

Egorov Research Group

Fall Recap

December 4th, 2023

Mohan Shankar



Transition State Theory (TST)

Background:

- Developed to explain chemical reaction rates
- Assumes particles behave classically

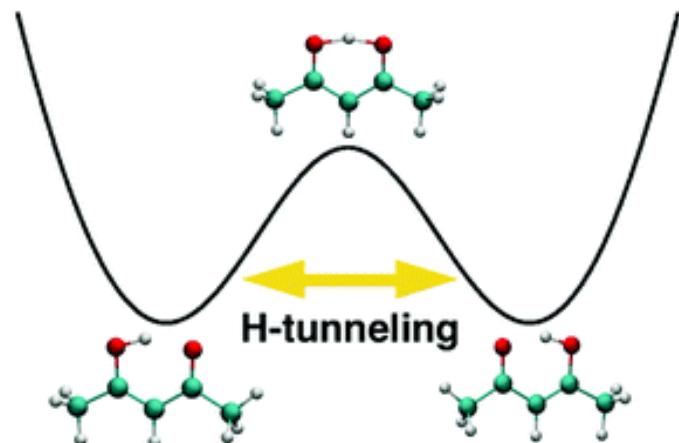
Arbitrary Elementary Rxn.



$$\text{rate} = k [A]^a + [B]^b$$

Examples:

- Nuclear reactions
- R-H functionalization rxns in catalysis



Phys. Chem. Chem.
Phys., 2021, 23, 7758

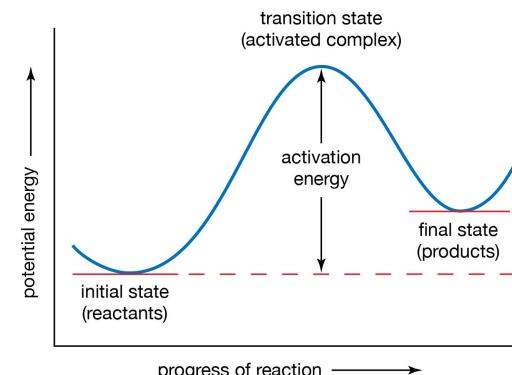
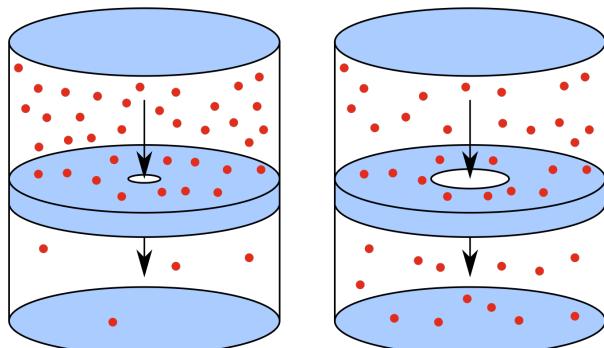
Quantum Effusion

Overview:

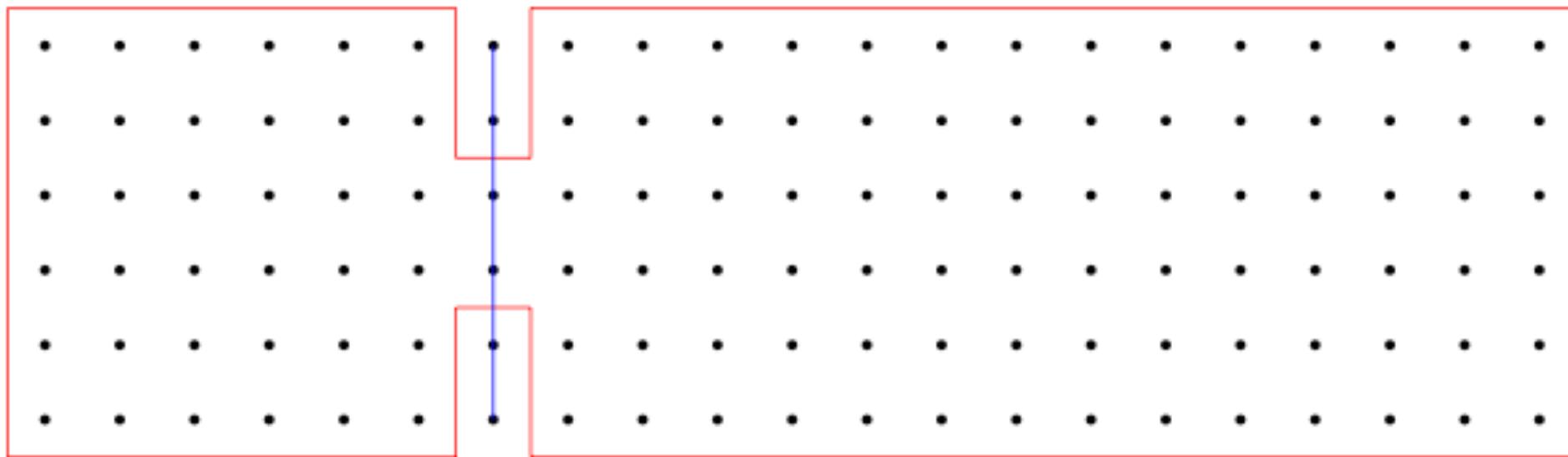
- Use modified 2D Particle-in-a-Box (P.I.B.) to model effusion → find exact thermal rate constants

Goal:

- Compare exact results to validate ring polymer molecular dynamics (RPMD) results → Quantum Transition State Theory (QTST)

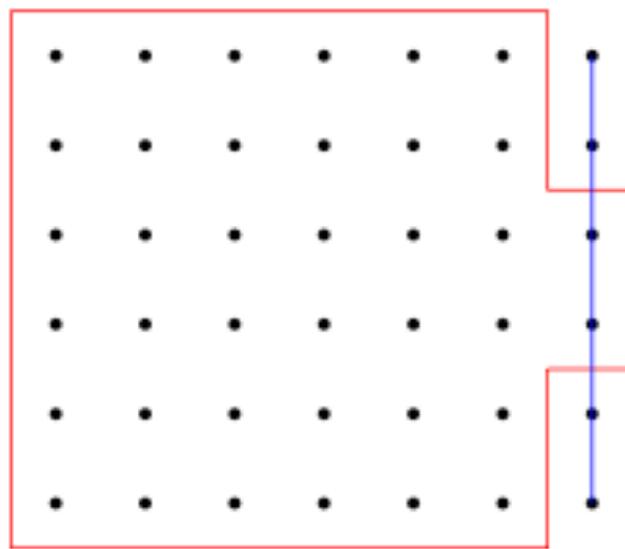


The System

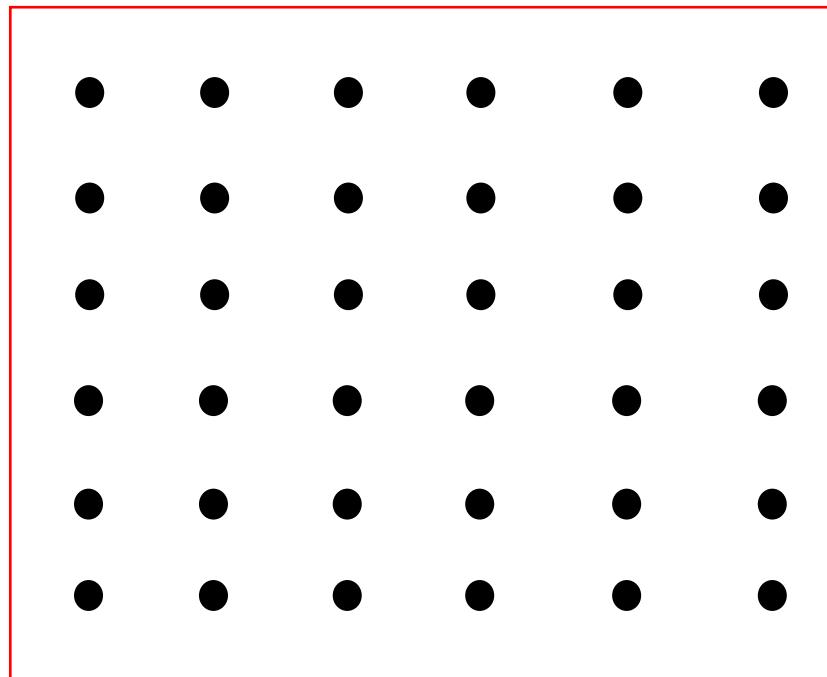


Sigurðarson, A.E. Calculation of the Quantum Mechanical Effusion Rate out of a 2D Box. BSc. Dissertation, School of Engineering and Natural Sciences University of Iceland, 2021.

The System



The System



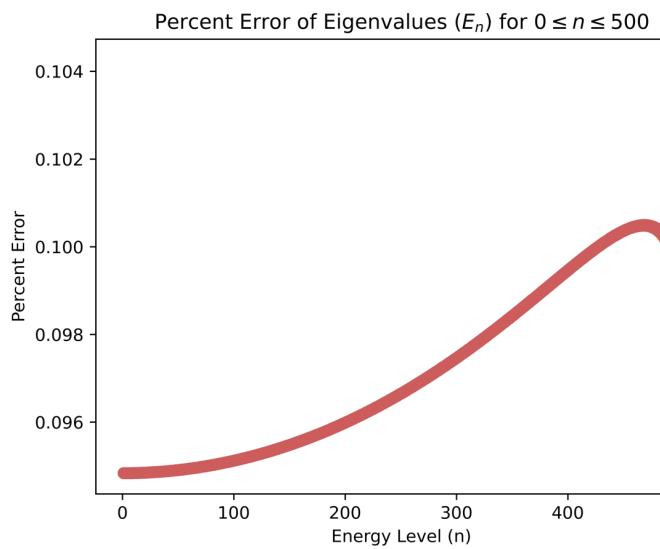
Walls $\rightarrow \psi = 0$
Inside the Box $\rightarrow \psi \neq 0$

Methods

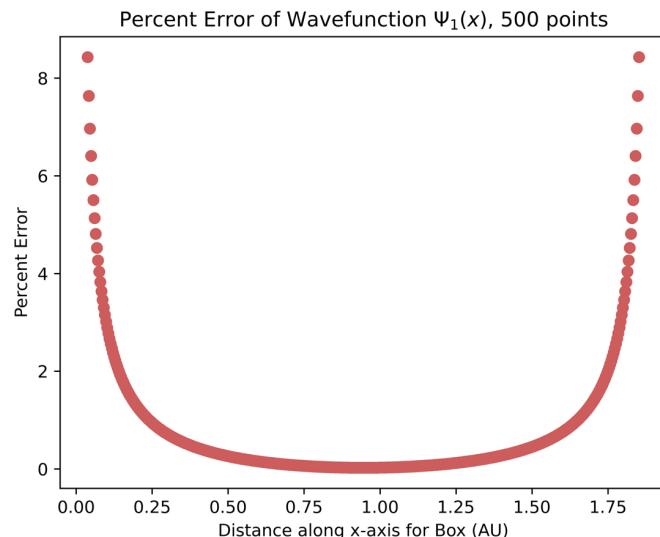
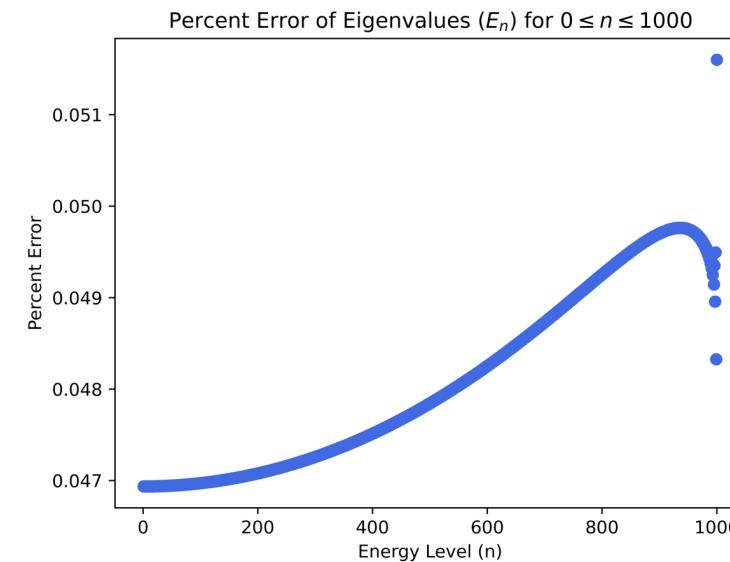
- Construct Hamiltonian Matrix
- Solve Time-Independent Schrödinger Equation ($\hat{H}\psi = E\psi$) at each point in the box
- Return eigenvalues and eigenvectors

$$\begin{bmatrix} \bullet & \bullet & \bullet \end{bmatrix} \xrightarrow{\text{Apply weights}} \begin{bmatrix} -\frac{\pi^2}{3} & \frac{2}{1^2} & -\frac{2}{2^2} \\ \frac{2}{1^2} & -\frac{\pi^2}{3} & \frac{2}{1^2} \\ -\frac{2}{2^2} & \frac{2}{1^2} & -\frac{\pi^2}{3} \end{bmatrix} * -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

