

USER-BOCS

$$\begin{aligned}
 W(\mathbf{R}, V) &\approx U_R(\mathbf{R}) + U_V(V) \\
 U_R(\mathbf{R}) &= U_b(\mathbf{R}) + U_{nb}(\mathbf{R}) \\
 U_V(V) &= \psi_1 N \frac{V}{\bar{v}} + \psi_2 N \left(\frac{V}{\bar{v}} - 1 \right)^2 \\
 \Delta \bar{P} &= -N \psi_1 / \bar{v} \\
 \Delta \kappa_T^{-1} &= 2N \psi_2 / \bar{v} \\
 P_{CG}(\mathbf{R}, \mathbf{P}, V) &= P_0(\mathbf{R}, \mathbf{P}) + F_V(V) \\
 P_0(\mathbf{R}, \mathbf{P}) &= \frac{2}{3V} K(\mathbf{P}) + \frac{1}{3V} \sum_I \mathbf{R}_I \cdot \mathbf{F}_I(\mathbf{R}) \\
 F_V(V) &= -\frac{dU_V(V)}{dV}
 \end{aligned}$$

We include a volume dependent term in the approximation to the many-body potential of mean force (PMF). In principle, the volume dependent function could contain more terms, but we typically find two to be sufficient. The two iteratively optimized coefficients ψ_1 and ψ_2 correspond to average pressure and compressibility corrections, respectively. The coarse-grained pressure is then evaluated as the standard formula employed in atomistic simulations plus the coarse-grained pressure correction, $F_V(V)$.

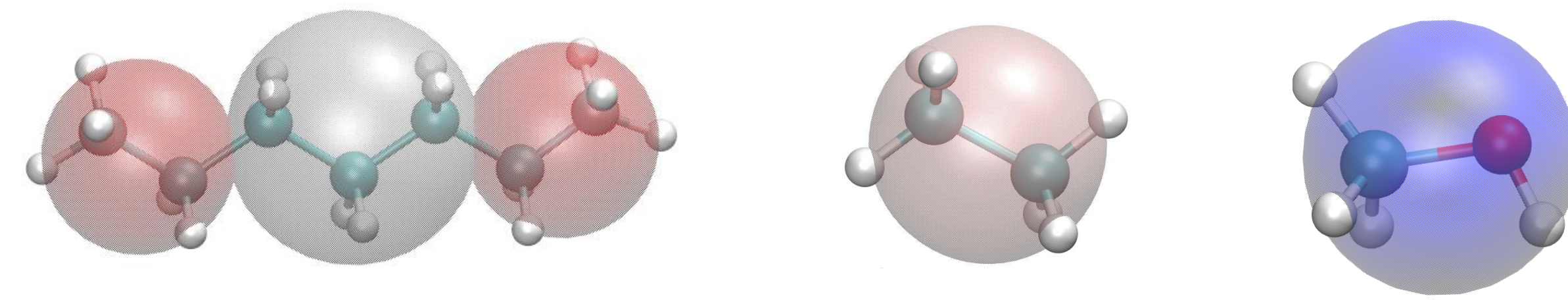


Figure 1. The coarse grained mappings used for heptane, ethane, and methanol. All mappings are done to atomistic centers of mass. Heptane has two equivalent end sites consisting of the terminal C_2H_5 groups with a central site consisting of the middle C_3H_6 . Ethane and methanol were both mapped to single site representations.

