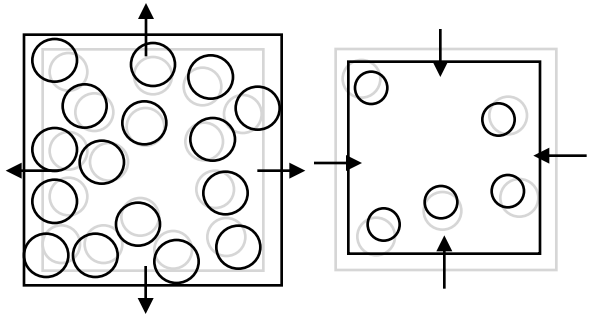
Gibbs Ensemble 2.

- 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

$$Q^{GE}(N,V,T) = \sum_{N_1=0}^{N} \int_0^V dV_1 Q(N_1,V_1,T) Q(N-N_1,V-V_1,T)$$

- Limiting distribution

$N_2 \equiv N - N_1$

$V_2 \equiv V - V_1$

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

- General algorithm. For each trial:
  - *with some pre-specified probability, select*
    - molecules displacement/rotation trial
    - volume exchange trial
    - molecule exchange trial
  - *conduct trial move and decide acceptance*

Molecule-Exchange Trial Move
Analysis of Trial Probabilities

- Detailed specification of trial moves and probabilities

Event [reverse event]	Probability [reverse probability]
Select box A [select box B]	1/2 1/2
Select molecule k [select molecule k]	$1/N_A$ $[1/(N_B+1)]$
Move to r^{new} [move back to r^{old}]	Scaled volume → $d\mathbf{s}/1$ $[d\mathbf{s}/1]$
Accept move [accept move]	$\min(1,\chi)$ $[\min(1,1/\chi)]$

Forward-step trial probability $\frac{1}{2}\times\frac{d\mathbf{s}}{N_A}\times\min(1,\chi)$

Reverse-step trial probability $\frac{1}{2}\times\frac{d\mathbf{s}}{N_B+1}\times\min(1,\frac{1}{\chi})$

χ *is formulated to satisfy detailed balance*

Molecule-Exchange Trial Move
Analysis of Detailed Balance

Forward-step trial probability $\frac{1}{2}\times\frac{d\mathbf{s}}{N_A}\times\min(1,\chi)$

Reverse-step trial probability $\frac{1}{2}\times\frac{d\mathbf{s}}{N_B+1}\times\min(1,\frac{1}{\chi})$

Detailed balance

$$\pi_i \quad \pi_{ij} \quad = \quad \pi_j \quad \pi_{ji}$$

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

$$\frac{1}{2}\times\frac{d\mathbf{s}}{N_A}\times\min(1,\chi)$$

Reverse-step trial probability

$$\frac{1}{2}\times\frac{d\mathbf{s}}{N_B+1}\times\min(1,\frac{1}{\chi})$$

Detailed balance

$$\pi_i \quad \pi_{ij} \quad = \quad \pi_j \quad \pi_{ji}$$

$$\frac{e^{-\beta U^{old}} V_A^{N_A} d\mathbf{s}^{N_1} V_B^{N_B} d\mathbf{s}^{N_B} dV_A}{\Lambda^{-3N} Q^{GE}}\left[\frac{d\mathbf{s}\min(1,\chi)}{2N_A}\right] = \frac{e^{-\beta U^{new}} V_A^{N_A-1} d\mathbf{s}^{N_A-1} V_B^{N_B+1} d\mathbf{s}^{N_B+1} dV_A}{\Lambda^{-3N} Q^{GE}}\left[\frac{d\mathbf{s}\min(1,\frac{1}{\chi})}{2(N_B+1)}\right]$$

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 $\frac{1}{2}\times\frac{d\mathbf{s}}{N_A}\times\min(1,\chi)$

Reverse-step trial probability $\frac{1}{2}\times\frac{d\mathbf{s}}{N_B+1}\times\min(1,\frac{1}{\chi})$

