Glasses and Jamming: lessons from hard disks in a narrow channel

Mike Moore

School of Physics and Astronomy, University of Manchester, UK

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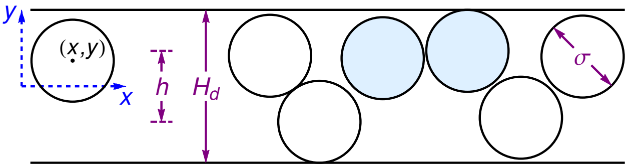
Co-Author:
Mike Godfrey, University of Manchester

Disks in a Narrow Channel

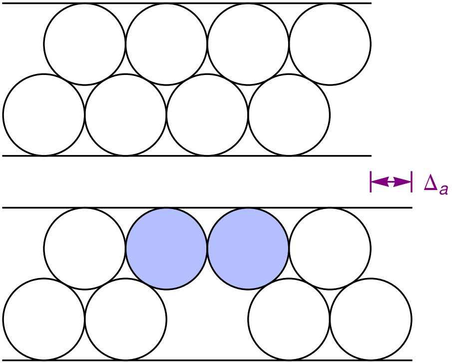


- Packing fraction $\phi = \frac{N\pi(\sigma/2)^2}{H_d L}$.
- $h = H_d - \sigma$ is the width available to the centres of the disks.

Three ranges for the width:

- $H_d < (1 + \sqrt{3}/2)\,\sigma$ – nearest-neighbour contacts only. (NN case).
- $(1 + \sqrt{3}/2)\,\sigma \le H_d \le 2\sigma$ – nearest and next-nearest neighbour contacts possible. (NNN case).
- $H_d > 2\sigma$ – disks can move past each other. This case cannot be solved with the transfer matrix approach.

The NN case case first. Figures for $H_d = (1 + \sqrt{3}/2)\,\sigma$.

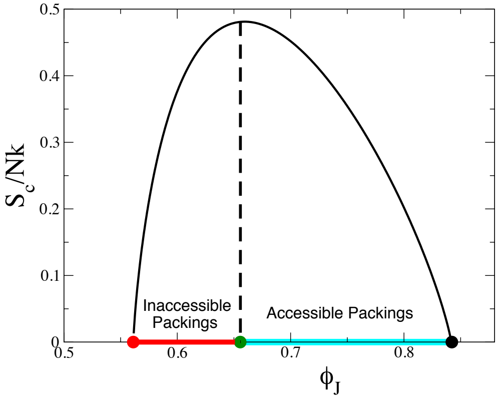


Upper Figure: the jammed state of maximum density. $\phi_{max} = 0.8418$.

Lower Figure: a jammed state with a defect. $\Delta_a = \sigma - \sqrt{\sigma^2 - h^2}$ is the extra length associated with the defect.
Note that it interrupts the zigzag structure.

Number of Jammed or Inherent States $S_c(\phi)$ for NN case

$S_c(\phi) = \ln N_J(\phi)/N.$



S. S. Ashwin, M. Z. Yamchi and R. K. Bowles , PRL **110**, 145701 (2013).

Philosophy of approach

- In theoretical physics we can basically solve exactly one-dimensional models or infinite dimensional models (i.e. mean-field theories).
- Mean-field theories for glasses and jamming e.g. RFOT and glass close-packing involve replica symmetry breaking ideas. The "transitions" , e.g. at ϕ_d, ϕ_K, ϕ_{GCP} probably "avoided" transitions in three dimensions.
- Narrow channels are effectively one-dimensional systems , so only "avoided" transitions can be expected for them too.
- Results from our calculation support an old picture of glassy behaviour where the growth of the long-relaxation times is associated with structural changes in the system, e.g. Charles Frank – icosahedra, Paddy Royall and Williams, Gilles Tarjus etc..
- In our system we can identify the structural features responsible for the growing time scale. It is the growth of zig-zag order.

