

Supplementary Material: Data-driven approximations to the bridge function yield improved closures for the Ornstein-Zernike equation

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POTENTIAL SYSTEMS

Fast-Diverging Potentials:

- Lennard Jones 6-12 (LJ)

$$\phi(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) \quad (1)$$

Lennard Jones is the classical potential used when simulating simple systems. It encapsulates two key effects, hard-sphere repulsion and long range Van der Waals attraction.

We study systems with $\epsilon \in \{0.65, 0.6, 0.55, 0.5\}$, and $\sigma = 1$.

- Morse

$$\phi(r) = \epsilon \left(\exp[-2\alpha(r - r_{min})] - 2 \exp[-\alpha(r - r_{min})] \right) \quad (2)$$

The Morse potential is qualitatively similar to LJ but allows slightly more freedom to tune the shape of the minimum. It is often used to model the interatomic interactions inside diatomic molecules such as N_2 .

We study systems with $\epsilon \in \{0.65, 0.6, 0.55\}$, $\alpha \in \{5, 9\}$, and $r_{min} = 1$.

- Generalised Pseudo-Hard-Sphere

The Mei Potential is a generalised form of LJ that offers more freedom to tune the shape of the potential.

$$\phi(r) = \psi \left(\frac{\lambda_r}{\lambda_a} \right)^\psi \epsilon \left(\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right) \quad (3)$$

where $\psi = \frac{\lambda_r}{\lambda_r - \lambda_a}$.

The Weeks-Chandler-Andersen (WCA) potential [1] is defined by truncating and shifting the LJ potential at its minimum, the resulting potential is purely repulsive. We have constructed the equivalent to WCA for the generalised Mei potential allowing us to test purely repulsive behaviour for a variety of exponents.

$$\phi(r) = \psi \left(\frac{\lambda_r}{\lambda_a} \right)^\psi \epsilon \left(\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right) - \phi_{Mei}(r_c) \quad (4)$$

This form can be used to mimic the discontinuous potential of an idealised hard-sphere system [2].

We study systems with $\epsilon \in \{1.0, 0.6\}$, $(\lambda_r, \lambda_a) \in \{(12, 6), (50, 49)\}$, and $\sigma = 1$.

- DLVO-type potentials

$$\phi(r) = \epsilon_h \left(\frac{\sigma}{r + \delta} \right)^{12} - \epsilon_h \left(\frac{\sigma}{r + \delta} \right)^8 + \epsilon_w \frac{\sigma \exp(-\kappa(r + \delta - 1)^4)}{r + \delta} \quad (6)$$

$$\phi(r) = \epsilon \left(\alpha \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^8 + \left(\frac{\sigma}{r} \right)^4 \right) \quad (7)$$

These two potentials are invented potentials designed to try and mimic the secondary stable minimum seen in DLVO theory.

For (6) we study a system with $\epsilon_h \in \{3, 5, 7\}$, $\epsilon_w = 1$, $\kappa \in \{10, 20, 30\}$, $\delta = 0.3$, and $\sigma = 1$.

For (7) we study systems with $\epsilon = 1$, $\alpha \in \{0.185, 0.2, 0.215, 0.23, 0.245\}$, and $\sigma = 1$.

Step-Diverging Potentials:

- Smooth Step Potential

$$\phi(r) = \epsilon_h \left(\frac{\sigma}{r} \right)^{12} + \frac{\epsilon_s}{1 + \exp[2\kappa(r - \delta)]} \quad (8)$$

Current closure relationships are known to fail for systems with features over multiple length scales making the smooth step a good choice of training system is we want to extend the generalisability of our inferred closure.

We study systems with $\epsilon_h = 1$, $\epsilon_s = 1$, $\kappa \in \{1, 3, 5, 7\}$, $\delta \in \{1, 1.5, 2\}$, and $\sigma = 1$.

