Multiresolution coarse-graining of polymer models

Ahmed E. Ismail
Department of Chemical Engineering
Massachusetts Institute of Technology

Krell Institute CSGF Fellows' Conference
17 July 2003

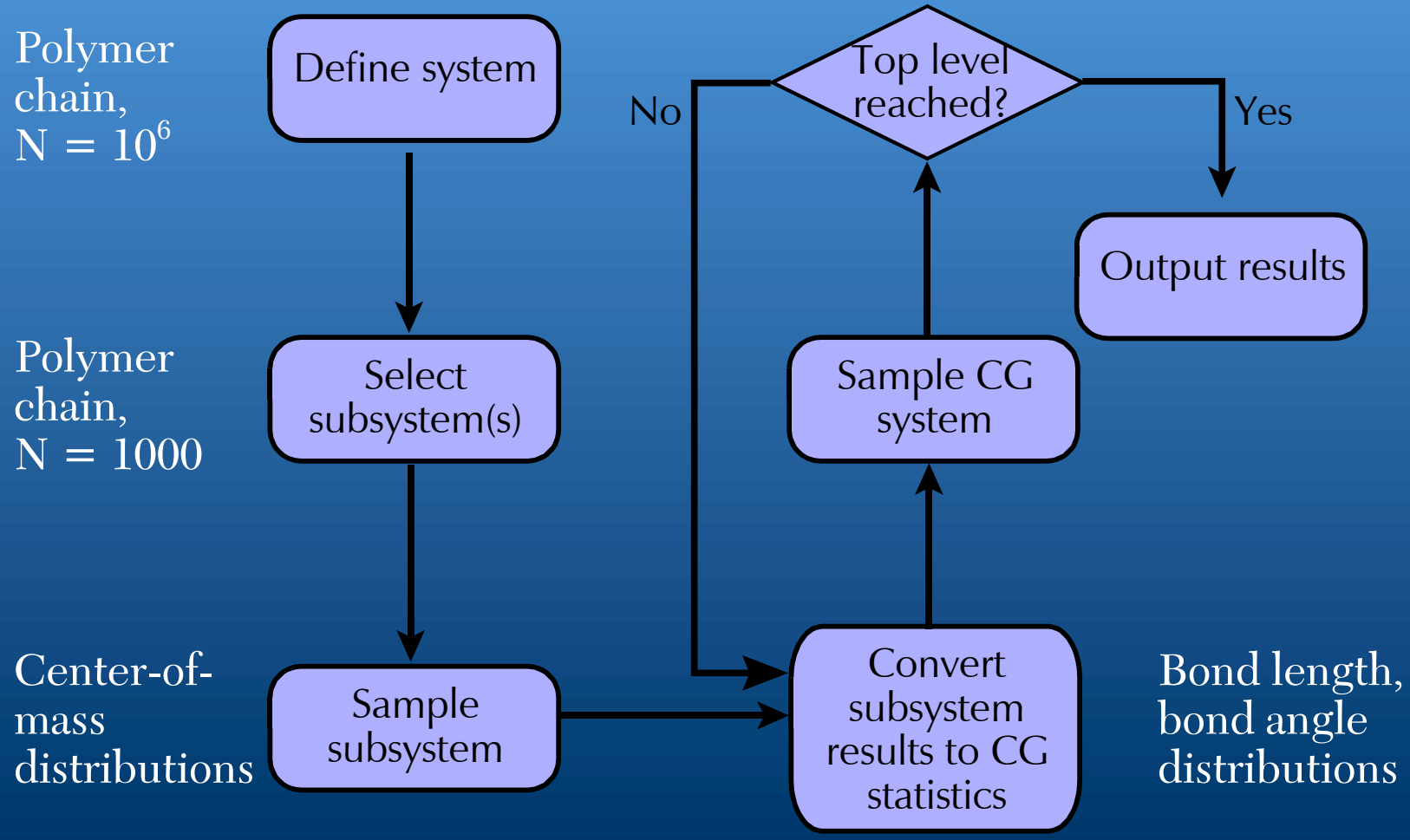
Motivations

Why?

- Better materials design requires a detailed understanding of polymer properties
  - Examples: size distributions, rigidity, density, morphology
- Atomistic simulations with current computational capabilities are still not feasible
  - Current limits: approximately 200,000 "atoms"
  - Moore's law won't help much: algorithms still $O(N^3)$