NN Equation of State

System can be regarded as a set of hard rods whose distance of closest approach on the x -axis is $\sigma(y_i, y_{i+1}) = [\sigma^2 - (y_i - y_{i+1})^2]^{1/2}$. The Helmholtz potential A_L is

$$\exp(-\beta A_L) = \frac{1}{\Lambda^{dN} N!} \int_{-h/2}^{h/2} \prod_i dy_i [L - \sum_{i=1}^{N} \sigma(y_i, y_{i+1})]^N$$

The sum is the total excluded volume of the hard rods. Define the Gibbs potential via

$$\exp(-\beta \Phi) = \int_0^\infty d\, L \exp(-\beta A_L) \exp(-\beta f L)$$

f is the force on the confining piston which keeps the N disks in a channel of length L.

$$\exp(-\beta \Phi) = \frac{1}{(\beta f)^{N+1} \Lambda^{dN}} \int_{-h/2}^{h/2} \prod_i dy_i \exp\left(-\beta f \sum_{i=1}^{N} \sigma(y_i, y_{i+1}) \right).$$

NN Transfer Matrix

$$\lambda_n \, u_n(y_1) = \int_{-h/2}^{h/2} e^{-\beta f \sigma(y_1,y)} \, u_n(y) \, dy \, .$$

As $N \to \infty$

$$\beta \Phi \to -N \ln \left(\lambda_1 / \beta f \Lambda^2 \right) .$$

λ_1 is the largest eigenvalue of the integral equation (i.e. transfer matrix).
The equation of state is $L = \partial \Phi / \partial f$.
The next largest eigenvalue λ_2 gives information on the correlation length.

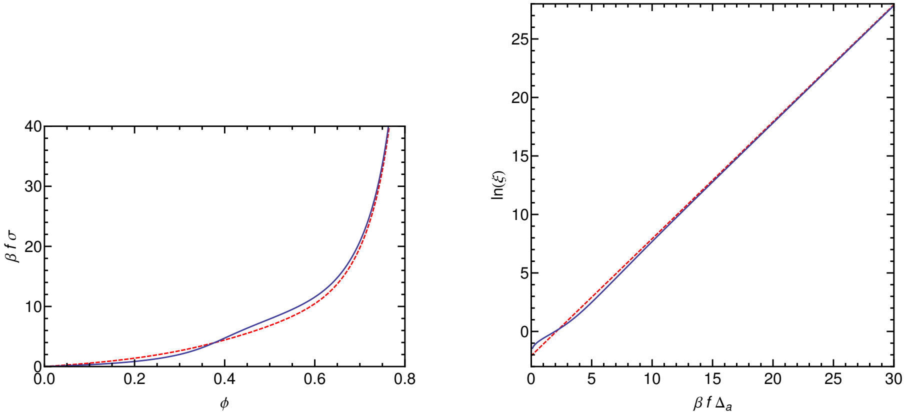
$$\xi = \frac{1}{\ln(\lambda_1/|\lambda_2|)}.$$

It describes the decay of the zig-zag correlation:

$$\langle y_i \, y_{i+s} \rangle \sim (-1)^s \exp(-s/\xi) \, ,$$

NN Equation of state and correlation length ξ

Numerically exact equation of state and zig-zag correlation length ξ.
Red lines are the defect based theory which becomes exact at high densities.



What we want to learn about: Hard Spheres in $d = 3$

- Fluid – fcc crystal first order transition at $\phi_c \approx 0.49$. No genuine phase transitions in one-dimensional channels.
- Onset of slow activated dynamics for hard spheres at $\phi > \phi_d = 0.58$. This is normally "explained" by mode-coupling theory. ϕ_d marks the onset of caging. There is a ϕ_d for the NN channel at ≈ 0.48.
- Random close packing density $\phi_{rcp} \approx 0.64$. A related feature exists for the NNN case of the narrow channel.
- ϕ_J dependence on compression rate can be understood in the channel.
- Numerical work for hard spheres becomes difficult for $\phi > 0.60$. A G-point ϕ_G where timescales diverge at finite pressure has been suggested (Berthier and Witten). S_c is supposed to vanish at the Kauzmann density ϕ_K. The Adam-Gibbs formula is supposed to relate $\tau_\alpha \sim \exp[A/S_c]$.
- Do these features arise in narrow channels?

