

Effect of shape anisotropy on the precipitation of dimeric nanoparticles

Md Moinuddin and Kaustubh Rane

Discipline of Chemical Engineering, Indian Institute of Technology Gandhinagar, Gujarat, India-
382355

Grand Canonical Transition Matrix Monte Carlo Simulations:

An efficient Transition Matrix Monte Carlo simulation algorithm was given by Fitzgerald *et al.* to study magnetic susceptibility and interfacial tension of 2D-Ising systems.¹ Later, it was implemented by Errington in isothermal-isobaric and grand canonical simulations.² We use Grand Canonical Transition Matrix Monte Carlo (GC-TMMC) method used by Errington to study our dimeric nanoparticles. The transition matrix Monte Carlo (TMMC) is a book-keeping scheme that allows biasing the GCMC simulations to adequately sample intermediate densities, meanwhile the unbiased probability distributions are also computed.^{1,2}

In standard Monte Carlo simulations by Metropolis *et al.*³ a new microstate t is generated from the old microstate s with a probability, $p(s \rightarrow t)$. The attempted new microstate t is accepted with an acceptance probability, $acc(s \rightarrow t) = \min \left[1, \frac{\pi(t)}{\pi(s)} \right]$. Here, $\pi(s)$ and $\pi(t)$ are probability of observing in microstate s and t , respectively. If the macrostates corresponding to the microstates s and t are denoted by S and T , respectively, then $\Pi(T) = \sum_{n \in N} \pi(t)$ and $\Pi(S) = \sum_{n \in N} \pi(s)$. Here, $\Pi(T)$ is the probability of observing the system in macrostate T . At each step, the attempted transitions are stored in a collection matrix,

$$C(S \rightarrow T) = C(S \rightarrow T) + acc(s \rightarrow t) \quad (1)$$

$$C(S \rightarrow S) = C(S \rightarrow S) + 1 - acc(s \rightarrow t) \quad (2)$$

The transition of system from macrostate S to T is given by macrostate transition probability,

$$P(S \rightarrow T) = \frac{C(S \rightarrow T)}{\sum_{\Delta S} C(S \rightarrow S + \Delta S)} \quad (3)$$

Using macrostate transition probability, the macrostate probability is obtained using detailed balance as follows.

$$\Pi(S)P(S \rightarrow T) = \Pi(T)P(T \rightarrow S) \quad (4)$$

For a single macrovariable, neighboring macrostates are attempted using the microstate transitions. In cases, where required states have relative transition probabilities differing by large values, makes it difficult to sample all the states connecting the two required states. Therefore, a biasing is applied to pass through all the states within the path of the required states. It is done using a weighting function $\eta(S)$, which helps in sampling all the states and is given by

$$\eta(S) = -\ln\Pi(S) \quad (5)$$

The acceptance criteria is modified as

$$acc(s \rightarrow t) = \min \left[1, \frac{\eta(t)\pi(t)}{\eta(s)\pi(s)} \right] \quad (6)$$

However, even after biasing, update of the collection matrix $C(S \rightarrow T)$ is done using unbiased acceptance criterion. For GC-TMMC, S and T denote different number of dimers/molecules in the simulation box. Typically, we only allow changes to adjacent states. For example, if $S \equiv N$ (number of dimers), then $T = N + 1$ or $N - 1$.

We start the GC-TMMC simulation with an empty cubic box of size $V = 1000D^3$. We attempt 30% particle displacement moves and 70% particle insertion and deletion moves. During insertion, the particle is rotated randomly and inserted, taking care of the rotational degree of freedom. A histogram of the number of visits to different states are observed. Since, it is a flat histogram technique, getting a smooth flat histogram of number of visits confirms a good sampling and equilibration. We use four-five independent runs to calculate an average property value. Since, we use massively parallel code (MPI), the time and number of cores used depend on the supercomputing facility used.

