Inducing liquid-crystal and crystalline order by increasing temperature in two-temperature active-rod fluid

Presented by

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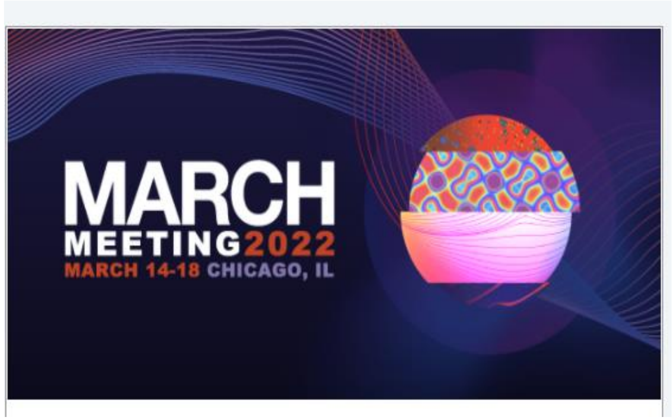
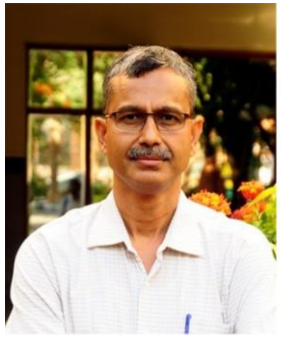
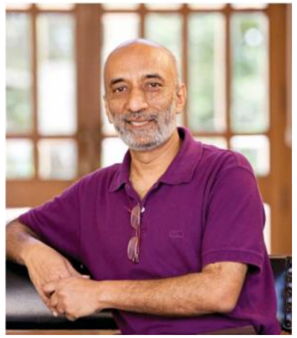






Prof. Prabal K. Maiti **Prof. Sriram Ramaswamy** **Prof. Chandan Dasgupta**

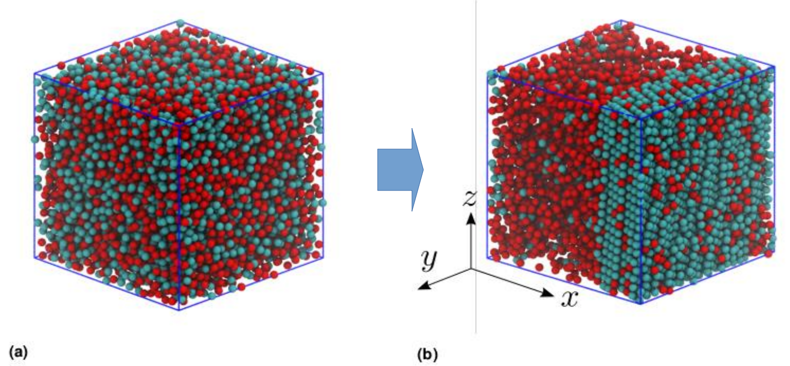
Motivation

Fish schools [1]

➢ Active matter :
- ❑ composed of "active agents"
- ❑ consume energy locally
- ❑ global non-equilibrium phase behaviours

➢ Example: flocks of birds, schools of fish, colony of bacteria , in the subcellular scale the cytoskeleton motor filaments.

Phase separation in Lennard-Jones (LJ) system



➢ Vectorial activity: Activity ∝ Self-propulsive force -> Vicsek model , Run and Tumble Particles (RTP), Active Brownian Particles (ABP).

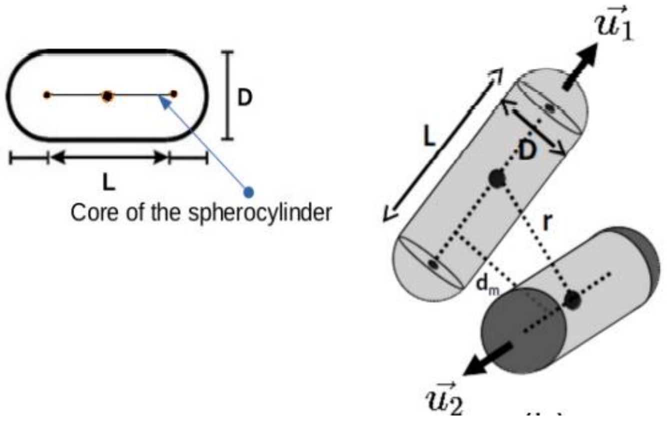
➢ Scalar activity : Activity does not have any preferred direction
- ❑ Example: Chromatin separation, phase separation in colloidal systems etc.
- ❑ Two-temperature model: Activity ∝ effective temperature difference

➢ **How two-temperature activity affects phase behaviors of Anisotropic active particles?**

- *[1] M. C. Marchetti, J. F. Joanny, S. Ramaswamy, T. B. Liverpool, J. Prost, M. Rao, and R. A. Simha, Rev.Mod. Phys. 85, 1143 (2013).*
- *[2] Ganai et al, Nucleic Acids Res. 42, 4145 – 4159 (2014).*
- *[3] A. Y. Grosberg and J.-F. Joanny, Phys. Rev. E 92, 032118 (2015).*
- *[4] S. S. N. Chari, C. Dasgupta, and P. K. Maiti, Soft Matter 15, 7275 (2019).*

The Model :
Soft Repulsive Spherocylinder (SRS)