Understanding the equation of state and ξ for the NN case at high densities

At high densities behaviour is controlled by defects. When disks are on opposite sides of the channel the excluded volume is

$$\sigma(1,2) = \sqrt{\sigma^2 - (h - z_1 - z_2)^2} \simeq \sqrt{\sigma^2 - h^2} + \frac{h}{\sqrt{\sigma^2 - h^2}}(z_1 + z_2).$$

(z_i denotes the distance of disk i from its confining wall at $y = \pm h/2$).
When the disks are on the same side i.e. within a defect, it is $\sigma(1,2) \simeq \sigma + \mathrm{O}\left[(z_1 - z_2)^2/\sigma\right]$; there is no term linear in z_1 or z_2.
For M defects, the total excluded volume is

$$\sum_{i=1}^{N-1} \sigma(y_i, y_{i+1}) \simeq (N-M)\sqrt{\sigma^2 - h^2} + M\sigma + \sum_{k=1}^{2M} \frac{hz_k}{\sqrt{\sigma^2 - h^2}} + \sum_{k=2M+1}^{N} \frac{2hz_k}{\sqrt{\sigma^2 - h^2}}$$

We can insert this into the expression for $\exp(-\beta\Phi)$ and integrate the z_i from 0 to ∞, with negligible error at large density.

$$\exp(-\beta\Phi) = \frac{1}{(2\beta f \Lambda^2)^N} \sum_M W_M \, e^{-\beta f[(N-M)\sqrt{\sigma^2-h^2}+M\sigma]} \left(\frac{\sqrt{\sigma^2-h^2}}{\beta f h}\right)^N 2^{2M},$$

where the combinatorial factor W_M is

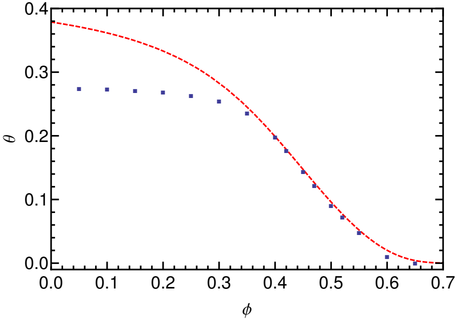
$$W_M = \frac{(N-M)!}{M!\,(N-2M)!}\,.$$

In the thermodynamic limit we can convert the sum over M to an integral over θ, where $M = \theta N$. Then on using steepest descents, at large $\beta f \sigma$

$$\theta \simeq 4\exp[-\beta f \Delta_a].$$

$\Delta_a = \sigma - \sqrt{\sigma^2 - h^2}$ is the extra length of the system containing one defect over that of the state of maximum density.

- The work done in increasing the length against the applied force is then $\Delta E = f\Delta_a$.
- The exponential is of the Boltzmann form $\exp(-\beta\Delta E)$.



Good agreement with the simulations of Bowles and Saika-Voivod as $\phi \to \phi_{\max}$.

The equation of state is

$$\beta f = \frac{2N}{L - N[(1-\theta)\sqrt{\sigma^2 - h^2} + \theta\sigma]}.$$

In the limit $\phi \to \phi_{max}$, $\theta \to 0$, so

$$\beta f \simeq \frac{2N}{L(1 - \phi/\phi_{\mathrm{max}})},$$

(cf Salsburg and Wood).
The correlation length

$$\xi \approx \frac{1}{8}\exp(\beta f \Delta_a).$$

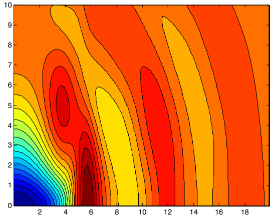
Notice that ξ is basically the distance between defects $1/\theta$ and grows exponentially rapidly as $\phi \to \phi_{max}$.

Summary: the static and thermodynamic properties of the NN model can be completely determined. Analysis in terms of defects is an excellent approximation at high densities.

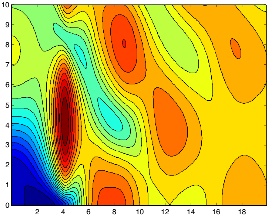
The Structure Factor $S(k_x, k_y)$

Plots are of $\log S(k_x, k_y)$.

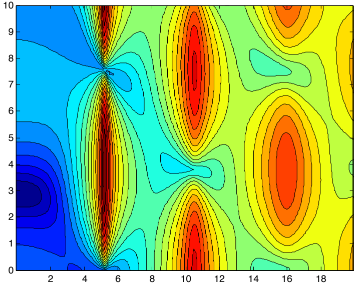
$\beta f \sigma = 3.5$, i.e. low density.



$\beta f \sigma = 7.5$, a density close to ϕ_d.