Detailed balance

$$\pi_i \quad \pi_{ij} \quad = \quad \pi_j \quad \pi_{ji}$$

$$\frac{e^{-\beta U^{old}} V_A^{N_A} d\mathbf{s}^{N_A} V_B^{N_B} d\mathbf{s}^{N_B} dV_A}{\Lambda^{-3N} Q^{GE}} \left[\frac{d\mathbf{s}\min(1,\chi)}{2N_A}\right] = \frac{e^{-\beta U^{new}} V_A^{N_A-1} d\mathbf{s}^{N_A-1} V_B^{N_B+1} d\mathbf{s}^{N_B+1} dV_A}{\Lambda^{-3N} Q^{GE}} \left[\frac{d\mathbf{s}\min(1,\frac{1}{\chi})}{2(N_B+1)}\right]$$

$$e^{-\beta U^{old}} \frac{1}{N_A}\chi = e^{-\beta U^{new}} \frac{V_B}{V_A}\frac{1}{N_B+1}$$

$$\chi = \frac{V_B}{V_A}\frac{N_A}{N_B+1} e^{-\beta\Delta U_{tot}}$$

Acceptance probability

Volume-Exchange Trial Move
Analysis of Trial Probabilities

- Take steps in $\lambda = \ln(V_A/V_B)$

$$d\lambda = \left(\frac{1}{V_A} + \frac{1}{V_B}\right) dV_A = \frac{V}{V_A V_B} dV_A$$

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

- Detailed specification of trial moves and probabilities

Event [reverse event]	Probability [reverse probability]
Step to λ^{new} [step to λ^{old}]	$d\lambda/\Delta$ $d\lambda/\Delta$
Accept move [accept move]	$\min(1,\chi)$ $[\min(1,1/\chi)]$

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

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

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

$$\pi_i \quad \pi_{ij} \quad = \quad \pi_j \quad \pi_{ji}$$

Limiting distribution

$$\pi(\mathbf{r}^N, N_A, V_A)\, d\lambda\, d\mathbf{s}^{N_A}\, d\mathbf{s}^{N_B} = \frac{d\lambda \Lambda^{3N}}{VQ^{GE}} \left[V_A^{N_A+1}\, d\mathbf{s}^{N_A} e^{-\beta U(\mathbf{s}^{N_A}, V_A)} \right] \left[V_B^{N_B+1}\, d\mathbf{s}^{N_B} e^{-\beta U(\mathbf{s}^{N_B}, V_B)} \right]$$

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

$$\pi_i \quad \pi_{ij} \quad = \quad \pi_j \quad \pi_{ji}$$

$$\frac{e^{-\beta U^{old}} V_{A,i}^{N_A+1} d\mathbf{s}^{N_1} V_{B,i}^{N_B+1} d\mathbf{s}^{N_B}}{\Lambda^{-3N} Q^{GE}} \left[\frac{d\lambda \min(1,\chi)}{\Delta}\right] = \frac{e^{-\beta U^{new}} V_{A,j}^{N_A+1} d\mathbf{s}^{N_A} V_{B,j}^{N_B+1} d\mathbf{s}^{N_B}}{\Lambda^{-3N} Q^{GE}} \left[\frac{d\lambda \min(1,\frac{1}{\chi})}{\Delta}\right]$$

Limiting distribution

$$\pi(\mathbf{r}^N, N_A, V_A) d\lambda d\mathbf{s}^{N_A} d\mathbf{s}^{N_B} = \frac{d\lambda \Lambda^{3N}}{V Q^{GE}} \left[V_A^{N_A+1} d\mathbf{s}^{N_A} e^{-\beta U(\mathbf{s}^{N_A}, V_A)}\right]\left[V_B^{N_B+1} d\mathbf{s}^{N_B} e^{-\beta U(\mathbf{s}^{N_B}, V_B)}\right]$$

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

$$\pi_i \quad \pi_{ij} \quad = \quad \pi_j \quad \pi_{ji}$$

$$\frac{e^{-\beta U^{old}} V_{A,i}^{N_A+1} d\mathbf{s}^{N_1} V_{B,i}^{N_B+1} d\mathbf{s}^{N_B}}{\Lambda^{-3N} Q^{GE}} \left[\frac{d\lambda \min(1,\chi)}{\Delta}\right] = \frac{e^{-\beta U^{new}} V_{A,j}^{N_A+1} d\mathbf{s}^{N_A} V_{B,j}^{N_B+1} d\mathbf{s}^{N_B}}{\Lambda^{-3N} Q^{GE}} \left[\frac{d\lambda \min(1,\frac{1}{\chi})}{\Delta}\right]$$