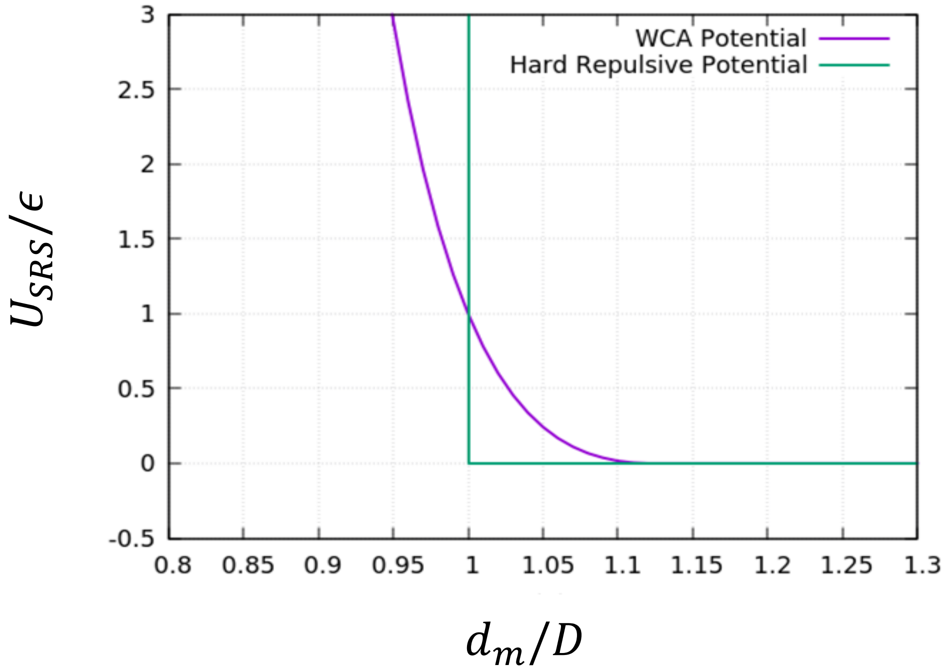
Schematic diagram of Spherocylinder



Weeks-Chandler-Anderson potential (WCA)

$$U_{SRS} = 4\varepsilon[(\frac{D}{d_m})^{12} - (\frac{D}{d_m})^{6}] + \epsilon \quad if \quad d_m < 2^{\frac{1}{6}} D$$

$$= 0 \quad if \quad d_m \geq 2^{\frac{1}{6}} D$$



- **Soft Repulsive Spherocylinder (SRS):** Spherocylinders are interacting through **Weeks-Chandler-Anderson potential (WCA)**
- **Aspect ratio = Length/Diameter**
- u_1, u_2 describe the orientations of the Spherocylinder 1 and 2 respectively
- r is the distance between their centers of masses.
- **d_m is the shortest distance that determines the interaction potential between them.**

Simulation methods:
Molecular Dynamics

- **We have performed Molecular Dynamics (MD) simulations** for a system of SRS with **aspect ratio L/D = 5 .**
- We use **Verlet algorithm** to update the positions and velocities of the particles
- We use **Quaternion based rigid-body dynamics** for rotational motion.
- The temperature was controlled using **Berendsen thermostat** with temperature relaxation time $\tau_T = 0.01$
- The pressure was controlled using **Berendsen barostat** with pressure relaxation time $\tau_T = 2.00$

Centre of mass motion:

$$x(t+\Delta t) = x(t) + v(t)\Delta t + \frac{a(t)}{2}(\Delta t)^2$$

$$v(t+\Delta t) = v(t) + \frac{a(t) + a(t+\Delta t)}{2}(\Delta t)$$

Rotation:

$$\frac{d\Omega_1}{dt} = \frac{I_2 - I_3}{I_1}\Omega_2\Omega_3 + \frac{T_1}{I_1}$$

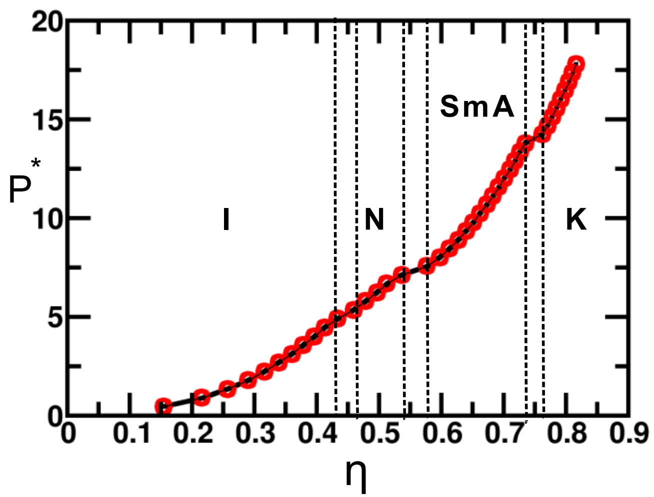
$$\frac{d\Omega_2}{dt} = \frac{I_3 - I_1}{I_2}\Omega_3\Omega_1 + \frac{T_2}{I_2}$$

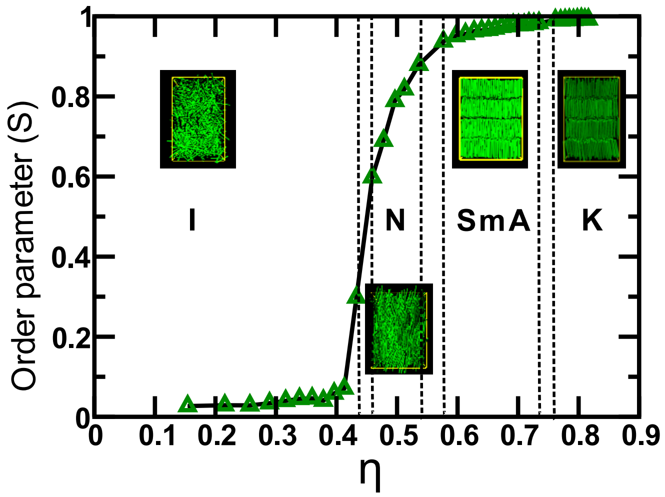
$$\frac{d\Omega_3}{dt} = \frac{I_1 - I_2}{I_3}\Omega_1\Omega_2 + \frac{T_3}{I_3}$$

- *I. P. Omelyan, Computers in Physics 12, 97 (1998).*
- *N. S. Martys and R. D. Mountain, Physical Review E 59, 3733 (1999).*
- *M. Rotunno, T. Bellini, Y. Lansac, and M. A. Glaser, The Journal of chemical physics 121, 5541 (2004).*
- *P. K. Maiti, Y. Lansac, M. A. Glaser, and N. A. Clark, Physical review letters 88, 065504 (2002).*

Equilibrium properties:

Equation of State of SRS for L/D = 5 at temperature T* = 5 :