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- Continuous Shouldered Well (CSW)

$$\phi(r) = \epsilon_h \left(\frac{\sigma}{r}\right)^{12} + \frac{\epsilon_s}{1 + \exp[2\kappa(r - \delta_s)]} - \epsilon_w \exp\left(-\frac{1}{2} \left(\frac{r - \delta_g}{\chi}\right)^2\right) \quad (9)$$

The CSW model is a core-softened model in the same manner as the smooth step but it has also been shown to recreate physical anomalies seen experimentally in fluids such as water [3].

We study systems with $\epsilon_h = 1$, $\epsilon_s = 2$, $\kappa \in \{2.5, 7.5\}$, $\delta_s \in \{1.2, 1.6\}$, $\epsilon_w = 1$, $\delta_g = 2.0$, $\chi \in \{0.1, 0.2\}$, and $\sigma = 1$.

- Repulsive Shoulder System Attractive Well (RSSAW)

$$\phi(r) = \epsilon_h \left(\frac{\sigma}{r}\right)^{14} - \lambda_1 \tanh(k_1[r - \sigma_1]) + \lambda_2 \tanh(k_2[r - \sigma_2]) \quad (10)$$

The RSSAW model is similar to the CSW model and exhibits the same complex behaviour [4]. Potentials of this form have been reported for colloidal particles and polymer-colloid mixtures making them important for the study of soft matter systems.

We study systems with $\epsilon_h = 1$, $\lambda_1 = 0.5$, $\lambda_2 = 0.3$, $\kappa_1 = 10$, $\kappa_2 = 10$, $\sigma_1 \in \{0.8, 1.15, 1.5\}$, $\sigma_2 \in \{1, 1.35\}$, and $\sigma = 1$.

Slow-Diverging Potentials:

- Soft-Sphere

$$\phi(r) = \epsilon \left(\frac{\sigma}{r}\right)^n \quad (11)$$

The soft-sphere potential is purely repulsive but allows for more interpenetration than other repulsive models.

We study systems with $\epsilon \in \{1, 6\}$, $n \in \{4, 6, 8, 10\}$, and $\sigma = 1$.

- Yukawa

$$\phi(r) = \frac{\epsilon \exp(-\kappa(r - \delta))}{r} \quad (12)$$

The Yukawa potential is a screened coulomb potential that is used to represent the effect of charges in ionic solutions.

We study systems with $\epsilon \in \{2, 4, 6\}$, $\kappa \in \{2.5, 3.5\}$, and $\delta = 0.8$.

Core-Overlapping Potentials:

- Hertzian

$$\phi(r) = \epsilon \left(1 - \frac{r}{r_c}\right)^{5/2} \quad (13)$$

The Hertzian potential effectively describes the interactions between weakly deformable bodies such as globular micelles. Soft-core potentials are qualitatively different from soft-sphere potentials in far as complete overlap is allowed.

We study systems with $\epsilon \in \{4, 6, 8, 10\}$ and $r_c \in \{2, 3\}$.

- Hat

$$\phi(r) = F_{max} \cdot \frac{r - r_c}{\sigma} \cdot \left(\frac{r + r_c}{2r_c} - 1\right) \quad (14)$$

The Hat potential is a standard conservative potential often used in Dissipative Particle Dynamics for simulating coarse grained fluids.

We study systems with $F_{max} \in \{4, 6, 8, 10\}$, $r_c \in \{2, 3\}$, and $\sigma = 1$.

- Gaussian

$$\phi(r) = \epsilon \exp\left(-\frac{1}{2} \left(\frac{r}{\sigma}\right)^2\right) \quad (15)$$

Gaussian shaped potentials have been used as reasonable approximations for the effective interaction between the centres of polymer chains (Flory-Krigbaum potential [5]).

We study systems with $\epsilon \in \{4, 6, 8, 10\}$ and $1/\sigma^2 \in \{1, 1.5, 2\}$.

SIMULATION DETAILS

ESPResSo is a highly flexible open-source Molecular Dynamics package designed for the simulation of soft matter systems. The simulation engine is written in C and C++ but is controlled via a Python interface.

Interaction potentials were specified using regularly spaced tabulated values, these are linearly interpolated in the core to evaluate the forces at each time step.