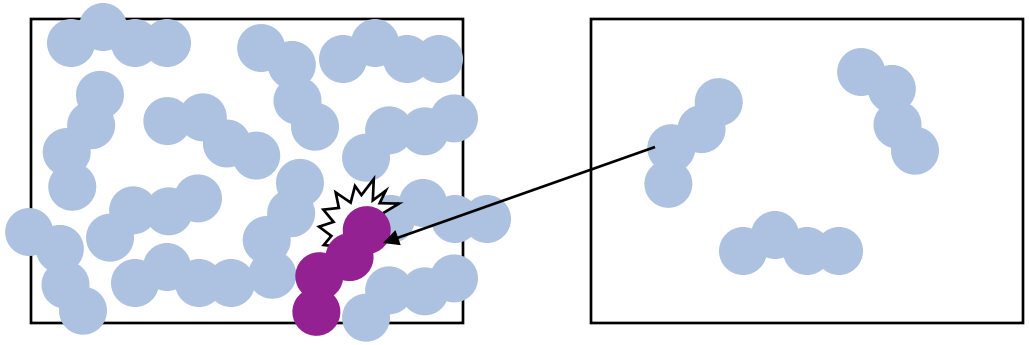
$$e^{-\beta U^{old}} V_{A,i}^{N_A+1} V_{B,i}^{N_B+1} \chi = e^{-\beta U^{new}} V_{A,i}^{N_A+1} V_{B,i}^{N_B+1}$$

$$\chi = \left(\frac{V_A^{new}}{V_A^{old}}\right)^{N_A+1} \left(\frac{V_B^{new}}{V_B^{old}}\right)^{N_B+1} e^{-\beta \Delta U_{tot}}$$