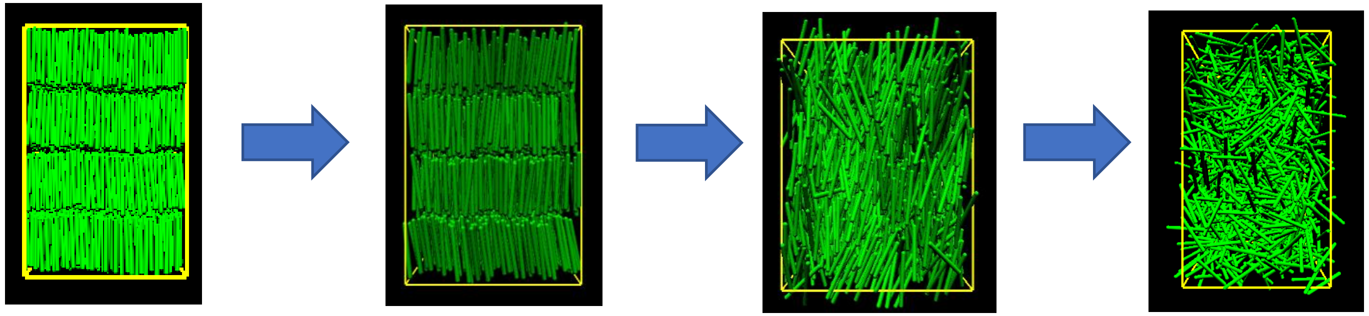


- **Nematic Order Parameter (S):** The scalar nematic order parameter ***S*** is the largest eigenvalue of ***Q***

$$Q_{ab} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{3}{2}u_i{}^a u_i{}^b - \frac{1}{2}\delta_{ab}\right)$$

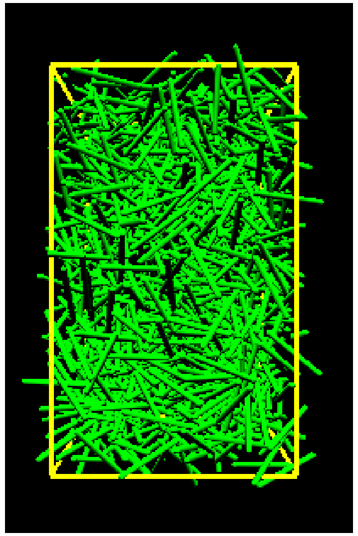
- **Equilibrium Phases:**

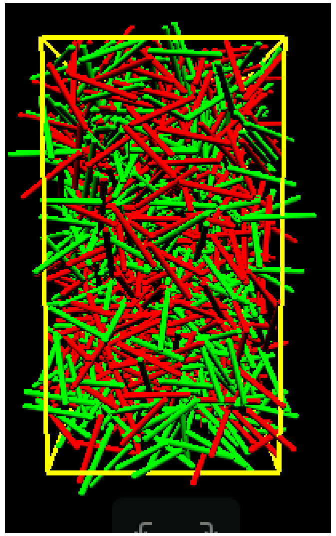
Crystal (K) **Smectic A (Sm A)** **Nematic (N)** **Isotropic (I)**



- Reduced pressure $P^* = PV_{sc} / k_B T$
  Packing fraction $\eta = NV_{sc} / V_{box}$
  Reduced Temperature $T^* = k_B T/\varepsilon$
  Volume of the Spherocylinder = $V_{sc} = \pi D^2(\frac{D}{6} + \frac{L}{4})$

Simulation Method for active-passive rod mixture:





Activity ➡ $\chi = \dfrac{T^*_{hot} - T^*_{cold}}{T^*_{cold}}$

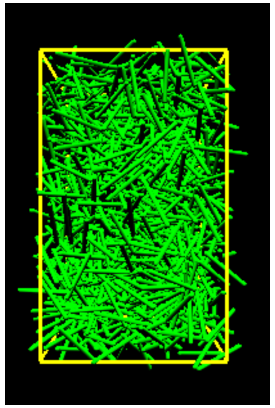
- T^*_{hot} is the imposed hot particles temperature.
- T^*_{cold} is the imposed cold particles temperature .
- We fix the cold particles' temperature at T^*_{cold} = 5 through out the simulation and slowly increase T^*_{hot} to increase the activity χ.

- **Red – Hot Particles – Active Particles**
- **Green – Cold Particles – Passive Particles**

- **The difference between the two temperatures scaled by the lower temperature provides a measure of the activity.**

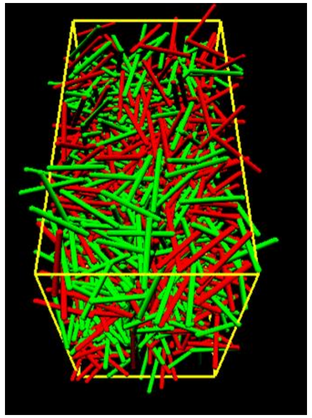
Results: Phase separation and ordering starting from Isotropic phase (η = 0.36)