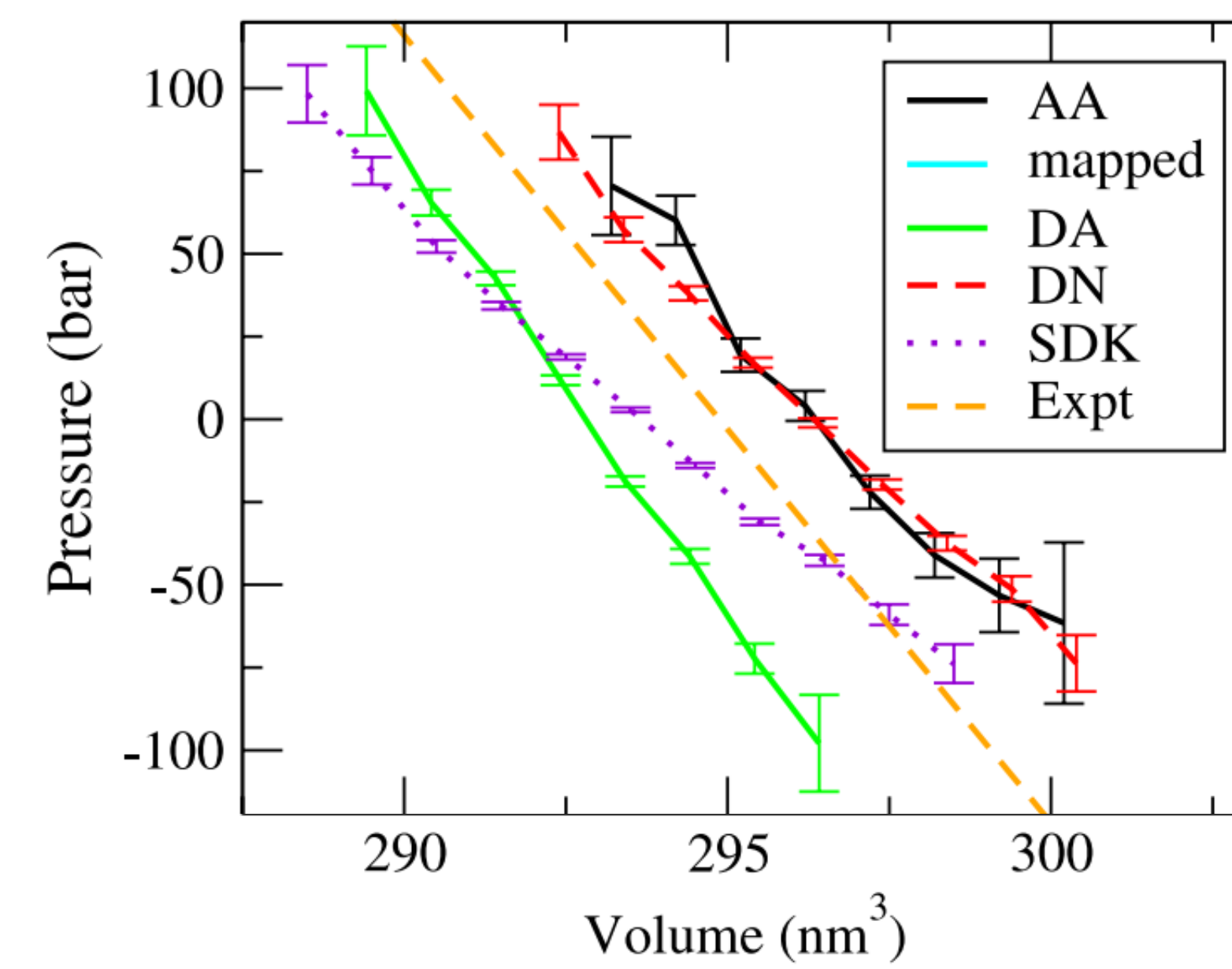