Coarse-graining paradigm

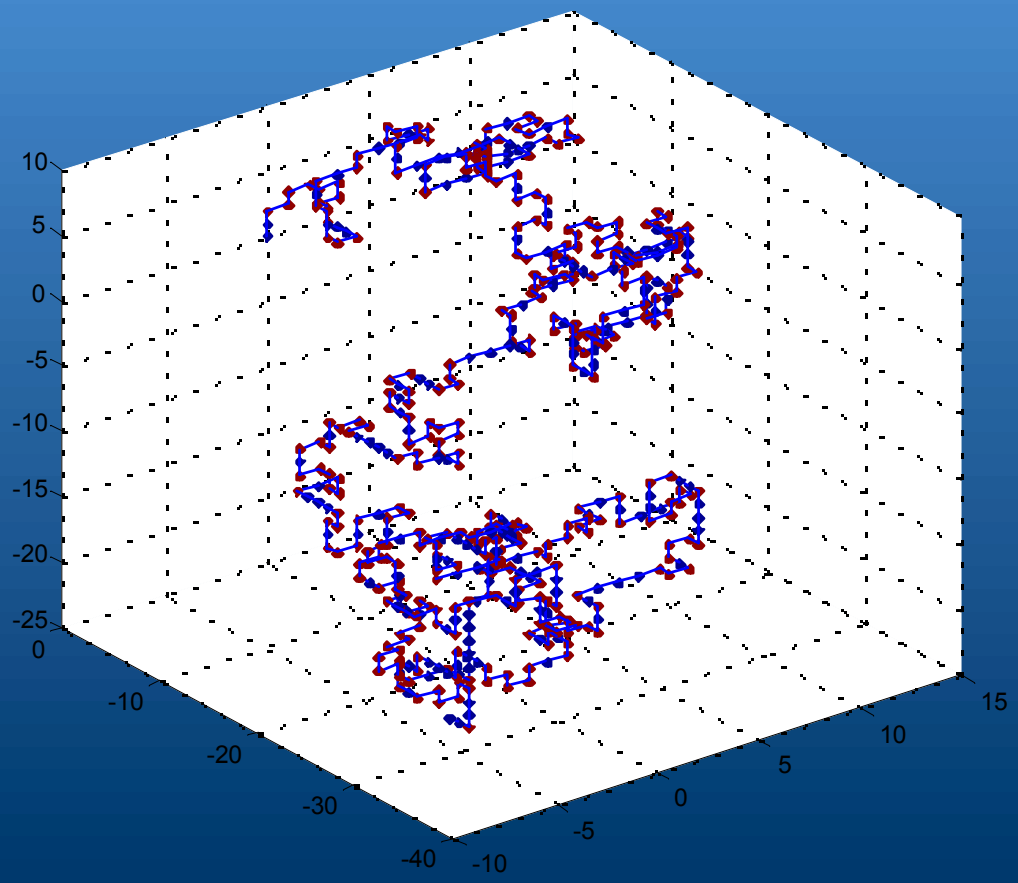
A "divide and conquer" hierarchical modeling scheme



Polymer models

Lattice (random walk) models

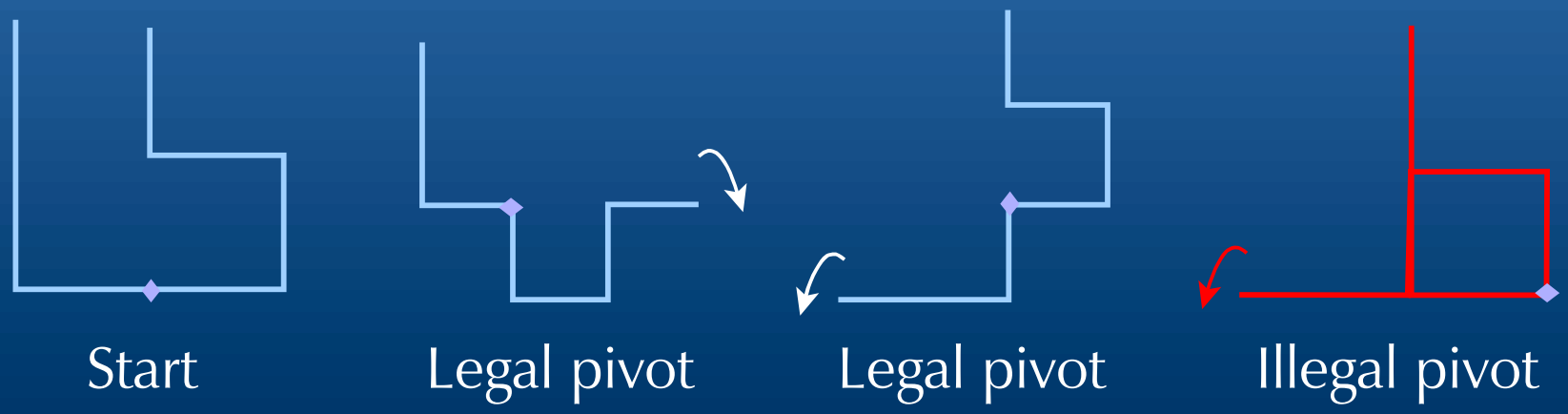
- Beads are restricted to the sites of a simple cubic lattice.
- Stiffness "penalty" associated with changes in direction.
- Non-bonded interactions also possible.



Pivot algorithm

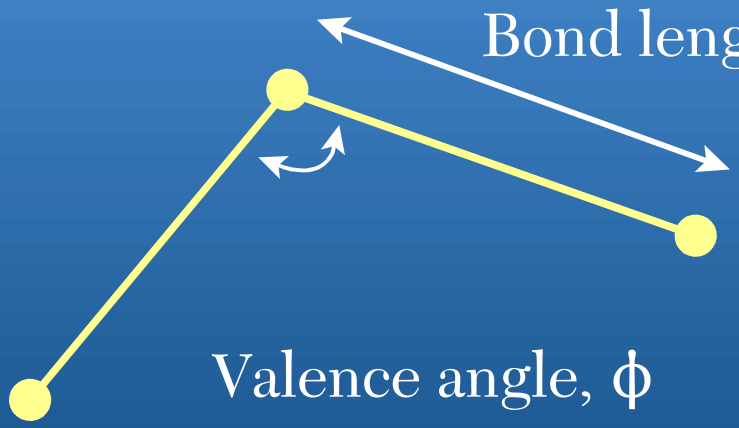
Very efficient algorithm for simulating single chains

