# Molecular Dynamics Simulations of Spherical Colloid Size Distribution Effects

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## Introduction

The mechanical stability of a colloidal gel depends on isostaticity networks formed during gelation [1, 2]. Molecular dynamics simulations allow a microscopic view into the percolation of these networks. This project uses the open-source simulator LAMMPS to quantify how particle contacts evolve for monodisperse and bidisperse colloidal spheres under a hybrid interaction potential.

## Methods

The Python and LAMMPS scripts used for gel initialization are adapted from a GitHub repository for shearing a polydisperse Morse gel [3]. A pairwise `yukawa/colloid` potential was added to account for long-range Coulombic repulsion.

$$V_{\text{Morse}} = D_0(e^{-2\alpha(r-r_0)} - 2e^{\alpha(r-r_0)})$$

$$V_{\text{Yukawa}} = \frac{A}{\kappa}e^{-\kappa(r-(R_i+R_j))}$$

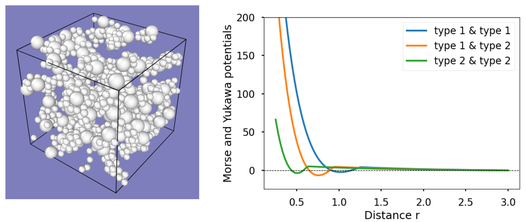


Fig. 1. (Left) Snapshot of simulation box with 1000 particles in OVITO. (Right) Sum of attractive and repulsive potentials applied for each pair of particle types.

- **Spherical particles with adapted potentials.** The adapted code models the colloid particles as monodisperse or bidisperse spheres. For each pairwise potential, a cutoff was defined, and parameters were made dependent on particle diameter.
- **Dissipative Particle Dynamics (DPD) thermostat.** Time integration consistent with the microcanonical ensemble was performed with `dpd/tstat`, which applies a dissipative pairwise force and a random force at every timestep to capture solvent effects so that solvent molecules do not have to be included.

$$\mathbf{F}_{\text{DPD}} = (F_{\text{dissipative}} + F_{\text{random}})\hat{\mathbf{r}_{\mathbf{ij}}}$$

Constant-energy time integration of the classical equations of motion was performed for $10^6$ timesteps of 0.001. DPD causes fluctuations in total potential energy.

### Simulation setup

Simulations were performed in a 3D cubic box with periodic boundary conditions. Quantities are in dimensionless `lj` (Lennard-Jones) units. The default particle diameter is 1.0. For bidisperse gels, some particles were assigned a diameter of 0.5 with probability corresponding to a 0.5 mass fraction (converted to a number fraction). The size of the simulation box was determined by the number density, entered as a separate parameter.

Parameters were chosen arbitrarily; rescaling is necessary before comparing to real systems. See the GitHub repository linked at the right for parameter definitions.

## Effect of pairwise potentials

In simple diffusion, the mean-squared displacement $\Delta x_{\text{MSD}} = \langle (x(t) - x(0))^2 \rangle$ grows linearly with time $t$, and $\log \Delta x_{\text{MSD}}$ grows linearly with $\log t$. A correct implementation of a pairwise potential should slow this growth. See "potential_check."

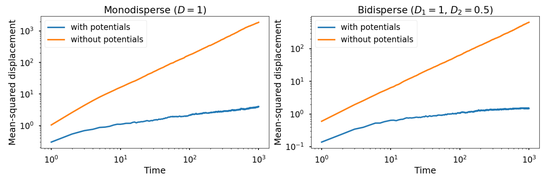


Fig. 2. Mean-squared displacement of 1000 particles with and without pairwise potentials.

The MSD plateaus on a log-log plot, consistent with the arresting effects of gelation.

## Neighbor counts

The number of neighbors of each particle (coordination number) was calculated at fixed time intervals. Particles are considered neighbors when the center-to-center distance is within a specified cutoff.

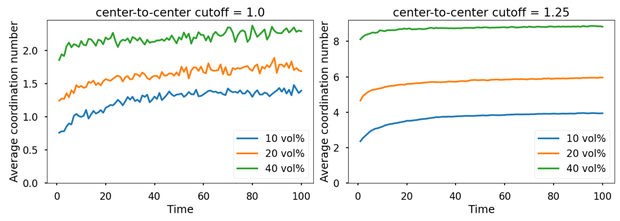


Fig. 3. Evolution of average coordination number in a monodisperse gel ($D = 1$), with two different cutoffs for counting neighbors. The simulation includes 1000 particles.

