Excess Entropy Scaling Applied to Coarse-Grained Polymer Models

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Introduction

Dynamics of coarse-grained (CG) models is greatly accelerated due to the removal of degrees of freedom and friction upon coarse-graining. Can this acceleration be predicted so that the dynamics can be corrected *a priori*?

In this work we apply excess entropy scaling relations to polymer models at different levels of resolution and attempt to quantify the accelerated dynamics in terms of changes in the excess entropy.

Self-diffusion coefficient

Einstein relation

$$D = \lim_{t \to \infty} \frac{1}{6t} \left\langle [\mathbf{r}_i(t) - \mathbf{r}_i(t_0)]^2 \right\rangle,$$

Slope of the MSD(t) curve as $t \to \infty$.

Entropy estimation

Excess entropy

$$S_{\text{exc}} = S - S_{\text{ig}}$$

Total entropy

$$S = S_0 + \Delta_{\text{b}} S + \Delta_{\text{nb}} S$$

Entropy change by thermodynamic integration (TI)

$$\Delta S = \frac{N}{k_B T^2} \int_0^1 \left(\left\langle \frac{\partial H}{\partial \lambda} \right\rangle_\lambda \langle H \rangle_\lambda - \left\langle \frac{\partial H}{\partial \lambda} H \right\rangle_\lambda \right) d\lambda$$

Excess entropy scaling

Reduced center of mass self-diffusion coefficient according to Rosenfeld [1]

$$D^* = D \frac{\rho_n^{1/3}}{\sqrt{k_B T / nm}},$$

where ρ_n is the chain density, n is the chain length, and m is the monomer mass. D^* and S_{exc} are related with

$$D^* = A \exp(\alpha S_{\text{exc}})$$

Iterative Boltzmann Inversion

Bottom-up approach to derive CG potentials by "fitting" the radial distribution function (RDF) of a fine-grained (FG) model.