Relative chemical potential

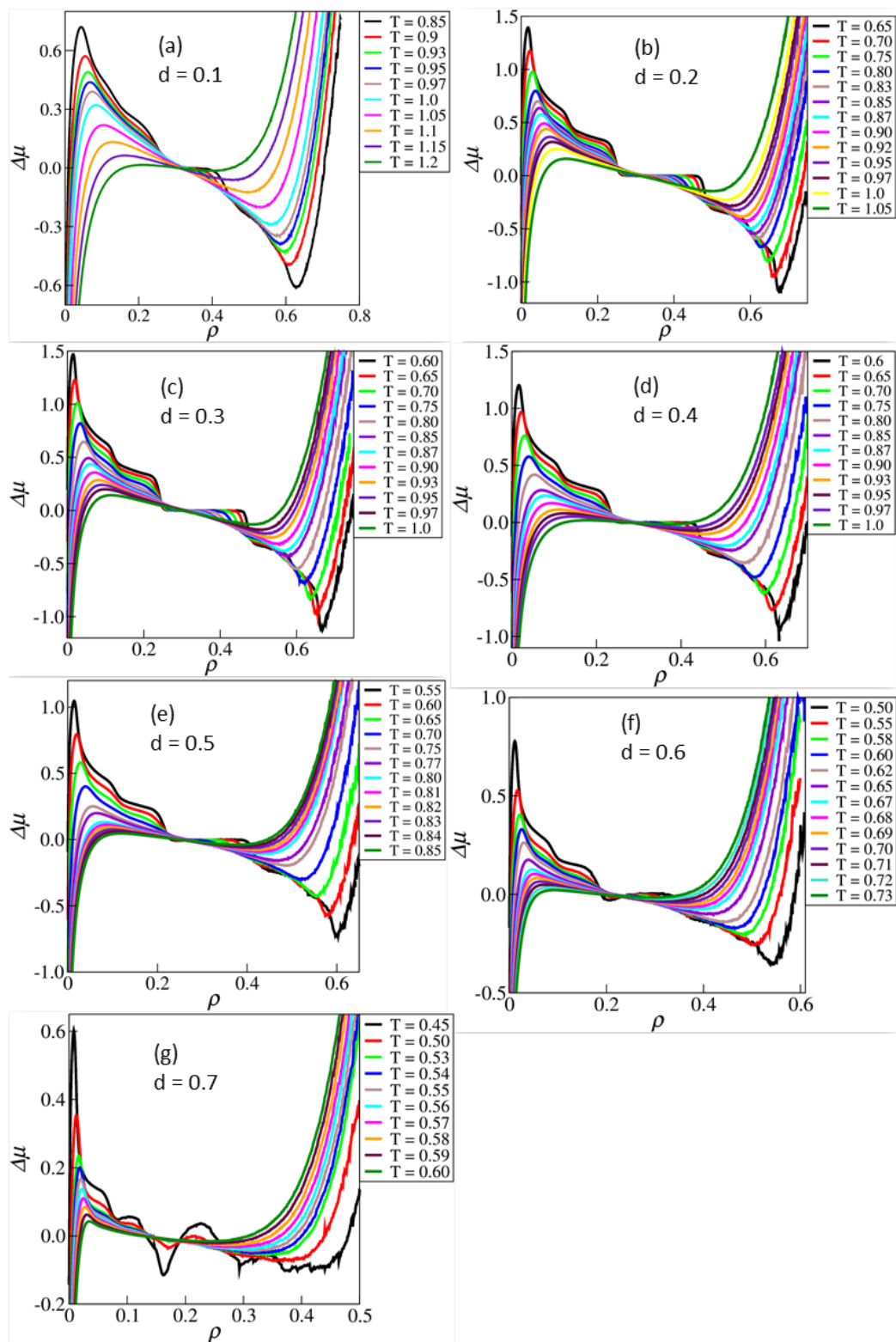


Figure S1. Relative chemical potential as a function of density (ρ) for dimers with $d = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6,$ and 0.7 with varying temperatures (T).