- Select a point along a chain, and rotate one side
- Check for self-avoidance of chain
- Accept or reject states according to Boltzmann weights
- *O(N)* steps between independent configurations
  - Determined "on the fly" using DDDA (M.T. Feldmann)



Properties to pass between scales

Distributions of bond lengths and dihedral angles

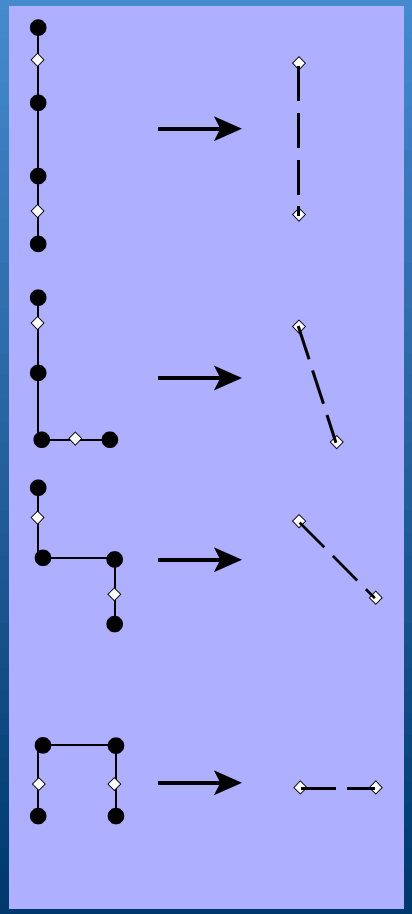


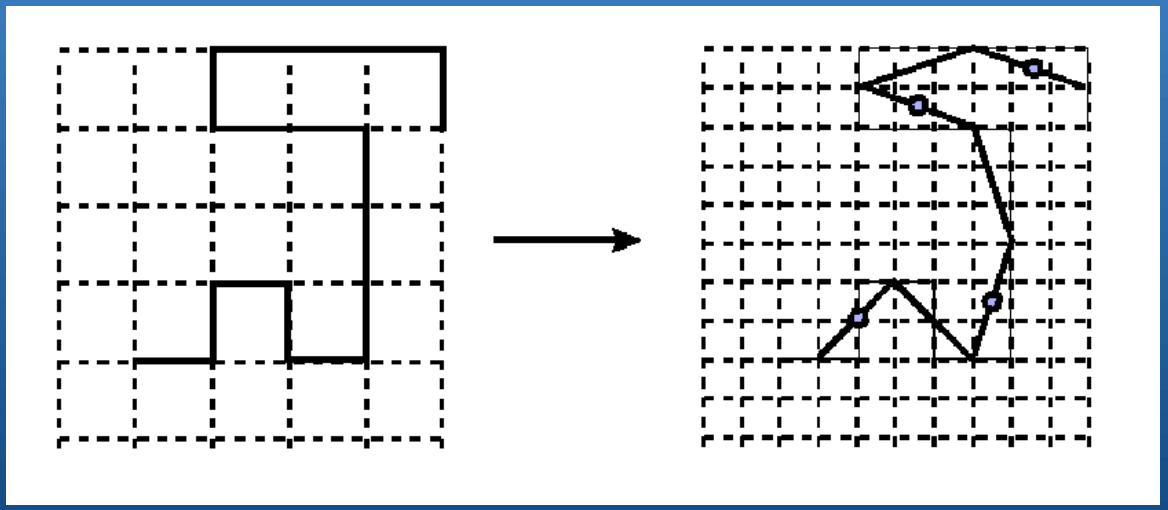
Bond length: distance between adjacent centers-of-mass of N_p consecutive particles along original chain