$$U_{n+1} = U_n + \gamma \Delta U_n$$

$$\Delta U_n = k_B T \ln \frac{g_n}{g_{\text{ref}}}$$

Computational details

- FG model: generic bead-spring polymer model with length 24 monomers.
- Total of 32 state points (ρ, T) in liquid phase.
- For each state point, bonded and non-bonded CG potentials were derived at two resolutions
- NVT simulations with LAMMPS [3].
- CG potentials derived with VOTCA [2].
- Thermodyamic integration: 21 points (for each state point at each resolution!) integrated with Simpson's rule.
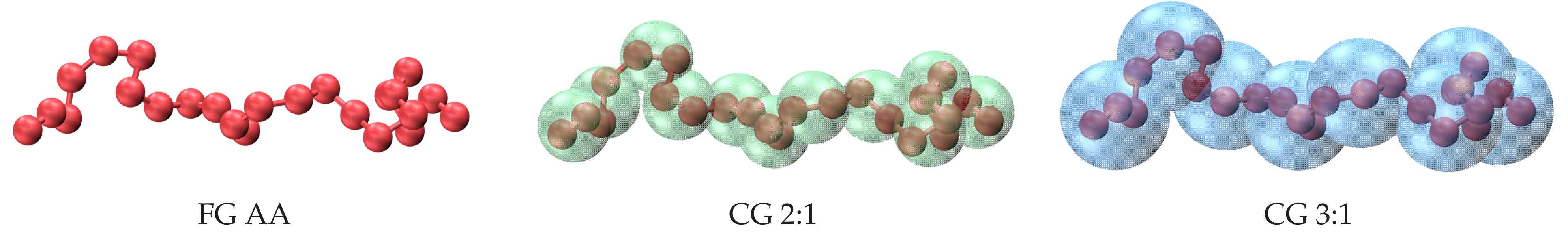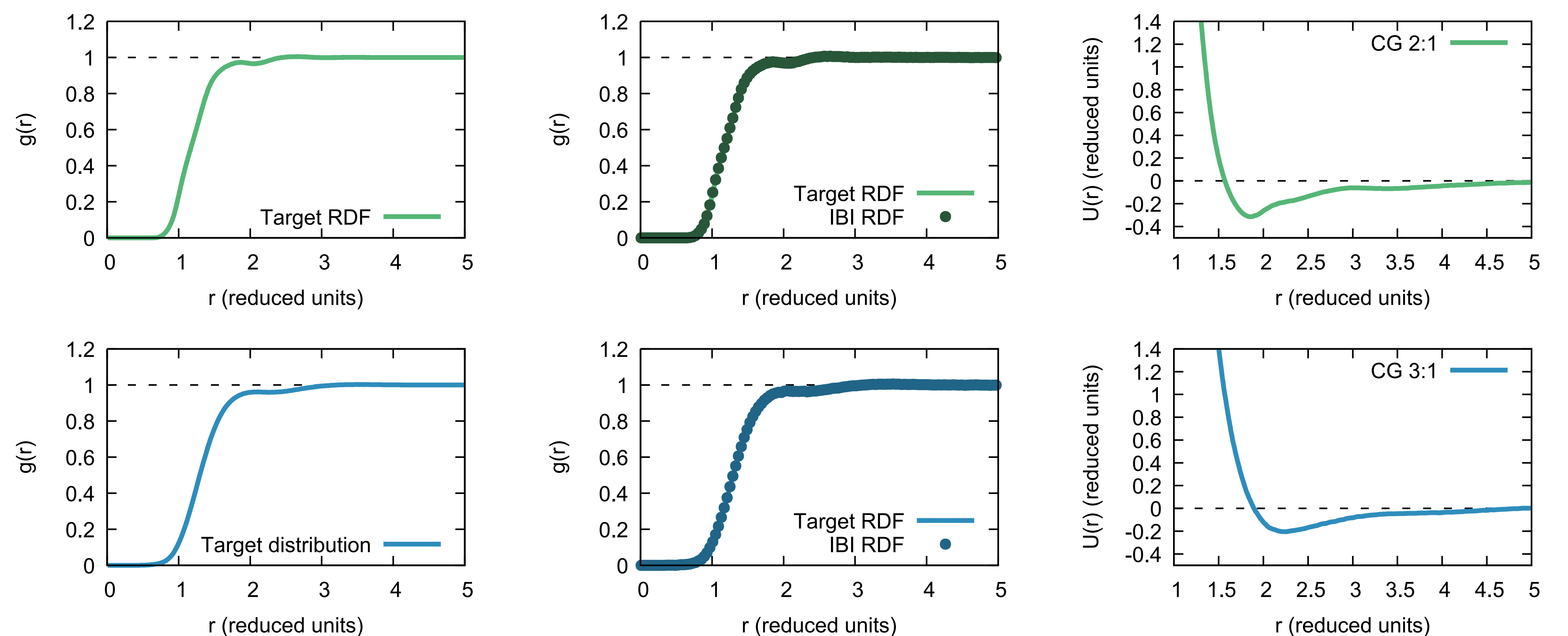
Acknowledgements

References

[1] Y. Rosenfeld *Phys. Rev. A* **15**, 2545-2549 (1977)

[2] V. Rühle et al. *J. Chem. Theory Comput.* **5**, 3211-3223 (2009)

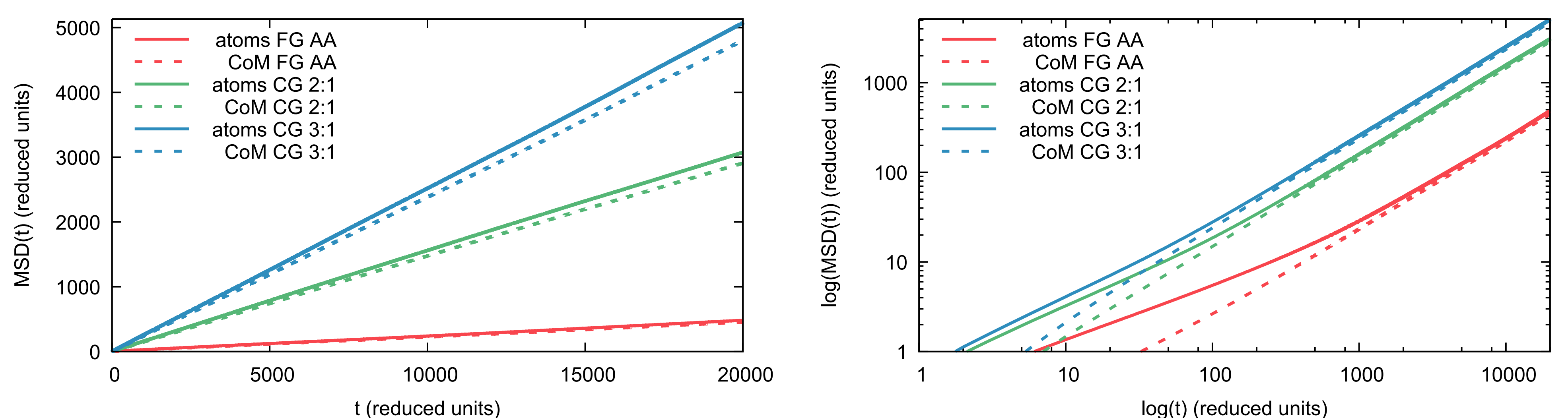[3] S. Plimpton *J. Comput. Phys.* **117**, 1-19 (1995)