Simulation snapshots of dense phase for the seven dimers

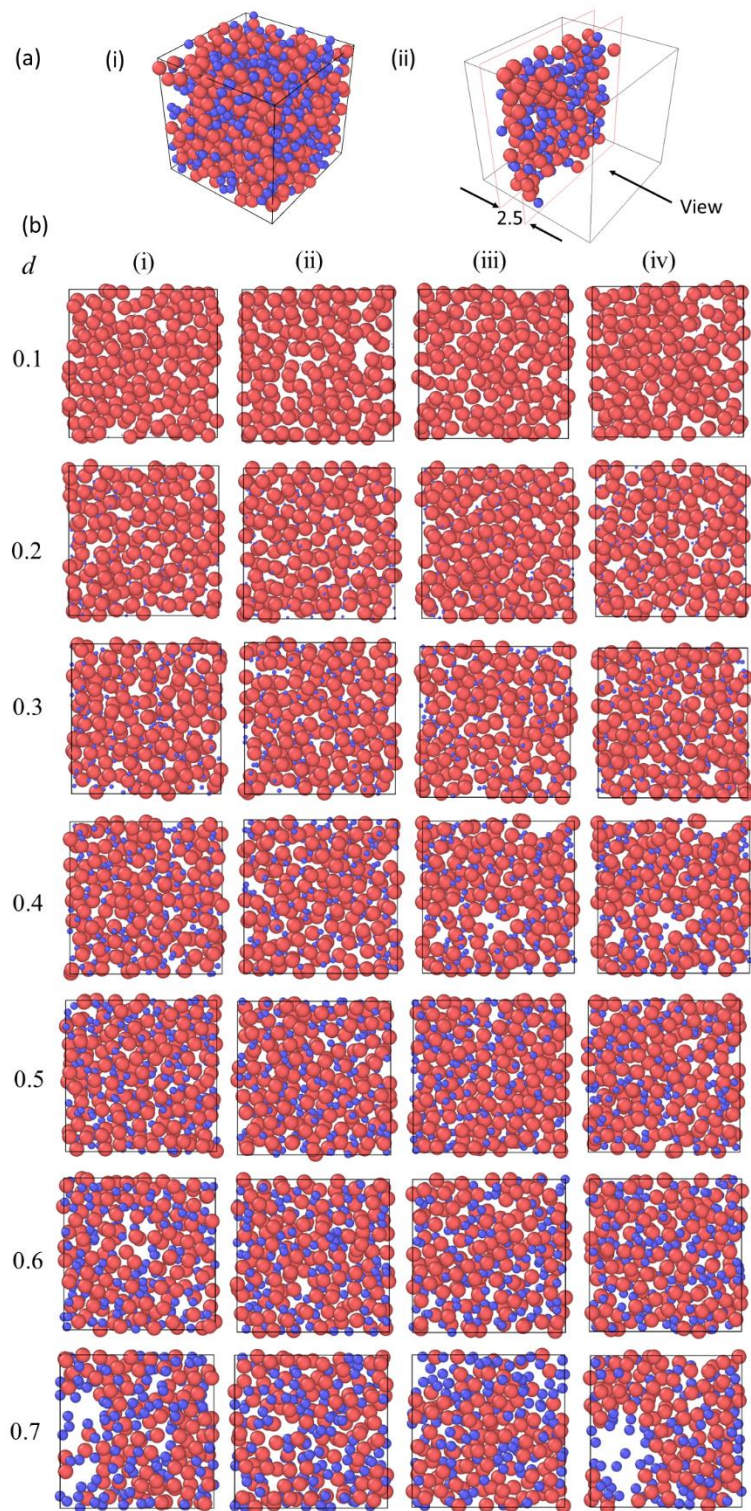


Figure S2. Snapshots from the grand canonical Monte Carlo (GCMC) simulations for the densities close to the coexisting dense phases (ρ_l) of seven dimers at $\frac{T}{T_c} = 0.725$. a) Figure showing the creation of slabs from the three-dimensional snapshot to view the internal structure. The arrow shows the viewing direction. We divide the simulation cell along x -axis into four slabs of thickness 2.5. Each slab only shows the particles whose centers are within the dimensions of the slab. Note that the snapshots are taken from the simulations performed with periodic boundary conditions along x, y and z directions. b) The dense phase configurations of seven dimers. Rows from top to bottom denote configurations of dimers with $d = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$, and 0.7 , respectively. Columns from left to right are slabs whose centers are located at different distances from one face of the simulation cell. Note that no two slabs overlap.

Discussions of simulations snapshots (Figures S2-S4) are presented in the discussions of Figure 7 of the main manuscript.