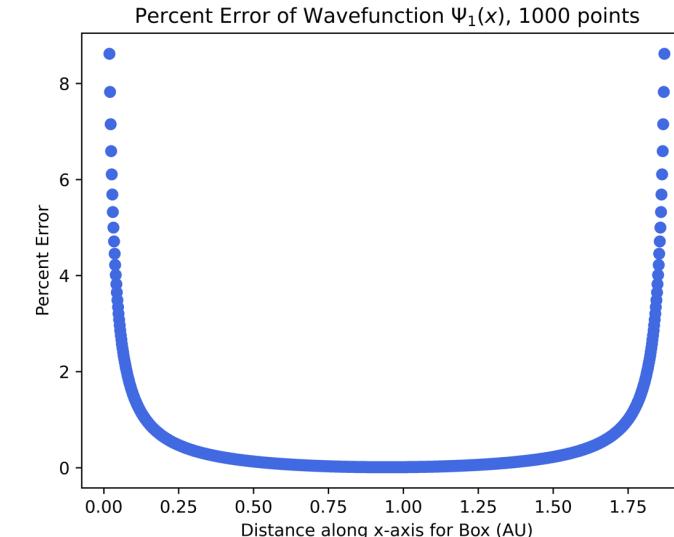
P.I.B. in \mathbb{R}^1



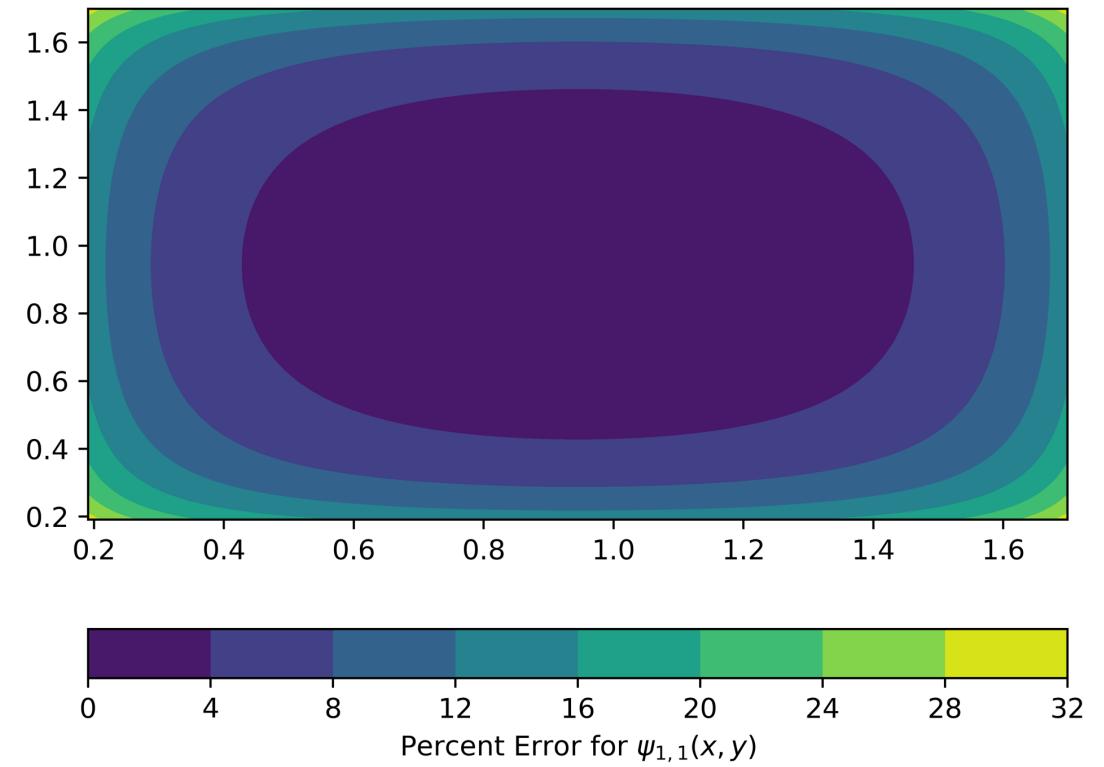
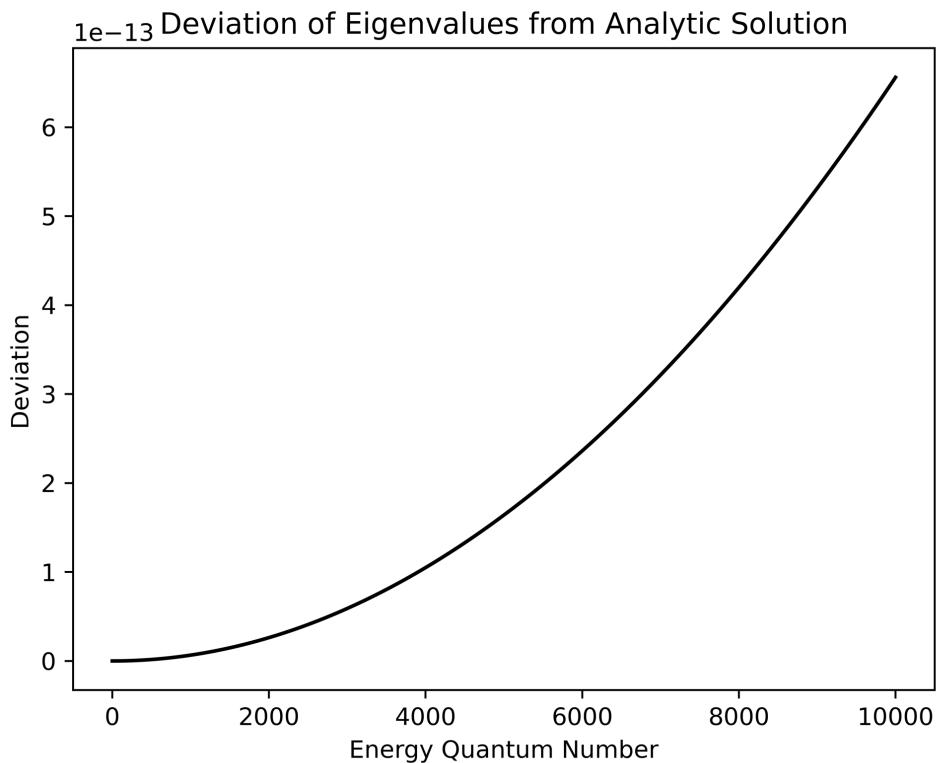
Inc. # of Points →



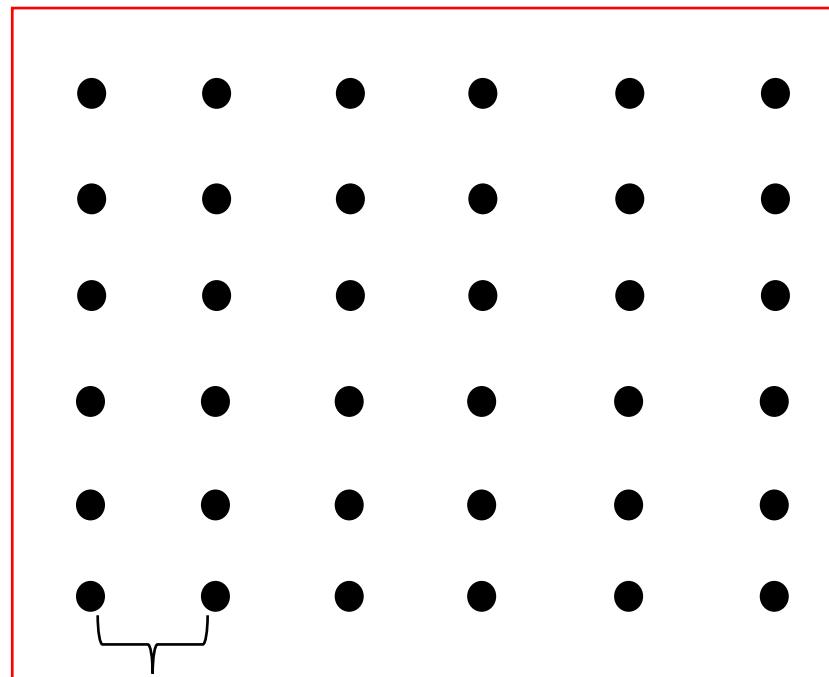
Inc. # of Points →



P.I.B. in \mathbb{R}^2

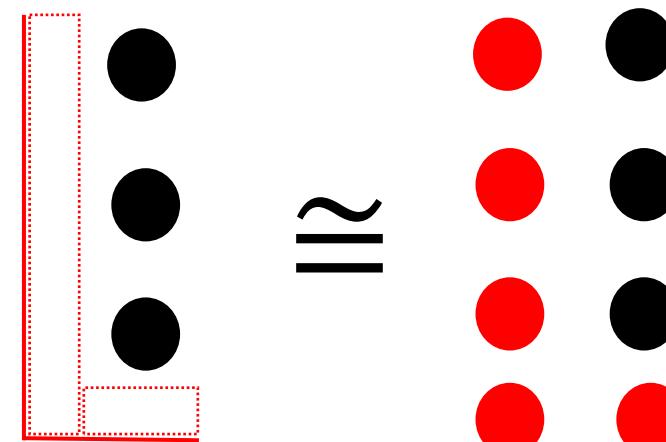
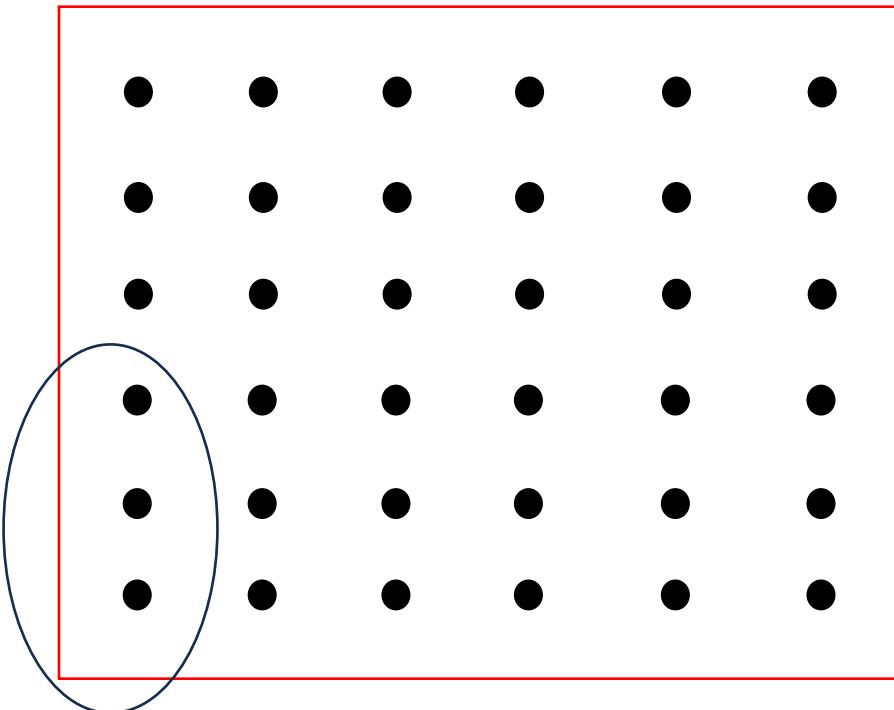


Grid Spacing Issue



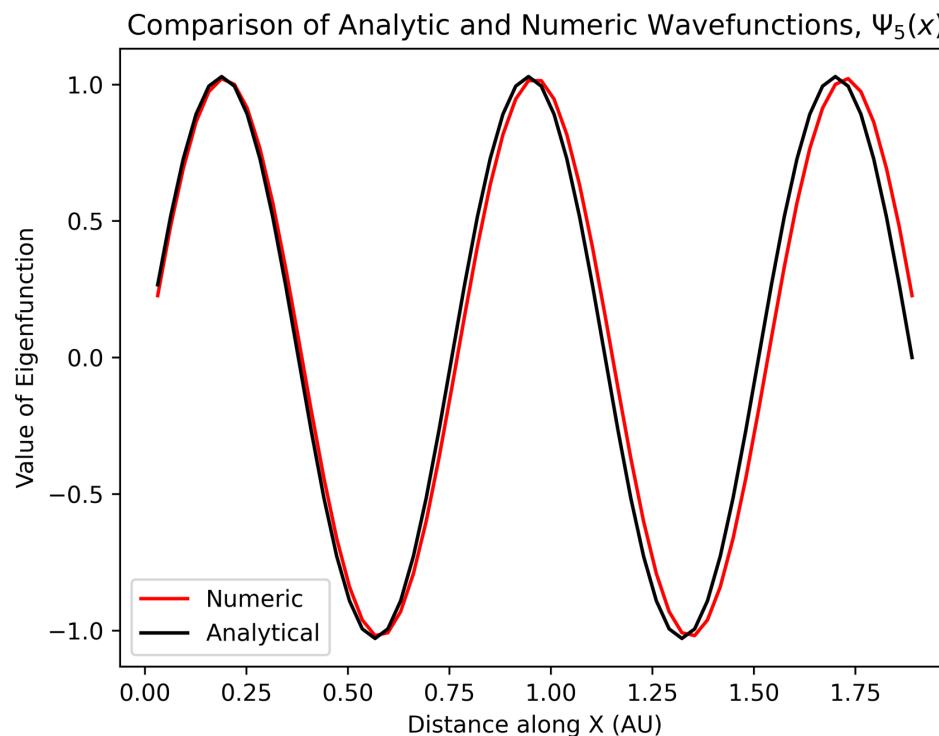
$$dx, dy = \frac{(L_{max} - L_{min})}{nx, ny \pm 1}$$