$\chi = 0\ , S = 0$



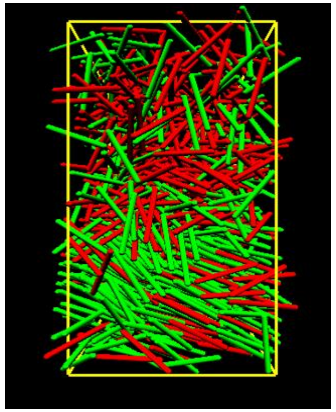
Initial phase: Isotropic

$\chi = 0.61\ , S_{cold} = 0.06\ , S_{hot} = 0.05$



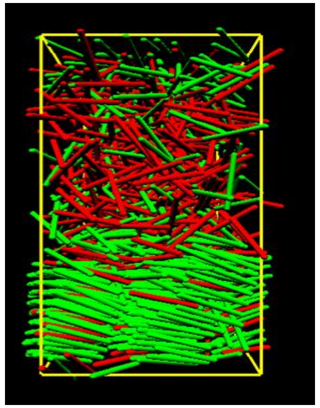
Hot: Isotropic
Cold: Isotropic

$\chi = 1.99, S_{cold} = 0.06\ , S_{hot} = 0.12$



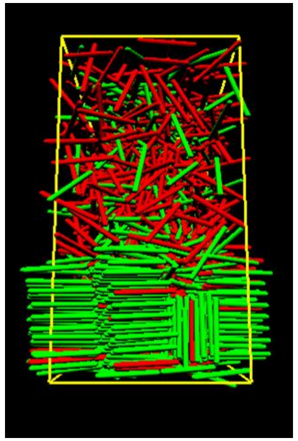
Hot: Isotropic
Cold: Nematic

$\chi = 2.5\ , S_{cold} = 0.54\ , S_{hot} = 0.17$



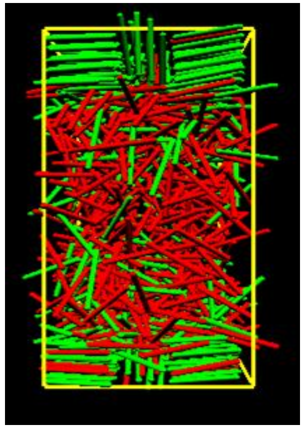
Hot: Isotropic
Cold: Nematic

$\chi = 3.5\ , S_{cold} = 0.46\ , S_{hot} = 0.12$



Hot: Isotropic
Cold: Domain Crystal

$\chi = 5\ , S_{cold} = 0.54\ , S_{hot} = 0.17$

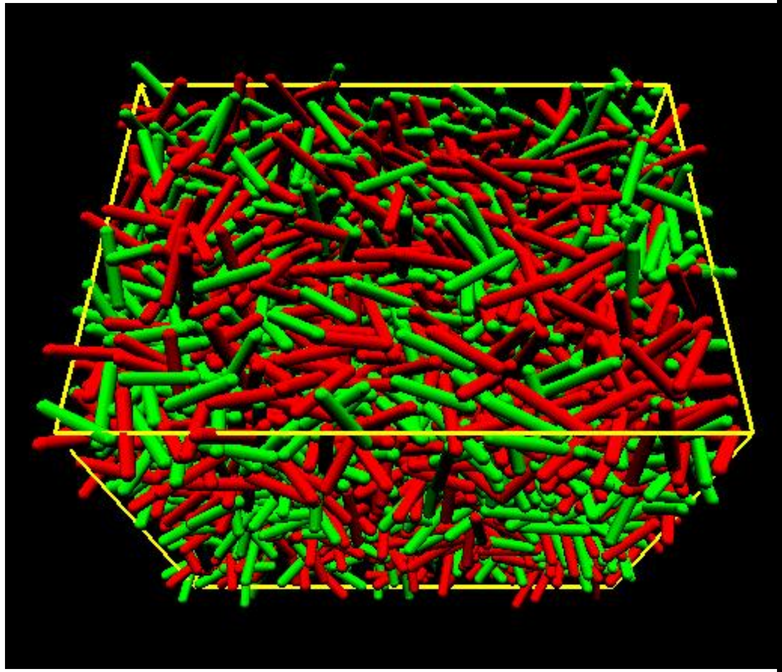


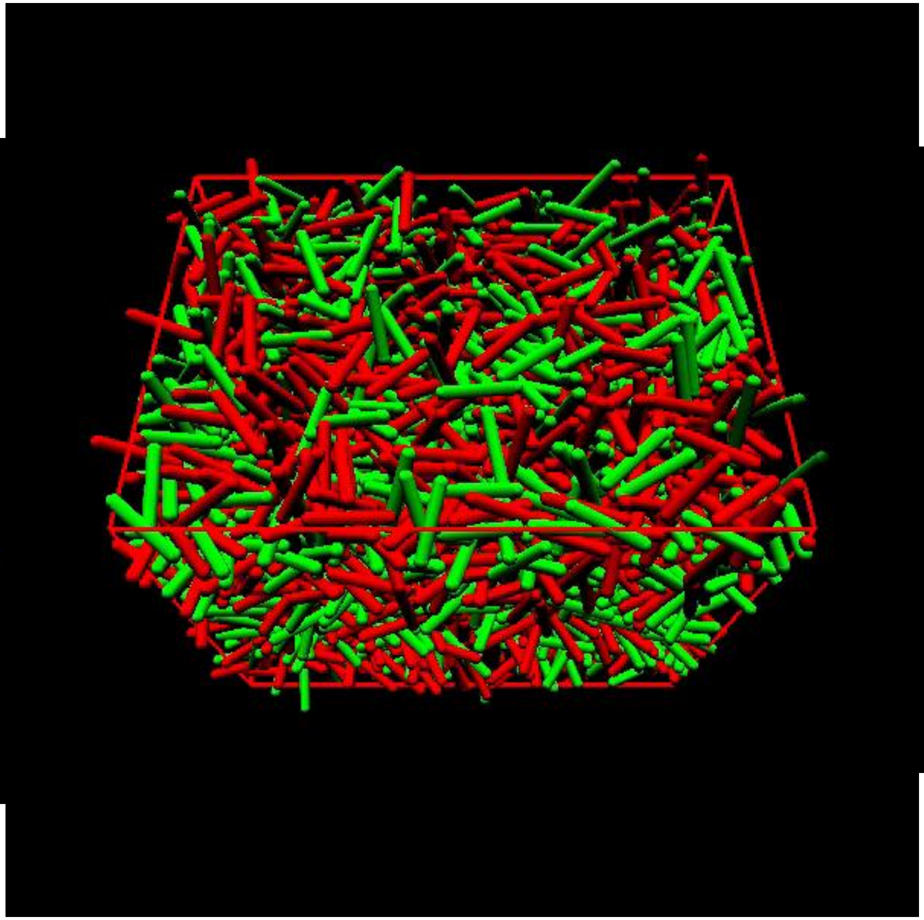
Hot: Isotropic
Cold: Domain Crystal

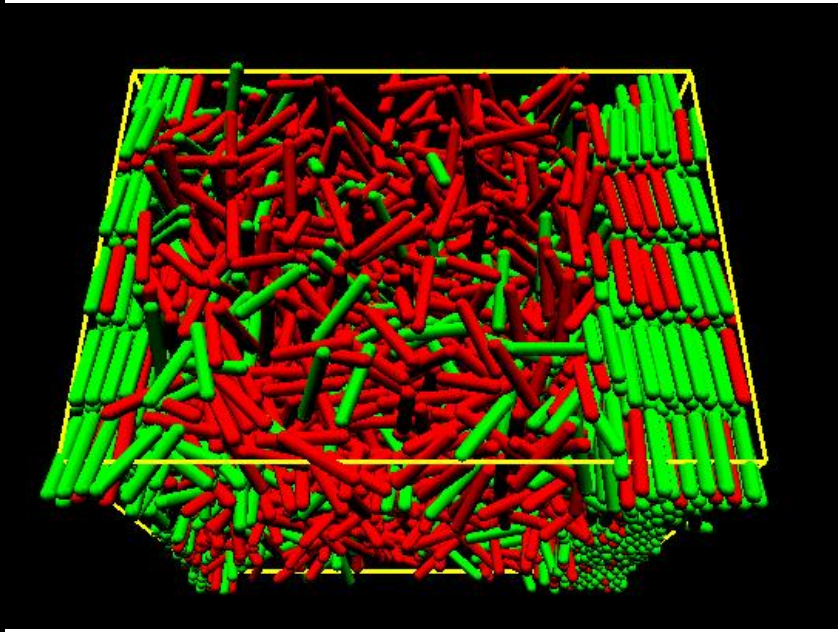
Results: Phase separation and ordering transition starting from an Isotropic phase