Acceptance probability

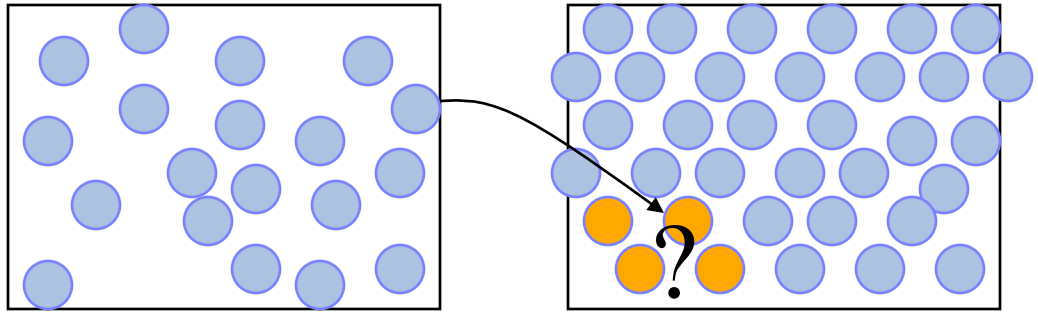
Gibbs Ensemble Limitations

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



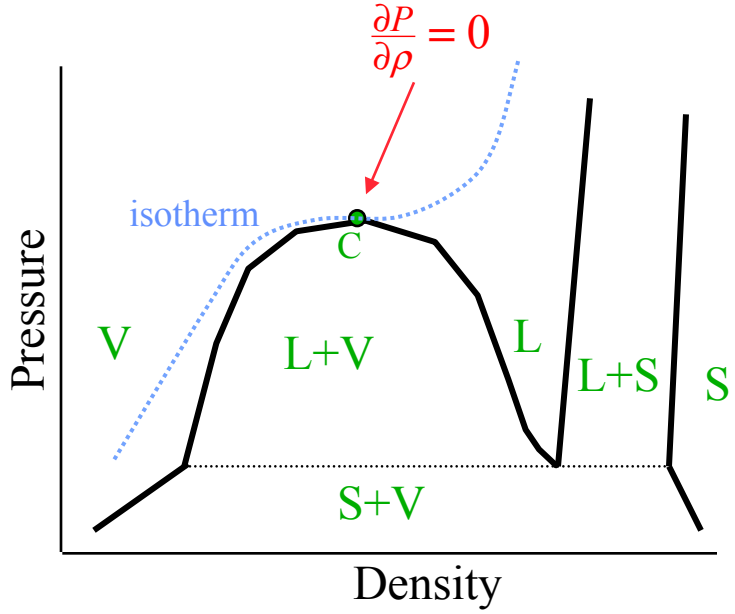
  - *Solid phases*

    $N = 4n^3$ (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*



$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right) \to \infty$$

$$\sigma_\rho^2 \propto \kappa \to \infty$$

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*

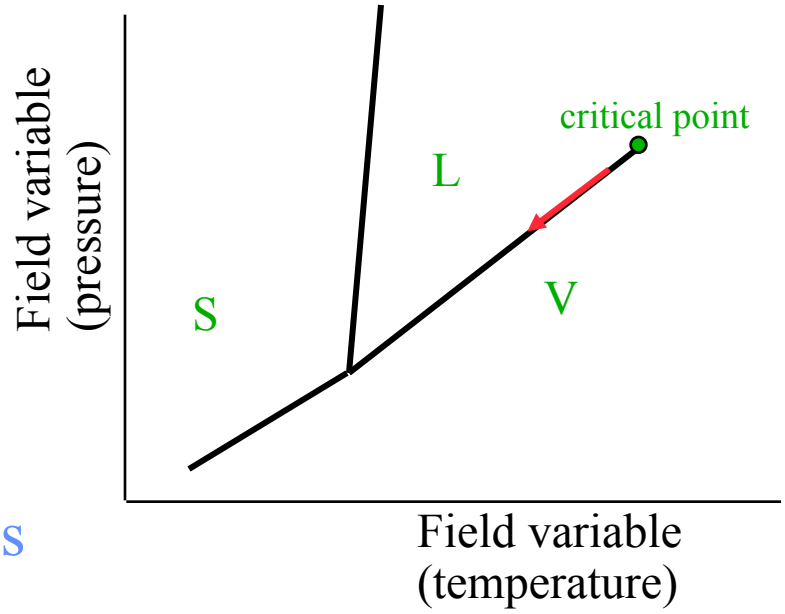
    surface free energy goes to zero

Gibbs-Duhem Integration

- GD equation can be used to derive Clapeyron equation

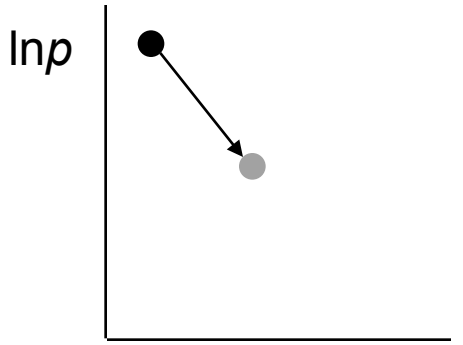
$$\left(\frac{\partial \ln p}{\partial \beta}\right)_{\sigma} = -\frac{\Delta h}{\Delta Z}$$

  - *equation for coexistence line*
- Treat as a nonlinear first-order ODE
  - *use simulation to evaluate right-hand side*
- Trace an integration path the coincides with the coexistence line