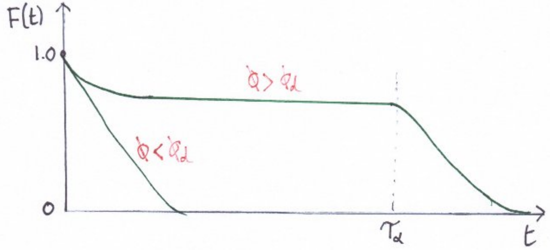
As the density is increased there is growing "crystalline" as well zig-zag order. Results for $\beta f \sigma = 20$.



Onset of Activated Dynamics in the NN model

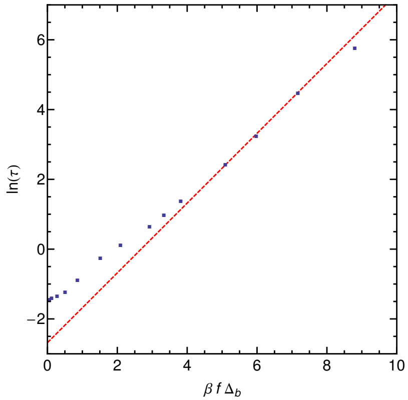
One can calculate using molecular dynamics the autocorrelation function

$$F(t) = \frac{1}{N}\sum_{i=1}^{N}\frac{\langle y_i(0)y_i(t)\rangle}{\langle y_i^2\rangle}.$$



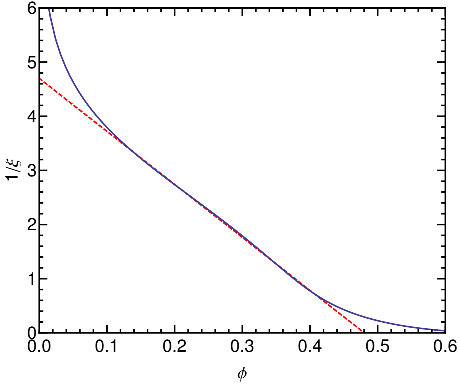
For $\phi > \phi_d \approx 0.48$ (Bowles et al.) the time scales are long and activated.

Activated Dynamics and Defects



τ is the time for a single defect to move. Data from MD simulation of Bowles and Saika-Voivod, PRE **73**, 011503 (2006). Red line: transition state theory i.e. activated dynamics.

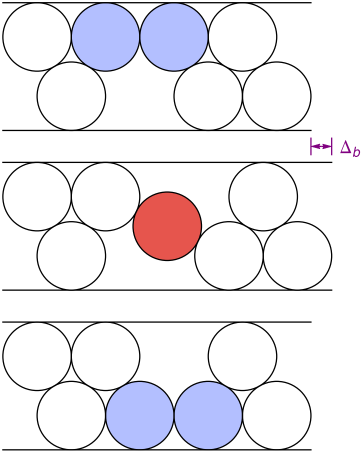
For three dimensional systems it has been suggested that there is perhaps a growing length scale associated with the growing time scale as ϕ_d is approached. Only in mean-field type theories does it truly diverge.



$$\xi \sim \frac{1}{1 - \phi/\phi_d}$$

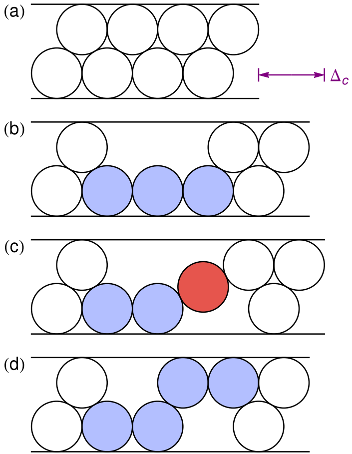
Transition State Theory For Motion of a Defect

The saddle point which has to be passed over to move the defect from (say) (3,4) to (4,5) in red. Extra length at the saddle point is $\Delta_b = \sqrt{4\sigma^2 - h^2} - \sigma - \sqrt{\sigma^2 - h^2}$. Then $1/\tau \sim \exp(-\beta f \Delta_b)$.



Transition state theory for creating Pairs of Defects

The saddle point for the creation of a pair of defects requires an extra length $\Delta_c = \sqrt{4\sigma^2 - h^2} + \sigma - 3\sqrt{\sigma^2 - h^2}$. Rate of pair defect creation $1/\tau_D \sim \exp(-\beta f \Delta_c)$.