Initial Structure
$\chi = 0$, $S = 0$

Phase separated configuration at
$\chi = 5$, $S_{cold} = 0.58$, $S_{hot} = 0.21$





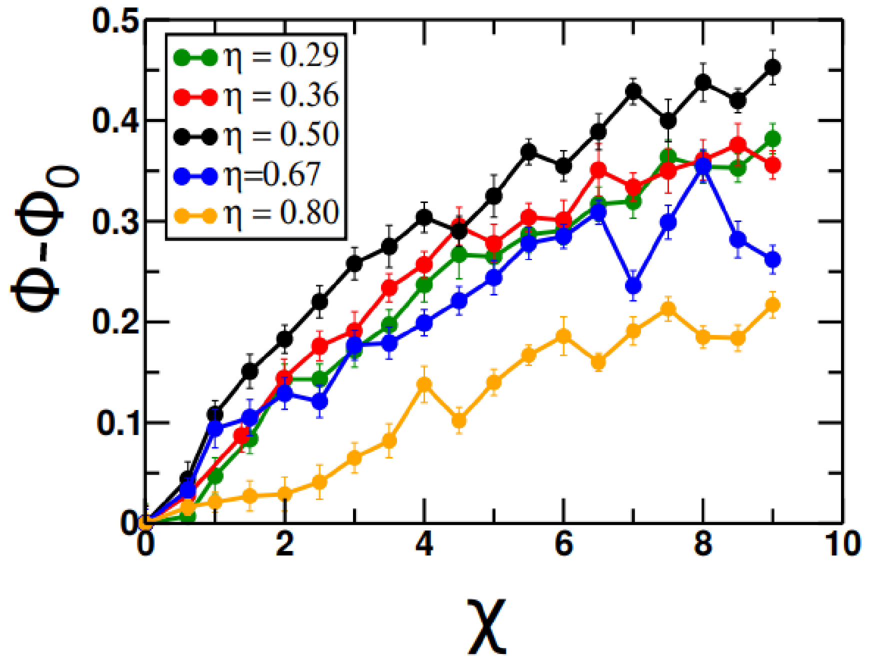


Initial phase:
Isotropic

Hot: Isotropic
Cold: Domain Crystal

Phase separation: Density order parameter (ϕ)

Density order parameter ϕ versus activity χ at different packing fractions η.



$$\phi = \frac{1}{N_{box}} \sum_{i=1}^{N_{box}} \left| \frac{\left(n_{hot}^{i} - n_{cold}^{i}\right)}{n_{tot}^{i}} \right|$$

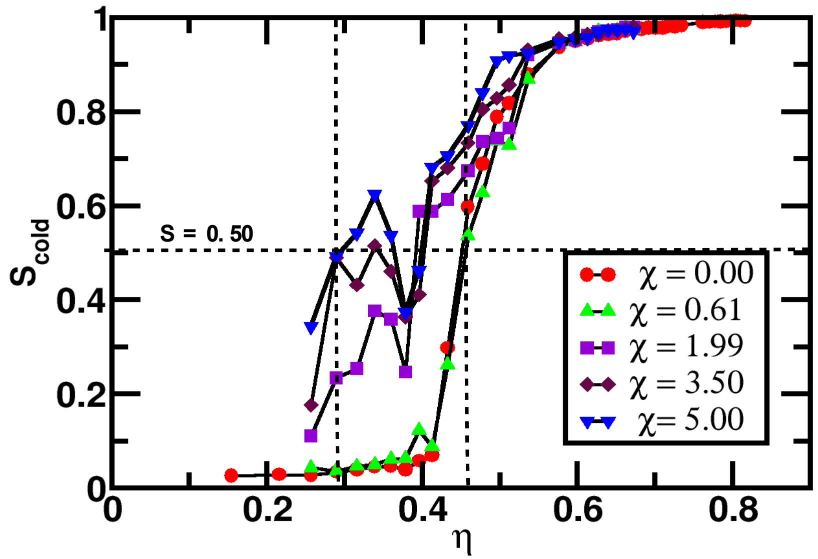
- n_{hot}^{i} and n_{cold}^{i} are the number of hot and cold particles in the i^{th} sub-box.
- $n_{tot}^{i} = n_{hot}^{i} + n_{cold}^{i}$
- N_{box} is the total number of sub-boxes.
- ϕ_0 is the initial value of density order parameter. As $\phi_0 \neq 0$ at $\chi = 0$ so we offset ϕ by its initial value ϕ_0.

