Reliable Density-Functional-Theory Calculations of Adsorption in Nanoporous Materials

Robert W. Maier, Edward J. Maginn
and Mark A. Stadtherr*

Department of Chemical Engineering
University of Notre Dame
Notre Dame, IN 46556 USA

AIChE Annual Meeting, Los Angeles, CA, Nov. 12–17, 2000
Session 92 (Molecular Thermodynamics of Adsorption I):
Paper 92g

*Fax: (219)631-8366; E-mail: markst@nd.edu

Density Functional Theory

- Popular tool for modeling adsorption phenomena
- Basic idea: Model system free energy and entropy as functionals of density distribution $\rho(r)$
- Lattice (discrete density distribution) or nonlattice models can be used
- Determine equilibrium density profile by solving appropriate minimization problem, generally by numerical solution of a nonlinear equation system for stationary points in the optimization problem
- This equation system may have multiple roots, especially in regions of phase transitions and hysteresis
- For reliable study of phase behavior using DFT, a solution technique is needed that can reliably find all roots of a nonlinear equation system

Solution Methods

- Local methods with multiple initial guesses
  - Broyden (e.g., Neimark and Ravikovitch, 1998)
  - Successive substitution (e.g., Lastoskie *et al.*, 1993)
  - No guarantee that all solutions are found

- Path tracking approach (Aranovich and Donohue, 1998, 1999)
  - No guarantee that all solutions are found

- We propose here using an interval-Newton/generalized-bisection (IN/GB) approach
  - **Mathematical and computational guarantee that all solutions are found**

IN/GB Approach

Problem: Solve $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ for all roots in initial interval $\mathbf{X}^{(0)}$

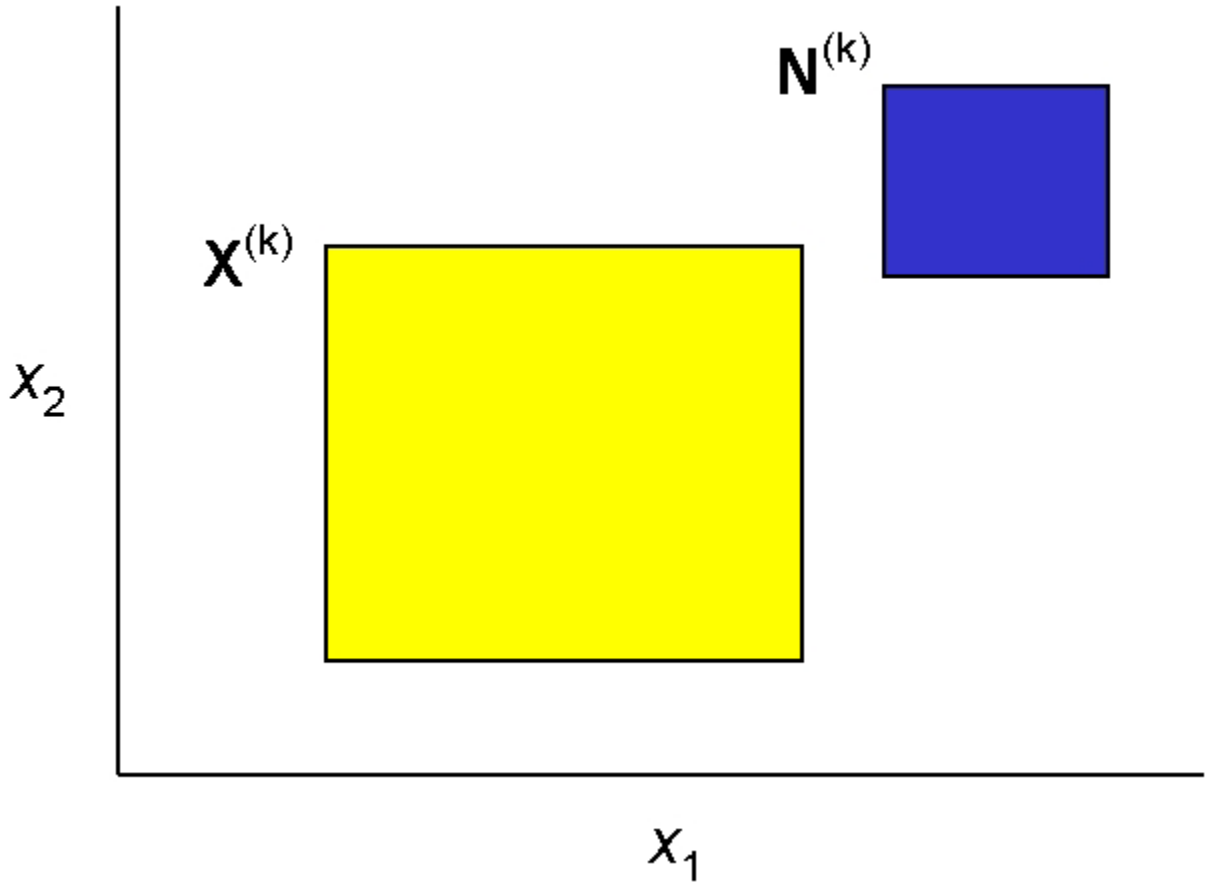
Basic iteration scheme: For a particular subinterval (box), $\mathbf{X}^{(k)}$, arising from some branching (bisection) scheme, perform root inclusion test:

- Compute the interval extension (bounds on range) of each function in the system
- If there is any range for which 0 is not an element, delete (prune) the box
- If 0 is an element of every range, then compute the *image*, $\mathbf{N}^{(k)}$, of the box by solving the interval Newton equation

$$F'(\mathbf{X}^{(k)})(\mathbf{N}^{(k)} - \mathbf{x}^{(k)}) = -\mathbf{f}(\mathbf{x}^{(k)})$$