Grid Spacing Issue

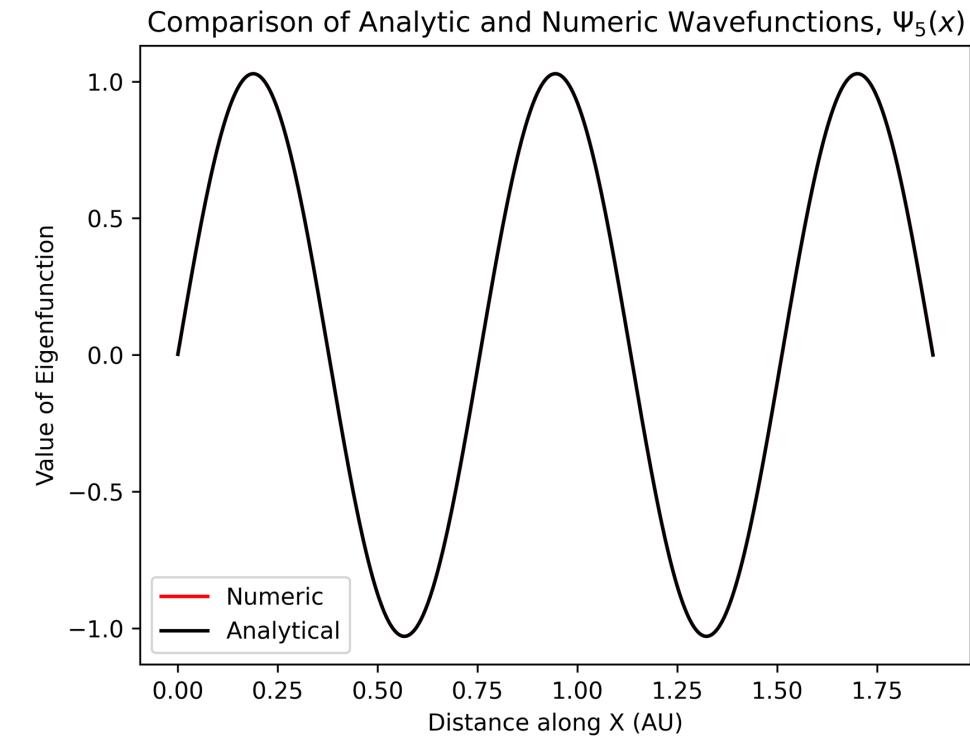


$$dx, dy = \frac{(L_{max} - L_{min})}{nx, ny \pm 1}$$

Increasing Points on Spacing Issue in \mathbb{R}^1



$\psi_5(x)$ where $nx = 60$

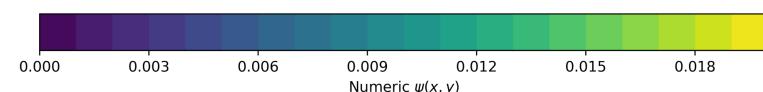
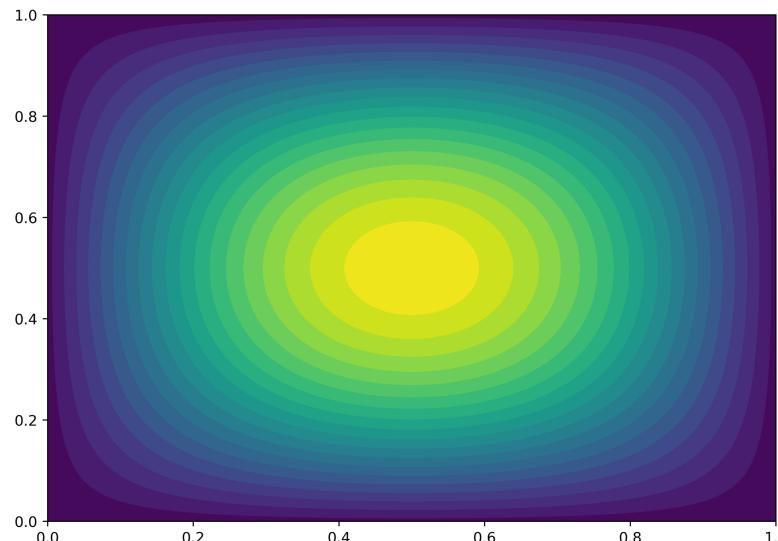


$\psi_5(x)$ where $nx = 600$

Future Avenues

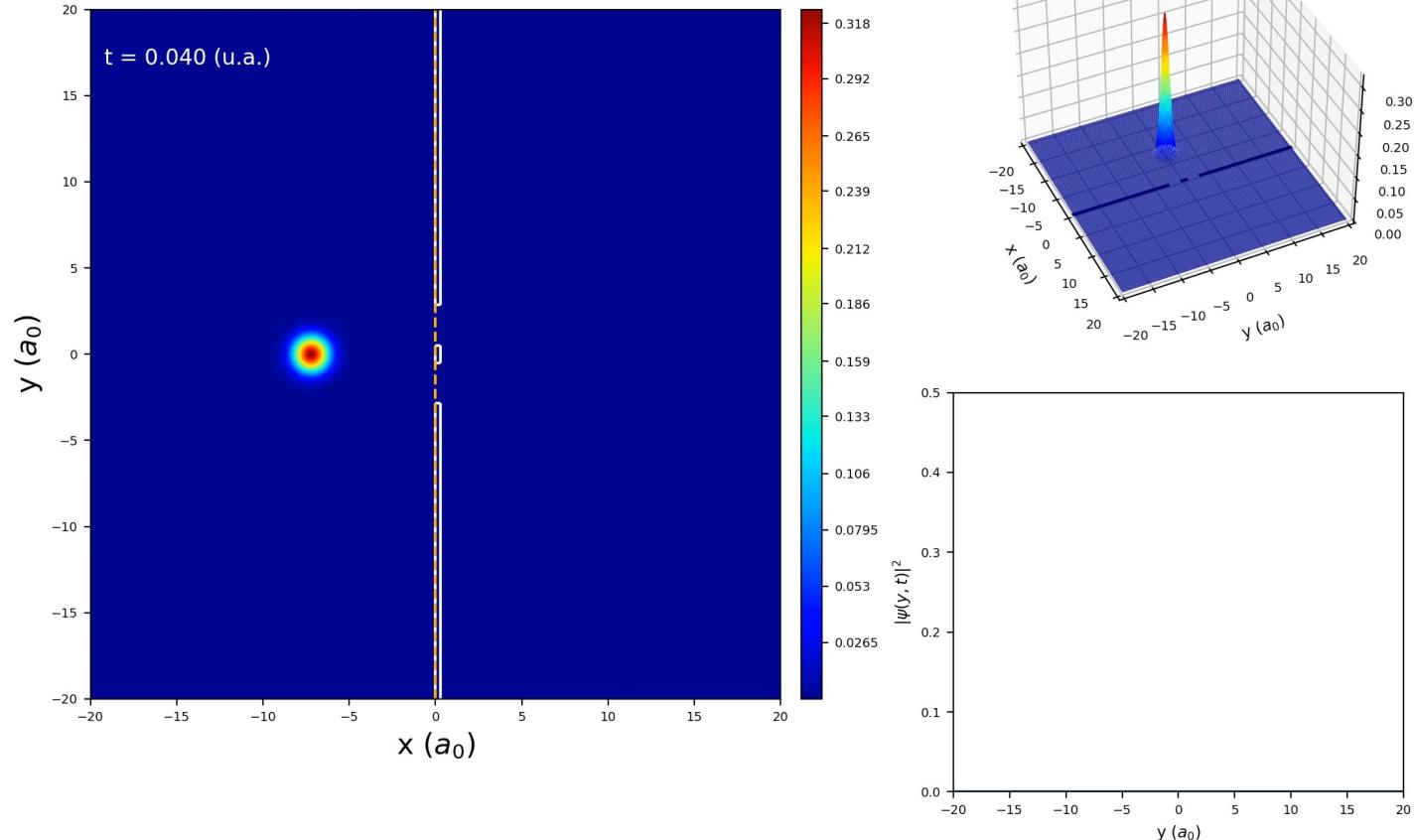
- Consider alternative population of Hamiltonian

$$\begin{bmatrix} \bullet & \bullet & \bullet \end{bmatrix} \xrightarrow{\text{Apply weights}} \begin{bmatrix} -2 & 1 & 0 \\ 1 & -2 & 1 \\ 0 & 1 & -2 \end{bmatrix}$$