Valence angle: Spherical angle formed by two adjacent center-of-mass bonds

Coarse-graining of bonds

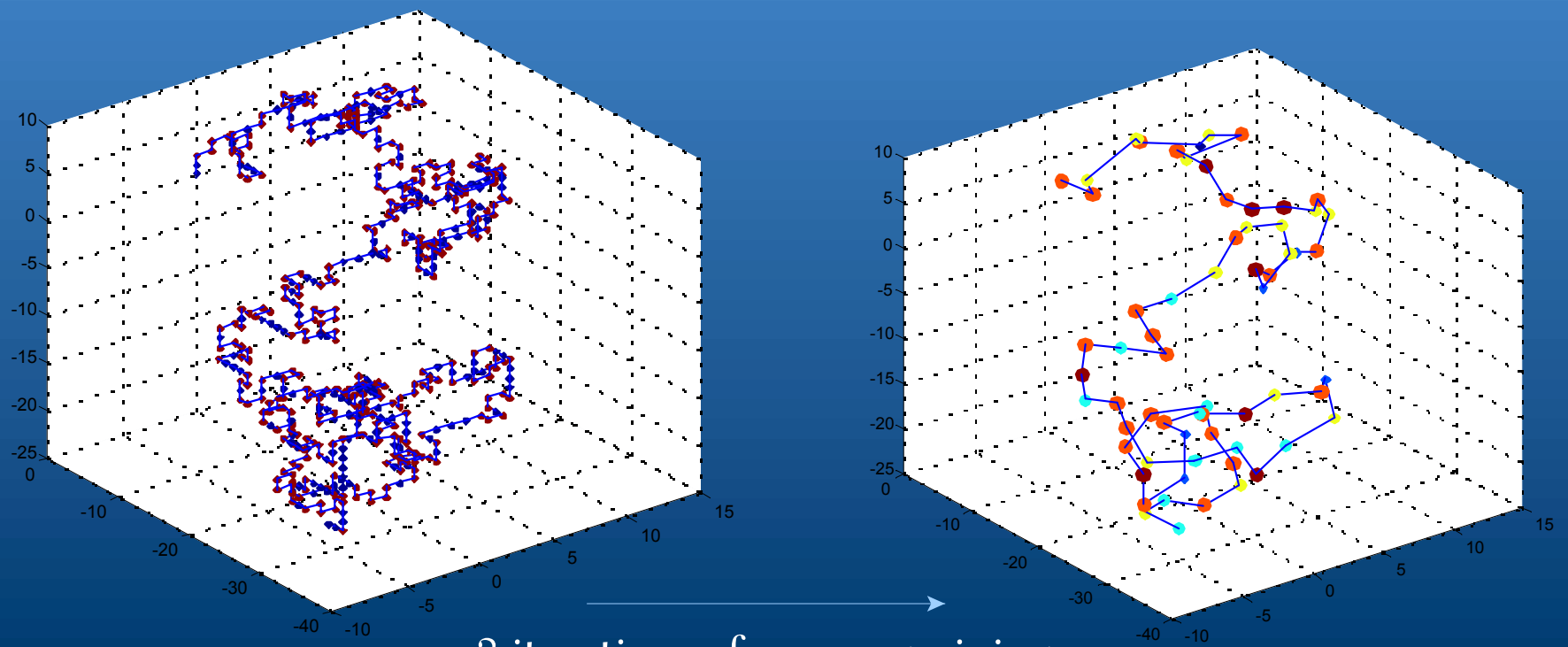
Beads are replaced by centers-of-mass; differences stored