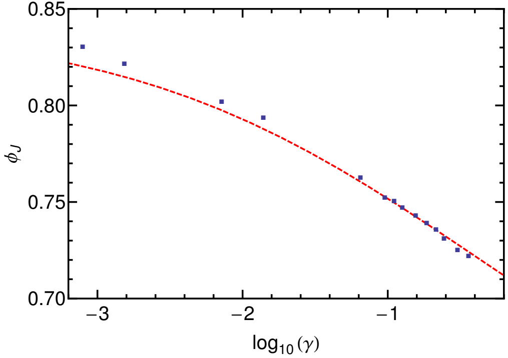


Diffusion Coefficient for Defects

- Defects are typically spaced by ξ and are created and annihilate in pairs.
- When they have moved a distance ξ by a diffusion like process they will typically annihilate.
- Time to annihilation τ_D is therefore $\sim D\xi^2$, where D is the diffusion coefficient.
- $D \sim \tau_D/\xi^2 \sim 1/\tau$. D is the rate $1/\tau$ for a defect to move a single place.
- Transition state estimates of τ_D and τ and the estimates of ξ at large densities are all consistent.

Jammed states and the Lubachevsky-Stillinger algorithm

The diameter of the disks is increased at a rate $\gamma = \sigma^{-1} d\sigma/dt$ in the molecular dynamics simulation until the system jams at a packing fraction ϕ_J.



(Ashwin, Yamchi and Bowles, PRL **110**, 145701 (2013)).

- The slower the compression rate, the higher the final jammed density ϕ_J.
- If there are M defects in the jammed state

$$\phi_J = \frac{N\pi\sigma^2}{4H_d[M\sigma + (N-M)\sqrt{\sigma^2 - h^2}]}$$
$$= \frac{\pi\sigma^2}{4H_d[\theta\sigma + (1-\theta)\sqrt{\sigma^2 - h^2}]}.$$

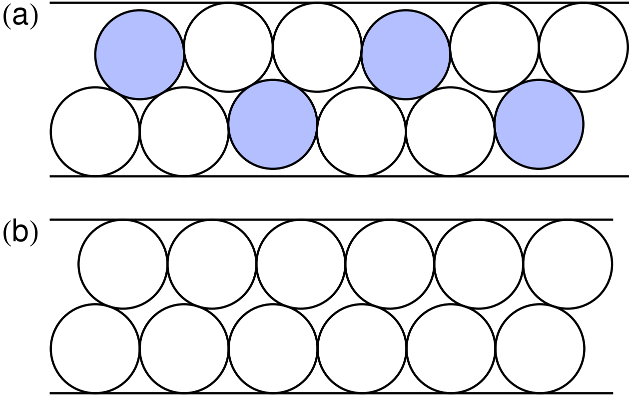
- The Kibble-Zurek hypothesis: the system will fall out of equilibrium when the rate of compression exceeds the rate at which defects can annihilate, $1/\tau_D$.
- At this point θ is frozen in and is not changed by the last stages of the LS compression.
- By equating $1/\tau_D(\theta)$ to γ we obtain the red line for ϕ_J versus γ.

Comments on the NN Model versus real glasses

- The structure factor $S(k_x, k_y)$ of the NN model in the vicinity of ϕ_d changes rapidly as a function of ϕ.
- The structure factor of real glasses and hard spheres hardly alters near ϕ_d. Glasses with very similar structure factors can have very different dynamics (Berthier and Tarjus).
- Maybe for them the important changes in the structure causing the change to activated dynamics shows up only in higher correlation functions, reflecting bond angles etc..

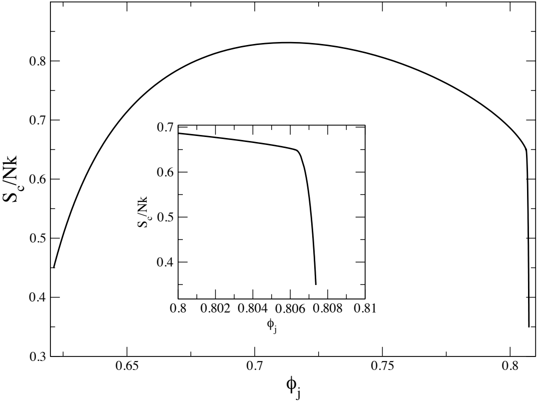
The NNN case

$(1+\sqrt{3}/2)(\approx 1.8660)\,\sigma < H_d < 2\sigma$: the NNN case. Figures for $H_d = 1.95\sigma$ when $\phi_{max} \approx 0.8074$ and $\phi_K \approx 0.8053$.