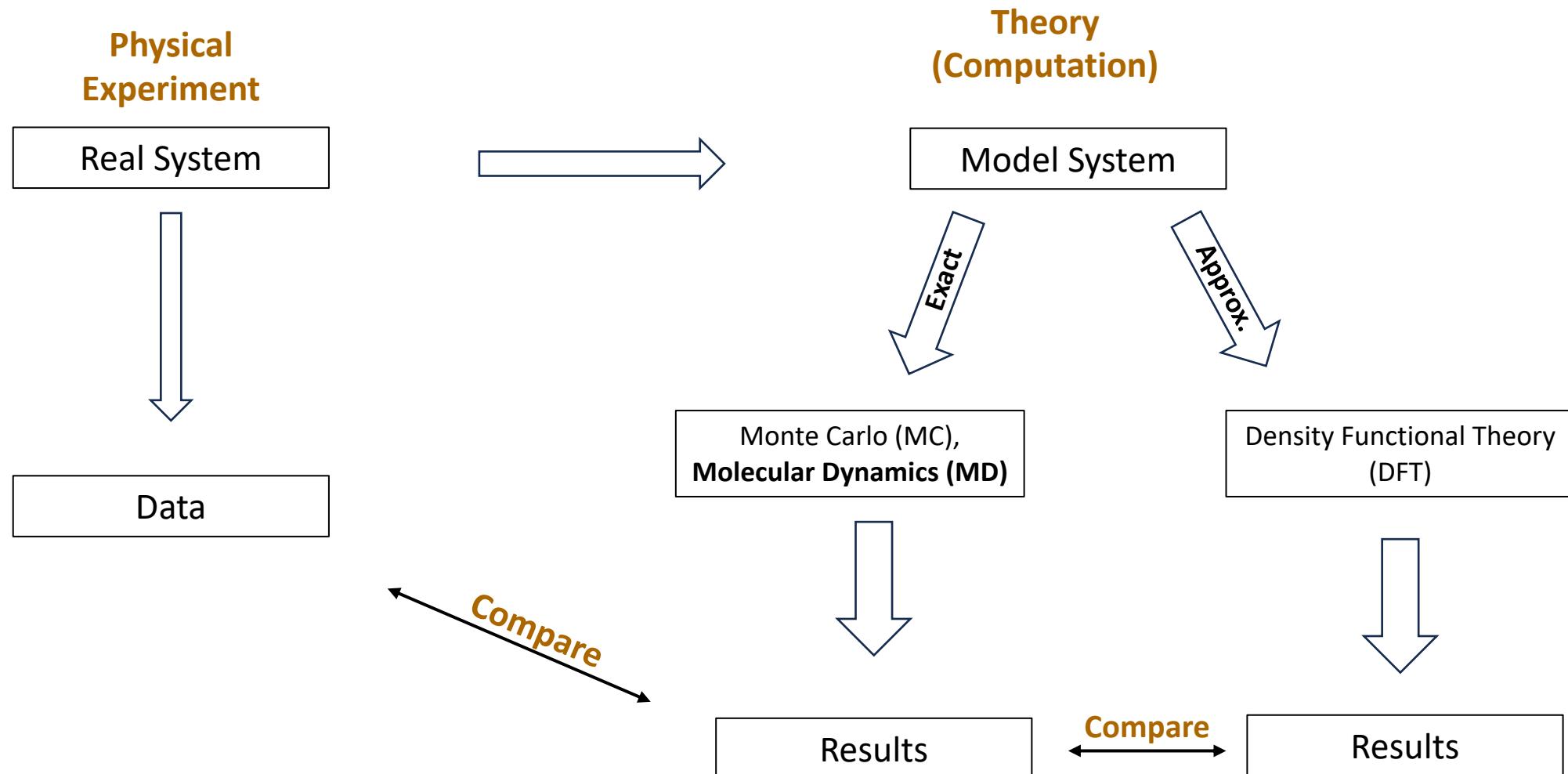


Future Avenues

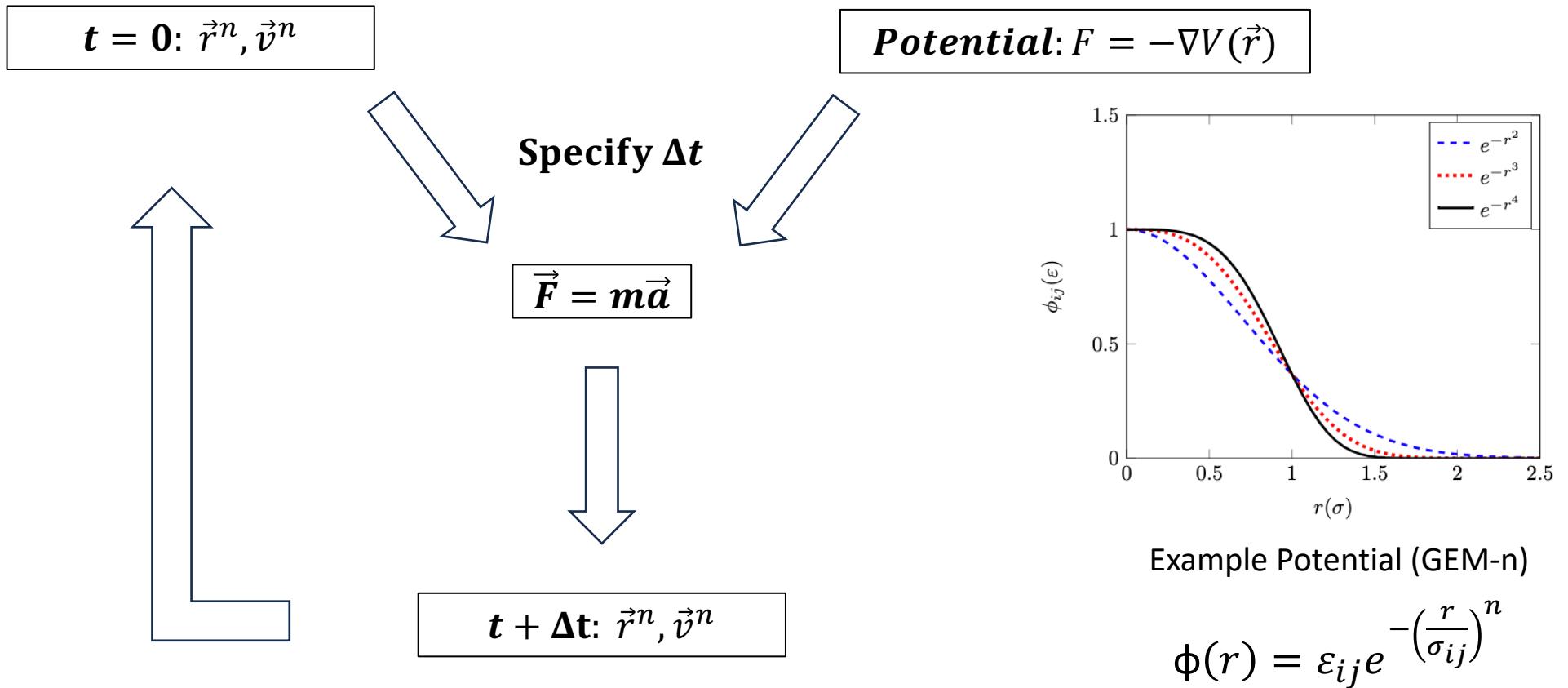
- Wavepacket Diffraction



“Experiment” in Stat Mech



Molecular Dynamics Schematic



Cluster Crystals

Experimental Results

- Confirmed by experiment to exist
- Self-assembling structure
- Dendrimers can be used to improve efficiency of drug molecules among other features

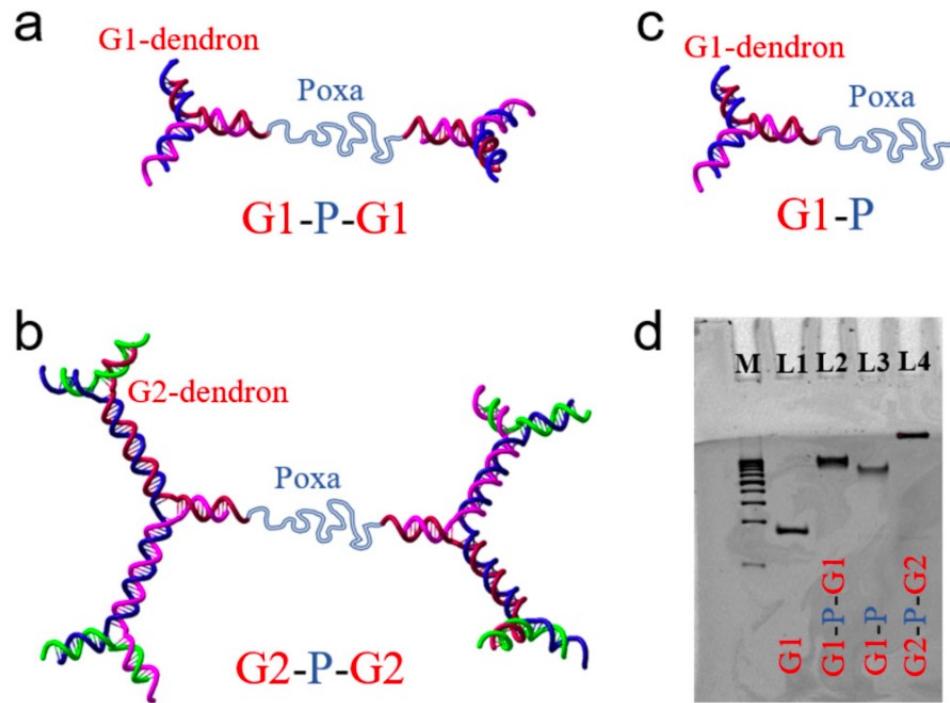
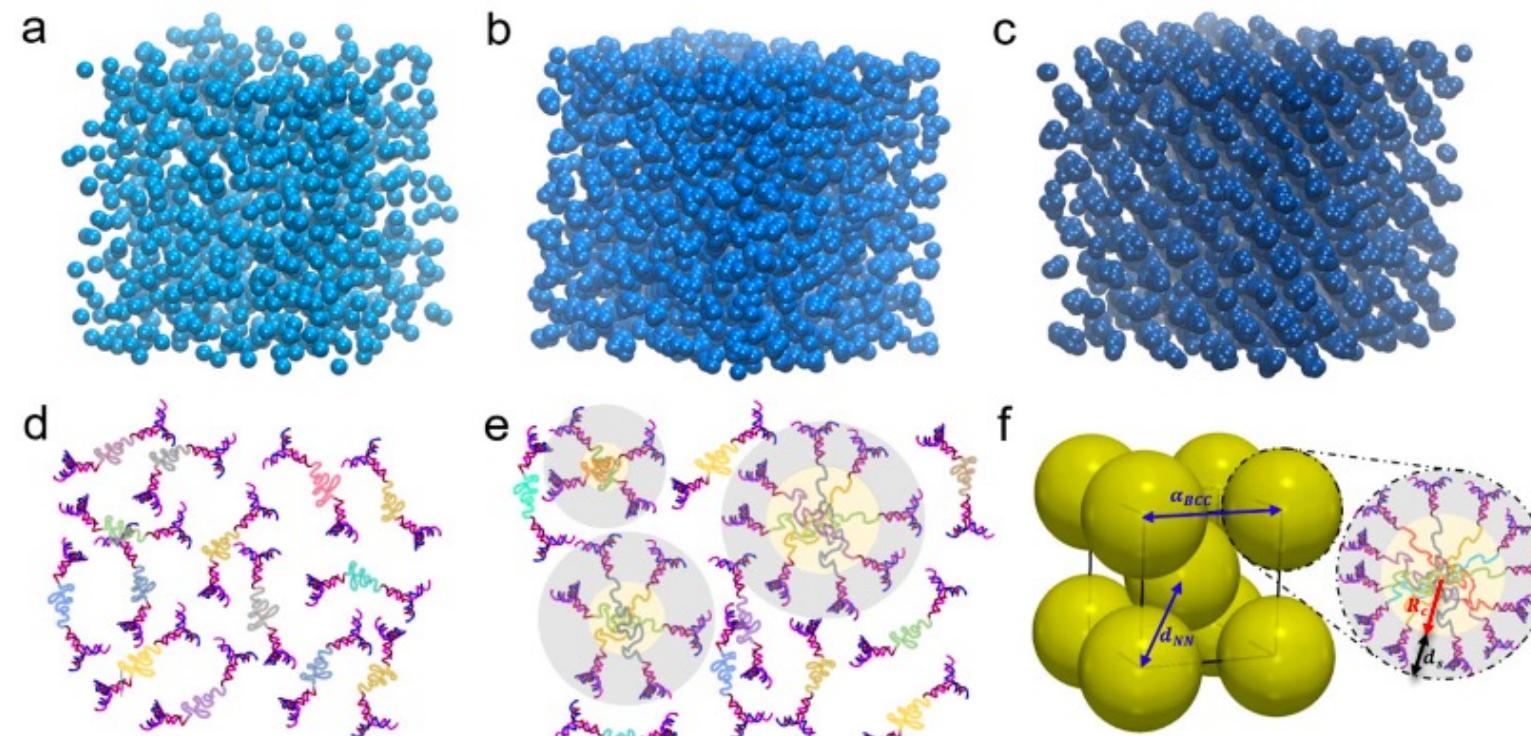


Fig. 1 Schematics and characterization of the tethered all-DNA dendrons.
a First generation of dendritic-linear-dendritic triblock (G1-P-G1). b Second generation of dendritic-linear-dendritic triblock (G2-P-G2). c First generation of dendritic-linear diblock (G1-P). d Non-denaturing polyacrylamide gel electrophoresis (PAGE) analysis. 10% PAGE: Lane M contains 50 base-pair (bp) DNA markers. Lanes 1-4 contain G1, G1-P-G1, G1-P, and G2-P-G2, respectively.

Cluster Crystals

Coarse-Graining → model particles as a sphere

- Main consideration is the physics



Stiakakis, E., Jung, N., Adžić, N. et al. Self assembling cluster crystals from DNA based dendritic nanostructures. *Nat Commun* **12**, 7167 (2021).
<https://doi.org/10.1038/s41467-021-27412-3>

GEM-n

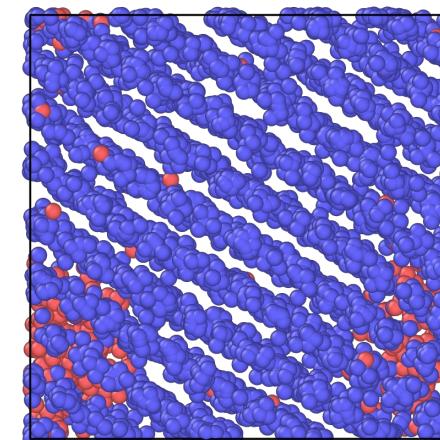
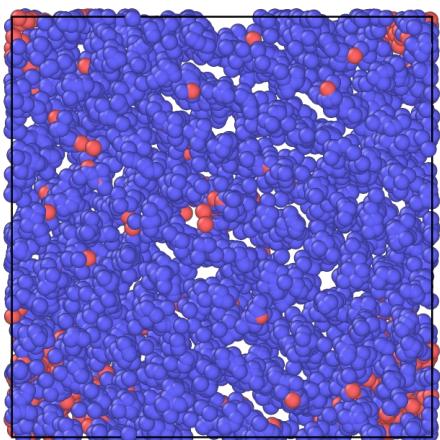
Explore interactive potential defined by:

$$\phi_{ij}(r) = \varepsilon_{ij} e^{-\left(\frac{r}{\sigma_{ij}}\right)^n}$$

$n \leq 2$: No Crystallization

$n > 2$: Crystallization

- Only repulsive interactions



GEM-n Overview

1

- GEM-2, GEM-4 Two Particle Types
- Compare to published results

S. D. Overduin and C. N. Likos 2009 EPL 85 26003.

$$\phi_{1,1}(r) = \varepsilon_{1,1} e^{-\left(\frac{r}{\sigma_{1,1}}\right)^{n_{1,1}}}$$
$$\phi_{1,2}(r) = \varepsilon_{1,2} e^{-\left(\frac{r}{\sigma_{1,2}}\right)^{n_{1,2}}}$$
$$\phi_{2,2}(r) = \varepsilon_{2,2} e^{-\left(\frac{r}{\sigma_{2,2}}\right)^{n_{2,2}}}$$

2

- GEM-4 Single Particle Type
- Compare to Collaborator's thesis

Mladek, B.M. Exotic phenomena in the phase behaviour of soft matter systems. Ph.D. Dissertation, Vienna University of Technology, 2007.

$$\phi_{1,1}(r) = \varepsilon_{1,1} e^{-\left(\frac{r}{\sigma_{1,1}}\right)^{n_{1,1}}}$$

3

- Dimer System
- Novel

$$\phi_{1,1}(r) = \varepsilon_{1,1} e^{-\left(\frac{r}{\sigma_{1,1}}\right)^{n_{1,1}}}$$
$$\phi_{1,2}(r) = \varepsilon_{1,2} e^{-\left(\frac{r}{\sigma_{1,2}}\right)^{n_{1,2}}}$$
$$\phi_{2,2}(r) = \varepsilon_{2,2} e^{-\left(\frac{r}{\sigma_{2,2}}\right)^{n_{2,2}}}$$