Recursive coarse-graining

Repeated application yields increasingly coarse description

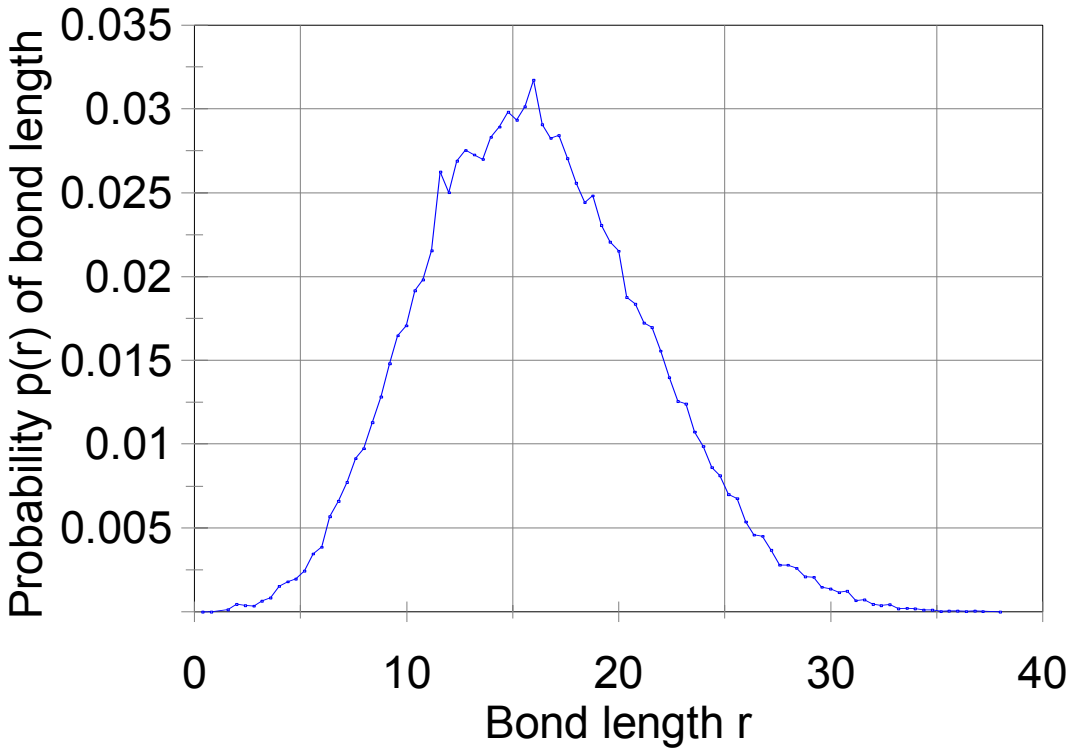


3 iterations of coarse-graining

Moving between scales

Distributions, not complete data, required

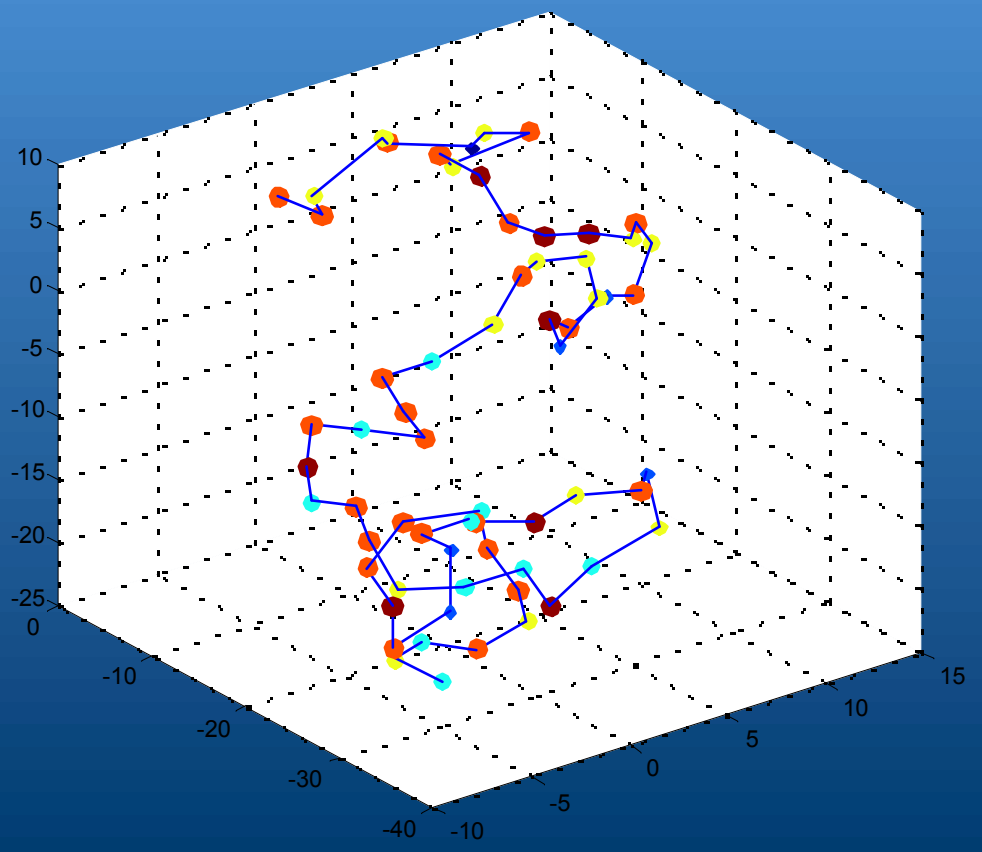
- It is not necessary to keep track of all of the details of the bond lengths of the system; just the overall probability distribution.



Polymer models

Bead-and-chain model

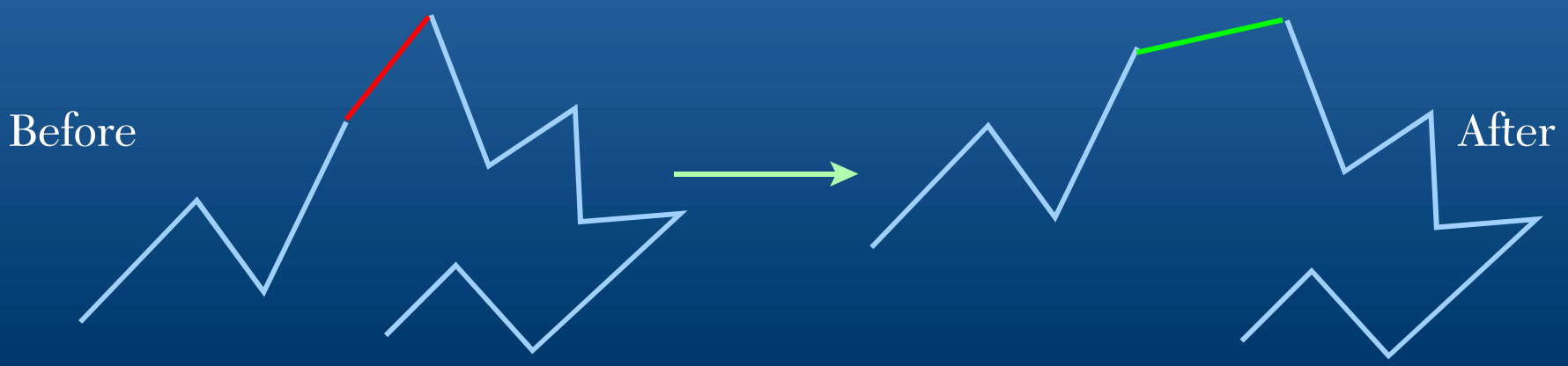
- Beads are connected to one another via flexible or rigid chains
- Energies function of distance between beads
- Particles have “excluded volume”