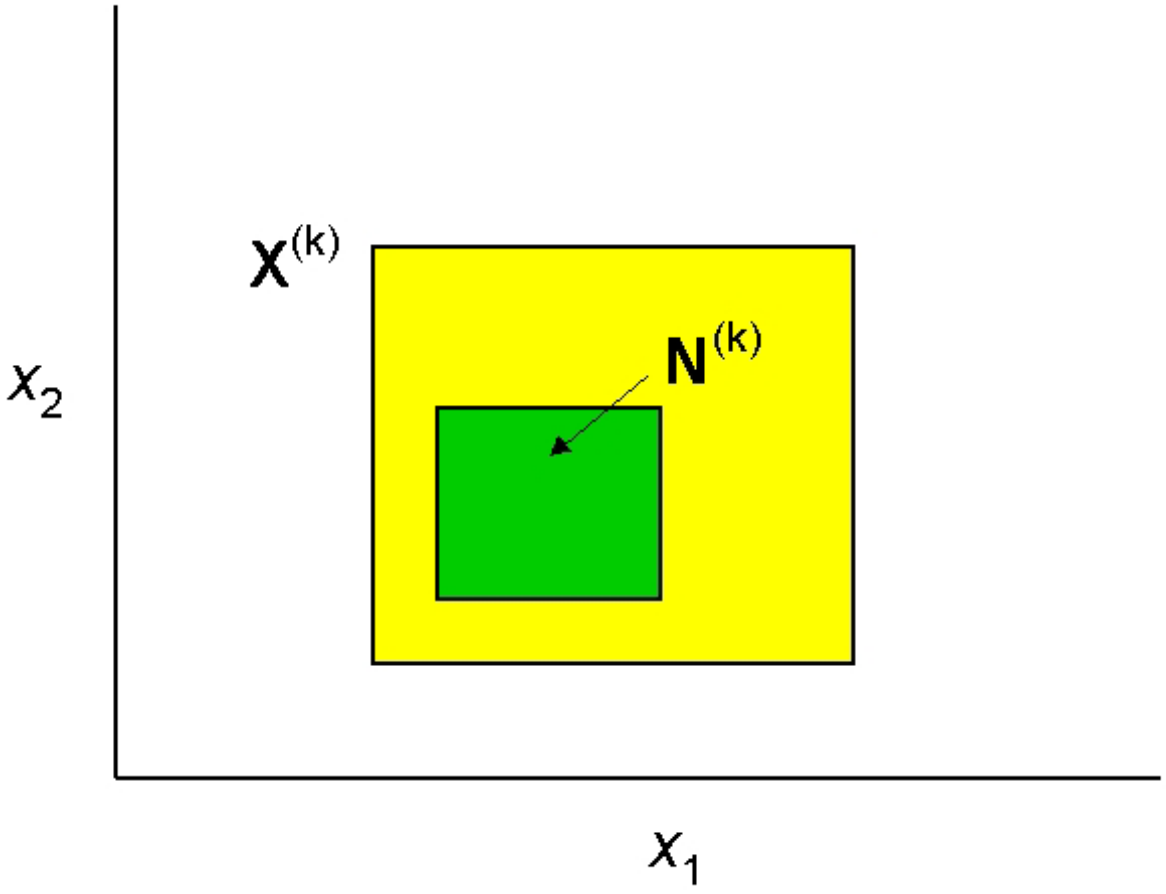
- $\mathbf{x}^{(k)}$ is some point in the interior of $\mathbf{X}^{(k)}$
- $F'\left(\mathbf{X}^{(k)}\right)$ is an interval extension of the Jacobian of $\mathbf{f}(\mathbf{x})$ over the box $\mathbf{X}^{(k)}$

Interval Newton Method



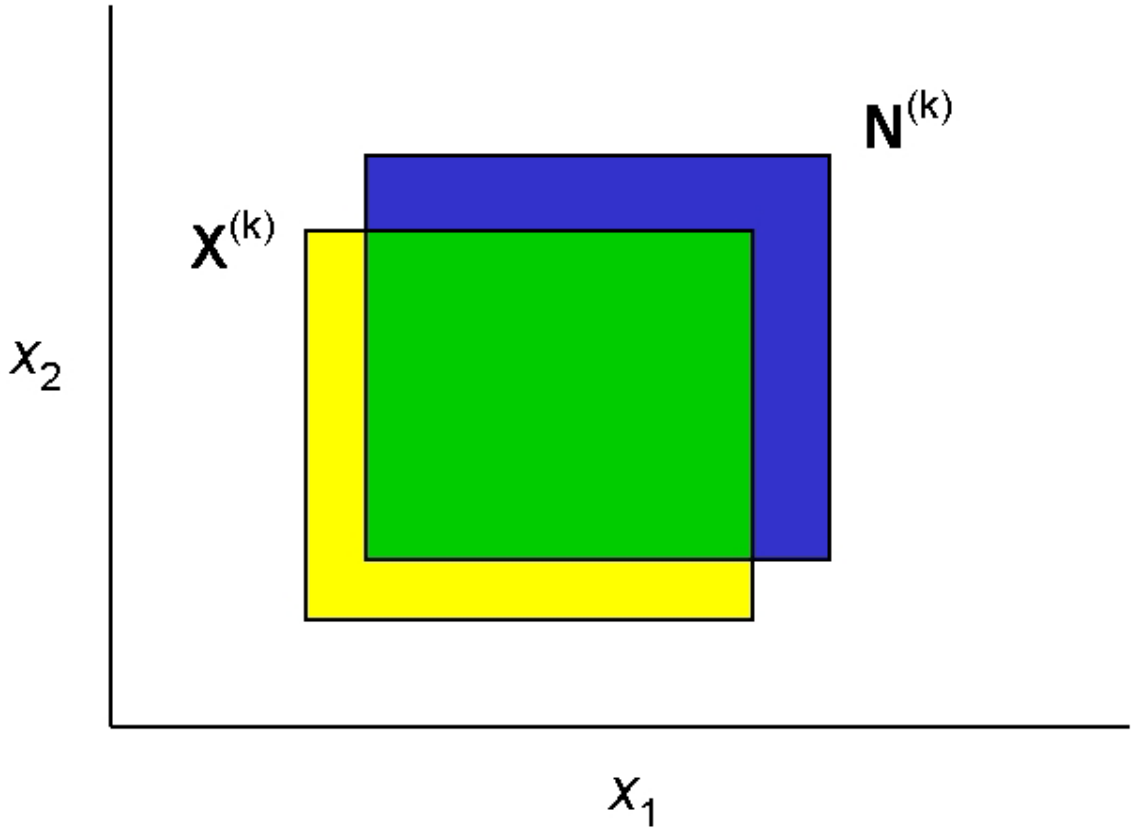
- There is no solution in $\mathbf{X}^{(k)}$

Interval Newton Method



- There is a *unique* solution in $\mathbf{X}^{(k)}$
- This solution is in $\mathbf{N}^{(k)}$
- Point Newton method will converge to solution

