

High-Performance Computing for Classical Density Functional Theory (HPC - cDFT): From Molecular Geometry to 3D Soft-Materials Structure

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1. Molecular Geometry as a Design Variable

Directional bonding and branched molecular architecture shape the organization of soft materials. Thermodynamic models often simplify this geometry by averaging molecular orientations or imposing reduced-dimensional descriptions [1–4]. My research examines when these approximations lose important structural information and develops a three-dimensional cDFT framework that retains molecular geometry.

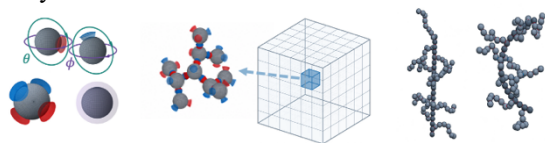


Figure 1. HPC-enabled 3D cDFT framework illustrating orientation-resolved versus averaged association (left), spatial discretization (center), and finite bottlebrush architectures (right).

Building on treatments of associating fluids [1–3] and bottlebrush polymers [4], my framework retains directional interactions and finite molecular connectivity in three dimensions. FFT evaluation makes nonlocal calculations tractable on million-point spatial grids, while multithreading provides a measured $7.3\times$ speedup for the benchmarked iteration updates. To solve the nonlinear equations governing the coupled density fields, a machine learning (ML)–inspired adaptive controller uses iteration history to predict updates and checks them against the full coupled residual. It combines Anderson acceleration, multi-secant modeling, regularized reduced Newton damping, and adaptive Picard mixing.

2. Directional Association under Confinement

Building on associating-fluid cDFT [1,3], I evaluate directional bonding through angular quadrature within a SAFT-based association functional, without the separately supplied bulk orientational correlation functions or learned orientational kernels [2]. Association therefore depends on molecular alignment as well as local density. Comparisons with scalar DFT, Monte Carlo, and molecular dynamics test the structural consequences of retaining these bonding directions. For water-like associating fluids under slit confinement, the orientation-resolved description reduces excessive density oscillations predicted by scalar DFT and improves agreement with particle simulations (Figure 2).

3. Resolving Finite Branched Architectures

The same question extends to permanent molecular connectivity in branched polymers. Zhang et al. [4] describe bottlebrush polymers using an infinite rigid backbone and radially varying segment density. My three-dimensional formulation retains a finite, flexible backbones and discrete

grafting sites in three dimensions. I benchmark the predicted segment densities against molecular dynamics simulations of the same molecular architecture and state conditions (Figure 3). From this, we can monitor and measure axial and azimuthal density variations and now study chain-end effects, uneven crowding, and asymmetric structures. The connection between bottlebrush architecture and material properties [5–6] motivates studies of structured polymer coatings and interfaces relevant to metal–organic frameworks (MOFs) and membranes.

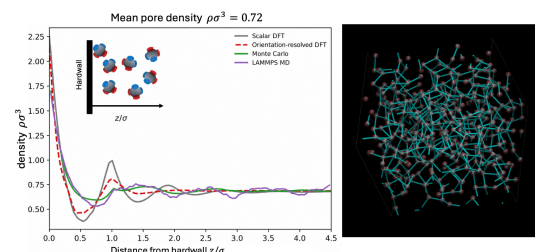


Figure 2. Slit confinement of water with H – bond strength $\beta\epsilon_{assoc} = 9$, in a 4nm nanopore. Orientation cDFT improves agreement with MC/MD. Geometric association in MD (right).

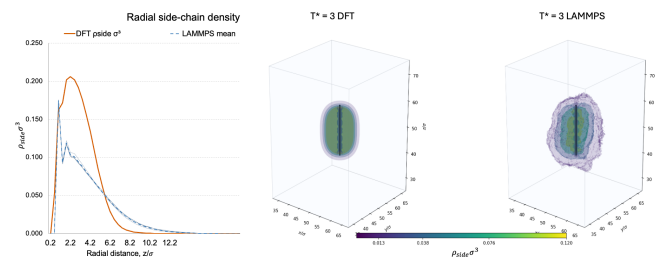


Figure 3. Radial side-chain density profiles (left) and corresponding 3D density fields from converged DFT (center) and the three-replica LAMMPS mean (right). MD shows a broader distribution than DFT.

4. Extending the Molecular Framework

Together, these studies examine how directional bonding and permanent connectivity govern molecular crowding and interfacial organization. Retaining these geometries provides a foundation for studying structured polymer coatings and confined fluids, with longer-term applications in protein folding, drug delivery, metal–organic frameworks, membrane interfaces, and separation processes. Future work will incorporate association cooperativity and steric constraints [9], dipolar interactions [7], and electrostatics [8], while exploring trained ML controllers to reduce the computational cost of solving the coupled three-dimensional fields.

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