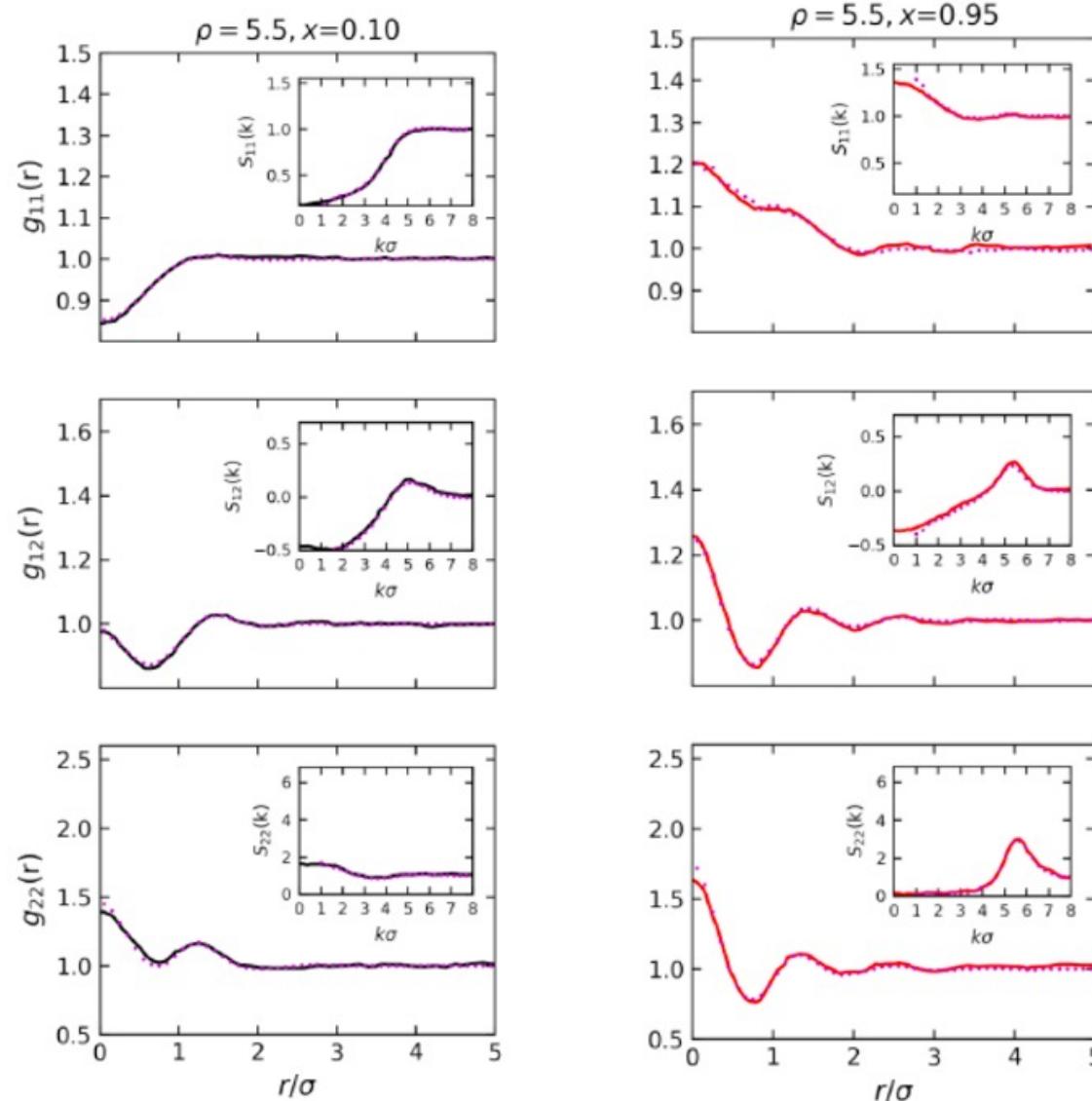
* {N, V, T} Ensemble
for All *

DFT/MD GEM-2,GEM-4 Comparison: $\frac{k_B T}{\varepsilon} = 1.0$

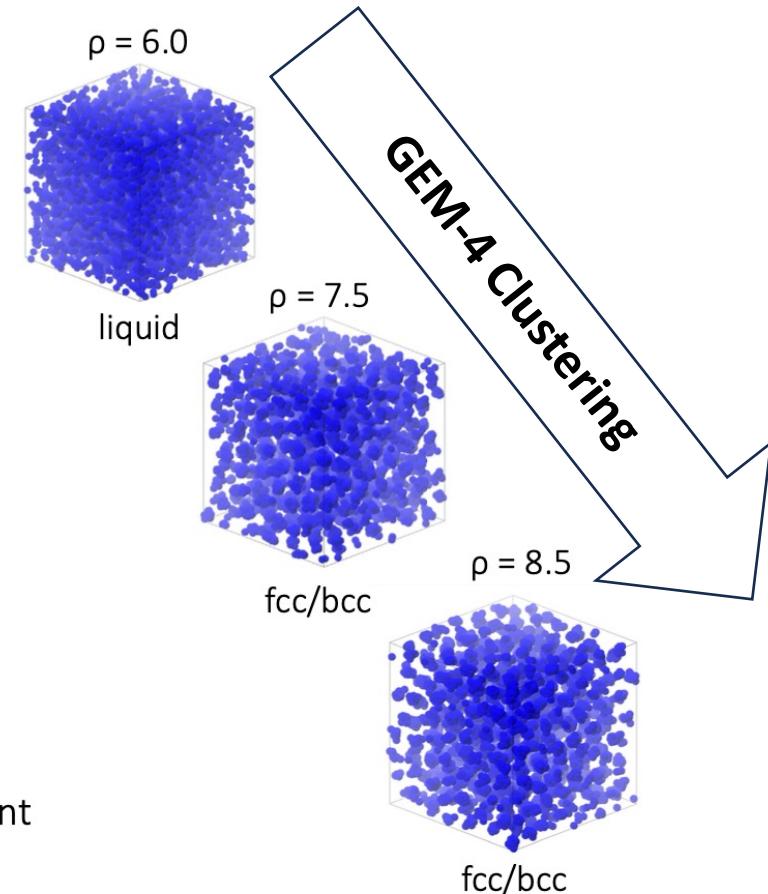
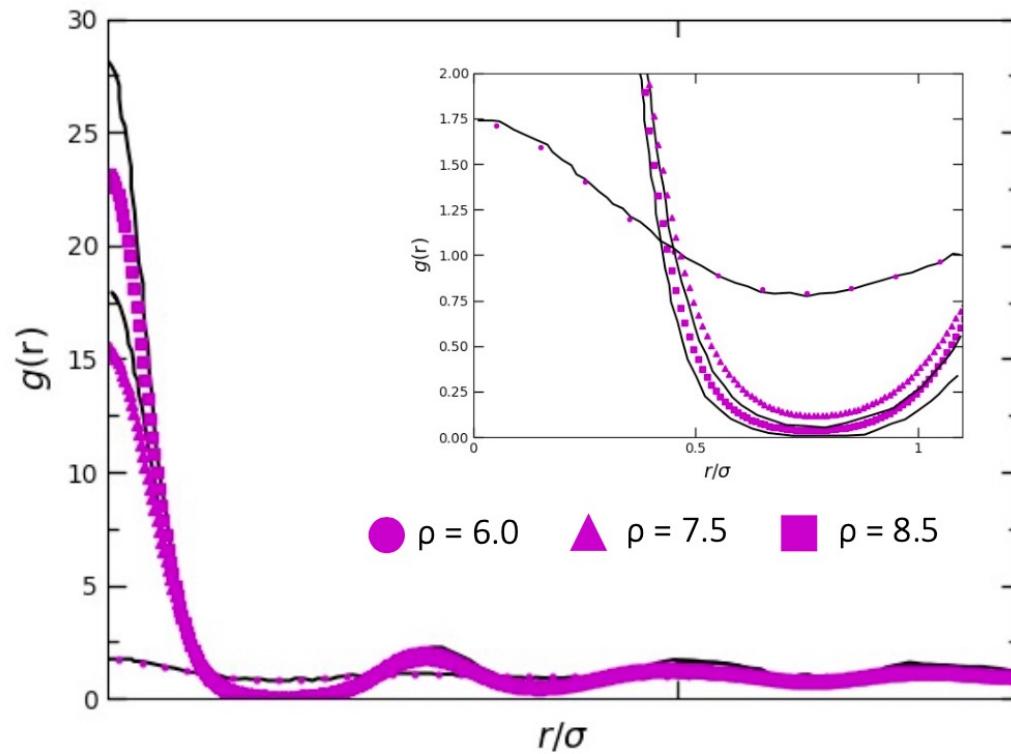
$$\phi_{1,1}(r) = \varepsilon e^{-\left(\frac{r}{\sigma}\right)^2}$$

$$\phi_{1,2}(r) = \varepsilon e^{-\left(\frac{r}{1.07\sigma}\right)^3}$$

$$\phi_{2,2}(r) = \varepsilon e^{-\left(\frac{r}{\sigma}\right)^4}$$

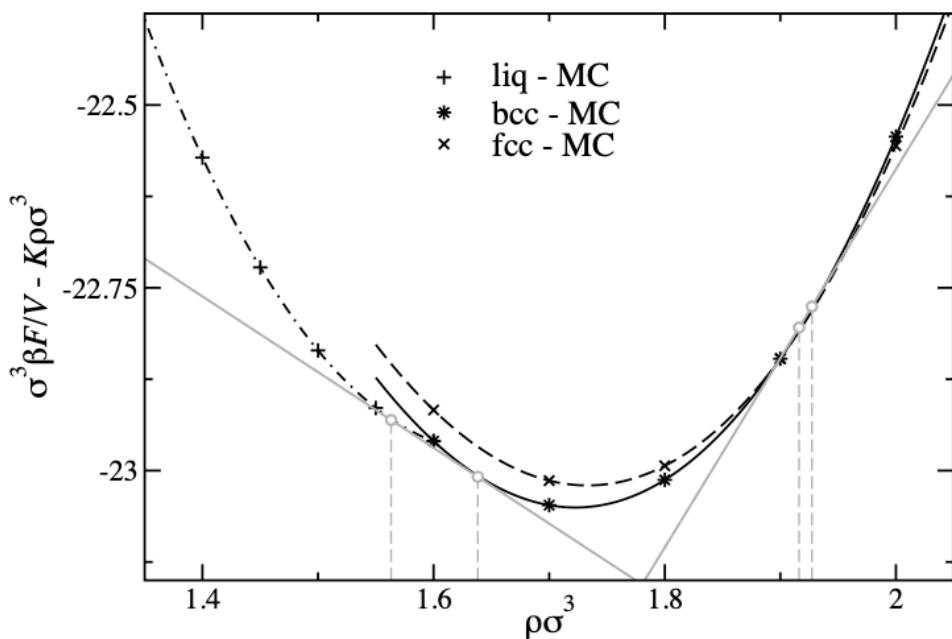


MC/MD GEM-4 Comparison: $\frac{k_B T}{\varepsilon} = 1.1$

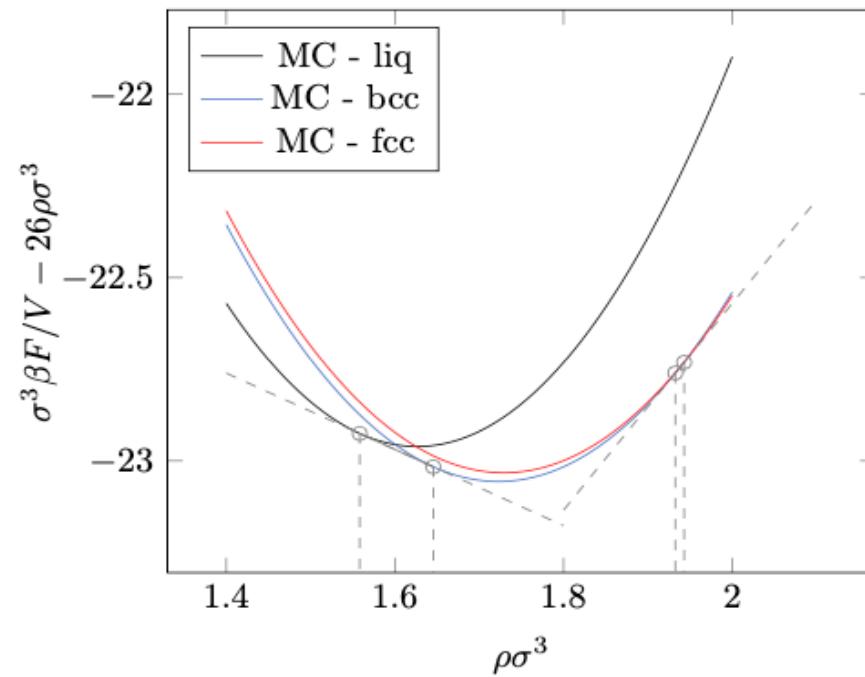


$$\phi_{1,1}(r) = \varepsilon e^{-\left(\frac{r}{\sigma}\right)^4}$$

Coexistence Recreation: $\frac{k_B T}{\varepsilon} = 0.2$

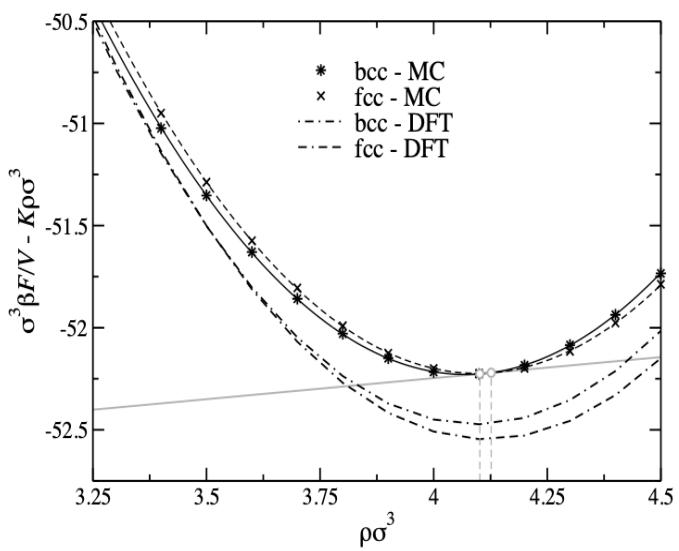
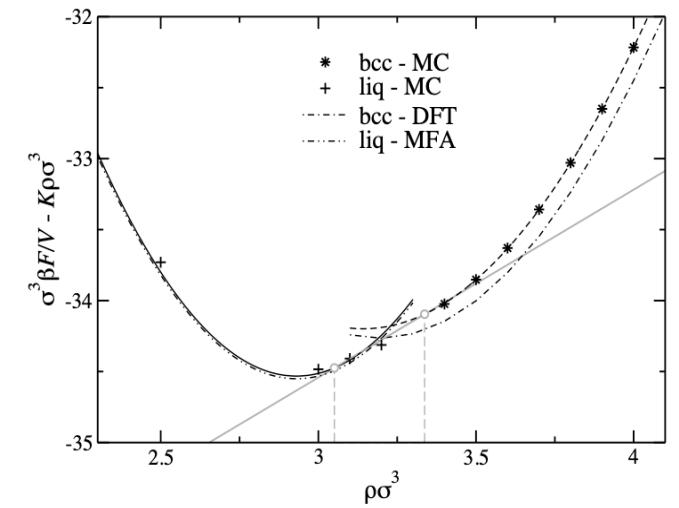