Coarse-grained algorithm

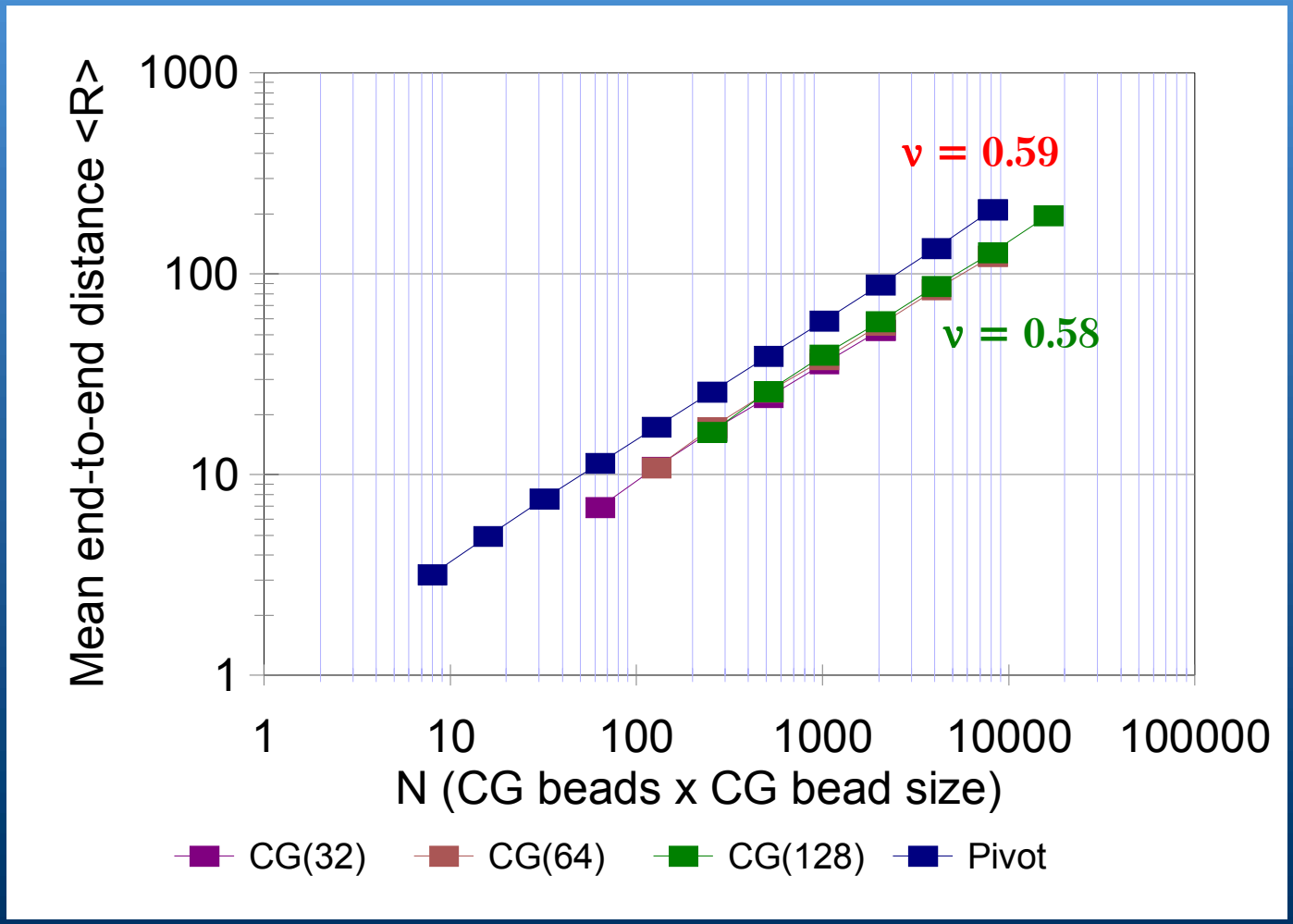
Generalized reptation-like moves

- Select a bond and generate new bond length and angle
- Drag one side of chain correspondingly
- Check for self-avoidance of new configuration
- Accept or reject state according to Boltzmann weights
- *O(N)* between independent configurations (DDDA)



