Hierarchical Self-Assembly in Binary Colloidal Systems

Jesse Funkhouser

The University of Texas at San Antonio, San Antonio TX, 78249

Name: *Jesse Funkhouser*
Status: *Junior, Undergraduate Student*
Department: *Chemical Engineering*
Area of Study: *Fuel & Energy*
UTSA Mentor(s):
Dr. Abelardo Ramirez-Hernandez
Dr. Luis Adrian Padilla Salas

WeARE Research Area

This research utilizes computational modeling of colloidal nanocrystals for energy applications. Colloidal nanocrystals can be created by grafting organic ligands onto hard core materials. Given the vast availability of organic ligands to choose from, colloidal nanocrystals of various structures and properties can be customized by tuning effective interaction potentials and manipulating the thermodynamic environment.

Motivation or Background

Although there are many loose definitions, a colloid may be considered as a microscopically heterogeneous system where one component has dimensions in between those of molecules and those of macroscopic particles [1]. Some popular examples include milk (liquid-liquid), smoke (solid-gas), and toothpaste (solid-liquid). Colloidal nanocrystals offer a rich platform to design materials with exquisite functionalities, including electronic and optoelectronic properties. Thus, the understanding of the fundamental processes leading to the self-assembly of these colloids can provide design rules to create new functional materials. By employing a coarse-grained model of two-dimensional colloidal phase behavior, extensive computer simulation experiments can take the place of physical experimentation and save time and money. The analysis provided herein provides a fundamental basis designed to be further explored. The various crystal structures revealed are only a small fraction of the possible structures that can be found with this approach, and with the immense number of distinct phases come distinguishing properties, such as unique responses to electromagnetic waves, that can be applied to optical technologies.

Objectives

1. Simulate various thermodynamic environments for a binary colloidal system at different compositions, by employing thermal annealing at different densities.
2. Explore resultant crystal structures and their dependence on temperature and density.

Methodology and Results

The interaction potentials between A and B particles were defined using a repulsive shoulder potential and the inspection of phase behaviors were executed by molecular dynamics simulations in the NVT (number-volume-temperature) ensemble. All calculations were performed using HOOMD-blue [3,4]. All visualizations were done with OVITO [2]. The first set contained 7225 particles, with a mole fraction of 0.35 B-particles. The parameter space of reduced densities and reduced temperatures (ρ^*, T^*) included $\rho^* \in [0.6, 1.4]$ in steps of $\delta\rho^* = 0.1$ and $T^* \in [0.10, 0.70]$ in steps of $\delta T^* = 0.05$. The second set contained 4000 particles, with a mole fraction of 0.5 B-particles. The parameter space included $\rho^* \in [0.6, 1.4]$ in steps of $\delta\rho^* = 0.1$ and $T^* \in [0.30, 0.70]$ in steps of $\delta T^* = 0.05$. The third and final set also contained 4000 particles, with a mole fraction of 0.7 B-particles. The parameter space included $\rho^* \in [0.6, 1.4]$ in steps of $\delta\rho^* = 0.1$ and $T^* \in [0.35, 0.70]$ in steps of $\delta T^* = 0.05$. Pictured below are examples of resultant structures.

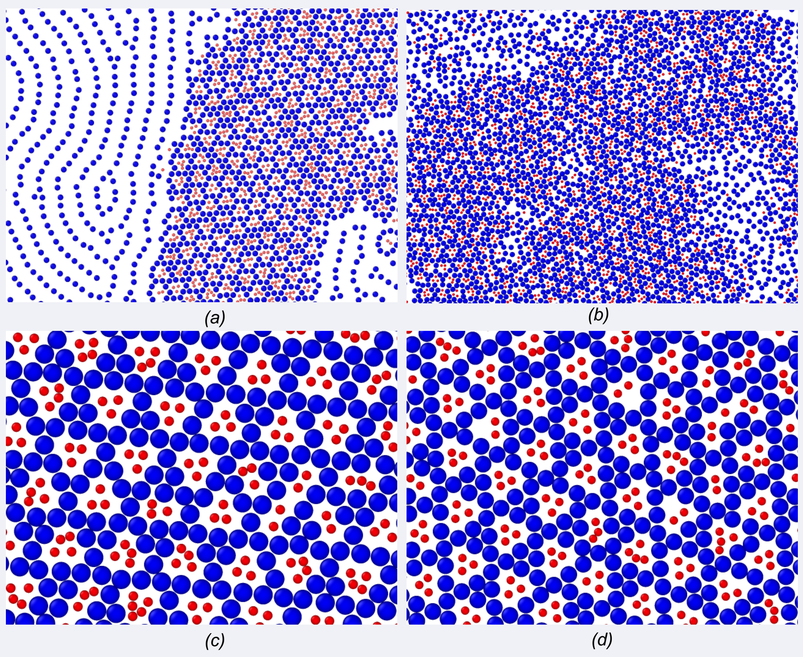

Fig. 1 – x_B=0.35

(a) ρ=0.6, T*=0.10. Solid. Lamellar lattice of A. Honeycomb lattice of A. Triangular forms of B inside honeycomb. (b) ρ*=0.9, T*=0.70. Three phases present: gas A and B (top left, bottom right), liquid A and B (positive diagonal), triangular lattice of B (bottom, center). (c) ρ*=0.9, T*=0.10. Solid. Triangular lattice of B inside triangular lattice of A. (d) ρ*=1.0, T*=0.20. Solid. Similar organization to (c).*