Original

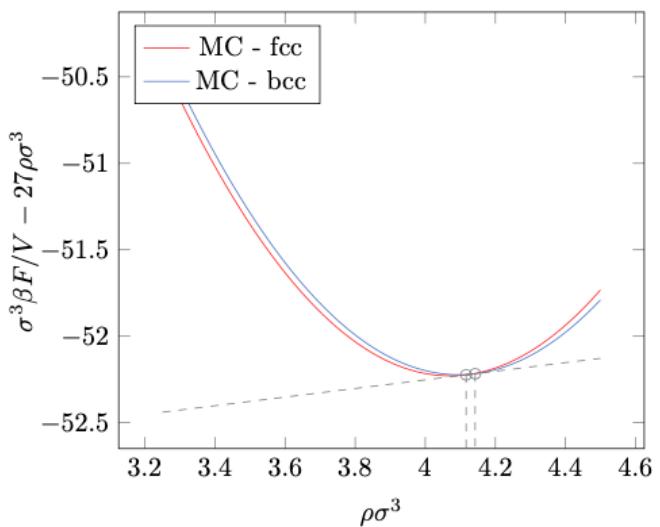
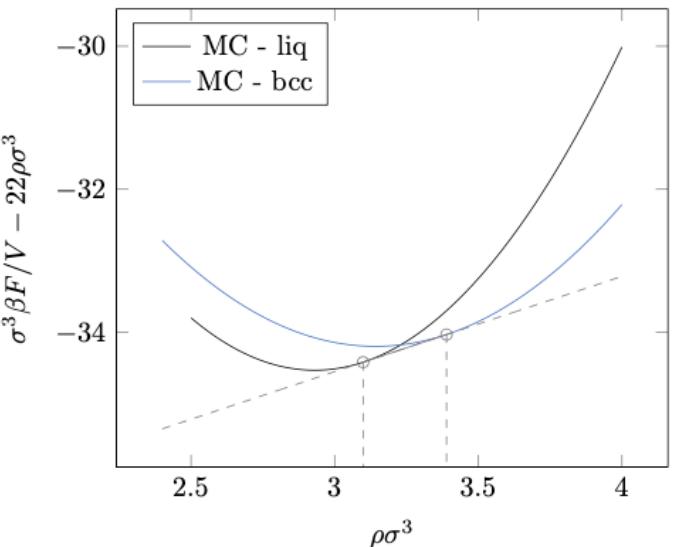


Recreation

Coexistence Recreation: $\frac{k_B T}{\varepsilon} = 0.5$



Originals



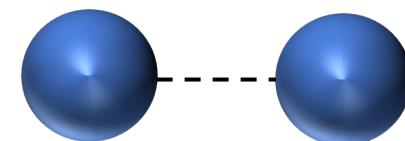
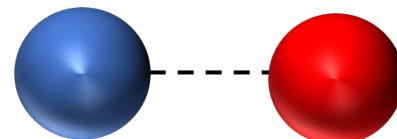
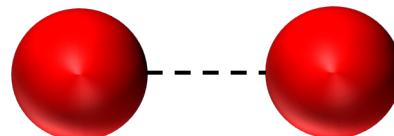
Recreations

Dimers

$$\textbf{GEM-2: } \phi_{1,1}(r) = \varepsilon_{1,1} e^{-\left(\frac{r}{\sigma_{1,1}}\right)^n}$$

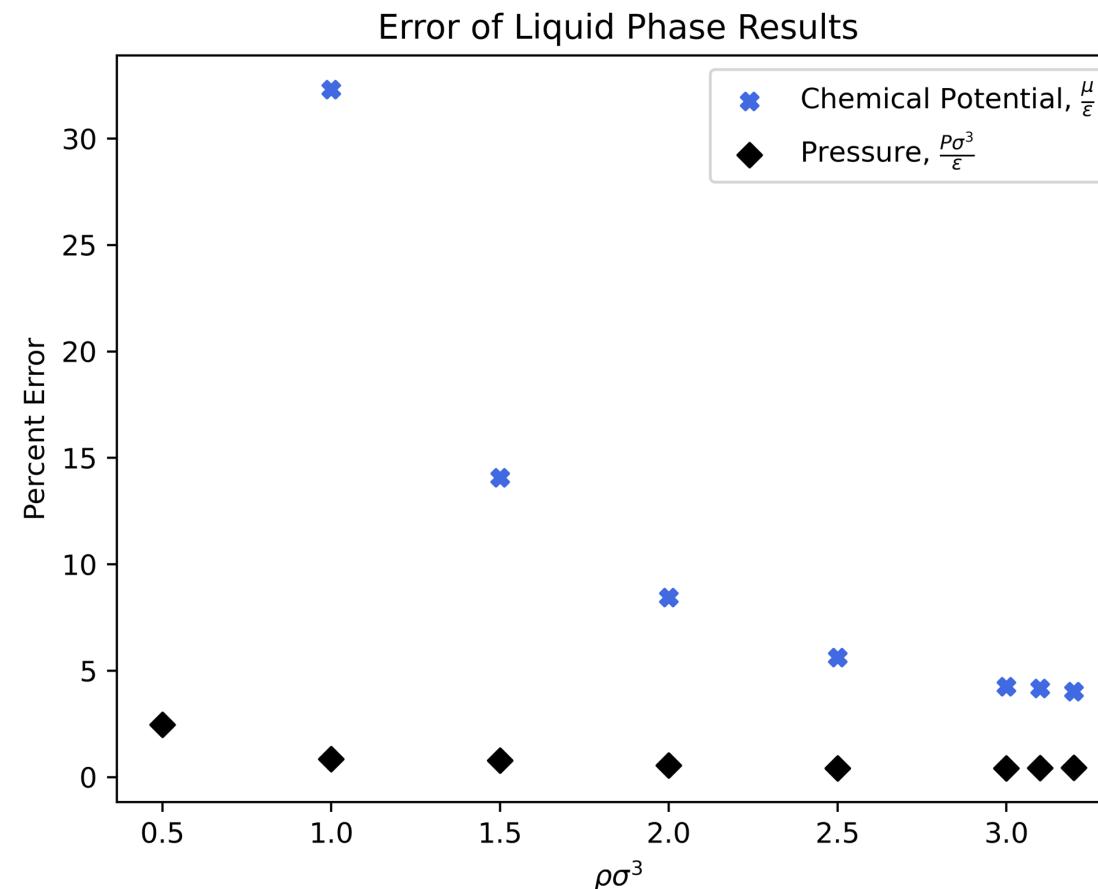
$$\textbf{GEM-2,4: } \phi_{1,2}(r) = \varepsilon_{1,2} e^{-\left(\frac{r}{\sigma_{1,2}}\right)^n}$$

$$\textbf{GEM-4: } \phi_{2,2}(r) = \varepsilon_{2,2} e^{-\left(\frac{r}{\sigma_{2,2}}\right)^n}$$



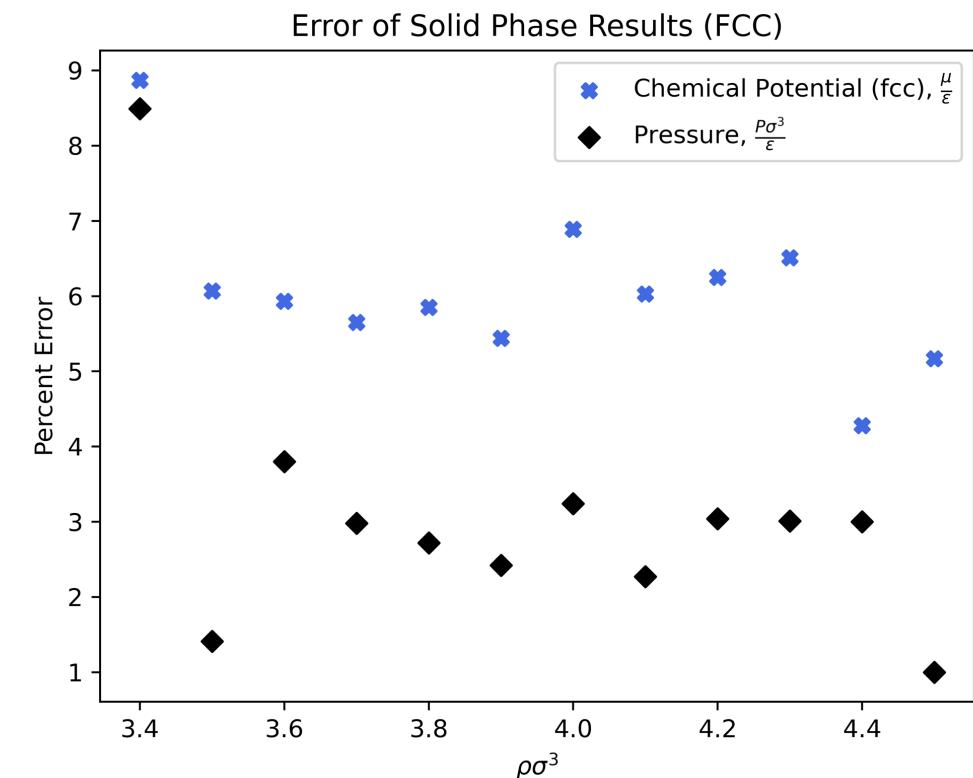
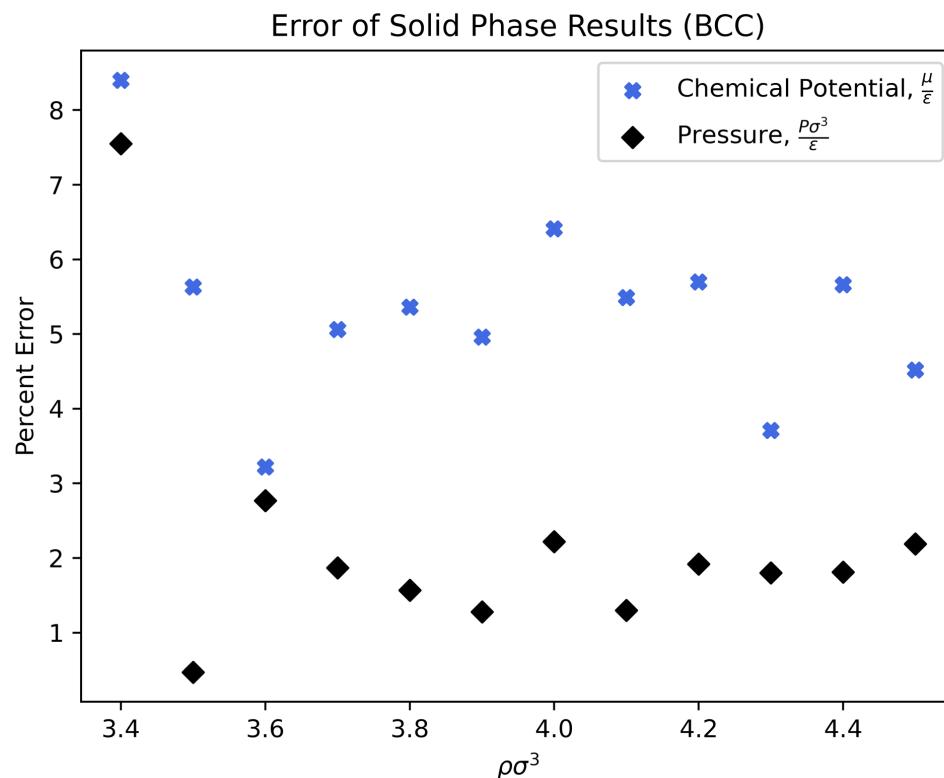
Dimer vs. GEM-4

Test Dimer system where $\epsilon_{2,2}$ and $\epsilon_{2,4} = 0$; $\frac{k_B T}{\epsilon} = 0.5$