Interval Newton Method



- Any solutions in $\mathbf{X}^{(k)}$ are in intersection of $\mathbf{X}^{(k)}$ and $\mathbf{N}^{(k)}$
- If intersection is sufficiently small, repeat root inclusion test
- Otherwise, bisect the intersection and apply root inclusion test to each resulting subinterval

Example Problems

- Solve the lattice-DFT model of Aranovich and Donohue (1999) for phase behavior in nanoscale pores

- Single component systems containing from $N = 2$ to $N = 20$ layers (1 to 10 independent variables) were considered (same problems solved by Aranovich and Donohue)

- For each system, the equation system was solved for the density profile (layer concentrations) $\rho_A(i), \quad i = 1, \ldots, N$ for many values of the bulk concentration ρ_A

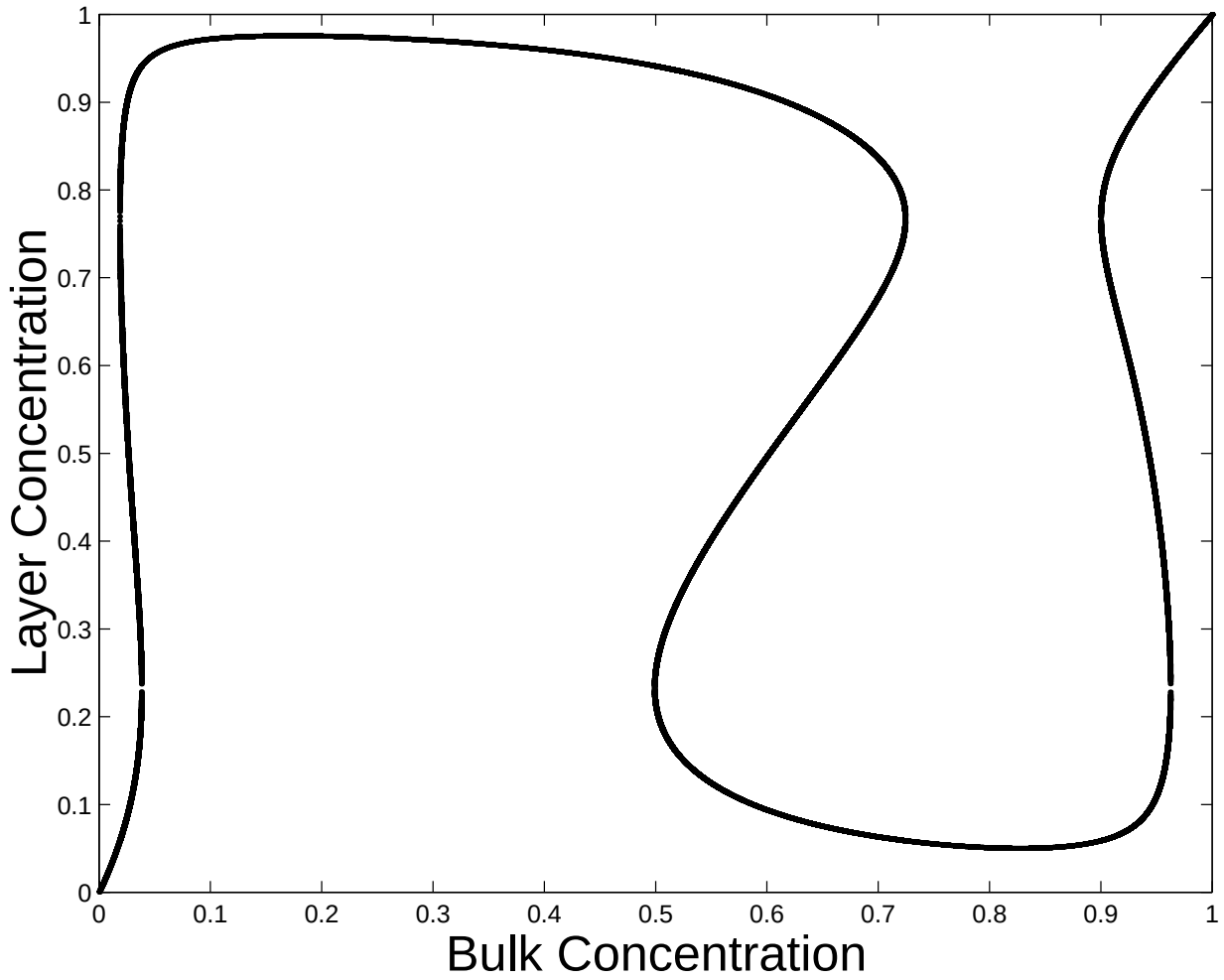
- An initial interval of [0,1] was used for each variable $\rho_A(i)$

