Bottom-up Coarse-graining

Denis Andrienko

Max Planck Institute for Polymer Research
Mainz, Germany

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Our dream

Quantum Chemistry

Ground/Excited states
Electrostatic multipoles
Polarizabilities

Statistical Physics

Advanced sampling techniques
Master Equation solvers
Long-range Interactions

Continuous Models

Drift-diffusion solvers
Self-consistent field techniques

no fitting parameters, quantitative accuracy
One-dimensional Ising model

\[ s_i = 1 \text{ (spin up)} \quad s_j = -1 \text{ (spin down)} \]

spins interact

\[ -J \text{ (energetically good)} \quad +J \text{ (entropically good)} \]

configurations

Low T

High T
Statistical Physics

Interaction between two neighboring sites only
\[ E_{i,i+1} = -J s_i s_{i+1} \]

Hamiltonian
\[ H = \sum_i E_{i,i+1} \]

Partition function
\[ Z = \sum_{i,s_i=\pm 1} \exp(-\beta H) = \sum_{s_i=\pm 1} \prod_i \exp(\beta J s_i s_{i+1}) \]

Can we invent a smart way of evaluating the partition function?
Real space renormalization group: Decimation

Partition function

\[ Z = \sum_{s_i = \pm 1} \prod_i \exp \beta J s_i s_{i+1} \]

Decimated partition function

\[ Z = \sum_{s_{2n}} \prod_{i=2n}^{s_{2n+1}} \exp \beta J (s_{2n}s_{2n+1} + s_{2n+1}s_{2n+2}) \]

Substitutions

\[ \exp \beta J s_i s_{i+1} = \cosh \beta J (1 + us_i s_{i+1}) \]
\[ u = \tanh \beta J \]

\[ Z = \sum \prod \cosh \beta J (1 + us_i s_{i+1}) \]
\[ Z = \sum \prod 2 \cosh^2 \beta J (1 + u^2 s_{2n}s_{2n+1}) \]

Similar sum but two times less sites. Repeat!
Coarse-grained Ising is again Ising!

\[ Z = \sum_{s_i} \prod_i \cosh \beta J (1 + u s_i s_{i+1}) \]

\[ Z = \sum_{s_{2n}} \prod_{i=2n} 2 \cosh^2 \beta J (1 + u^2 s_{2n} s_{2n+1}) \]

Our first bottom-up coarse-grained model

new coupling constants

\[ \tanh \beta J' = \tanh^2 \beta J \]

\[ \beta J' = \frac{1}{2} \ln \cosh \beta J \]

Check coupling constants when \( n \to \infty \)
Coupling constants

1. No long-range order in 1D systems with finite interaction range
2. Fluctuations in 1D always eliminate phase transition

Generalize to more complex systems?

\[ \beta J' = \frac{1}{2} \ln \cosh \beta J \]

Graphical solution

\[ K = \beta J \]

Attraction points

\[ \beta J = 0 \text{ - stable } (T \to \infty) \]
\[ \beta J = \infty \text{ - unstable} \]

At some length-scale the coupling always becomes small, no matter how strong the microscopic coupling was
Summary

1. Chose blocks: two spins combined into one
   Mapping operator: Ising -> CG Ising

2. Integrate out “unneeded” degrees of freedom
   Effective CG potential

3. Project effective potential on a CG force-field
   No need, CG Ising has the same $Z(s)$ as Ising $Z(s)$
Coarse-graining of particle-based systems

Atomistic system
polypyrrole chain

\[ r^n = \{ r_1, \ldots, r_n \} \]

\[ p^n = \{ p_1, \ldots, p_n \} \]

Coarse-grained system
10 PPY repeat units

\[ n < N \]

coordinates

momenta

Hamiltonian

\[ h(r^n, p^n) = \sum_{i=1}^{n} \frac{1}{2m_i} p_i^2 + u(r^n) \]

\[ H(R^N, P^N) = \sum_{i=1}^{N} \frac{1}{2M_i} P_i^2 + U(R^N) \]
Canonical (NVT) ensemble

\[ p(\mathbf{r}^n) \sim \exp[-\beta u(\mathbf{r}^n)] \]  
Boltzmann

\[ P(\mathbf{R}_N) \sim \exp[-\beta U(\mathbf{R}_N)] \]

\[ p(\mathbf{p}^n) \sim \exp \left[ -\beta \sum_{i=1}^{n} \frac{p_i^2}{2m_i} \right] \]  
Maxwell

\[ P(\mathbf{P}_N) \sim \exp \left[ -\beta \sum_{i=1}^{N} \frac{P_i^2}{2M_i} \right] \]