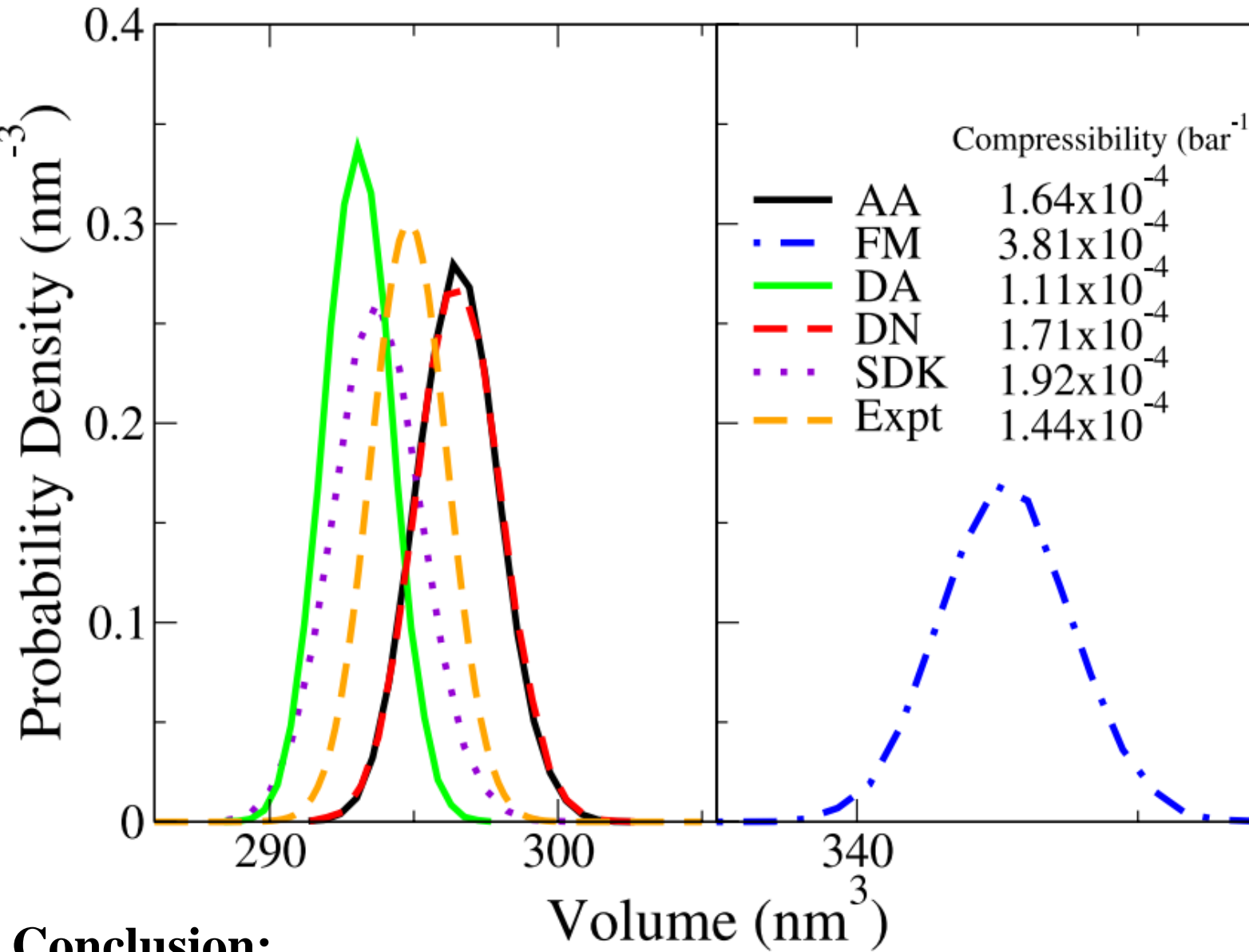
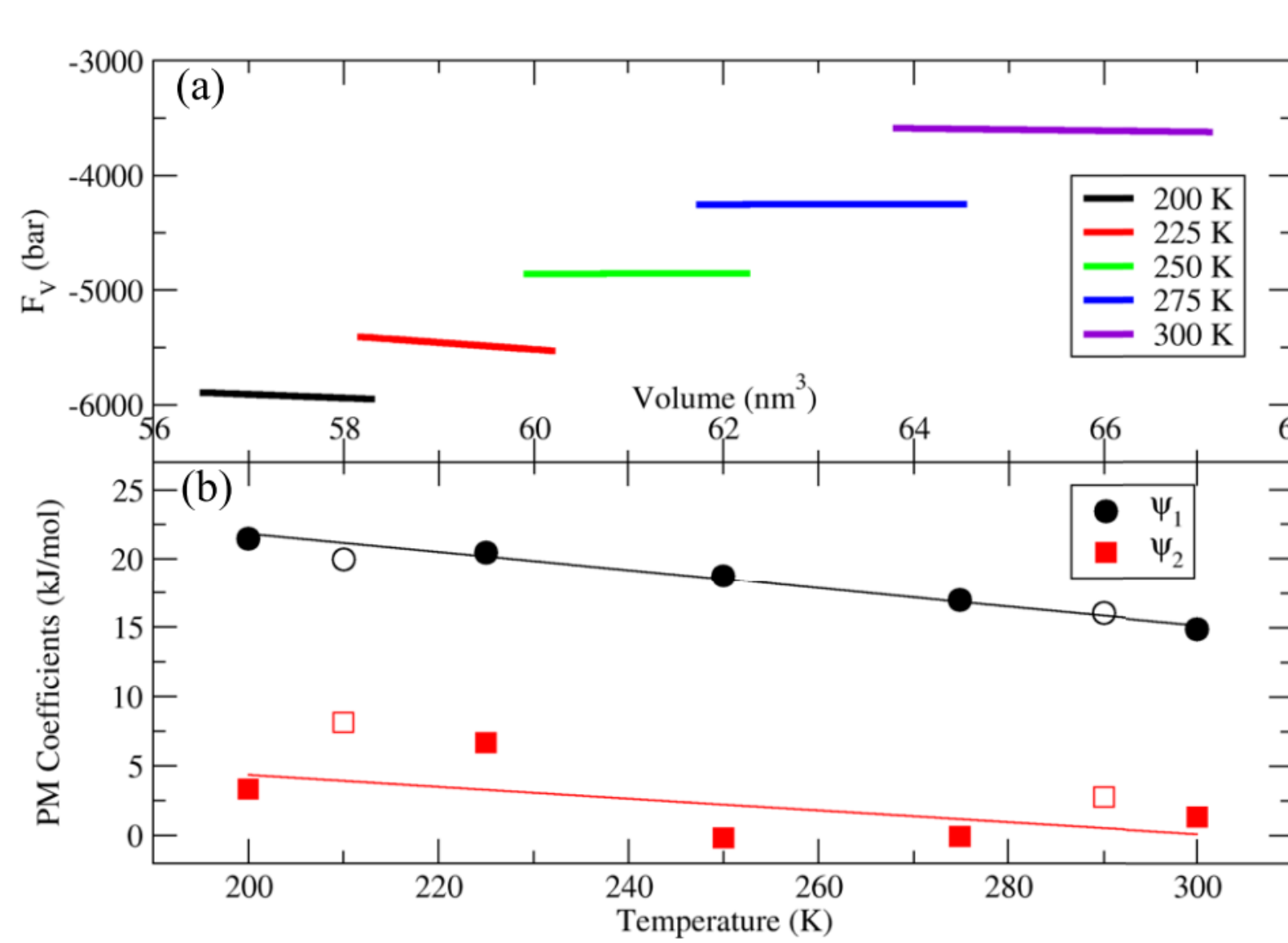