- All computations were done using a Sun Ultra 10/440 workstation

Example 1

$N = 2$

$z_1 = 1,\ z_2 = 3,\ \epsilon_{AA}/kT = -1.4,\ \epsilon_{AS}/kT = -1.0$

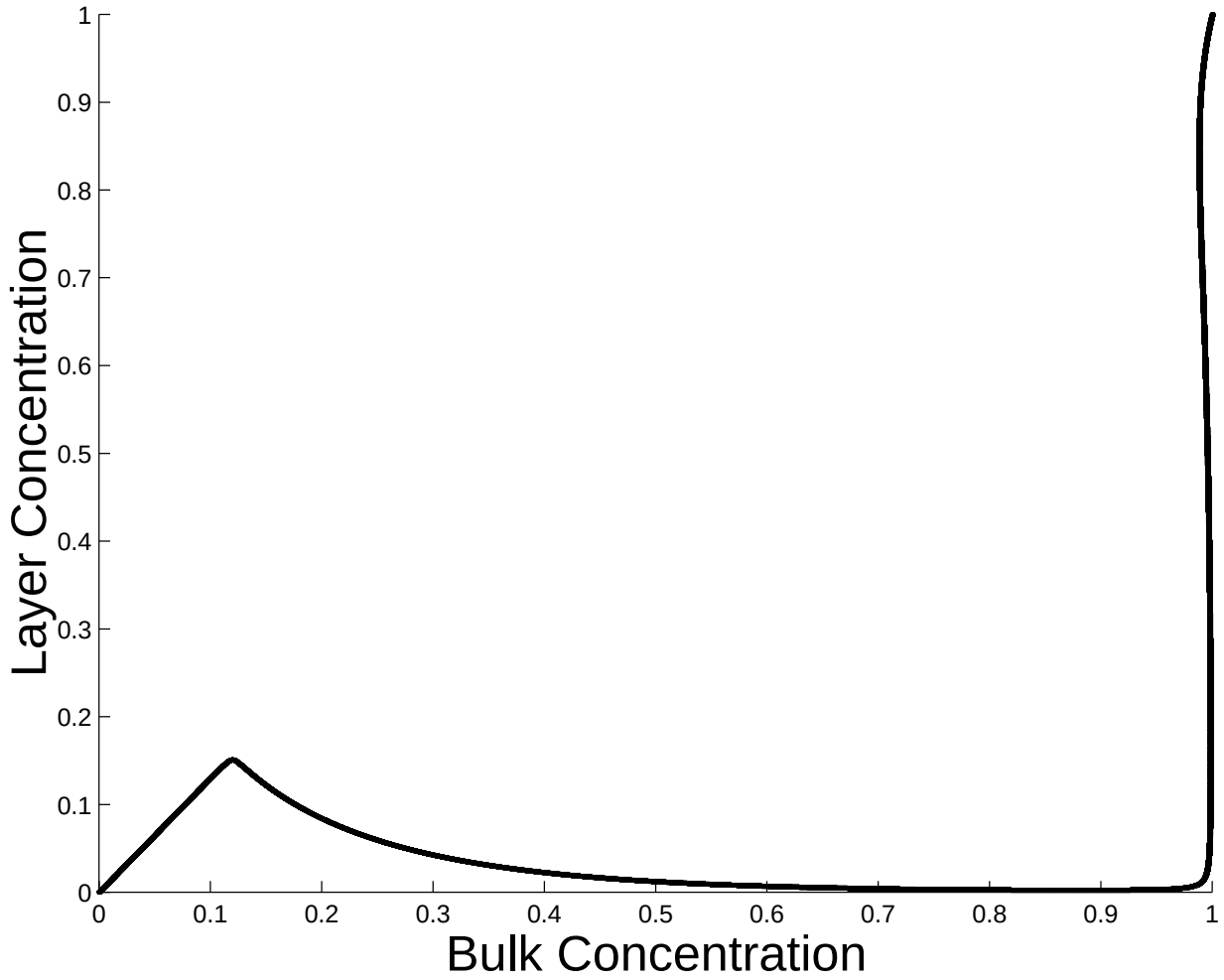


Example 2

$N = 2$

$z_1 = 1$, $z_2 = 3$, $\epsilon_{AA}/kT = -1.9$, $\epsilon_{AS}/kT = -.258$

Result using path tracking method of Aranovich and Donohue (1998).

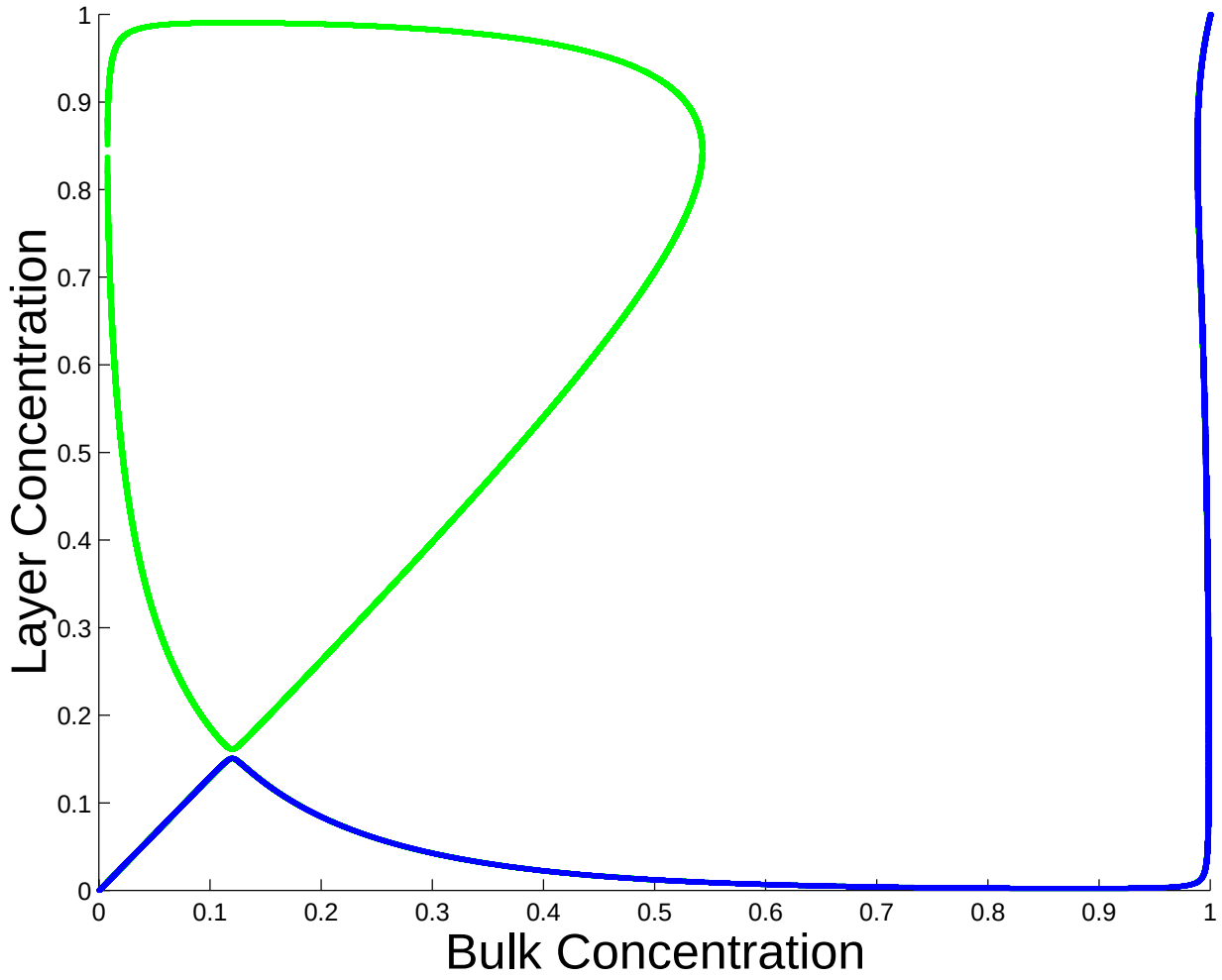


Example 2 (cont'd)