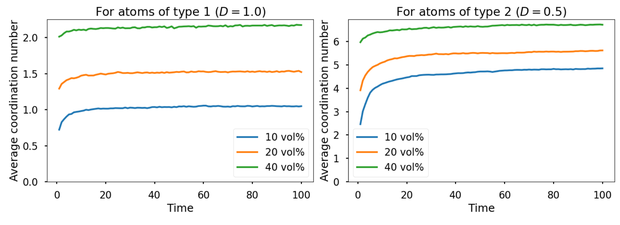


Fig. 4. Evolution of average coordination number in a bidisperse gel, with the $j$ cutoff defined as $(D_i + D_j)/2 + D_i/4$ for particle $i$, so that particles whose surfaces are within $0.25D_i$ of particle $i$'s surface are considered neighbors. The simulation includes 1000 particles ( 500 of each size).

- At the same total volume fraction, atoms with $D = 1$ approach a much lower coordination number when smaller atoms are present (also observed for a surface-to-surface cutoff of 0; see "volumefrac_neighbors" folder).
- At a $0.25D$ surface-to-surface neighbor cutoff, monodisperse gels with $D = 1$ approach similar neighbor counts as particles with $D = 0.5$ in the bidisperse gels.

## Atom-level forces

Force over time was extracted for individual atoms using "forces.py." The normalized autocorrelation function $R$ (defined below) was computed in "plotforces.py."

$$R(F, t_{\text{lag}}) = \frac{\langle F(t)F(t_{\text{lag}})\rangle}{\langle F(t)^2\rangle}$$

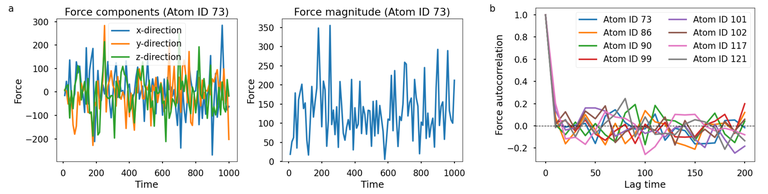


Fig. 5. (a) Force components and magnitude over time for an arbitrarily selected type 1 ($D = 1$) atom in a bidisperse gel with 10 vol% colloid, in the absence of `dpd/tstat`. (b) Autocorrelation function of the force magnitude for a selection of $D = 1$ atoms.

Even when random energy dissipation is excluded, memory of the current force (measured by autocorrelation) decays quickly at the level of an individual atom.

## Conclusions

In a simple model with interacting spheres, post-gelation coordination number depends on particle size distribution at constant colloid volume fraction.

### Future work

Validate the DPD thermostat by including a specific solvent explicitly, and determine the appropriate parameters to enable comparison to experiment.

Vary the temperature and look for changes in the force memory of atoms.

## GitHub repository

This work was conducted as a final project for PHYS 25000 (Autumn 2025). The simulation code can be found at `https://github.com/msong2026/lammps-gels`. Sample LAMMPS scripts by Christopher Ness [4] were also consulted.

## Acknowledgments

I am grateful to members of the Jaeger Lab for providing feedback on my early simulations, and especially to Qinghao Mao for providing assistance with LAMMPS.

## References

[1] Hideyo Tsurusawa et al. "Direct link between mechanical stability in gels and percolation of isostatic particles". In: *Science Advances* 5.5 (2019), eaav6090. DOI: `10.1126/sciadv.aav6090`.

[2] Lilian C. Hsiao et al. "Role of isostaticity and load-bearing microstructure in the elasticity of yielded colloidal gels". In: *Proceedings of the National Academy of Sciences* 109.40 (2012), pp. 16029–16034. DOI: `10.1073/pnas.1206742109`.

[3] Peter Crowther. *Bulk creep Molecular Dynamics simulations*. `https://github.com/merrygoat/creep-sheared-gels`. 2020.

[4] Christopher Ness. "Simulating dense, rate-independent suspension rheology using LAMMPS". In: *Computational Particle Mechanics* 10.6 (2023), pp. 2031–2037. DOI: `10.1007/s40571-023-00605-x`.