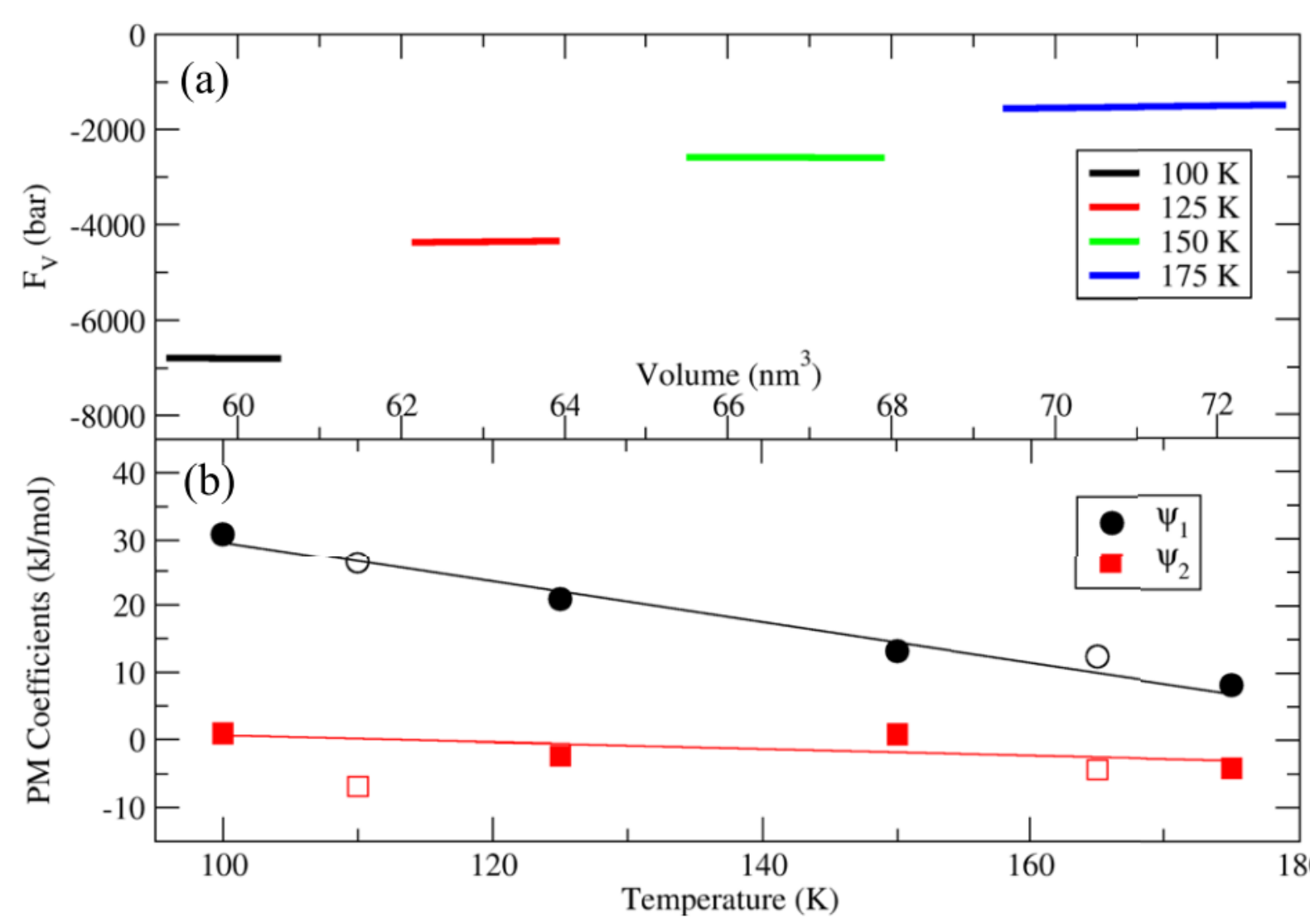