Models

FG: bead-spring chains with harmonic bonds and Lennard-Jones interaction for non-bonded monomers.
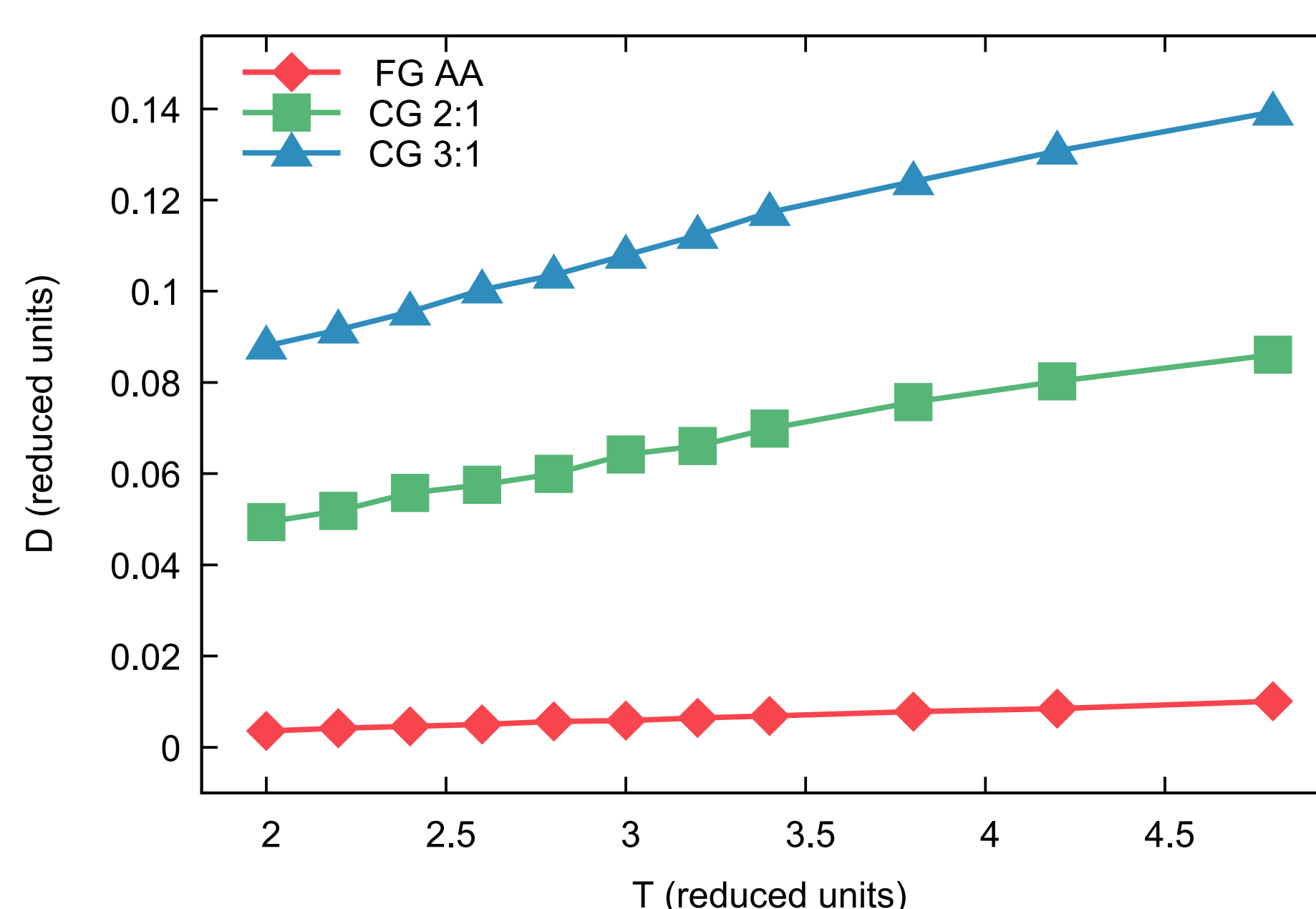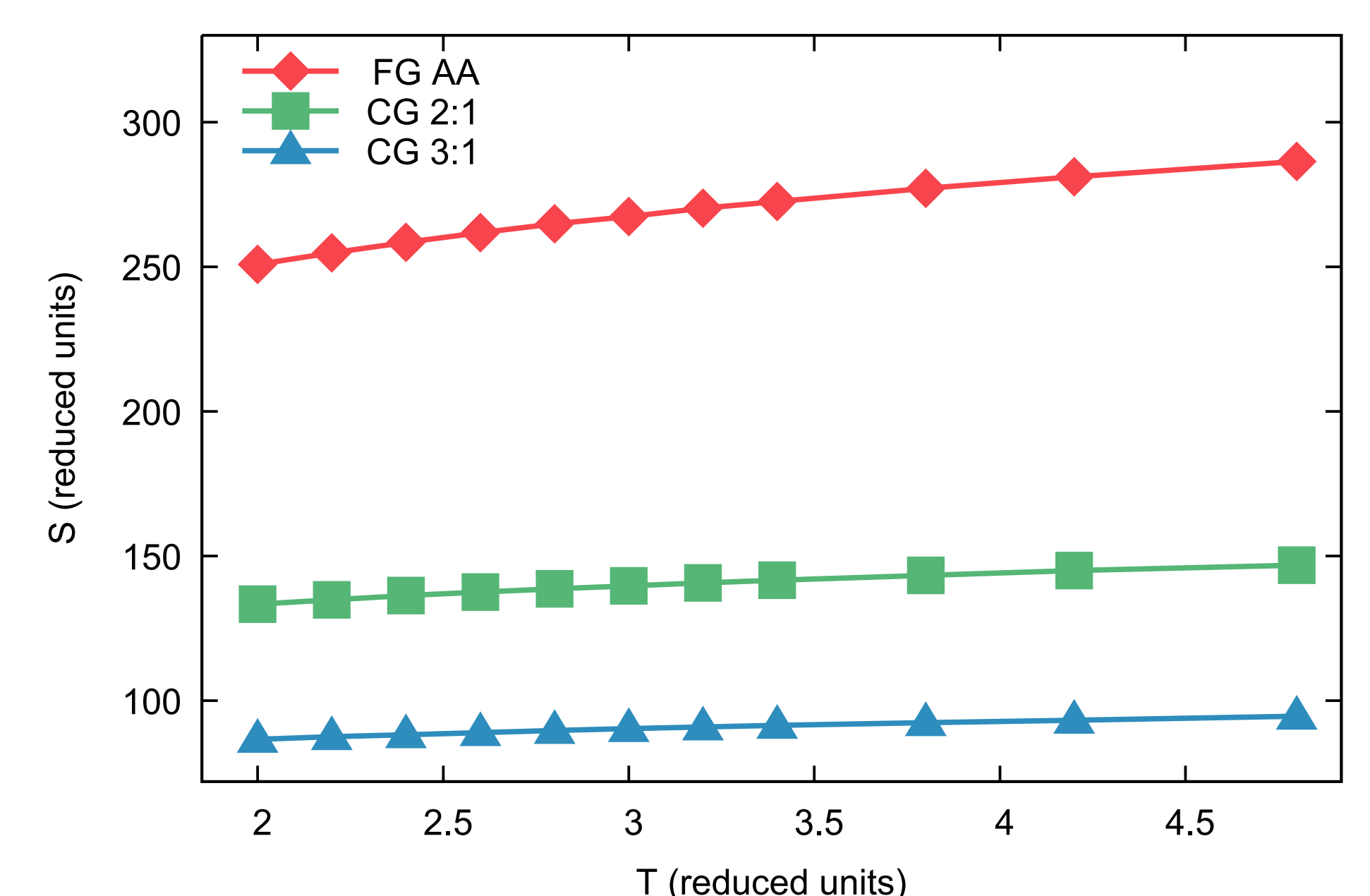