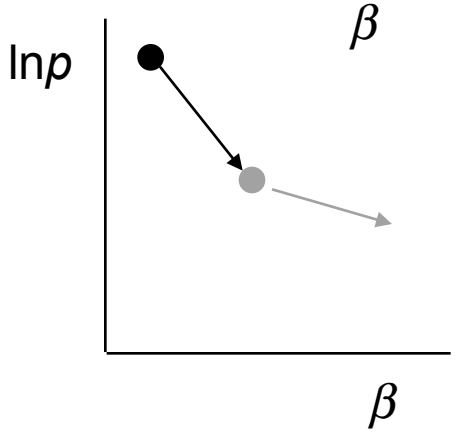


GDI Predictor-Corrector Implementation

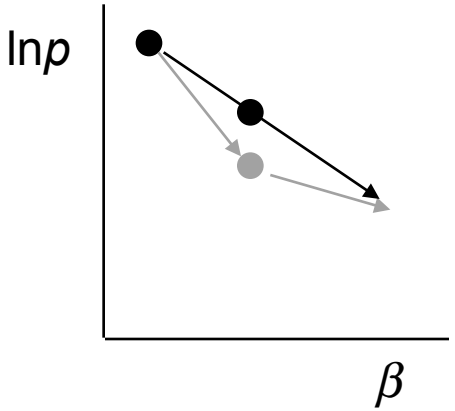
- Given initial condition and slope (= $-\Delta h/\Delta Z$), predict new (p,T) pair.



- Evaluate slope at new state condition…



- …and use to correct estimate of new (p,T) pair



GDI Simulation Algorithm

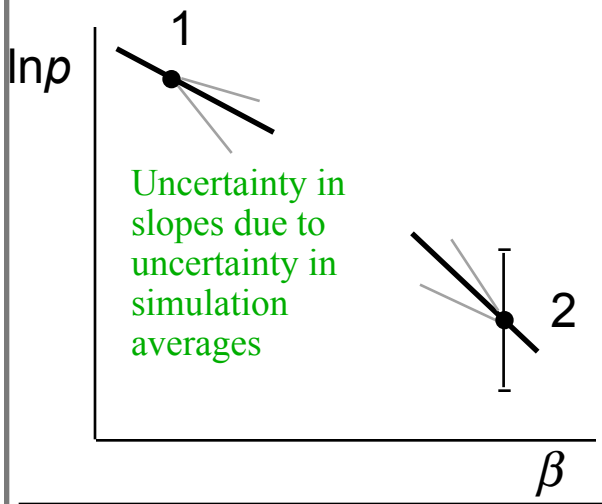
- Estimate pressure and temperature from predictor
- Begin simultaneous NpT simulation of both phases at the estimated conditions
- As simulation progresses, estimate new slope from ongoing simulation data and use with corrector to adjust p and T
- Continue simulation until the iterations and the simulation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

Each simulation yields a coexistence point.
Particle insertions are never attempted.

GDI Sources of Error

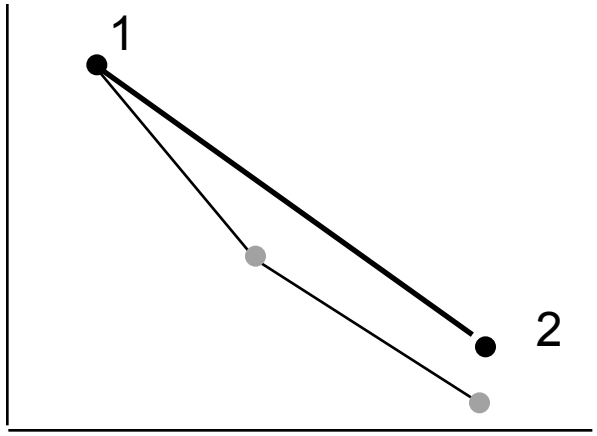
- Three primary sources of error in GDI method

Stochastic error



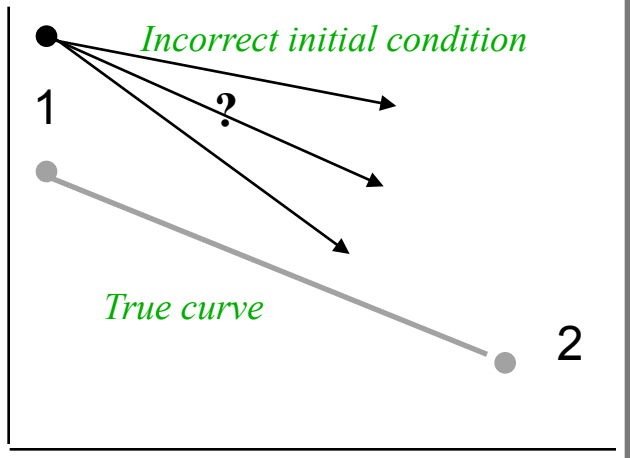
Quantify via propagation of error using confidence limits of simulation averages