➢ **Phase separation increases monotonically with χ for all the packing fractions.**

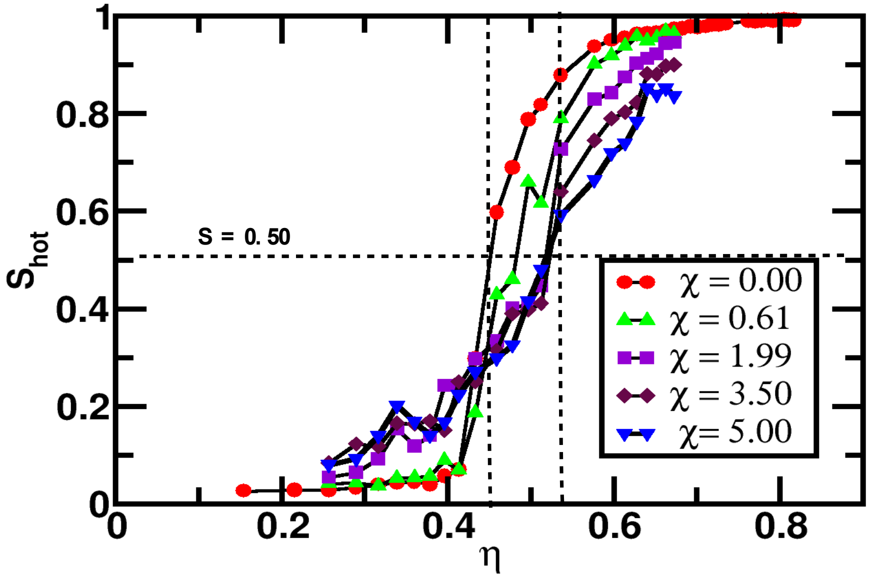
➢ **The amount of phase separation increases with η up to Nematic phase then decreases in the smectic and crystal phase.**

Shifting of Isotropic-Nematic (I-N) Phase Boundary

Nematic Order Parameter of Cold particles (S_{cold})



Nematic Order Parameter of Hot particles (S_{hot})

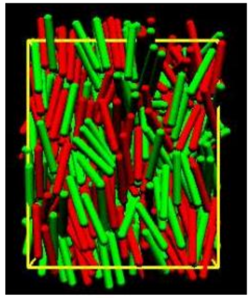


- **For cold particles, I-N phase boundary shifts towards lower packing fractions compared to the location of equilibrium I-N phase boundary.**
- **For hot particles, I-N phase boundary shifts towards higher packing fractions compared to the location of equilibrium I-N phase boundary.**

Ref. J. Chattopadhyay, S. Pannir-Sivajothi, K. Varma, S. Ramaswamy, C. Dasgupta, and P. K. Maiti, ***Phys. Rev. E,104, 054610 (2021).***

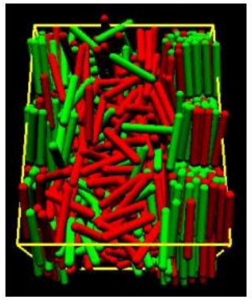
Segregated phases starting from different initial equilibrium phases

Starting from Nematic phase (η = 0.50)



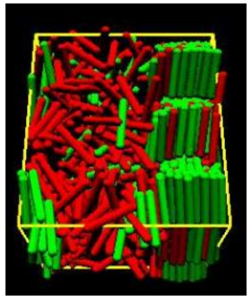
$\chi = 0.00$

$S = 0.75$-N



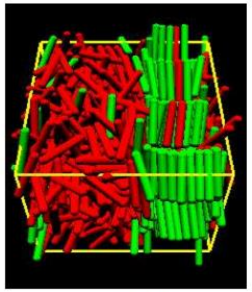
$\chi = 2.00$

$S_{cold} = 0.97$- SmA
$S_{hot} = 0.10$- I



$\chi = 5.00$

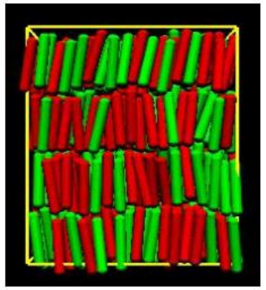
$S_{cold} = 0.99$- K
$S_{hot} = 0.10$- I



$\chi = 9.00$

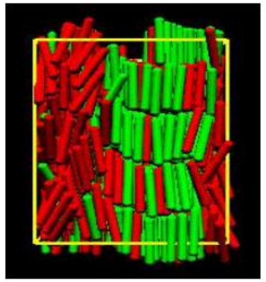
$S_{cold} = 0.99$- K
$S_{hot} = 0.08$- I

Starting from Smectic phase (η = 0.67)



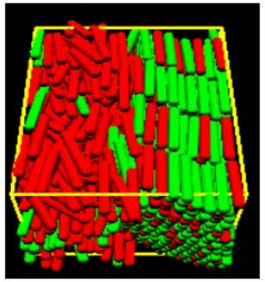
$\chi = 0.00$

$S = 0.97$-Sm



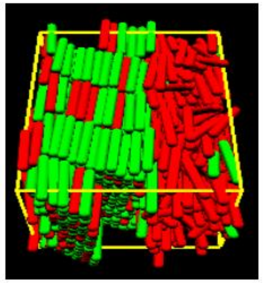
$\chi = 2.00$

$S_{cold} = 0.99$- K
$S_{hot} = 0.92$- N



$\chi = 5.00$

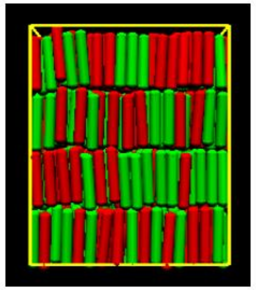
$S_{cold} = 0.99$- K
$S_{hot} = 0.81$- N



$\chi = 9.00$

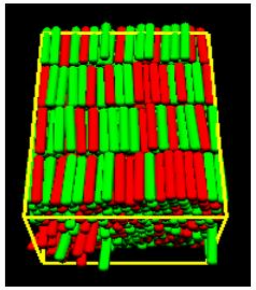
$S_{cold} = 0.99$- K
$S_{hot} = 0.63$- N

Starting from Crystal phase (η = 0.80)