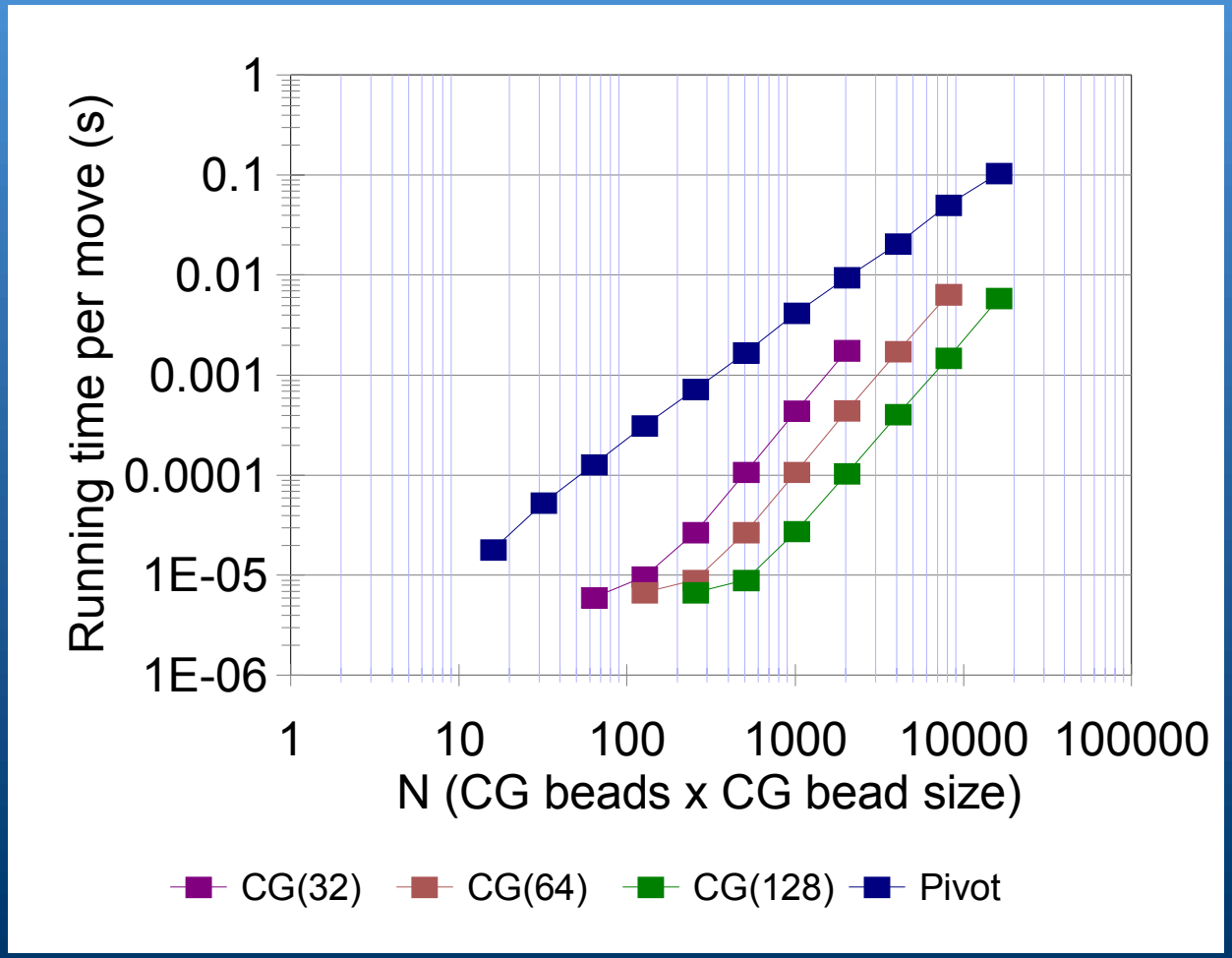
Coarse-graining v. atomistic model

Scaling preserved across CG scales



Coarse-graining v. atomistic model

Performance of CG model orders of magnitude faster



Pivot algorithm: $O(N)$.
CG algorithm: $O(N^2)$, unoptimized.

But $N_{cg} \quad N_p$, so CG algorithm is still much faster.

Also, CG running time is independent of resolution scale.

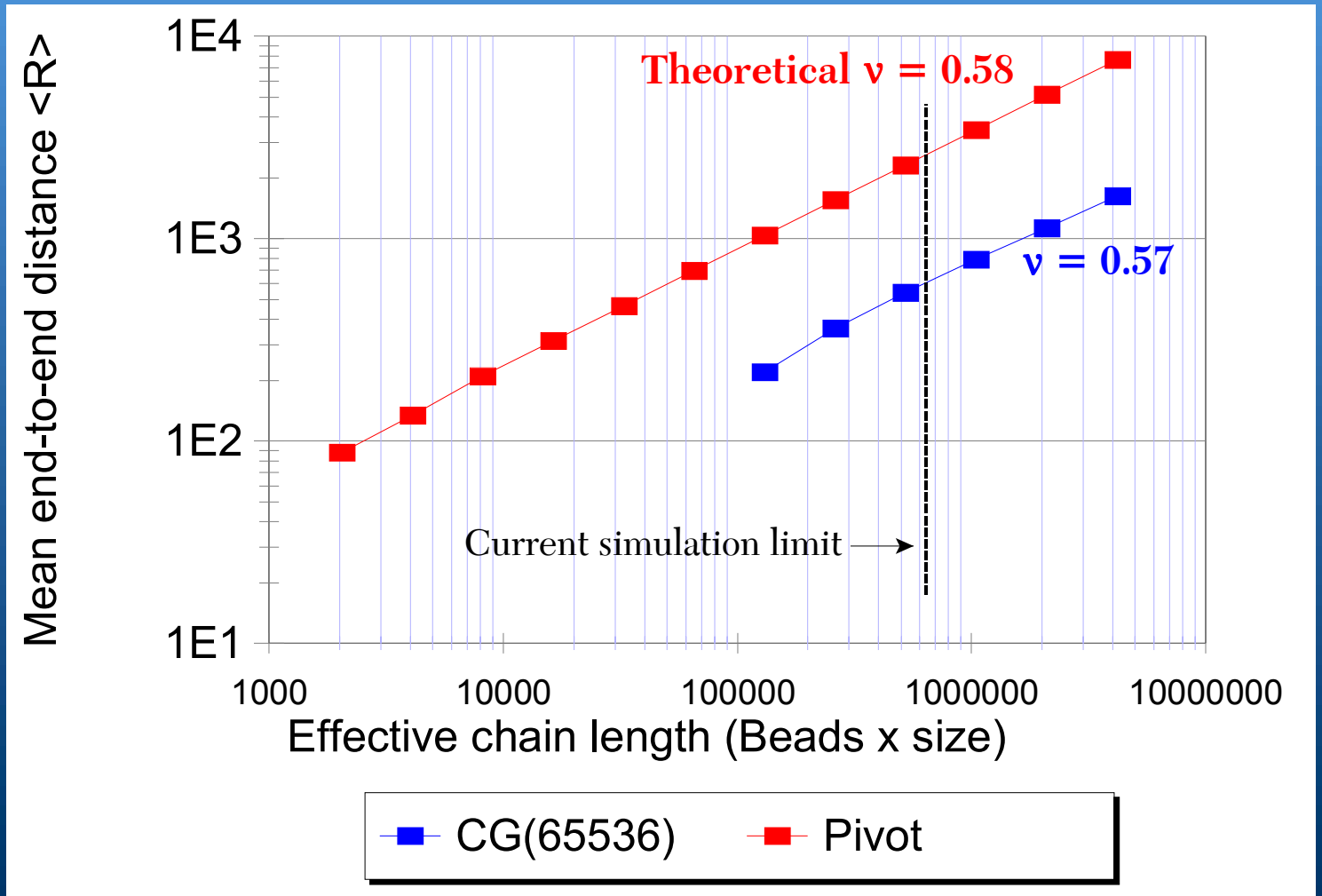
Extending the model

Making the model truly "multiresolution"

- Our coarse-grained algorithm *doesn't care where its inputs come from*:
  - Experimental data
  - Detailed atomistic simulation
  - Another coarse-grained simulation at a finer scale.
- We can peform simulations at one scale, and feed the resulting data into the simulation at a coarser scale.