For each state point investigated the density was specified and the box size was fixed at 20σ where σ is the scale parameter of the density which numerically we set to 1. The number of particles under consideration was scaled accordingly. We consider reduced densities in the range 0.4-0.8 at increments of 0.1.

The system is integrated using the Velocity Verlet algorithm [6, 7]. The resulting global errors in the velocities and positions are $O(\Delta t^2)$. A time step of $\Delta t = 0.005$ was used in this work.

A Langevin thermostat is used to control the system temperature. The Langevin thermostat introduces stochastic momentum fluctuations that both regulate the temperature and are necessary to recreate the fluctuations observed in the canonical ensemble (NVT) making it superior to a rescaling thermostat that would suppress such fluctuations. We opt to set the temperature of the thermostat to $1/K_b$ and adjust energy scales in the parameterisations of the potentials.

To minimise the chances of a quasi-stable solid phase forming particle positions are randomly initialised to ensure a low symmetry starting arrangement. At the start of each simulation run a static energy minimisation is performed via gradient descent without the thermostat to remove any overlaps present between hard-sphere potentials. Warm-up runs were then carried out with the thermostat to allow the system to equilibrate. Equilibrium was taken to be the point at which the kinetic temperature over a short windowing period is consistent with the reference temperature of the thermostat.

For computational efficiency the potentials used are truncated at $r_{cut} = 3\sigma$. The potentials have also been adjusted to fix the potential and force at the cut-off. Often this is treated with caution as it introduces systematic errors when measuring the thermodynamic properties of a reference system. However, as the structural correlation functions are causally determined by Newton's laws their validity is unaffected by adjusting the potential. Verlet lists are used to efficiently handle the truncation of the potential. A skin length of 0.2 times the cut-off length was chosen in line with common practice [8].

The radial distribution function and structure factor were measured from the simulation. To get the structure factor in a timely manner we only take measurements along $\{100\}$ type directions within the system such that evaluating $S(q)$ is $O(N)$ in the number of particles. The default approach that evaluates $S(q)$ for every valid grid

point scales as $O(N^3)$.

In total for each state point 1024 samples were taken at intervals of 16 time steps. The variances were handled using the Flyvbjerg-Peterson blocking approach [9].

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- [1] John D. Weeks, David Chandler, and Hans C. Andersen. Role of repulsive forces in determining the equilibrium structure of simple liquids. *The Journal of Chemical Physics*, 54(12):5237–5247, 1971.
 - [2] J Jover, AJ Haslam, A Galindo, G Jackson, and EA Müller. Pseudo hard-sphere potential for use in continuous molecular-dynamics simulation of spherical and chain molecules. *The Journal of Chemical Physics*, 137(14):144505, 2012.
 - [3] Miha Lukšič, Barbara Hribar-Lee, and Orest Pizio. Phase behaviour of a continuous shouldered well model fluid. a grand canonical monte carlo study. *Journal of molecular liquids*, 228:4–10, 2017.
 - [4] Yu D Fomin, EN Tsiok, and VN Ryzhov. Complex phase behavior of the system of particles with smooth potential with repulsive shoulder and attractive well. *The Journal of chemical physics*, 134(4):044523, 2011.
 - [5] P. J. Flory and W. R. Krigbaum. Statistical mechanics of dilute polymer solutions. ii. *The Journal of Chemical Physics*, 18(8):1086–1094, 1950.
 - [6] Loup Verlet. Computer "experiments" on classical fluids. i. thermodynamical properties of lennard-jones molecules. *Phys. Rev.*, 159:98–103, 1967.
 - [7] William C. Swope, Hans C. Andersen, Peter H. Berens, and Kent R. Wilson. A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters. *The Journal of Chemical Physics*, 76(1):637–649, 1982.
 - [8] Daan Frenkel and Berend Smit. *Understanding Molecular Simulation*. Academic Press, Inc., 2001.
 - [9] Henrik Flyvbjerg and Henrik Gordon Petersen. Error estimates on averages of correlated data. *The Journal of Chemical Physics*, 91(1):461–466, 1989.