Figure 2 (top left). The pressure-volume equations of state for the different CG models of heptane. Employing the optimized coefficients (DN) reproduces the equation of state of the AA model.

Figure 3 (bottom left). The volume distributions for simulations of different CG models of heptane. The CG model employing the optimized coefficients (DN) quantitatively reproduces the atomistic model's volume distribution.



Figures 4-5 (top right, bottom right). The pressure corrections (a) and volume potential coefficients (b) for simulations of CG models of ethane (Fig 4) and methanol (Fig 5). Lower temperatures require stronger pressure corrections. Furthermore, the ψ_1 coefficient varies linearly with temperature.



Coarse Graining of Inhomogeneous Environments

$$\begin{aligned}
 U_{CG}(\mathbf{R}) &= U_b(\mathbf{R}) + U_{nb}(\mathbf{R}) \\
 U_{nb}(\mathbf{R}) &= U_2(\mathbf{R}) + U_\rho(\mathbf{R}) \\
 U_\rho(\mathbf{R}) &= \sum_I u_\rho(\rho_I) \\
 \rho_I &= \sum_J \bar{w}(R_{IJ}) \\
 \mathbf{F}_{\rho;I}(\mathbf{R}) &= \sum_{J \neq I} - \left(\frac{du_\rho(\rho_I)}{d\rho_I} + \frac{du_\rho(\rho_J)}{d\rho_J} \right) \bar{w}'(R_{IJ}) \hat{\mathbf{r}}_{IJ} = \sum_{J \neq I} \mathbf{F}_{\rho;IJ}(\mathbf{R})
 \end{aligned}$$

We include a local density potential in our basis set of coarse-grained particle interactions. The local density is defined by an indicator function, $w(r)$. Although the local density potential incorporates many body effects, the resulting forces have a convenient pairwise decomposition. Accordingly, it scales similarly to standard non-bonded pair potentials.