$N = 2$

$z_1 = 1,\ z_2 = 3,\ \epsilon_{AA}/kT = -1.9,\ \epsilon_{AS}/kT = -.258$

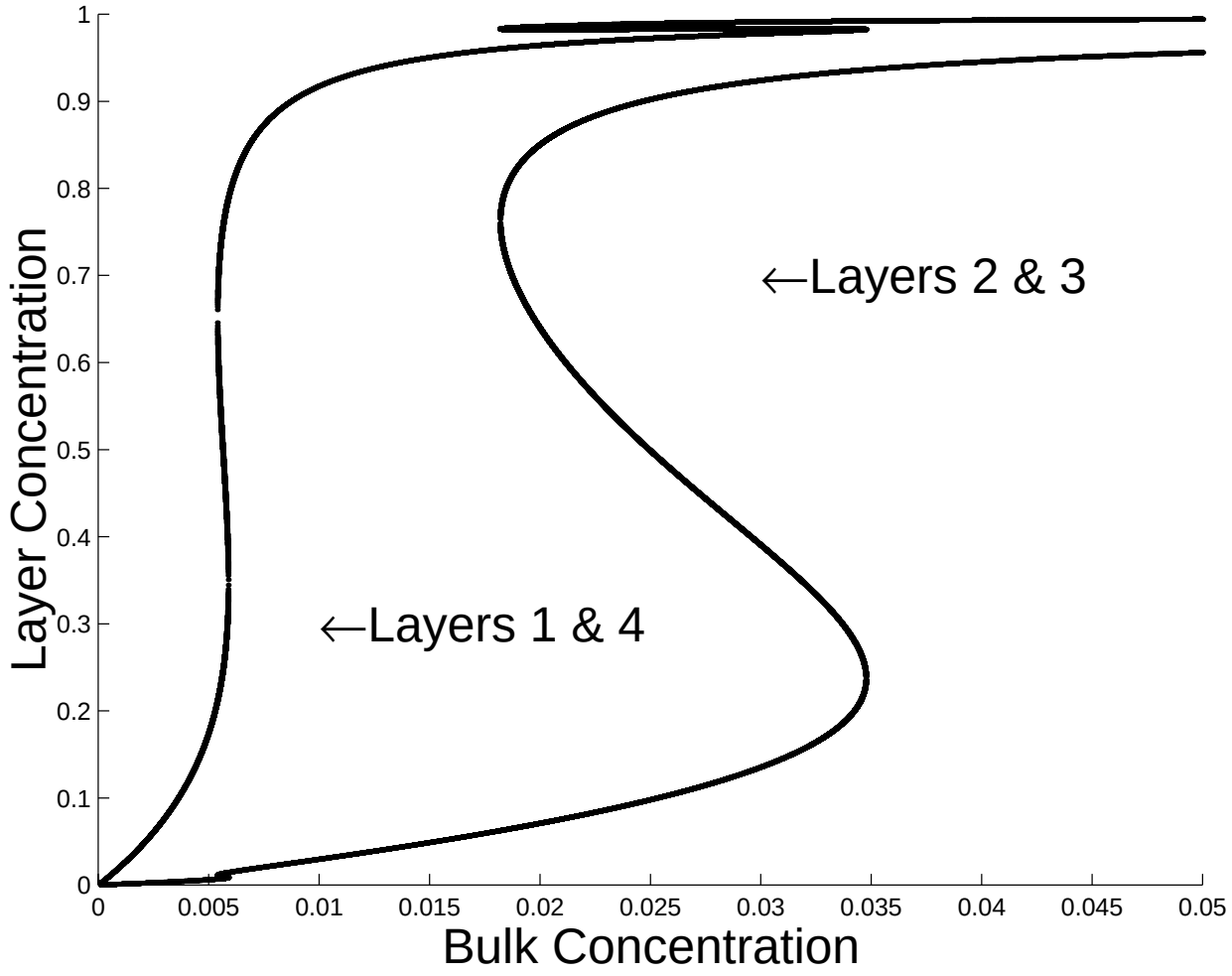
Result using IN/GB approach.



Example 3

$N = 4$

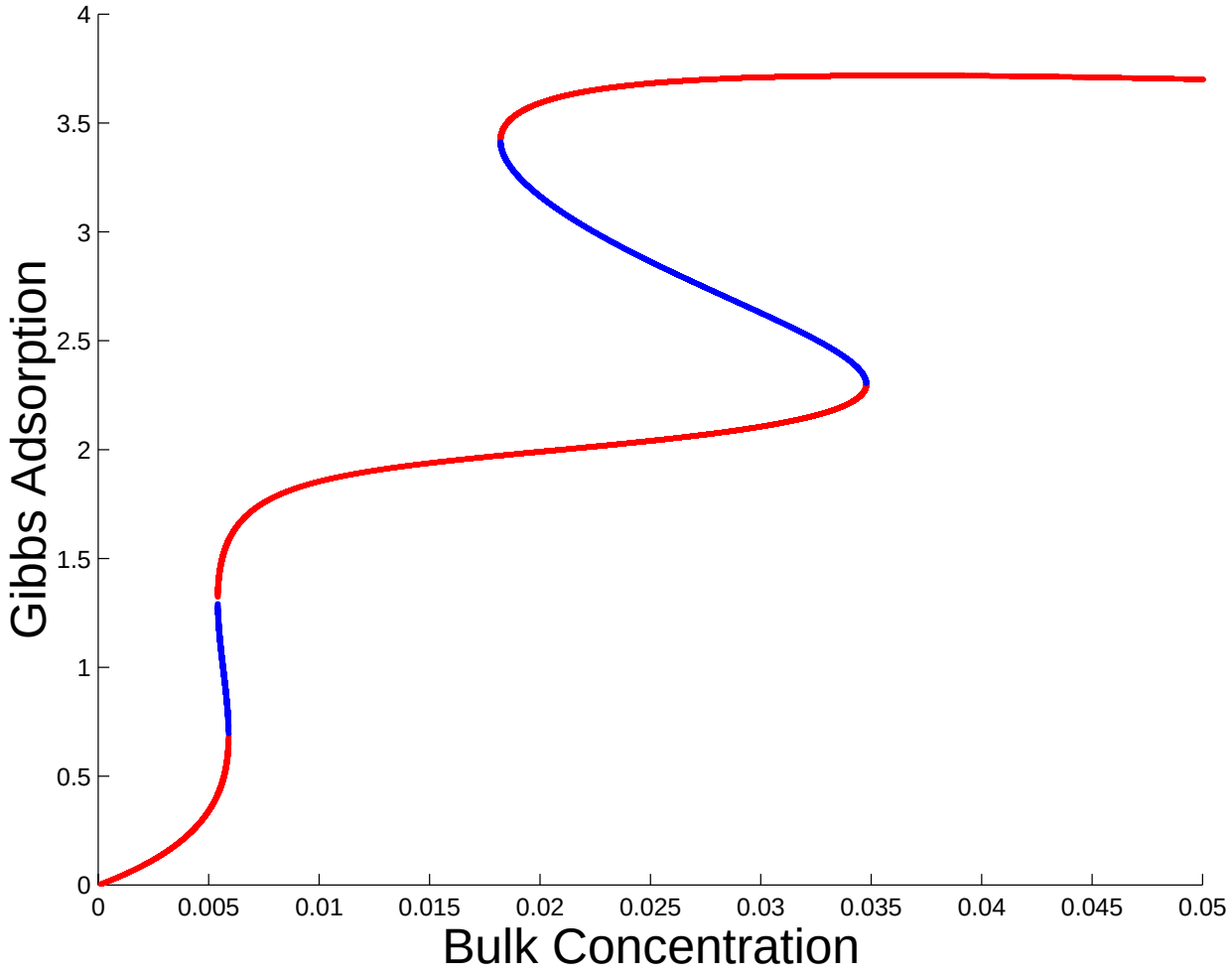
$z_1 = 1$, $z_2 = 4$, $\epsilon_{AA}/kT = -1.1$, $\epsilon_{AS}/kT = -3.0$