FG AA — CG 2:1 — CG 3:1

Coarse-Grained Derivation

Mean Square Displacement
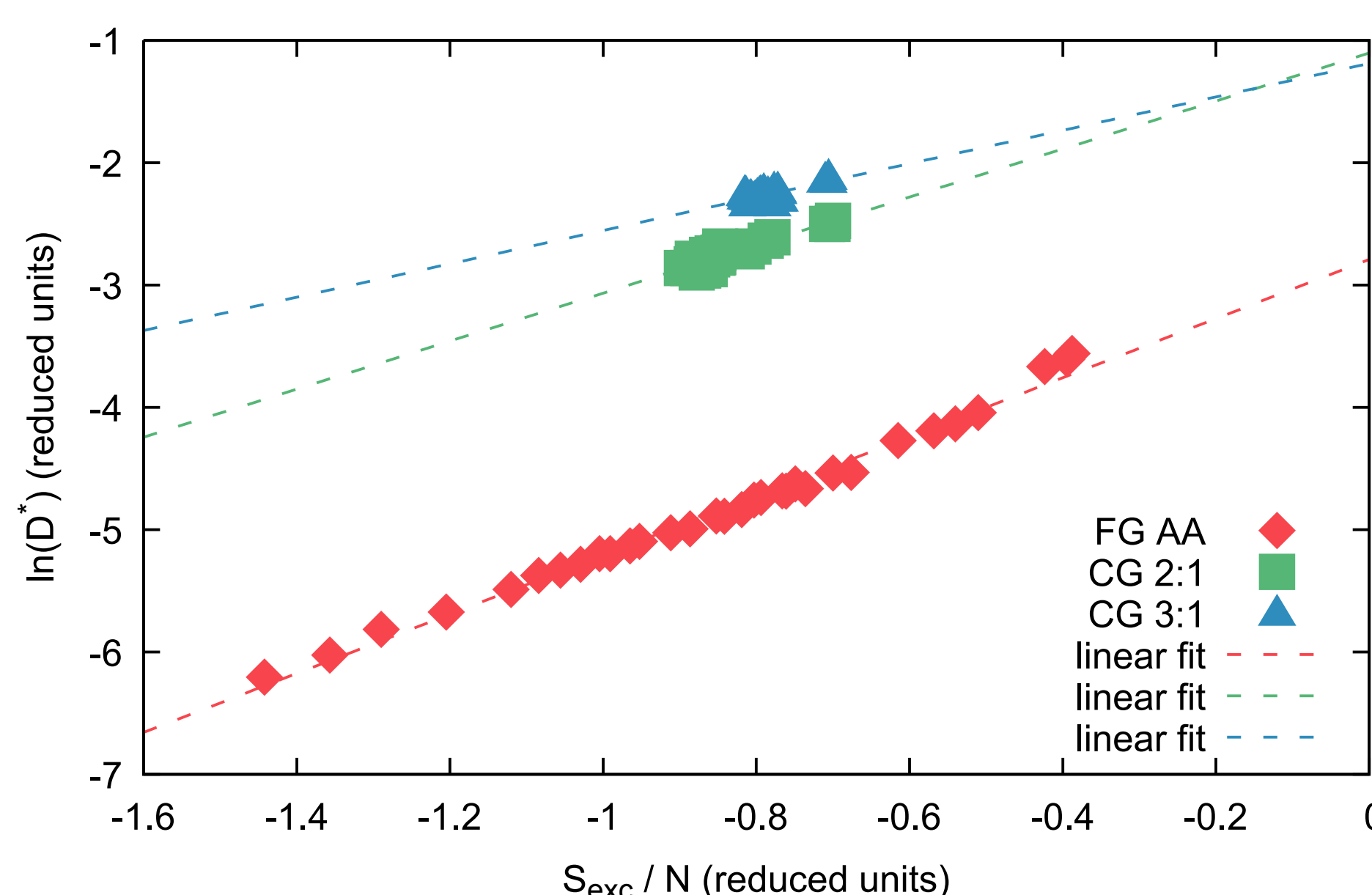

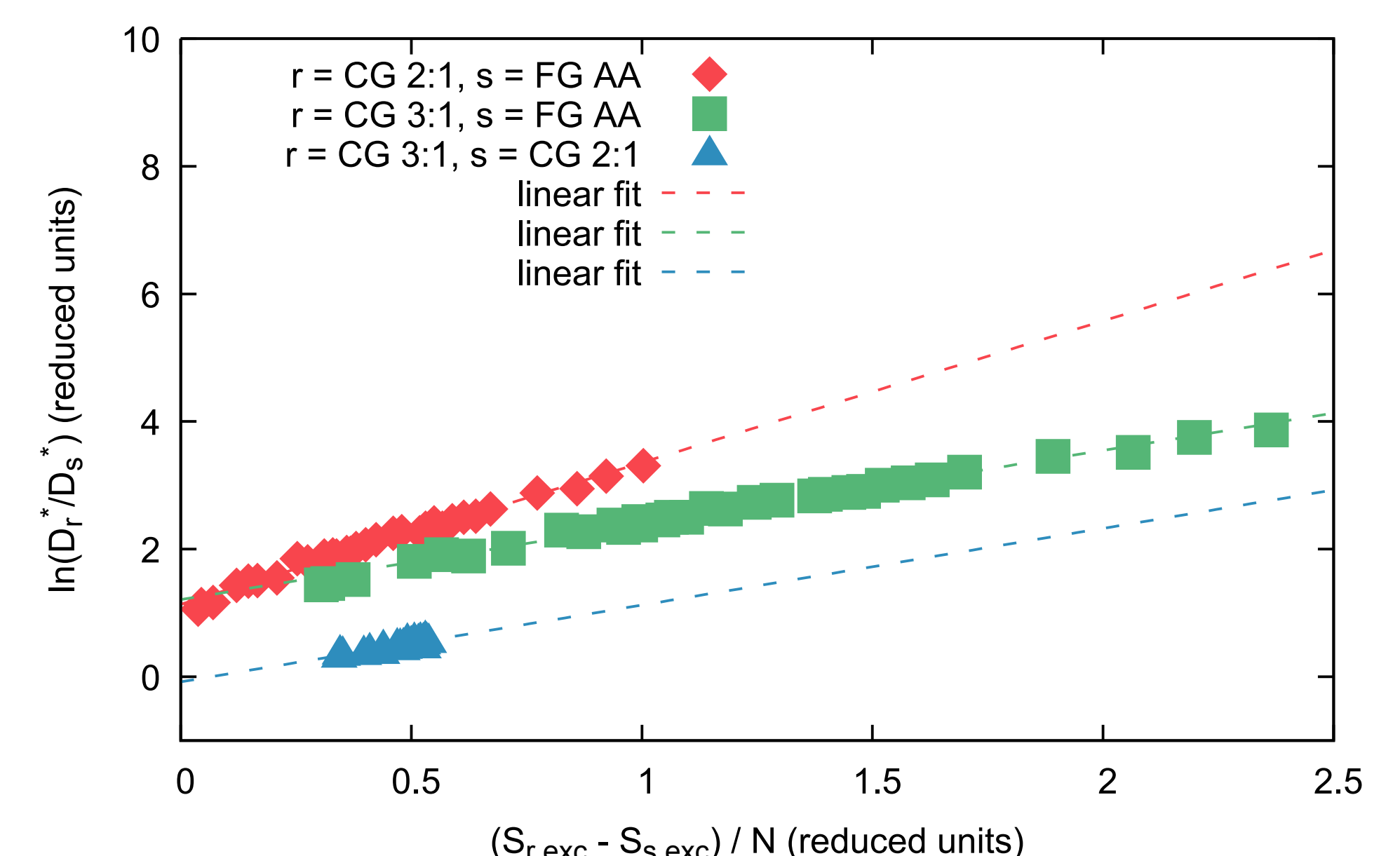
Self-Diffusion Coefficient

Total Entropy

Rosenfeld Scaling

$R^2_{\text{FG}} = 98.2\%$ $R^2_{\text{CG2:1}} = 94.6\%$ $R^2_{\text{CG3:1}} = 87.9\%$

Comparing

$R^2_{\text{CG21-FG}} = 97.9\%$ $R^2_{\text{CG31-FG}} = 98.1\%$ $R^2_{\text{CG31-CG21}} = 91.3\%$

Conclusions and Outlook

- Rosenfeld's excess entropy scaling relation [1] holds for coarse-grained resolutions.
- Excess entropy change due to coarse-graining can be linearly correlated to change in diffusion coefficient.
- **Acceleration of the dynamics is proportional to the entropy loss → Predictions?**
- Next: apply this method to realistic polymer, e.g. polystyrene, and try to predict accelerations.