Simulation snapshots of dense phase for the seven dimers

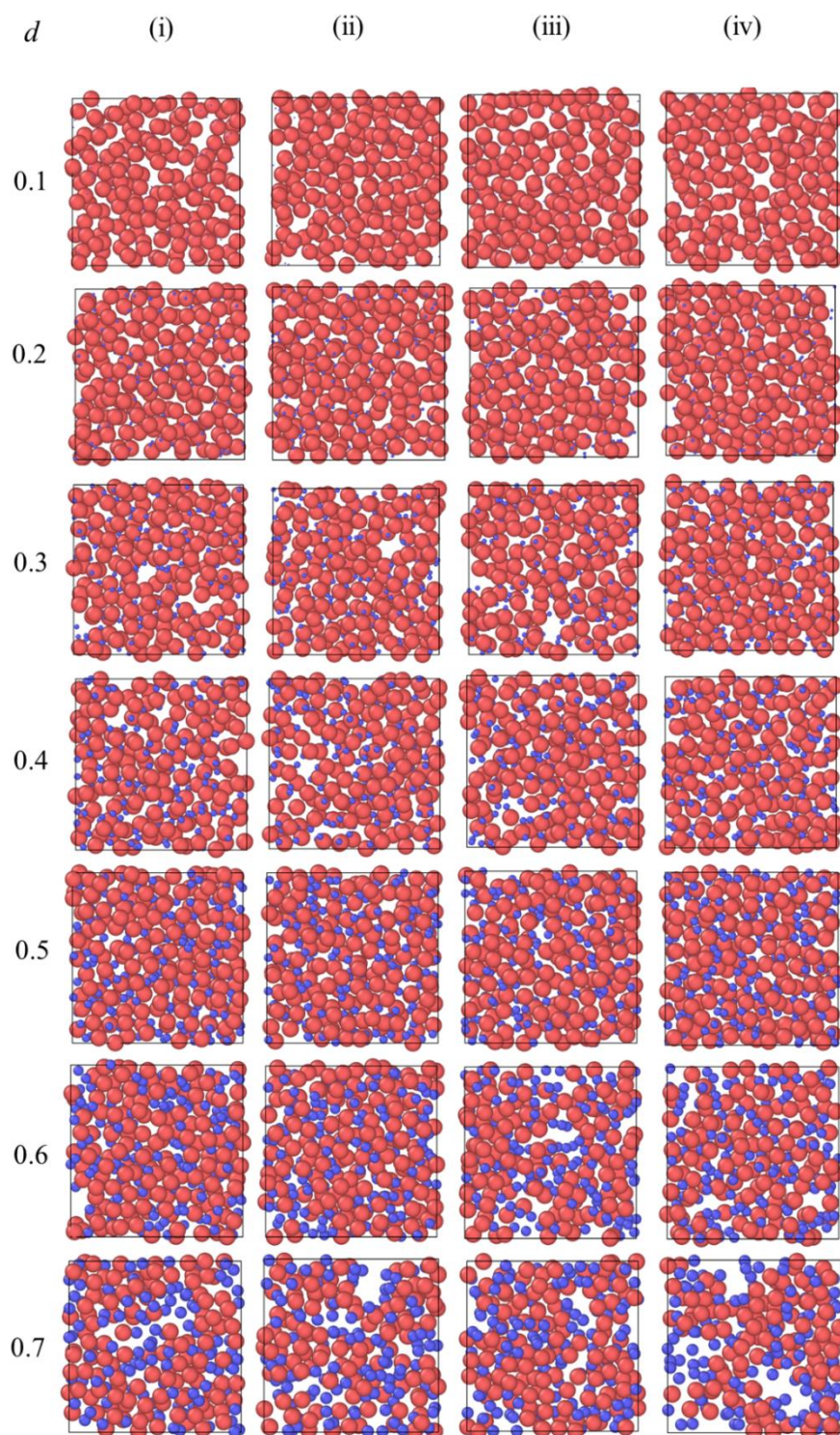


Figure S3. Same as the caption of Figure S2.