Example 3 (cont'd)

Plot of Gibbs adsorption $\Gamma = \sum_{1=1}^{N} [\rho_A(i) - \rho_A]$

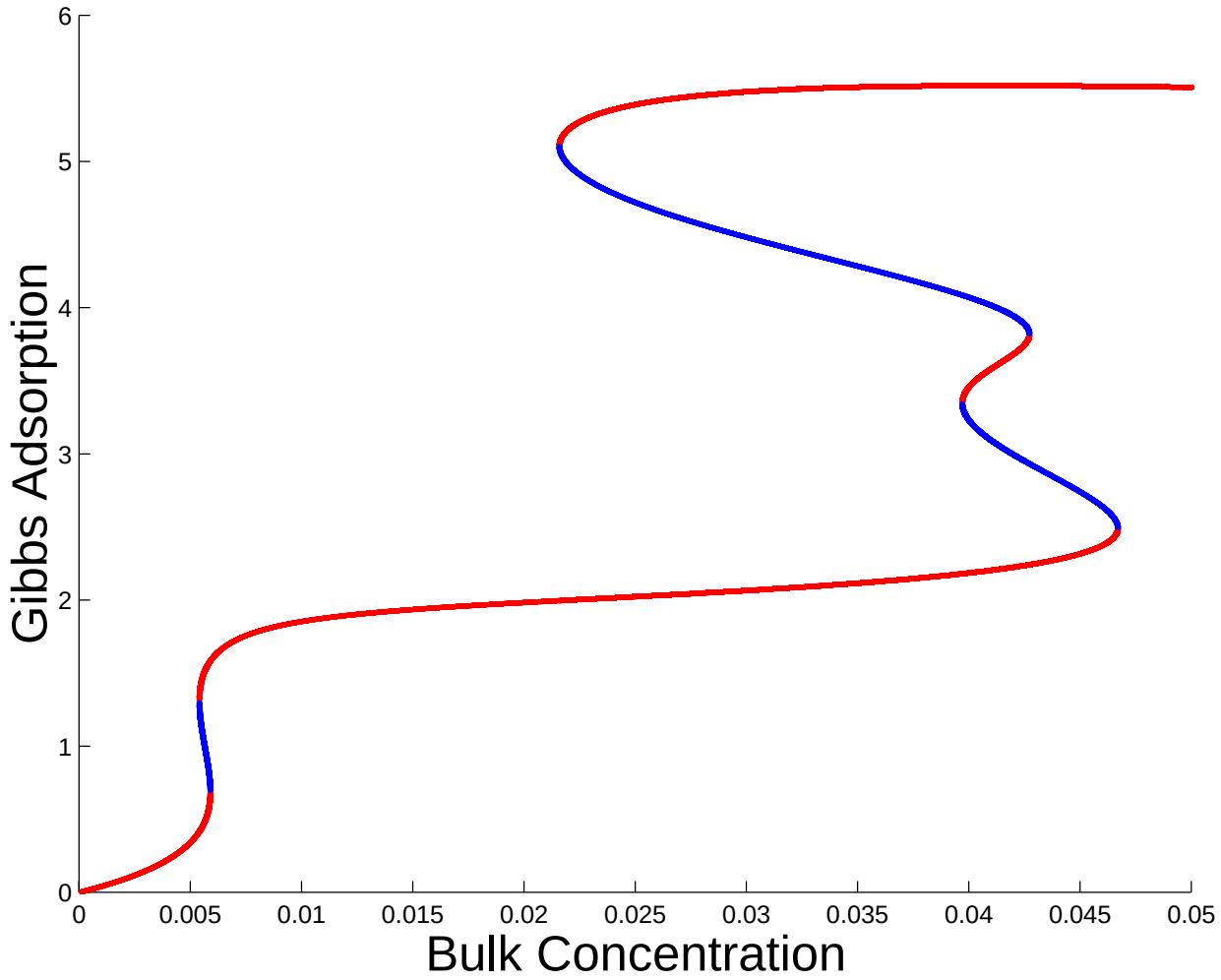
Red $\rightarrow$ local (or global) minimum in optimization problem (stable or metastable state)