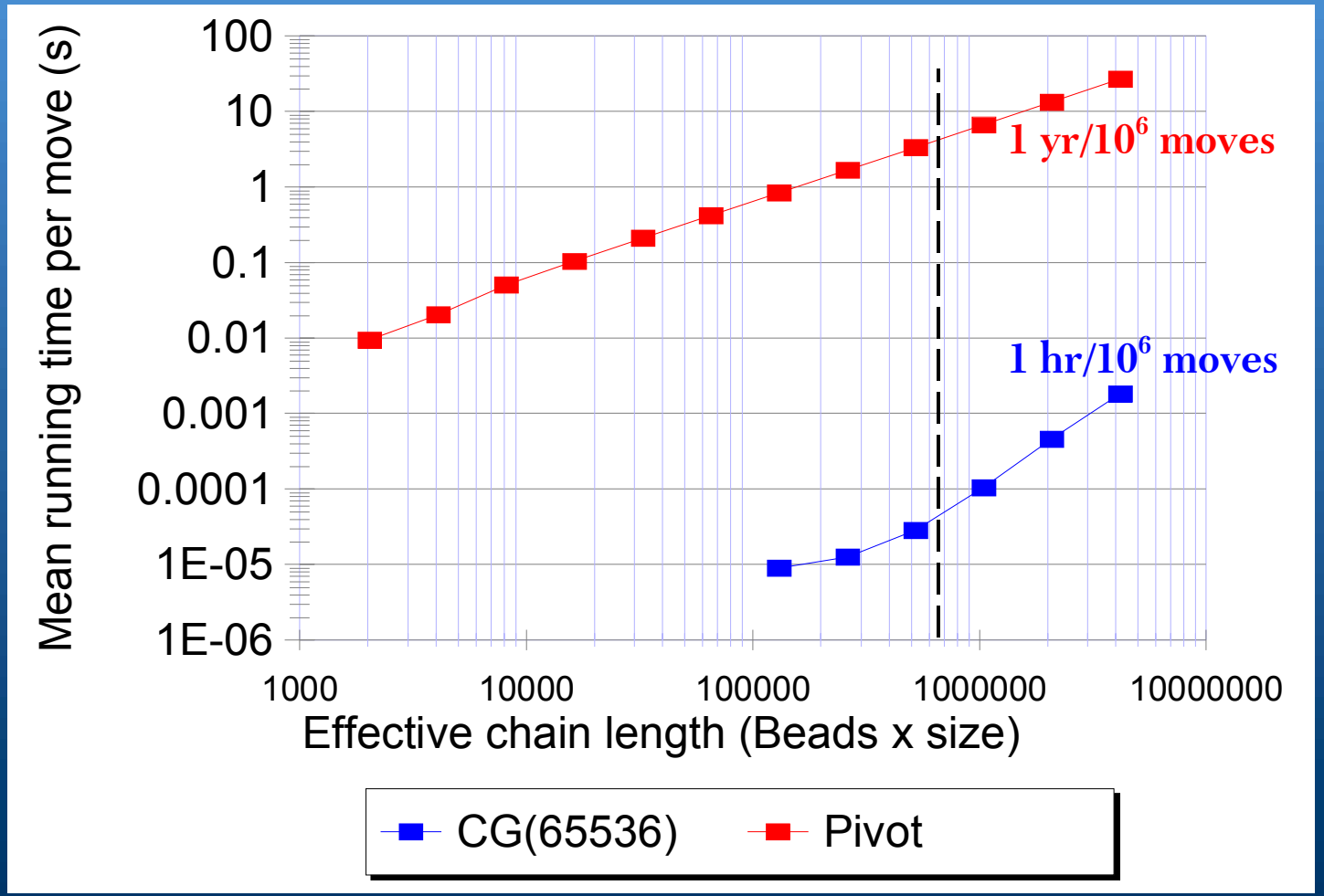
Hierarchical model results

Four-stage simulation (1, 128, 2048, 65536)



Hierarchical model results

Four-stage model performance comparison



Conclusions

A highly-efficient coarse-graining method

- Without correcting potentials or other "fixes," correct scaling results are obtained, even across multiple levels of simulation.
- *Unoptimized performance* is orders of magnitude faster than efficient atomistic simulations.
- Easily able to simulate system lengths currently unobtainable via direct atomistic simulations.

Applications

Extensions of the model

- Multiple chains and polymer melts
- Fitting of coarse-grained potential models
- Extensions to sample problems
  - Polymer-colloid interactions
  - Charged polymers
  - Phase diagrams
  - Polydisperse models

Acknowledgments

- G. C. Rutledge, G. Stephanopoulos
- D. Blankschtein, B. L. Trout
- M. S. Dyer, O. Karsligil, M. Bathe
- M. T. Feldmann, CACR (Caltech)
- DOD/Battelle (NDSEG)
- DOE/Krell Institute

Questions?