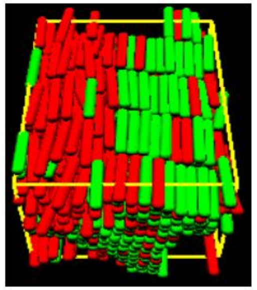
$\chi = 0.00$

$S = 0.99$-K



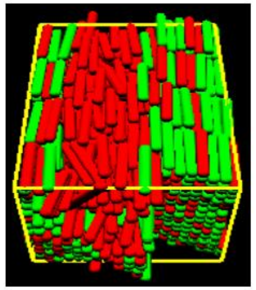
$\chi = 2.00$

$S = 0.99$- K



$\chi = 5.00$

$S_{cold} = 0.99$- K
$S_{hot} = 0.94$- N



$\chi = 9.00$

$S_{cold} = 0.99$- K
$S_{hot} = 0.92$- N

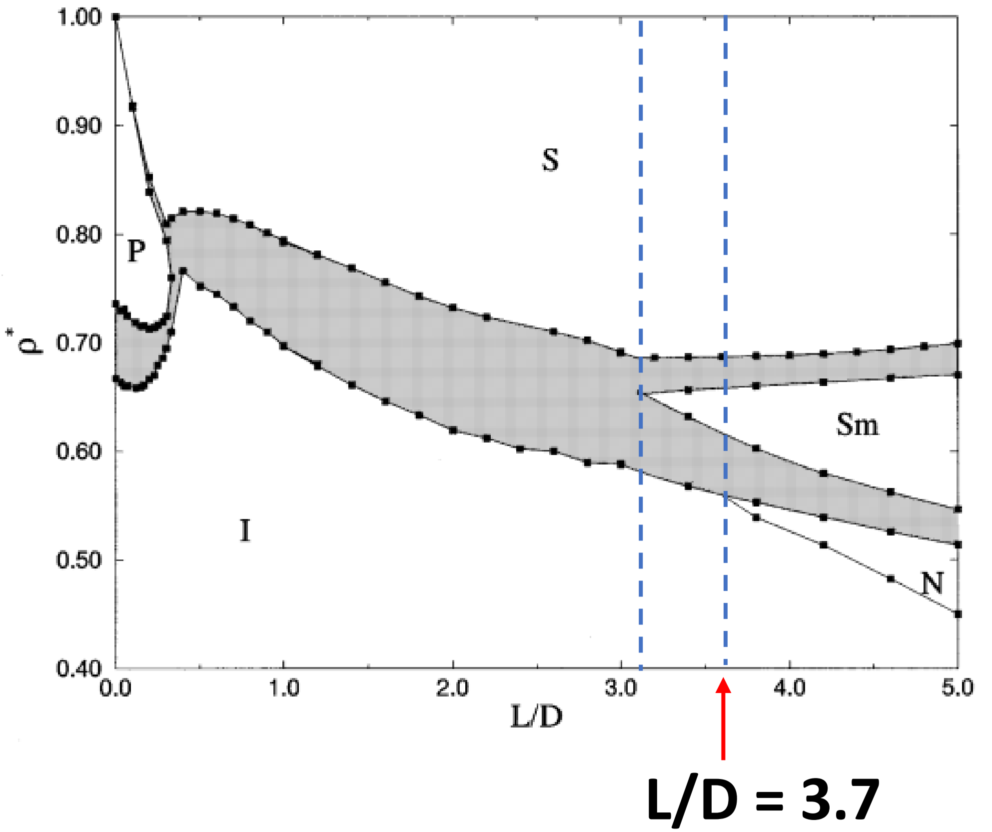
- **Hot particles -> previous less ordered state**
- **Cold particles -> next higher ordered state**

Ref. J. Chattopadhyay, S. Pannir-Sivajothi, K. Varma, S. Ramaswamy, C. Dasgupta, and P. K. Maiti, ***Phys. Rev. E,104, 054610 (2021).***

Onsager's limit

- Onsager showed analytically that Isotropic - Nematic (I-N) phase transition is **not possible** for the aspect ratio **below 3.7** for Hard Spherocylindes (HSC).

- Bolhuis-Frenkel have studied the phase diagram of HSC for a range of aspect ratio computationally and showed that HSC with **L/D > 3.7 shows 4 different phases in equilibrium**:
- **(1) Crystal (2) Smectic A (3) Nematic and (4) Isotropic**

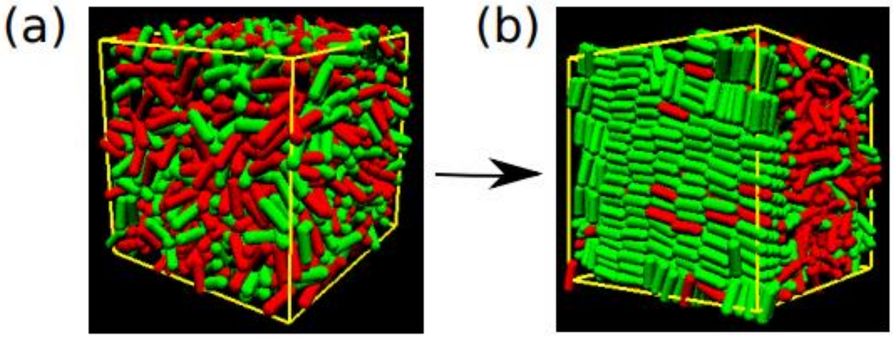


Ref: (1) L. Onsager, Ann. N.Y. Acad. Sci. 51, 445 ,1949
(2) Peter Bolhuis, and Daan Frenkel,The Journal of Chemical Physics,106, 666 (1997)
(3) S. C. McGrother, D. C. Williamson, and G. Jackson, J. Chem. Phys. 104,6755 (1996)
(4) A. Cuetos, B. Mart´ınez-Haya, L.F. Rull, and S. Lago, J.Chem. Phys. 117, 2934 (2002)

Phases in active-passive SRS of different aspect ratios

L/D = 2, η = 0.45

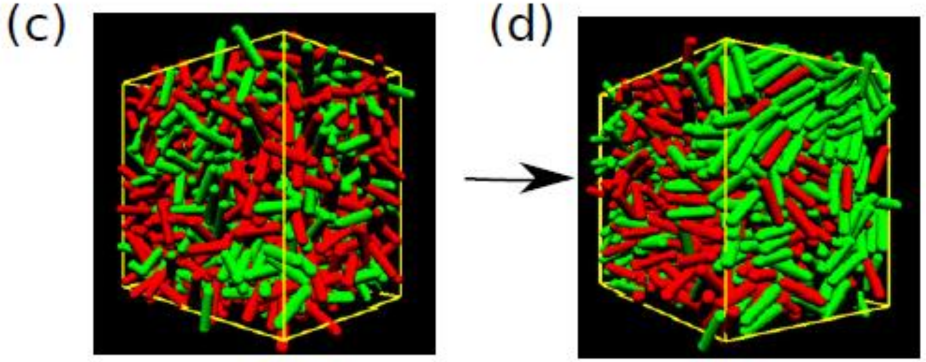
Isotropic at χ = 0 Smectic in cold zone at χ = 9