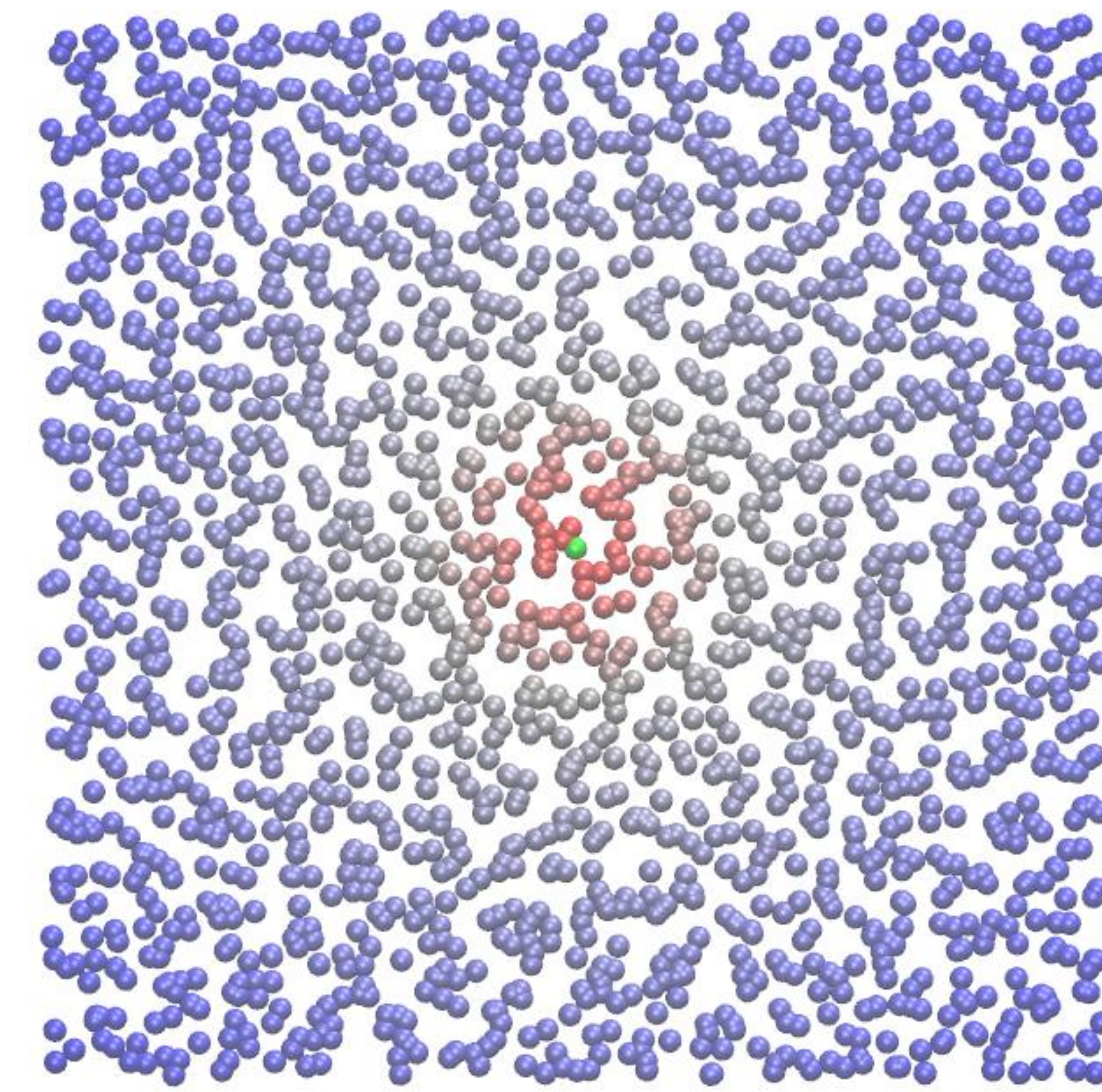
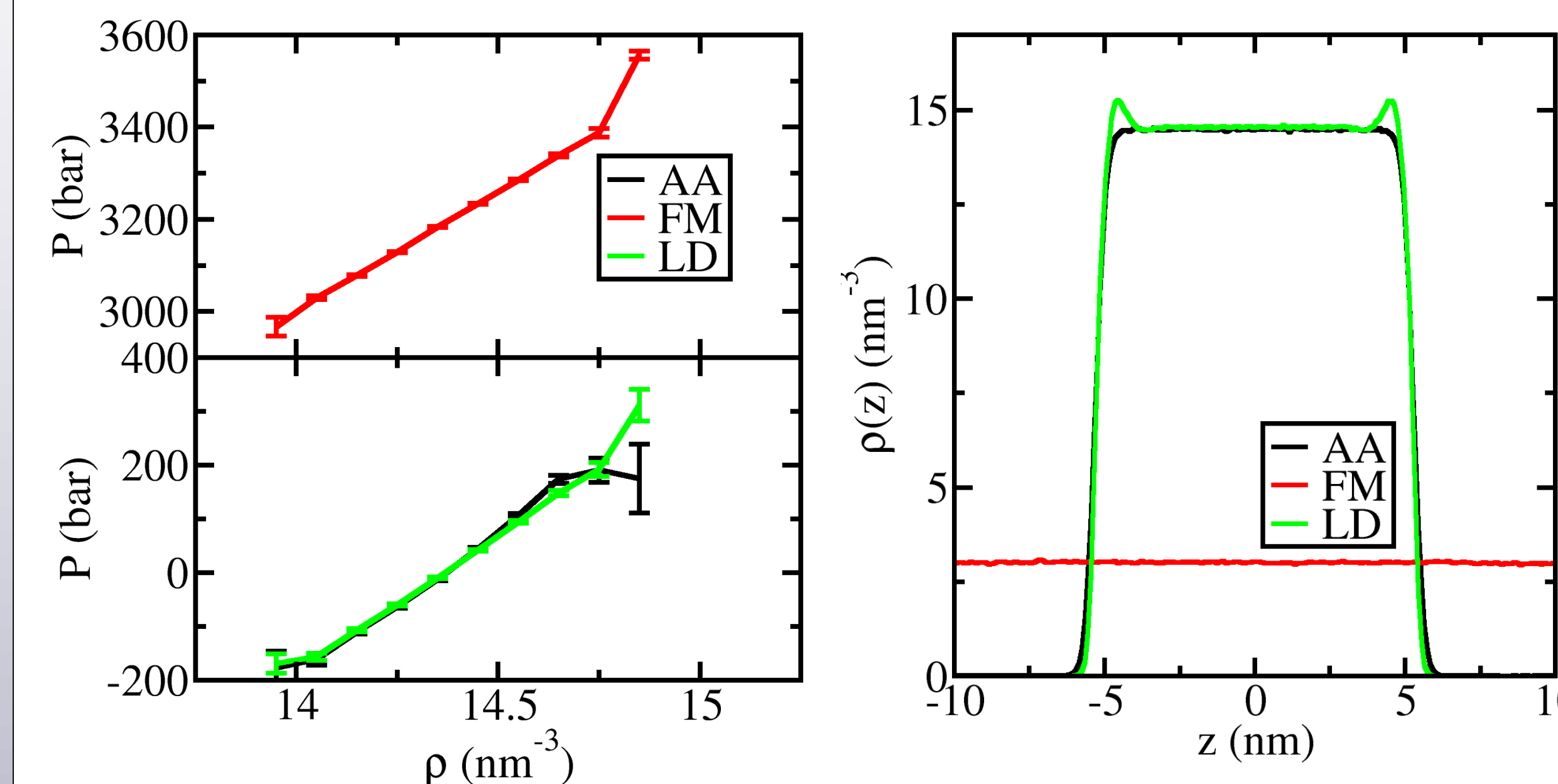
