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 \( f(x) = 0 \) for all roots in initial interval \( X^{(0)} \)

Basic iteration scheme: For a particular subinterval (box), \( X^{(k)} \), 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, \( N^{(k)} \), of the box by solving the interval Newton equation

\[
F'(X^{(k)})(N^{(k)} - x^{(k)}) = -f(x^{(k)})
\]

- \( x^{(k)} \) is some point in the interior of \( X^{(k)} \)
- \( F'(X^{(k)}) \) is an interval extension of the Jacobian of \( f(x) \) over the box \( X^{(k)} \)
Interval Newton Method

- There is no solution in $X^{(k)}$
Interval Newton Method

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

- Any solutions in \( X^{(k)} \) are in intersection of \( X^{(k)} \) and \( N^{(k)} \)
- 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) $\rho_A(i), \ i = 1, \ldots, N$ for many values of the bulk concentration $\rho_A$

- 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

\[ N = 2 \]
\[ z_1 = 1, \ z_2 = 3, \ \epsilon_{AA}/kT = -1.9, \ \epsilon_{AS}/kT = -0.258 \]

Example 2 (cont’d)

\[ N = 2 \]
\[ \varepsilon = 1, \varepsilon_2 = 3, \frac{\varepsilon_{AA}}{kT} = -1.9, \frac{\varepsilon_{AS}}{kT} = -0.258 \]

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

Red $\rightarrow$ local (or global) minimum in optimization problem (stable or metastable state)
Example 4

\(N = 6\)
\(z_1 = 1, z_2 = 4, \frac{\epsilon_{AA}}{kT} = -1.1, \frac{\epsilon_{AS}}{kT} = -3.0\)
Example 5

\[ N = 8 \]
\[ z_1 = 1, \ z_2 = 4, \ \frac{\epsilon_{AA}}{kT} = -1.4, \ \frac{\epsilon_{AS}}{kT} = -4.0 \]
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

<table>
<thead>
<tr>
<th>Layers (N)</th>
<th>Variables (N/2)</th>
<th>Average Solution Time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>19</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>316</td>
</tr>
</tbody>
</table>

- 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