Example 4

$N = 6$

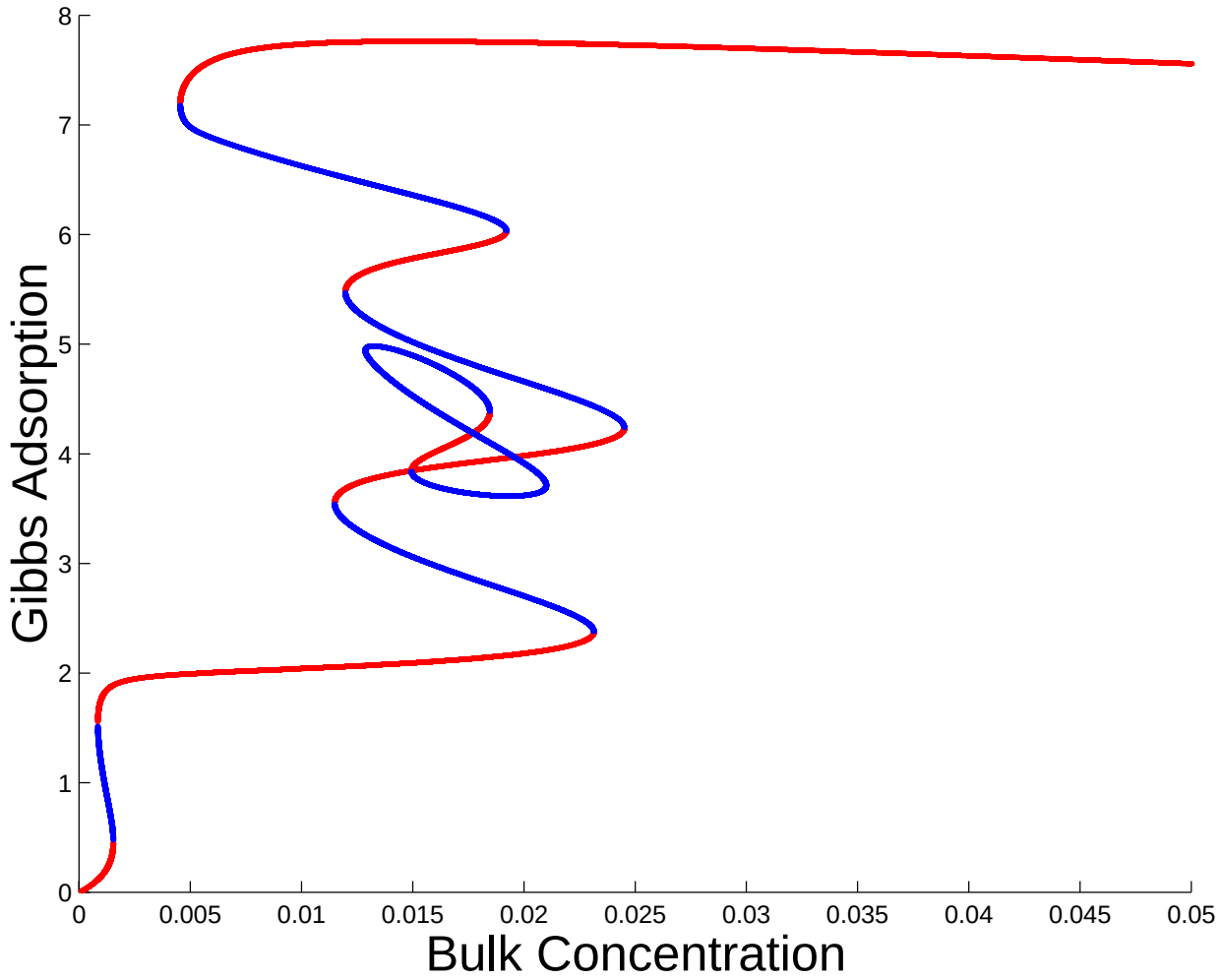
$z_1 = 1,\ z_2 = 4,\ \epsilon_{AA}/kT = -1.1,\ \epsilon_{AS}/kT = -3.0$



Example 5

$N = 8$

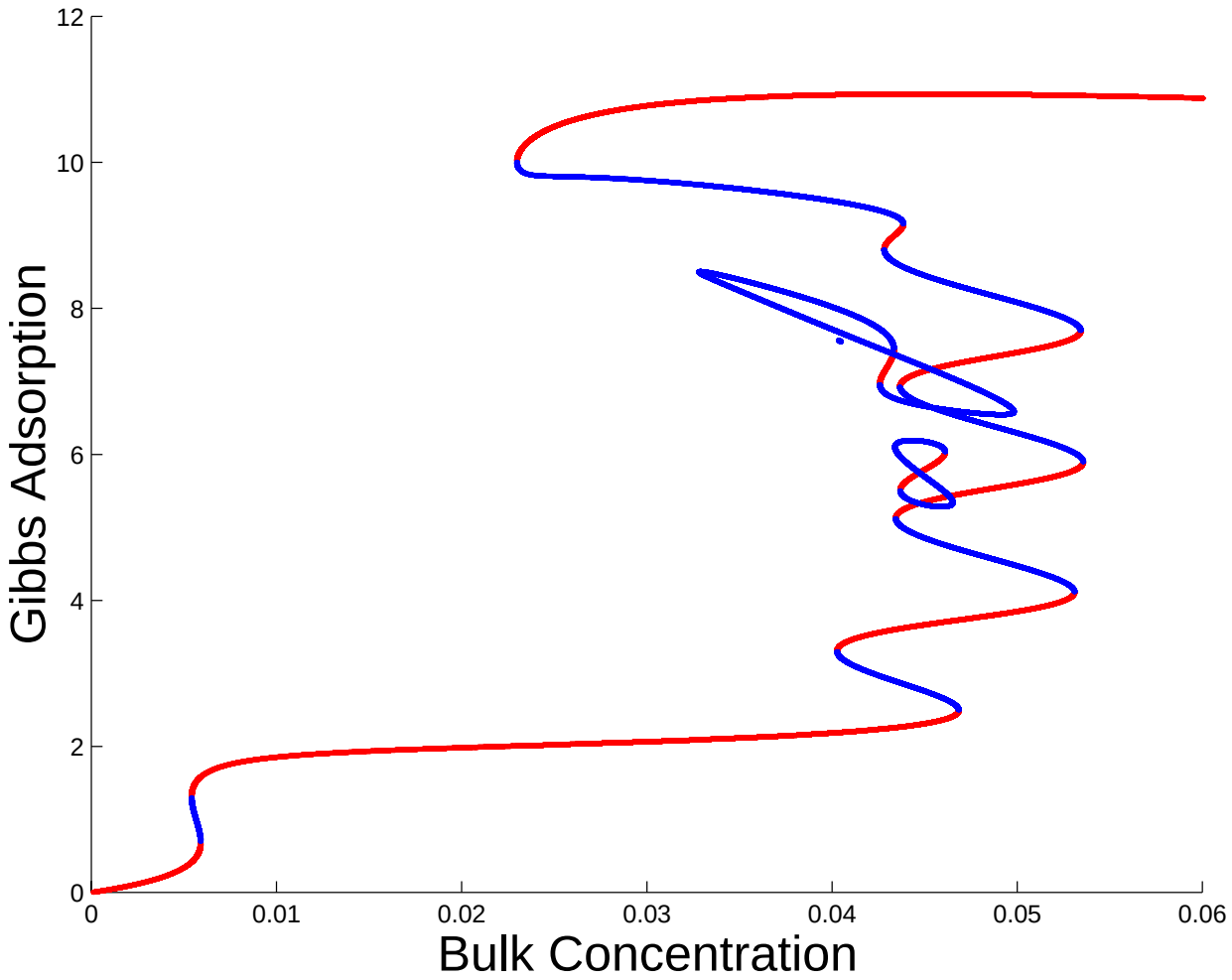
$z_1 = 1,\ z_2 = 4,\ \epsilon_{AA}/kT = -1.4,\ \epsilon_{AS}/kT = -4.0$