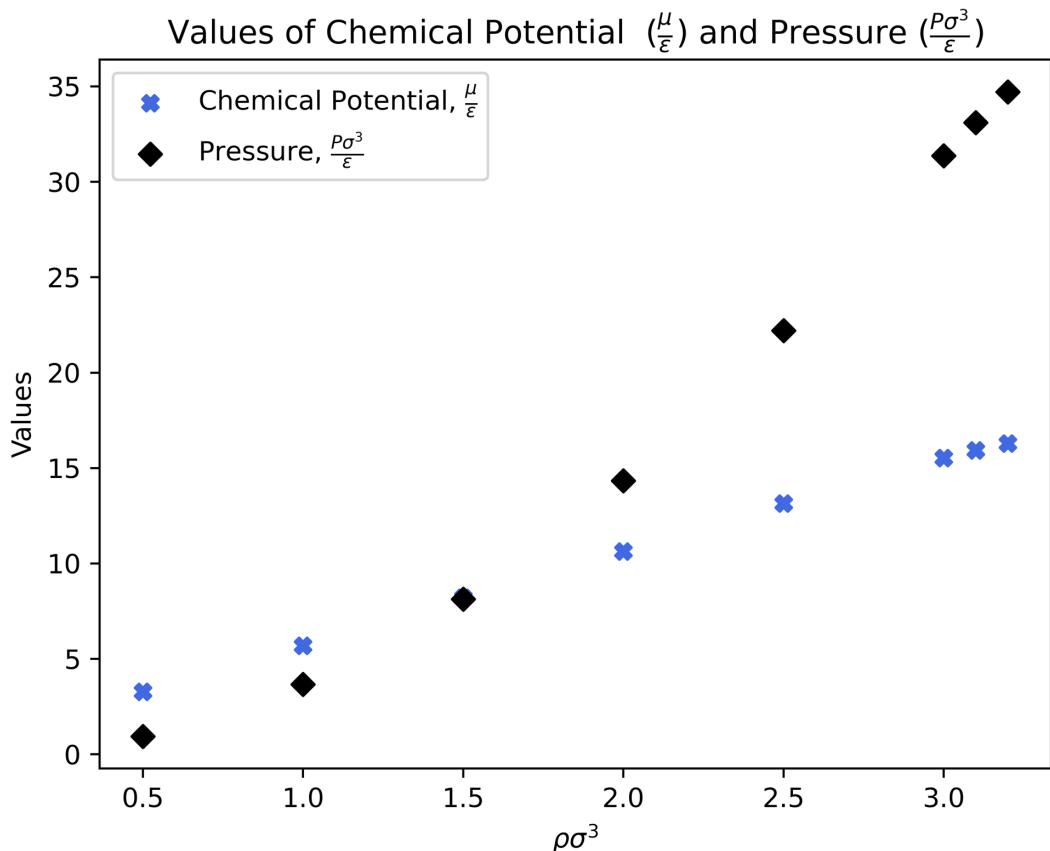
Dimer vs. GEM-4

Test Dimer system where $\varepsilon_{2,2}$ and $\varepsilon_{2,4} = 0$; $\frac{k_B T}{\varepsilon} = 0.5$



Future Avenues

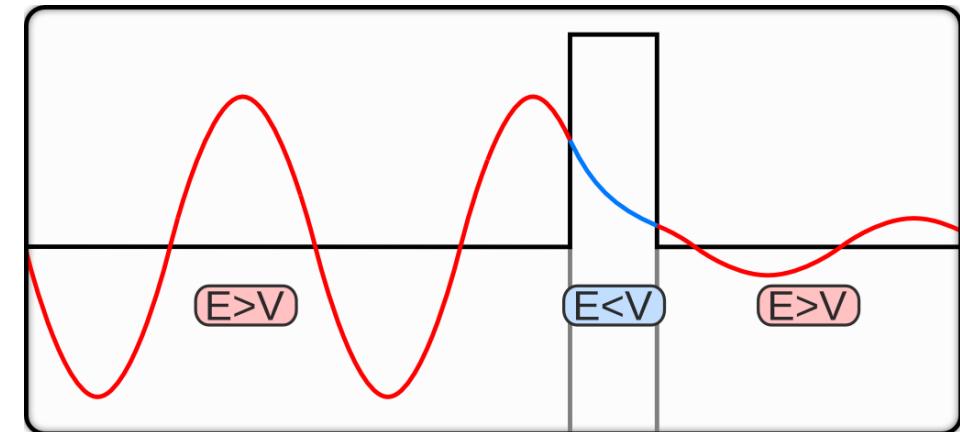
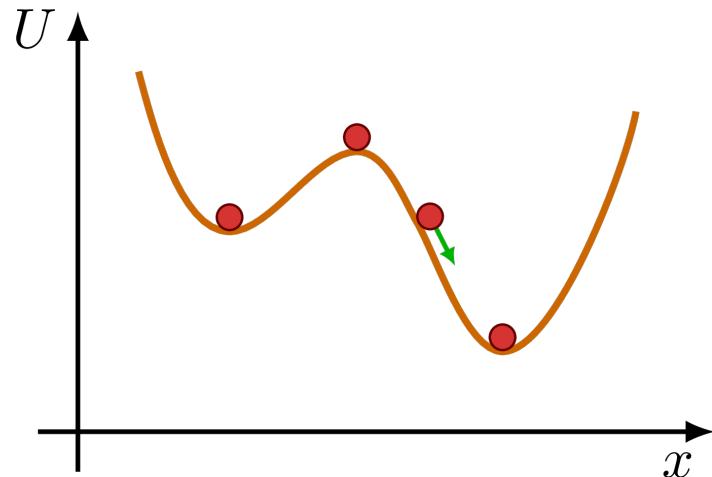
Dimer system where $\varepsilon_{2,2}$ and $\varepsilon_{2,4} \neq 0$



Thank You!
Any Questions?

Tunneling and Zero Point Energy

Tunneling:



Zero Point Energy:

$$E_n = \frac{\hbar^2 \pi^2}{8ml^2} \rightarrow \Delta x \Delta p \approx \hbar \rightarrow \Delta x \sim l \rightarrow \Delta p \sim \frac{\hbar}{l} \rightarrow E_{min} = \frac{\Delta p^2}{2m} \neq 0$$

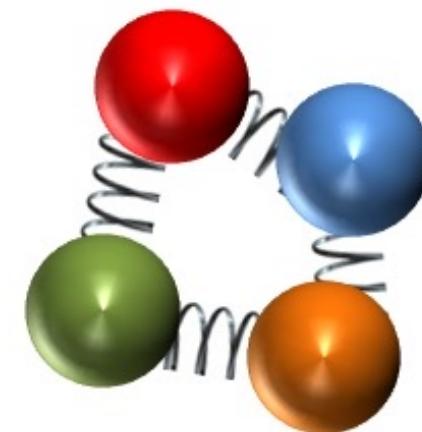
RPMD

Classical Mechanics



Classical Particle

Quantum Mechanical Path Integral



Ring Polymer

RPMD

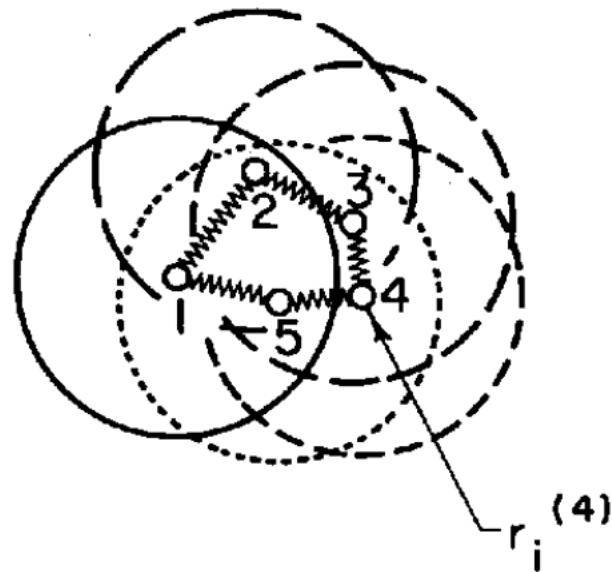
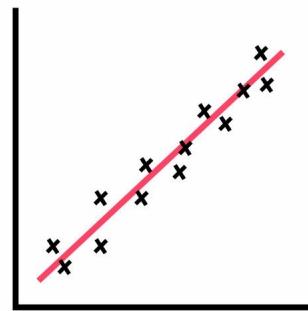


FIG. 1. A molecule in the classical isomorphism with $P = 5$, and the meaning of the coordinates $r_i^{(t)}$. The numbered small circles represent the locations of the i th atom at the P different states (points on a quantum path). Equivalently, the numbers label the P distinguishable atoms in the i th molecule of the isomorphic classical fluid. The large circles represent schematically the interaction spheres associated with the different atoms. The wavy lines depict the harmonic springs whose Boltzmann factors are proportional to the single particle $\rho_0(r_i^{(t)}, r_i^{(t+1)}; \beta/P) = E(|r_i^{(t)} - r_i^{(t+1)}|; \beta/P)$.

Chandler, D. Wolynes, P.G.
Exploiting the isomorphism
between quantum theory and
classical statistical mechanics of
polyatomic fluids.
J. Chem. Phys. 74, 4078–4095
(1981)

Correlation Functions

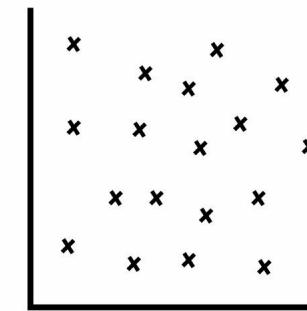
- Describes a statistical relationship between quantities



Positive
Correlation



Negative
Correlation



No
Correlation

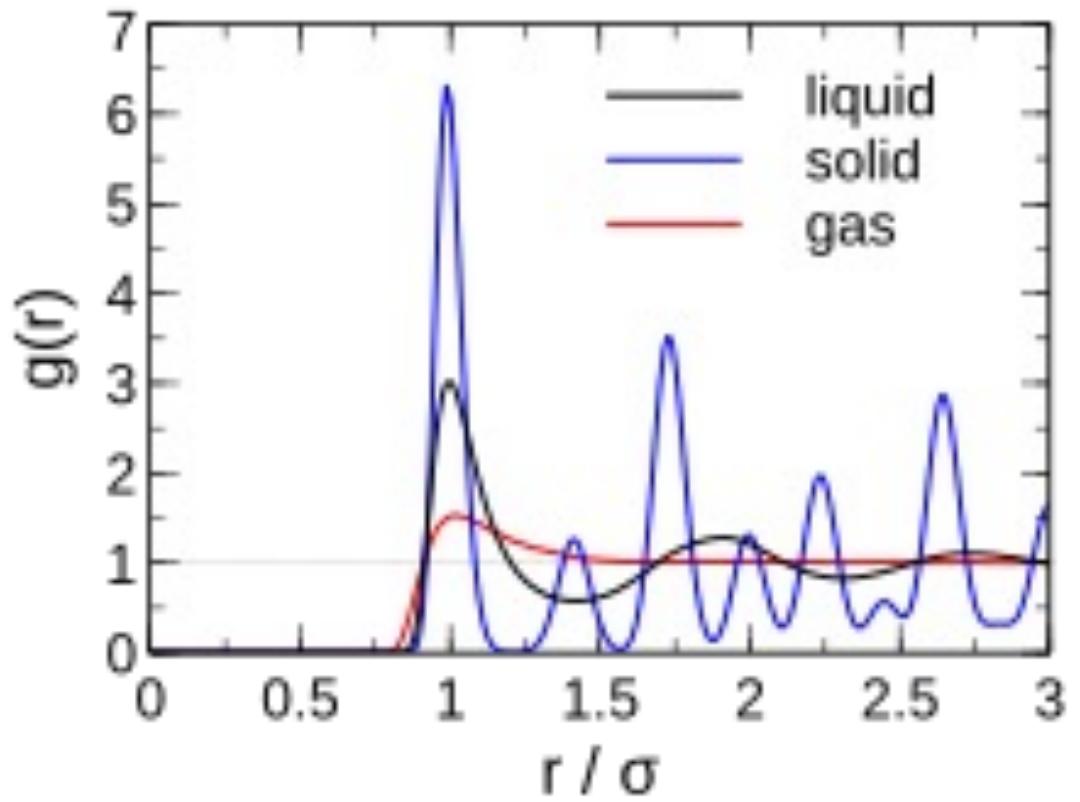
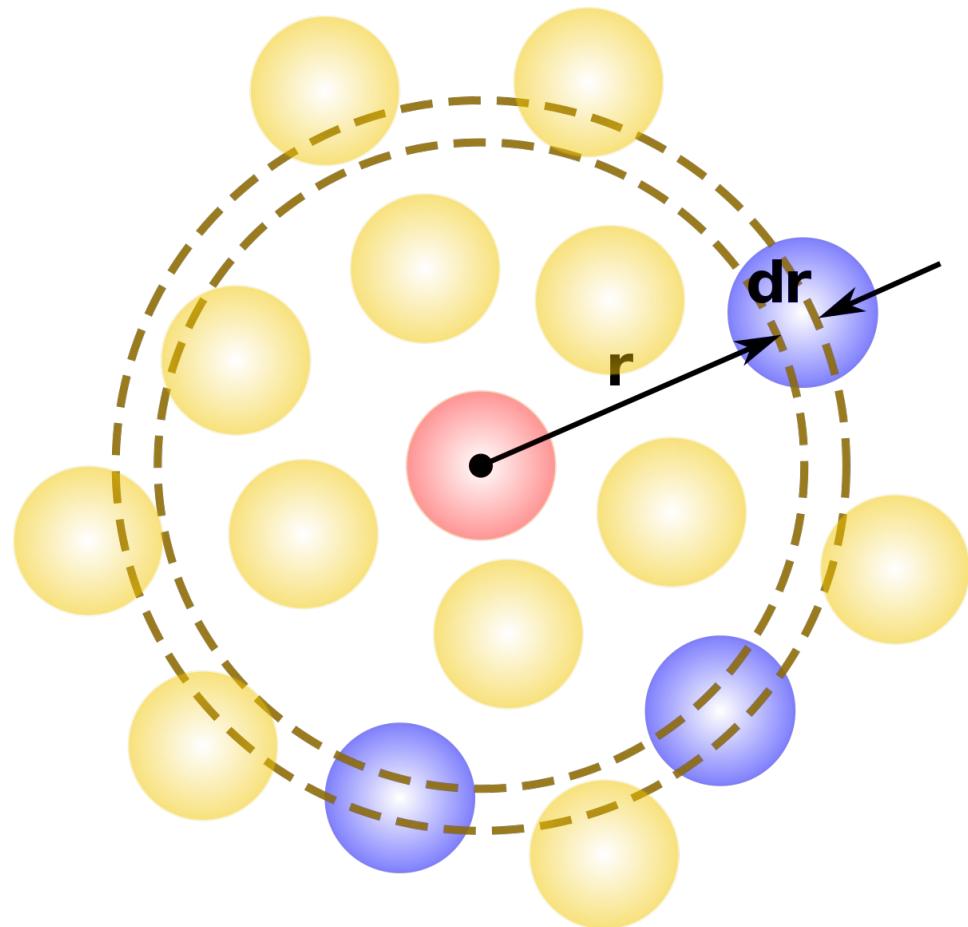
Kinetics with Correlation Functions