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

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*

$$\frac{\partial \beta A}{\partial \lambda} = \left\langle \frac{\partial \beta U}{\partial \lambda} \right\rangle$$

  - *mixtures*

Semigrand Ensemble

- Thermodynamic formalism for mixtures

$$d(\beta A) = U d\beta - \beta P dV + \beta\mu_1 dN_1 + \beta\mu_2 dN_2 \quad +\beta\mu_1 dN_2 - \beta\mu_1 dN_2$$

- Rearrange $d(\beta A) = U d\beta - \beta P dV + \beta\mu_1 d(N_1 + N_2) + \beta(\mu_2 - \mu_1) dN_2$

$$= U d\beta - \beta P dV + \beta\mu_1 dN + \beta\Delta\mu_2 dN_2$$

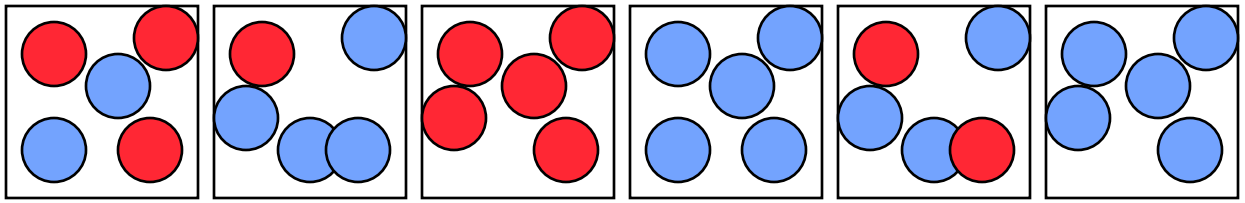
- Legendre transform $d(\beta Y) \equiv d(\beta A - \beta\Delta\mu_2 N_2)$

$$= U d\beta - \beta P dV + \beta\mu_1 dN - N_2 d(\beta\Delta\mu_2)$$

  - *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

$$\pi\left(\mathbf{r}^N, \mathbf{p}^N, N_2\right) = \frac{1}{\Upsilon}\frac{1}{h^{3N} N!} e^{-\beta E(p^N, r^N, N_2)} e^{+N_2\beta\Delta\mu_2}$$