Example 6

$N = 12$

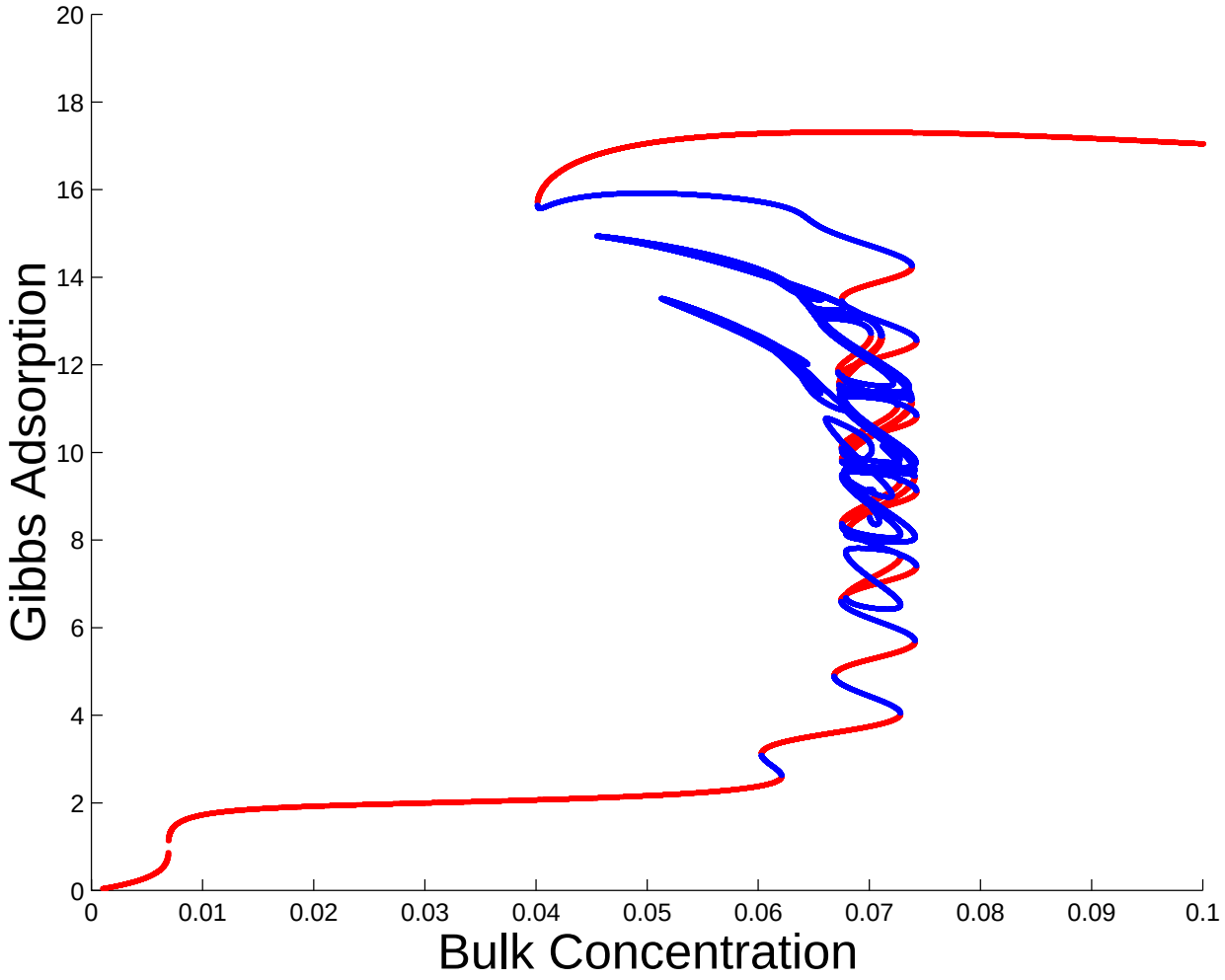
$z_1 = 1,\ z_2 = 4,\ \epsilon_{AA}/kT = -1.1,\ \epsilon_{AS}/kT = -3.0$



Example 7

$N = 20$

$z_1 = 1,\ z_2 = 4,\ \epsilon_{AA}/kT = -1.0,\ \epsilon_{AS}/kT = -3.0$



Computational Performance

Layers (N)	Variables (N/2)	Average Solution Time (ms)
2	1	1
4	2	2
6	3	3
8	4	6
12	6	19
20	10	316

- Average solution time is the average CPU time required to obtain all solutions of the nonlinear equation system for a particular given value of the bulk concentration

- Times are on a Sun Ultra 10/440 workstation

Concluding Remarks

- Interval Newton approach provides an efficient and completely reliable method for solving DFT models of adsorption in nanoscale pores

- Other types of problems solved using IN/GB
  - Fluid phase stability and equilibrium (e.g. Hua et al., 1998)
  - Location of azeotropes (Maier *et al.*, 1998, 1999, 2000)
  - Location of mixture critical points (Stradi *et al.*, 2000)
  - Solid-fluid equilibrium (Xu *et al.*, 2000)
  - Parameter estimation (Gau and Stadtherr, 1999, 2000)
  - General process modeling problems—up to 163 equations (Schnepper and Stadtherr, 1996)

- Continuing advances in hardware and software (e.g., compiler support for interval arithmetic from Sun Microsystems) will make this approach even more attractive

Acknowledgments

- ACS PRF 30421-AC9 and 35979-AC9
- NSF EEC97-00537-CRCD
- EPA R826-734-01-0

For more information:

- Contact Prof. Stadtherr at markst@nd.edu
- See also
  http://www.nd.edu/~markst