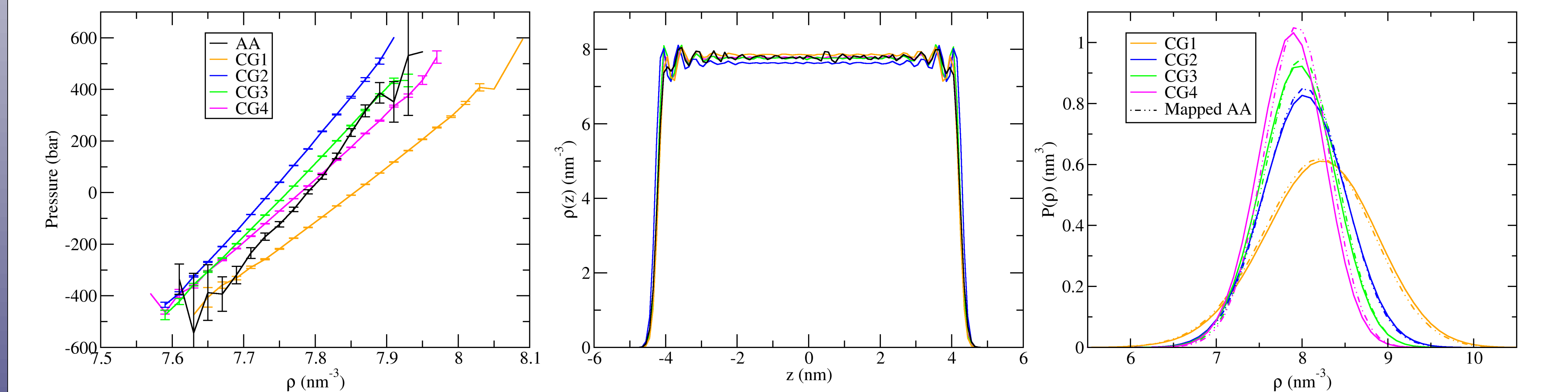