Simulation snapshots of dense phase for the seven dimers

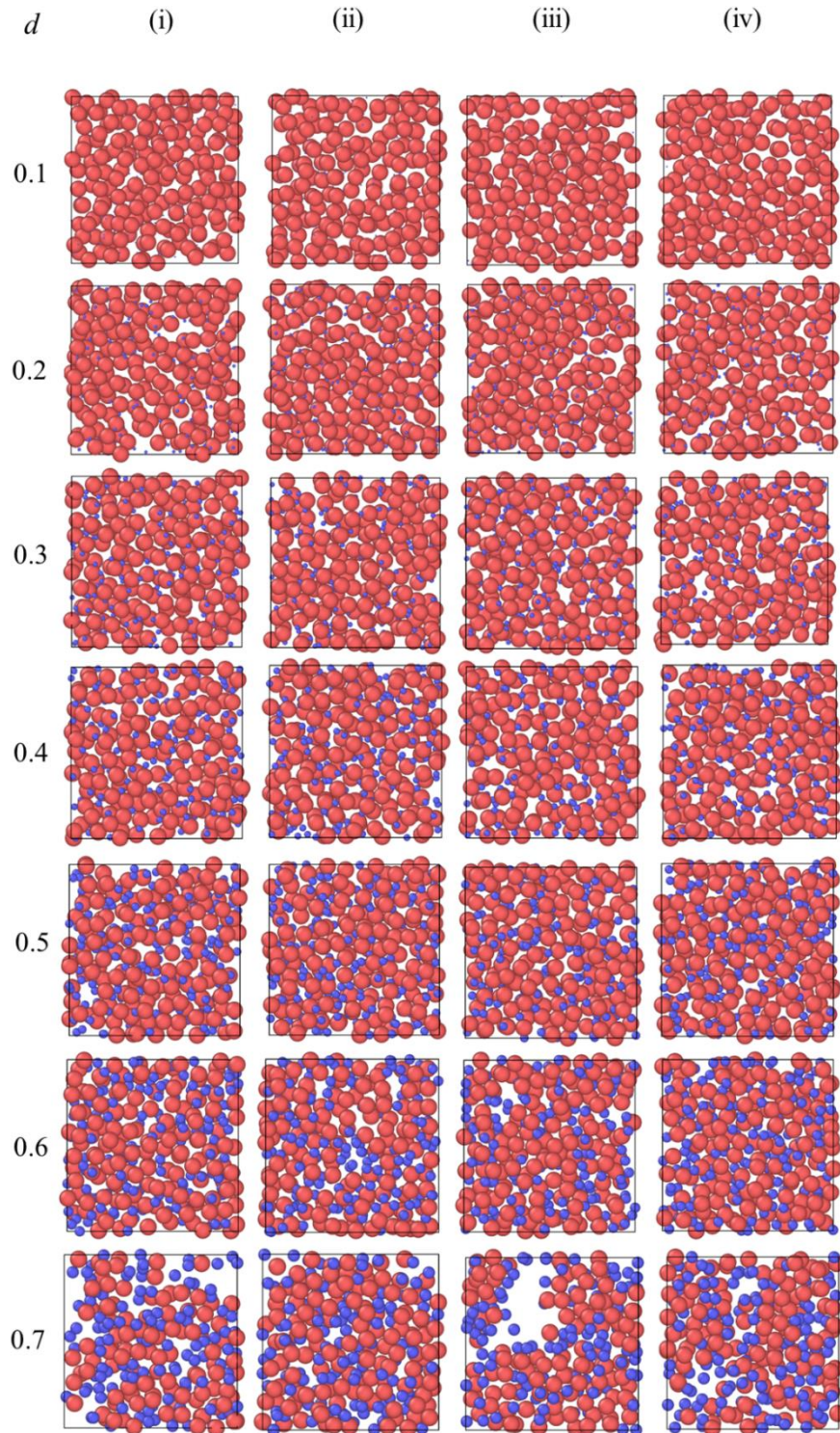


Figure S4. Same as the caption of Figure S2.

Simulation snapshots of Figure S2 to S4 including Figure 7 are obtained using Ovito-an open visualization tool.⁴