Configurational Entropy for the NNN case

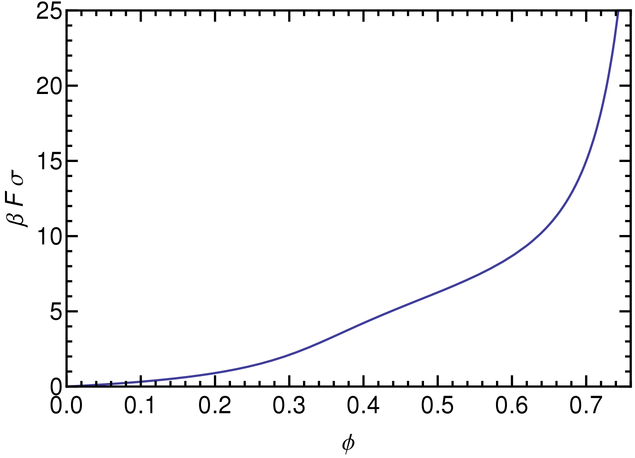
$H_d = 1.95\sigma$, $\phi_{max} = 0.8074$



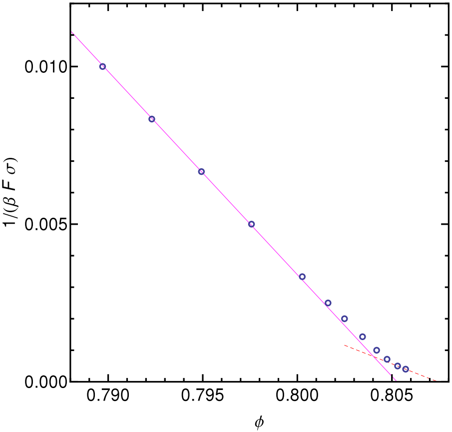
(from S. S. Ashwin and R. K. Bowles, PRL **102**, 235701 (2009)).

NNN equation of state

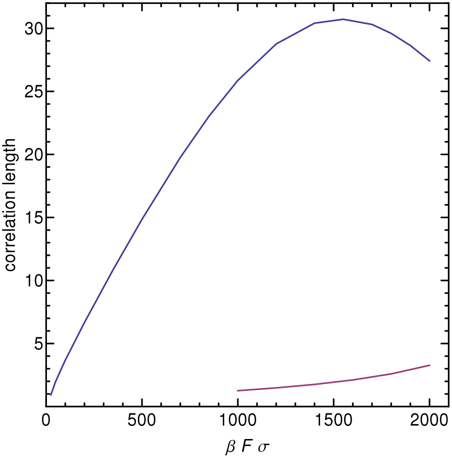
The transfer matrix for the NNN problem is complicated.



Is there a feature in the equation of state associated with the "kink" in S_c?



There is an "apparent" divergence of $\beta F \sigma$ for $\phi = \phi_K \approx 0.8053 < \phi_{max}$.



$\xi_3 = 1/\ln(\lambda_1/\lambda_3)$, corresponding to "crystalline" order as in the $S(k)$ of the hard rod gas as $\phi \to \phi_{max}$.
$\xi_c = 1/\ln(\lambda_1/|\lambda_c|)$, corresponding to the growth of buckled crystalline order.

Comments on the NNN model

- (a) The "kink" in S_c,(b) the apparent divergence in the pressure (force), and (c) the peak in ξ_3 are all close to $\phi = \phi_K$.
- There is no true singularity at ϕ_K: the "transition" is avoided.
- Question: Does behaviour near ϕ_K mimic what is expected for hard spheres at ϕ_{rcp}?
- At ϕ_{rcp}, the pressure apparently diverges, just as at ϕ_K, and the jammed states for $\phi > \phi_{rcp}$ have increasing amounts of fcc order.
- The correlation length associated with ϕ_d in the NNN model is still the length scale associated with the growing zig-zag order i.e. $\xi = 1/\ln(\lambda_1/|\lambda_2|)$.
- There are multiple length scales, e.g. ξ, ξ_3 and ξ_c (and therefore time) scales in the system.