Flux: Number of particles per unit time through a point, $x = s$

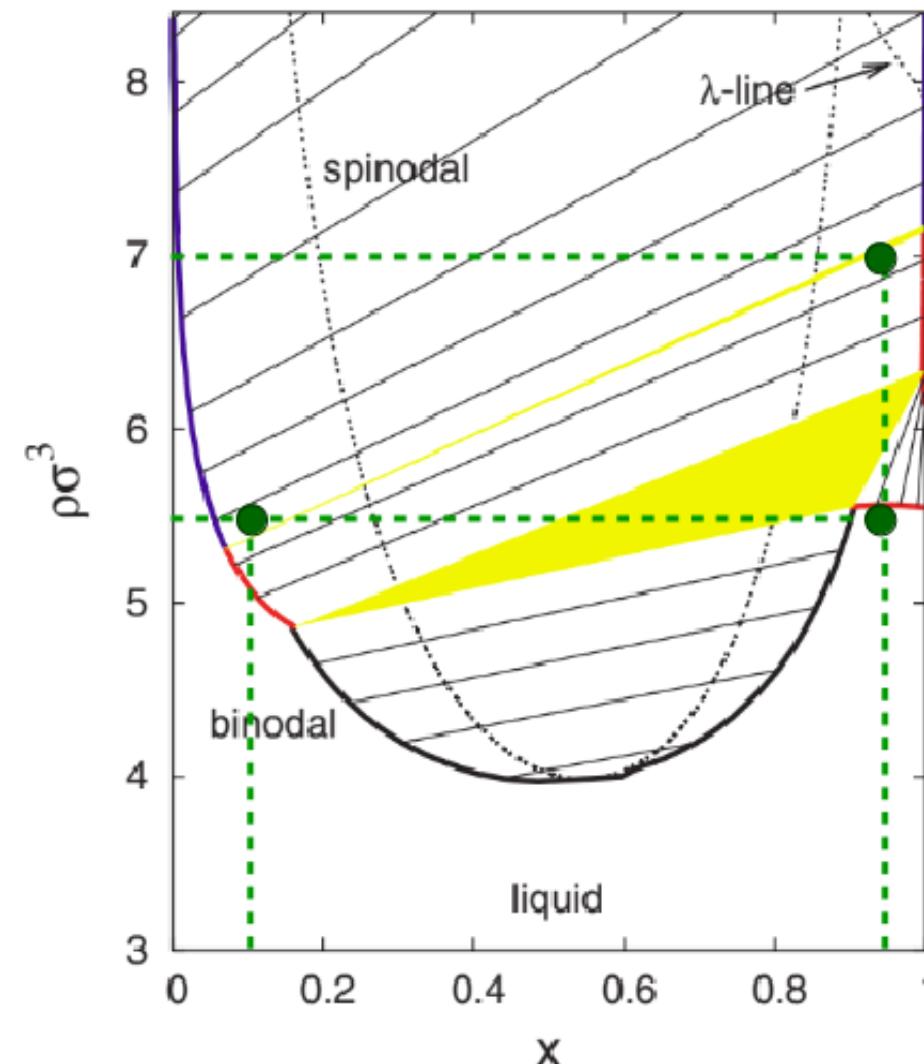
$$\hat{F}(s) = -\frac{i\hbar}{2m} \left\{ \delta(x - s) \frac{d}{dx} + \frac{d}{dx} \delta(x - s) \right\}$$

$$j(s, t) \equiv \langle \psi | \hat{F}(s) | \psi \rangle = -\frac{i\hbar}{2m} \left\{ \psi(s, t)^* \frac{\partial \psi(s, t)}{\partial s} - \frac{\partial \psi(s, t)^*}{\partial s} \psi(s, t) \right\}$$

Radial Distribution Function, $g(r)$



Likos Phase Diagram



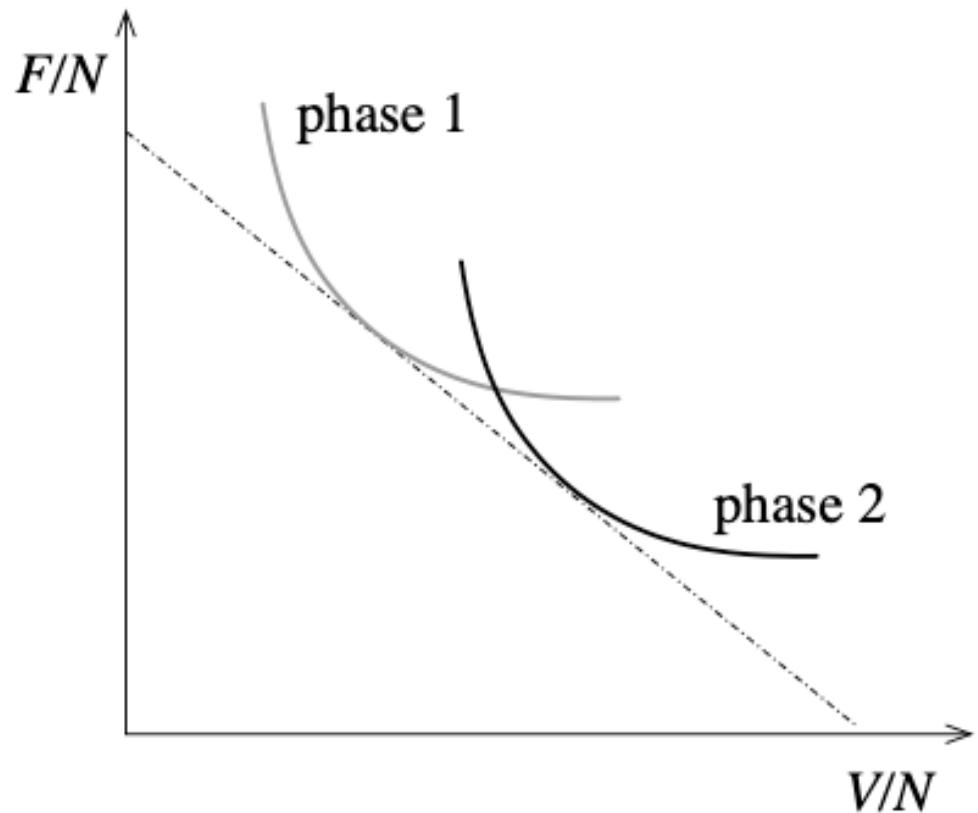
Langevin Dynamics

Langevin thermostat maintains temperature by modifying Newton's Eqns. of motion

$$\dot{p}_i = -\nabla F_i - \xi_i p_i + F(t) \quad \begin{cases} V(x) = \text{Potential} \\ F(t) \equiv \text{random force} \\ \xi \equiv \text{friction constant} \end{cases}$$

$$\dot{r}_i = \frac{p_i}{m_i} \quad \sigma_i^2 = 2 m_i \gamma_i k_B T / \Delta t$$

Common Tangent Construction



$$P_1 = P_2 \rightarrow P = -\left(\frac{\partial F}{\partial V}\right) \rightarrow \text{Equal Slopes}$$

$$\mu = \frac{F}{N} + \frac{PV}{N}$$

$$\mu_1 = \mu_2 \rightarrow \text{Equal Intercept}$$

Coexistence

Determine coexistence by the following:

$$0 = \mu_c = \frac{F(\mu_c) + P(\mu_c) - \mu(\mu_c)N}{N_c}$$

μ_c is the work necessary to introduce a new lattice site

- All other quantities are constrained by μ_c leading to the expression above (Note: {N, V, T} Ensemble)

Methods of Acquisition:

- Density Functional Theory (DFT) $\rightarrow F(\mu_c)$
- Widom Insertion $\rightarrow \mu(\mu_c)$
- LAMMPS logfile $\rightarrow P(\mu_c)$

Mladek Phase Diagram

$k_B T/\varepsilon$	structure	$\rho\sigma^3$	n_c	$\beta F/N$	μ/ε	$P\sigma^3/\varepsilon$
0.5	liquid	0.5	-	-0.259	1.18	0.66
		1.0	-	2.143	3.34	2.26
		1.5	-	4.343	5.39	4.83
		2.0	-	6.451	7.39	8.32
		2.5	-	8.508	9.34	12.70
		3.0	-	10.505	11.18	17.78
		3.1	-	10.900	11.51	18.80
		3.2	-	11.277	11.81	19.75
		3.4	6.900	11.993	11.75	19.54
		3.5	7.096	12.328	12.00	20.42
		3.6	7.300	12.658	12.26	21.34
		3.7	7.492	12.984	12.52	22.31
		3.8	7.692	13.308	12.79	23.32
		3.9	7.892	13.628	13.05	24.33
4.5	bcc	4.0	8.100	13.946	13.31	25.37
		4.1	8.300	14.262	13.59	26.44
		4.2	8.492	14.575	13.86	27.60
		4.3	8.688	14.887	14.13	28.76
		4.4	8.896	15.196	14.39	29.89
		4.5	9.088	15.503	14.67	31.11
		5.0	10.072	17.020	16.02	37.51
		3.4	7.004	12.015	11.70	19.37
		3.5	7.207	12.346	11.95	20.23
		3.6	7.410	12.674	12.20	21.13
		3.7	7.613	12.999	12.45	22.07
		3.8	7.813	13.318	12.73	23.06
		3.9	8.020	13.635	12.99	24.06
		4.0	8.219	13.950	13.25	25.12
4.5	fcc	4.1	8.418	14.263	13.52	26.19
		4.2	8.621	14.572	13.79	27.30
		4.3	8.824	14.880	14.05	28.42
		4.4	9.031	15.187	14.32	29.55
		4.5	9.230	15.492	14.58	30.72

Table C.2: MC results for the cluster size n_c , free energy F , chemical potential μ and pressure P at fixed temperature $k_B T = 0.5$ for various densities and structures in equilibrium (i.e., $\mu_c = 0$). Error estimates in the various values are as follows: $n_c : \pm 0.005$, $\beta F/N : \pm 0.001$, $\mu/\varepsilon : \pm 0.02$, $P\sigma^3/\varepsilon : \pm 0.01$

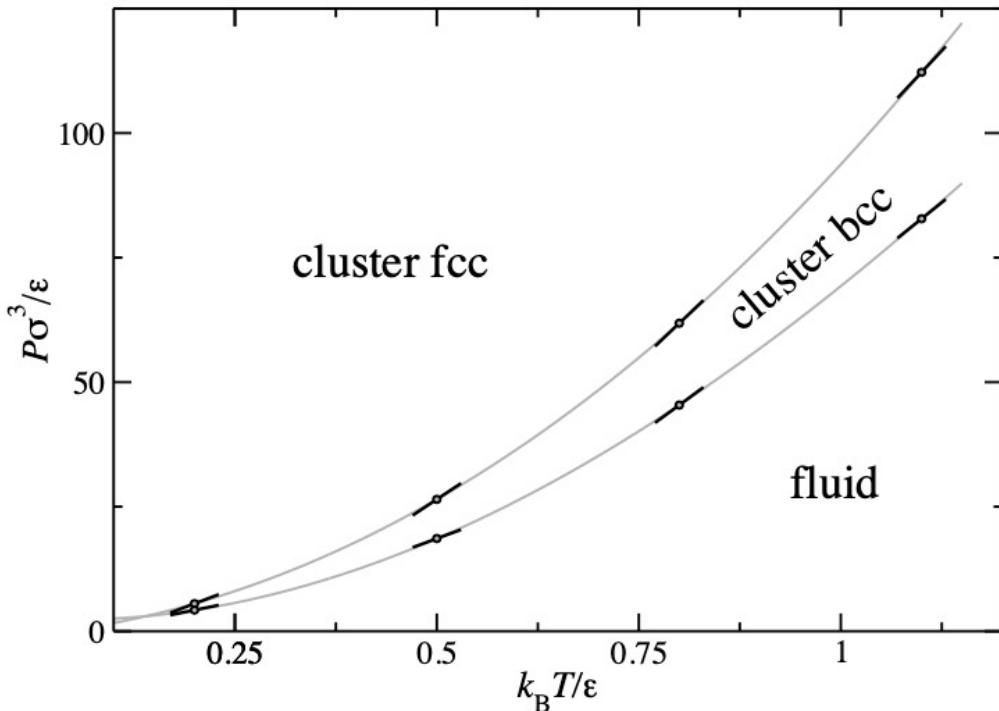


Figure 7.53: P - T phase diagram (points) as obtained from MC simulations with the corresponding Clausius-Clapeyron tangents (black segments) to the coexistence curve. The grey lines interpolate the simulation data and are guides to the eye. Their intersection point indicates a triple point at $k_B T/\varepsilon \approx 0.15$.