Radial distribution function of dense phase for the seven dimers

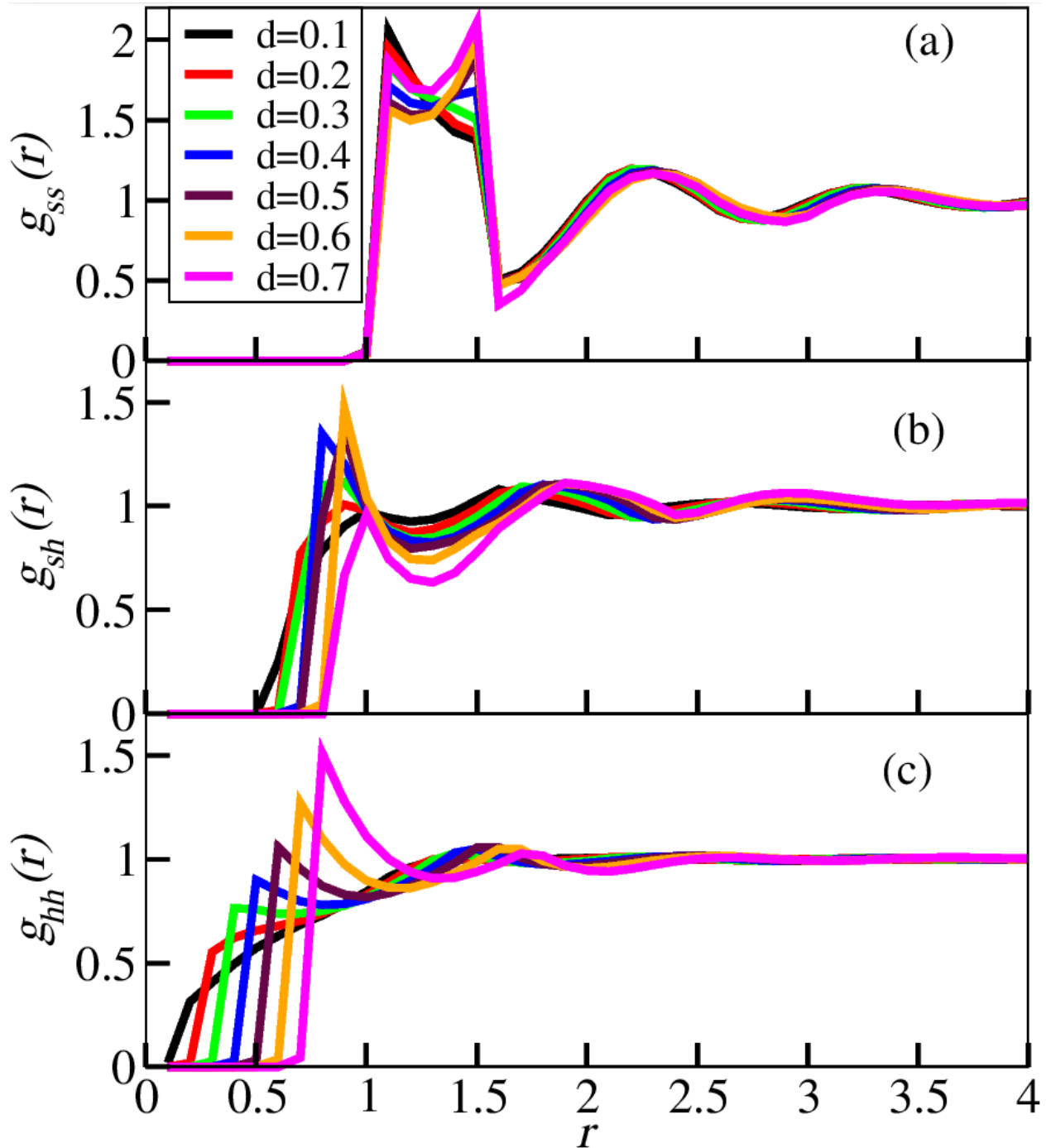


Figure S5. Radial distribution function of the precipitated phase close to the dense phase peak of $\ln\Pi$ vs ρ at $T/T_c = 0.725$ between (a) attractive sites, $g_{ss}(r)$, (b) attractive-hard sphere sites, $g_{sh}(r)$, and (c) hard sphere sites, $g_{hh}(r)$ for hard sphere diameters, $d = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6,$ and 0.7 . Black, red, green, blue, brown, orange, and magenta curves represent values for $d = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6,$ and 0.7 , respectively.

References

- 1 M. Fitzgerald, R. R. Picard and R. N. Silver, *Europhys. Lett.*, 1999, **46**, 282–287.
- 2 J. R. Errington, *J. Chem. Phys.*, 2003, **118**, 9915–9925.
- 3 N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, *J. Chem. Phys.*, 1953, **21**, 1087–1092.
- 4 A. Stukowski, *Modelling Simul.Mater. Sci. Eng.*, 2010, **18**, 015012