Total probability

\[ p_{rp}(\mathbf{r}^n, \mathbf{p}^n) = p_r(\mathbf{r}^n)p_p(\mathbf{p}^n) \]

\[ P_{RP}(\mathbf{R}_N, \mathbf{P}_N) = P_R(\mathbf{R}_N)P_P\mathbf{P}_N \]

Physical intuition

\[ p_{rp}(\mathbf{r}^n, \mathbf{p}^n) = P_{RP}(\mathbf{R}_N, \mathbf{P}_N) \]

Mapping operators

\[ R_I = M_{RI}(r^n) = \sum_{i=1}^{n} c_{II_i} r_i \]

\[ P_I = M_{PI}(p^n) = M_I \sum_{i=1}^{n} \frac{c_{II_i} p_i}{m_i} \]

\( c_{II_i} \) is an \( N \times n \) matrix

\( \sum_i c_{II_i} = 1 \) (translational invariance)

Propane CM: 4 x 1, 3 x 1, 4 x 1 block matrix

Here: linear mapping operators only
You will have to specify \( c_{II_i} \) in the VOTCA input files!
Conditional probabilities

Equilibrium probability density for CG variables

\[ \rho_R(R^N) = \int dr^np_r(r^n)\delta(M_{RI}^N(r^n) - R^N) \]

\[ \rho_P(P^N) = \int dp^np_p(p^n)\delta(M_{PI}^N(p^n) - P^N) \]

delta function sorts microscopic states in appropriate coarse-grained states

Consistency of the CG and the atomistic models

\[ P_{RP}(R^N, P^N) = \rho_{RP}(R^N, P^N) \]
The CG interaction potential is the potential of mean force
The CG force is a conditioned expectation value of the atomistic force

\[ P_{RP}(R^N, P^N) = p_{RP}(R^N, P^N) \]

is equivalent to

\[ M_I = \left( \sum_{i \in I} \frac{c_{ii}^2}{m_i} \right)^{-1} \]

momentum space:

\[
\exp[-\beta U(R^N)] \sim \int d\mathbf{r}^n \exp[-\beta u(\mathbf{r}^n)] \delta(M_{RI}^N(\mathbf{r}^n) - R^N)
\]

coordinate space:

\[ F_I(R^N) = \langle \mathcal{F}_I(\mathbf{r}^n) \rangle_{R^N} \]
Force-field basis set functions

PMF provides **exact** mapping of the atomistic onto CG system.

PMF requires many-body potential functions $G_I(R^N)$, MD force-fields provide a **limited** set of many-body potentials (angles, dihedrals).
In a nutshell

coarse-graining

Atomistic model

Coarse-grained model

Force Matching
Inverse Monte Carlo
Relative Entropy
Iterative Boltzmann Inversion
Conditional Reversible Work

backmapping
Variational principle

Project the many-body potentials on the functions provided by the force-field

\[ \chi^2[G] = \frac{1}{3N} \left\langle \sum_{I=1}^{N} \left| \mathcal{F}_I (r^n) - G_I \left( M^N_R(r^n) \right) \right|^2 \right\rangle \]

The global minimum of the functional \( \chi \) for \( G \) in the vector space of CG force fields is achieved when \( G \) is \( F \)

This is exactly what force-matching (MSCG) is doing: projecting many-body PMF onto the CG force-field basis functions

Force matching, **MultiScale Coarse-Graining**

It is a non-iterative method.
Example: hexane in vacuum

Forces have off-plane components which are not present in the basis set of the coarse-grained force-field

Example: water model (SPC/E)

Pair potential is not reproducing the local tetrahedral structure

Structure-based coarse-graining

What if we do not have forces?
(e.g. Monte Carlo is used for sampling)

CG procedure can be reformulated in terms of correlation functions

\[
\begin{align*}
\text{correlation function} & \quad \text{simple liquid} \\
\rho_1(r_1) & \quad \rho - \text{density} \\
\rho_2(r_1, r_2) & \quad g(r) - \text{pair distribution function} \\
\rho_3(r_1, r_2, r_3) & \\
\ldots
\end{align*}
\]

Normally \( \rho \) and \( g(r) \) are used (easy to compute)
Henderson theorem

A classical analogue of the Hohenberg-Kohn theorem in DFT

\[ g(r) \equiv U(r) \]

pairwise potential \( U(r) \) is unique

All structure-based methods matching \( \rho \) and \( g(r) \) converge to the same coarse-grained potential