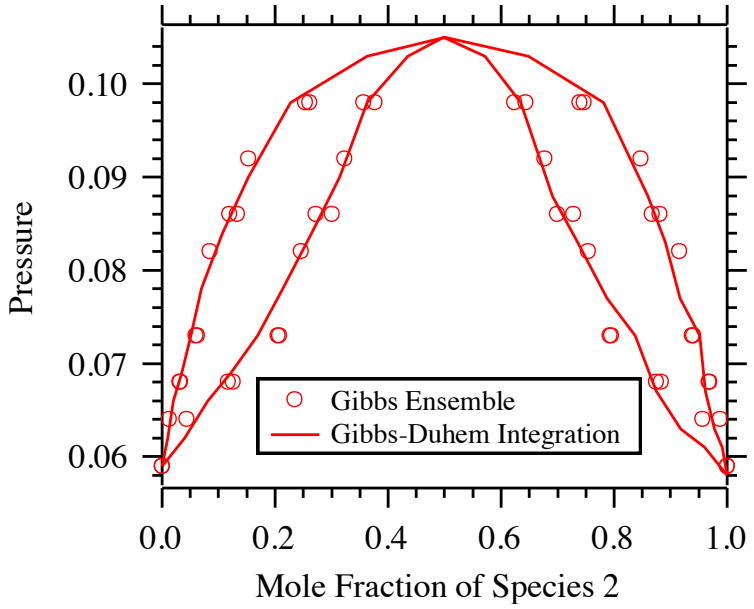
GDI/GE with the Semigrand Ensemble

- 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

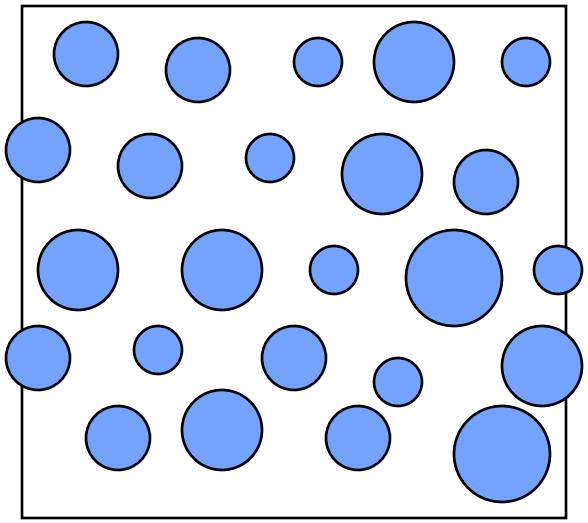
$\sigma_{11} = 1$	$\varepsilon_{11} = 1$
$\sigma_{12} = 1$	$\varepsilon_{12} = 0.75$
$\sigma_{22} = 1$	$\varepsilon_{22} = 1$



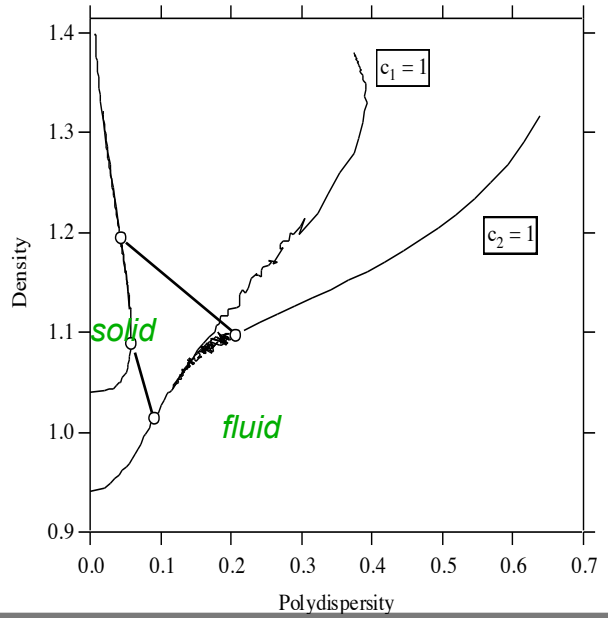
GDI with the Semigrand Ensemble

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

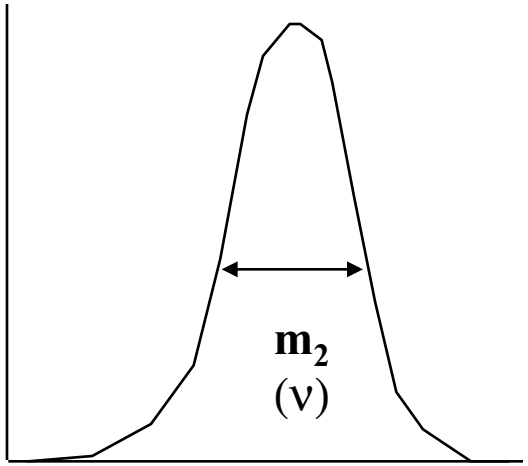
$$\left(\frac{dp}{dv}\right)_{sat} = \frac{\Delta m_2 / 2v^2}{\Delta(V/N)}$$



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



Composition (Fugacity)



Diameter

Other Views of Coexistence Surface

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

$$\left(\frac{dP^{sat}}{d\beta}\right)_{azeo} = -\frac{h^L - h^V}{\beta(v^L - v^V)}$$