Figure 6. Contributions to the central green particle's local density. Particles' contributions diminish as they get farther from the particle under consideration.



Figures 7-8. Data from simulations of atomistic methanol (black) and two one site CG models. The first CG model (FM, red) comes from force matching a nonbonded pair force from a bulk liquid simulation. The resulting force field is much too repulsive; the internal pressure of the CG model at atomistic densities is approximately 3200 bar too high and a liquid slab simulation vaporizes. Adding in a LD potential (LD, green) enables reasonable reproduction of the equation of state and liquid slab density profile. The LD potential was initially parameterized via pressure matching and then modified.



Figures 9-11. Results from simulations of atomistic glycerol and four one site CG models of glycerol. For each CG model, we used the multi-scale coarse-graining method to parameterize both the pair potential and the LD potential. Different colors indicate different indicator functions ($w(r)$) employed to define the local density. They reasonably reproduce the atomistic equation of state, liquid slab density profile, and local density PDF, respectively.

Conclusion:

Local density potentials provide the cohesion that is frequently absent from bottom-up coarse-grained models that only use standard pair potentials to describe the intermolecular interactions. As a result, the new models can accurately reproduce equations of state and liquid-vapor interfaces. Iterative pressure matching and force matching both provide reasonable local density potentials.

References:

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Conclusion:

The USER-BOCS package in LAMMPS implements a correction to the barostat that accounts for the volume dependence of the many-body potential of mean force. The BOCS software package provides tools to parameterize both the configuration dependent coarse-grained potentials as well as the volume potential. The resulting models are capable of reproducing equations of state for bulk liquids in addition to structural properties. The BOCS software package is available at <http://github.com/noid-group/BOCS>

References:

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