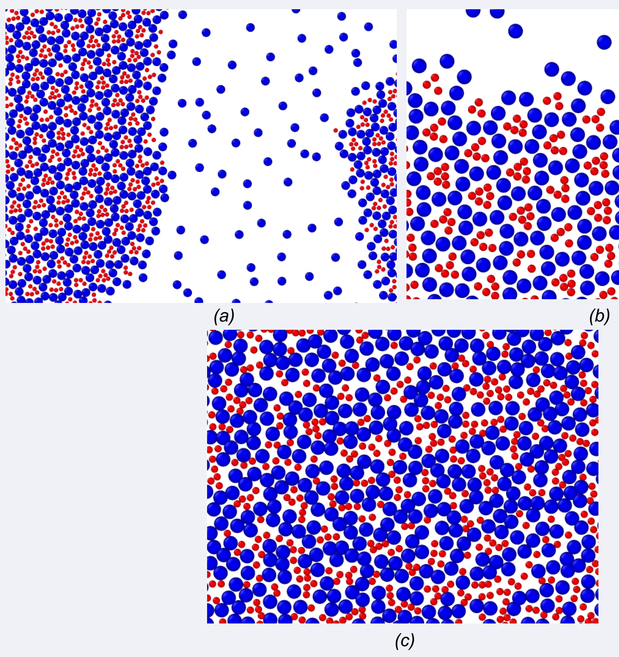

Fig. 2 – x_B=0.50

(a) ρ=0.6, T*=0.40. Coexistence. Honeycomb lattice of A and clusters of about 6 B particles in triangular shared with gaseous A phase. (b) ρ*=0.7, T*=0.3. Similar construction to (a). (c) ρ*=1.4, T*=0.7. Liquid A and B.*

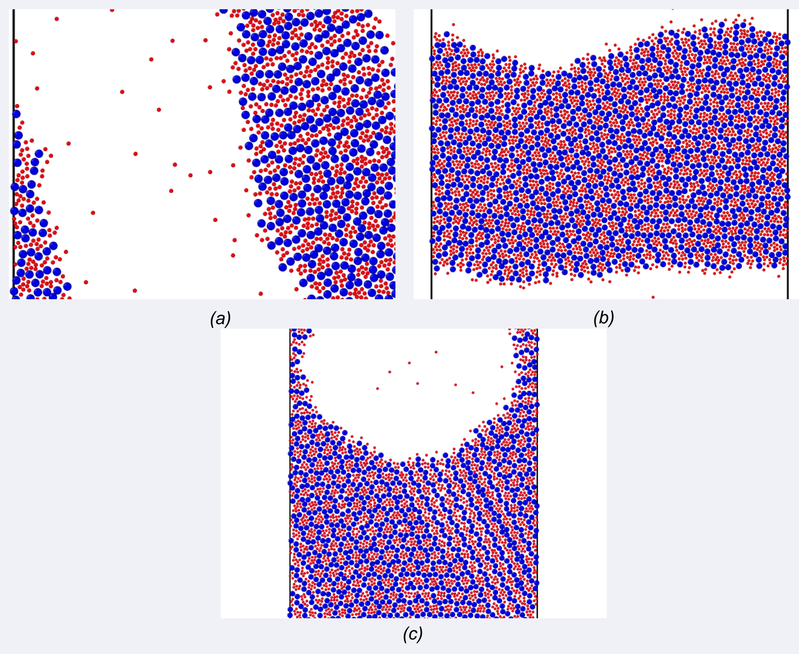

Fig. 3 – x_B=0.70

(a) ρ=1.0, T*=0.70. Coexistence. Rods of A and B merge into honeycomb lattice of A that contains large clusters of B. (b) ρ*=0.7, T*=0.35. Solid. Loosely organized, glass-like phase of A and B. (c) ρ*=1.2, T*=0.55. Solid. Like (a), rod and honeycomb lattices are interchangeable.*

Skills and Experience

- Conceptual knowledge of soft matter including polymers and colloids and their thermodynamic properties
- Foundational knowledge of molecular dynamics simulations
- Python coding familiarity and applicability
- MATLAB coding capabilities
- Spreadsheet utilization
- Use of High-Performance Computing Systems

What I Learned

I have expanded my knowledge of chemistry through the study of soft matter such as polymers and colloids. I also dove into the pool of coding and built a solid foundation in the Python and MATLAB languages. This foundation was then applied to the use of UTSA's cluster computer Shamu where HOOMD software was used to perform calculations. These results were then analyzed through the use of various software including the visualization programs Ovito and VMD.

Future Plans

Further analysis will be performed in order to build a more complete representation of the physical properties of the colloid system. This will include but is not limited to thermodynamic descriptors relating to density such as internal energy, pressure, compressibility factor, and specific heat, radial distribution functions, bond orientational order parameters, and phase diagrams.

Acknowledgments

This work is supported by the USDA National Institute of Food and Agriculture, Interdisciplinary Hands-on Research Traineeship and Extension Experiential Learning in Bioenergy/Natural Resources/Economics/Rural project, U-GREAT (UnderGraduate Research, Education And Training) program (2016-67032-24984).

References

[1] Hamley, I. W. *Introduction to Soft Matter – Revised edition, 2007.*
[2] A. Stukowski, Visualization and analysis of atomistic simulation data with OVITO – the Open Visualization Tool Modelling Simul. Mater. Sci. Eng. 18 (2010), 015012
[3] J. A. Anderson, C. D. Lorenz, and A. Travesset. General purpose molecular dynamics simulations fully implemented on graphics processing units Journal of Computational Physics 227(10): 5342-5359, May 2008. 10.1016/j.jcp.2008.01.047
[4] J. Glaser, T. D. Nguyen, J. A. Anderson, P. Lui, F. Spiga, J. A. Millan, D. C. Morse, S. C. Glotzer. Strong scaling of general-purpose molecular dynamics simulations on GPUs Computer Physics Communications 192: 97-107, July 2015. 10.1016/j.cpc.2015.02.028