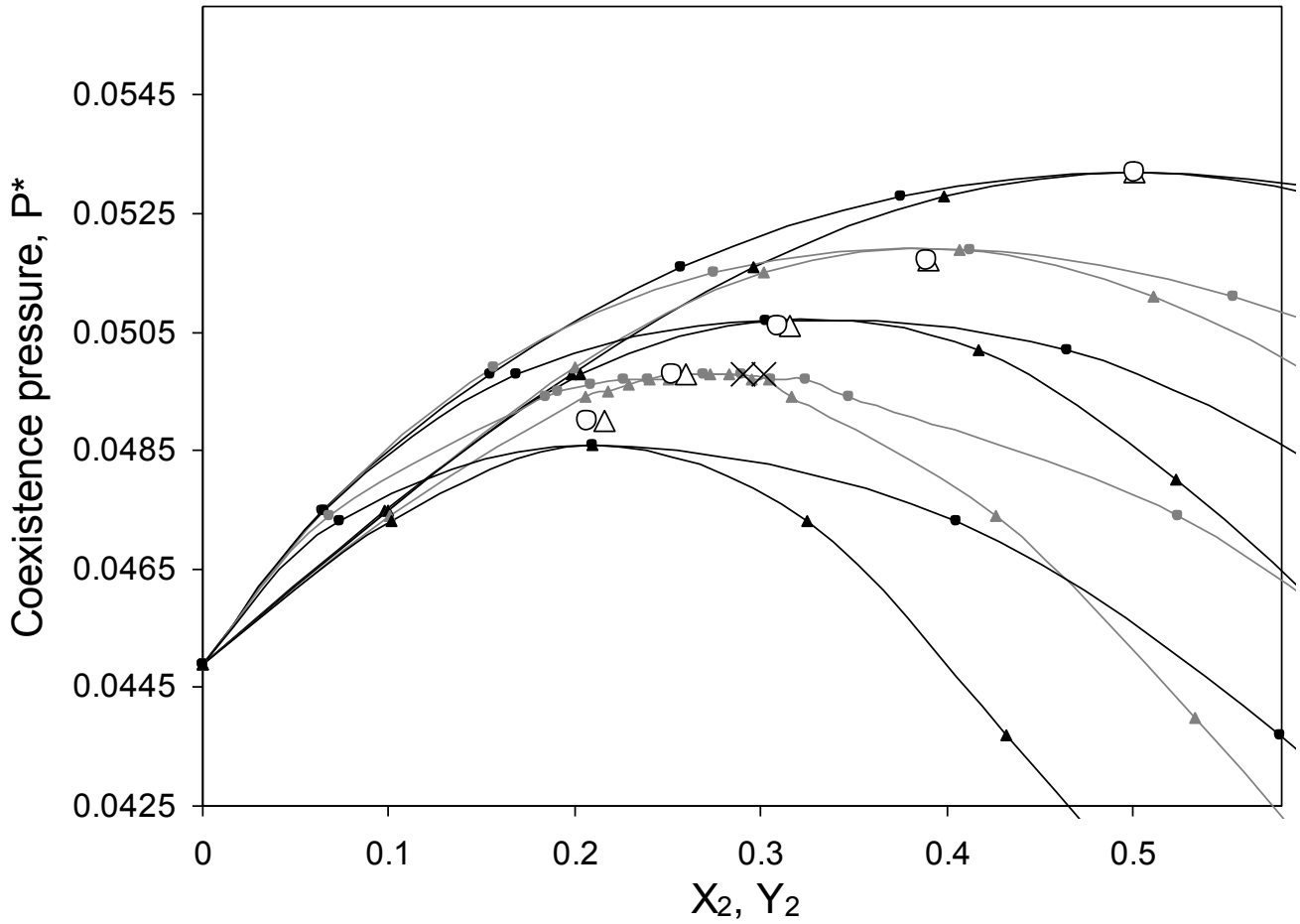
$$\left(\frac{d(\beta\Delta\mu)}{d\beta}\right)_{azeo} = \frac{\left\{\left(\frac{\partial X_1}{\partial\beta}\right)_{P,\beta\Delta\mu} - \left(\frac{\partial Y_1}{\partial\beta}\right)_{P,\beta\Delta\mu}\right\} + \left\{\left(\frac{\partial X_1}{\partial P}\right)_{\beta,\beta\Delta\mu} - \left(\frac{\partial Y_1}{\partial P}\right)_{\beta,\beta\Delta\mu}\right\}\left(\frac{dP^{sat}}{d\beta}\right)_{azeo}}{\left\{\left(\frac{\partial Y_1}{\partial\beta\Delta\mu}\right)_{P,\beta} - \left(\frac{\partial X_1}{\partial\beta\Delta\mu}\right)_{P,\beta}\right\}}$$

  - *integrate as in standard GDI method*

    right-hand side involves partial molar properties

Tracing of Azeotropes

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



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