Liquid state theory – Yvon-Born-Green equation

Pair potential of mean force

\[-W'_\xi(r) = F_\xi(r) + \sum_{\xi'} dr' G_{\xi \xi'}(r, r') F_{\xi'}(r')\]

Direct force Correlation function

integrated

\[W_\xi(r) = U_\xi(r) + \sum_{\xi'} W_{\xi \xi'}(r, r')\]

no correlations between DOF

\[\delta U_\xi(r) = w_\xi(r) - W_\xi(r) \sim k_B T \ln [P_\xi(r)/p_\xi(r)]\]

Iterative Boltzmann Inversion

\[ \delta U(r) = k_B T \ln \frac{g(r)}{g_{\text{ref}}(r)} \]

IBI: iterative, local, no correlations.
Robust, but it is not clear if it works for mixtures.

Inverse Monte Carlo

\[ H = \sum_{i,j} U(r_{ij}) = \sum_{\alpha} S_\alpha U_\alpha \]

\[ \delta\langle S_\alpha \rangle = \langle S_\alpha \rangle - S_\alpha^{\text{ref}} = \sum_{\gamma} \frac{\partial \langle S_\alpha \rangle}{\partial U_\gamma} \delta U_\gamma + \mathcal{O}(\delta U^2) \]

\[ A_{\alpha\gamma} = \frac{\partial \langle S_\alpha \rangle}{\partial U_\gamma} = \frac{\partial}{\partial U_\gamma} \frac{\int dq S_\alpha(q) \exp[-\beta H(q)]}{\int dq\exp[-\beta H(q)]} \]

\[ A_{\alpha\gamma} = \beta \left( \langle S_\alpha \rangle \langle S_\gamma \rangle - \langle S_\alpha S_\gamma \rangle \right) \]

In the first order we need only averages (RDF) and correlations

Inverse Monte Carlo

\[ \langle S_\alpha \rangle - S^\text{ref}_\alpha = \sum_\gamma A_{\alpha\gamma} \delta U_\gamma \]

\[ A_{\alpha\gamma} = \beta (\langle S_\alpha \rangle \langle S_\gamma \rangle - \langle S_\alpha S_\gamma \rangle) \]

\[ \delta U = A^{-1} [\langle S \rangle - S^\text{ref}] \]

- non-local, iterative, particle-particle correlations are included
- \( A \) is tricky to invert

IMC implementation

Global initialization
- Initialize global variables (paths to scripts, executables and user-defined scripts)

Iteration initialization
- Convert target distribution functions into internal format, prepare input files, copy data of the previous step

Prepare sampling
- Prepare input files for the external sampling program

Sampling
- Canonical ensemble sampling with molecular dynamics, stochastic dynamics or Monte Carlo techniques

Calculate updates
- Analysis of the run. Evaluation of distribution functions, potential updates $\Delta U^{(n)}$

Postprocessing of updates
- Smoothing, extrapolation of potential updates. Ad-hoc pressure correction.

Update potentials
- $U^{(n+1)} = U^{(n)} + \Delta U^{(n)}$

Postprocessing of potentials
- Smoothing, extrapolation of potentials $U^{(n+1)}$

Continue? (yes/no)
- Evaluation of the convergence criterion either for $\Delta U^{(n)}$ or distribution functions. Check the number of iterations.

Finish
Examples: SPC/E water

IBI and IMC reproduce RDF and give similar potentials
Examples: Efficiency

IMC converges faster but needs longer iterations
Less computational costs for IBI
Test your CG model!

Bond-angle correlations are not reproduced affects chain stiffness, end-to-end distance
Coarse-graining provides a systematic way to parameterize a force-field based on selected properties of a reference system.

Can be based on

- Distribution functions:
  - Boltzmann inversion
  - Iterative Boltzmann Inversion
  - Inverse Monte Carlo
  - Relative Entropy (talk of Sikandar)
- Many-body potential of mean force
  - force matching
  - MSCG
- Desired thermodynamic property
  - Simplex algorithm
Versatile Object-oriented Toolkit for Coarse-graining Applications

\texttt{votca.org}

open source
C++, test suite, hg repository, wiki pages, bug tracker, mailing list

\textbf{votca-csg} modules (coarse-graining)
Google code: votca project

\textbf{votca-ctp} modules (charge transport)
Google code: votca-ctp project

\textbf{Happy coarse-graining!}