A_{SRS} at $T^* = 5$	A_{HSC}	Equilibrium Phases at $\chi = 0$	Phases at $\chi \neq 0$
5	5.28	I, N, Sm, K	I, N, Sm, K, Multi-domain K
3	3.20	I, Sm, K	I, **N**, Sm, K
2	2.11	I, K	I, **Sm**, K

L/D = 3, η = 0.33

Isotropic at χ = 0 Nematic in cold zone at χ = 4

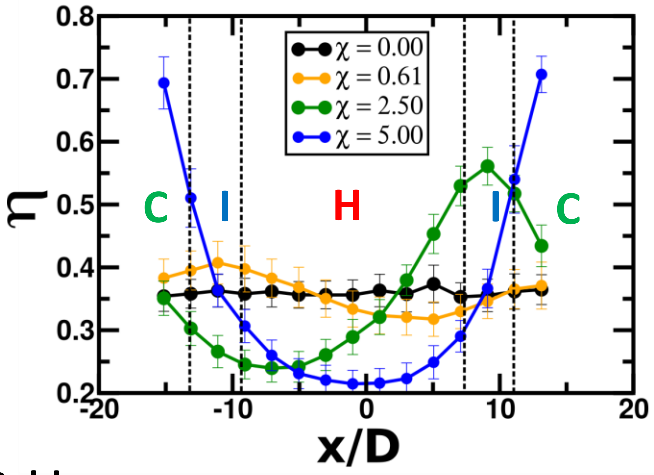


- **I-N for L/D = 3 which is below Onsager's limit.**
- **We observe Smectic phase for L/D = 2, Nematic phase for L/D = 3 and multi-domain Crystal for L/D = 5 which are not observed in equilibrium.**

Scalar activity induced isotropic-nematic transition for rods having aspect ratio below Onsager's limit, *J. Chattopadhyay, S. Ramaswamy, C. Dasgupta, and P. K. Maiti (to be submitted)*

Interfacial Properties

Packing fractions (η)

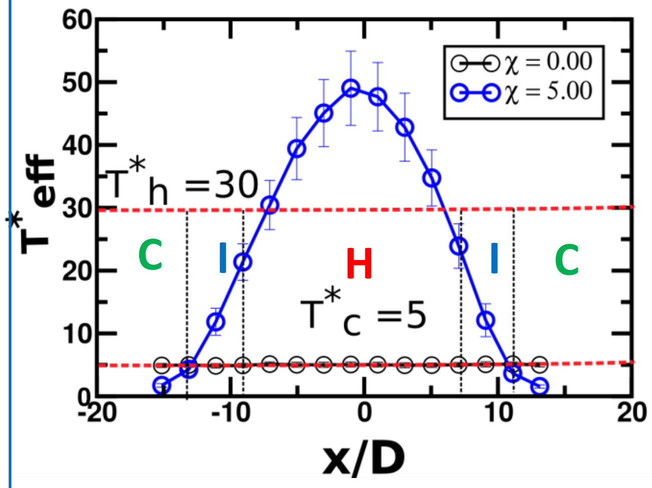


- C – Cold zone
- I – Interfacial zone
- H-Hot zone

$$\eta(i) = \frac{n(i)}{v(i)} v_{hsc}$$

➢ **η decreases from cold to hot zone**

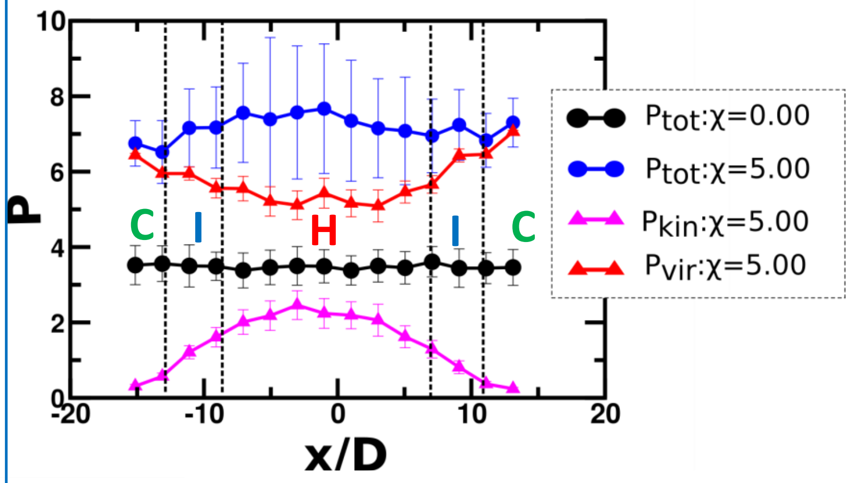
Effective temperature (T^*_{eff})



$$5 \times \frac{1}{2} k_B T_{eff}(i) = \frac{1}{n(i)} \sum_{j=1}^{n(i)} \left(\frac{1}{2} m v_j^2 + \frac{1}{2} I \omega_j^2 \right)$$

➢ **T^*_{eff} increases from cold to hot zone**

Pressure (P)



$$P_{\text{kin}}(i) = \frac{1}{3 \times V(i)} \sum_{j=1}^{n(i)} m v_j^2,$$

$$P_{\text{vir}}(i) = \frac{1}{3 \times V(i)} \sum_{j=1}^{n(i)-1} \sum_{k>j} \vec{r}_{jk} \cdot \vec{f}_{jk},$$

$$P(i) = \langle P_{\text{kin}}(i) + P_{\text{vir}}(i) \rangle_{ss}.$$

➢ **P_{kin} increases, P_{vir} decreases from cold to hot zone**

➢ **P_{tot} remains balanced to maintain mechanical stability**

Conclusions and Future Outlook

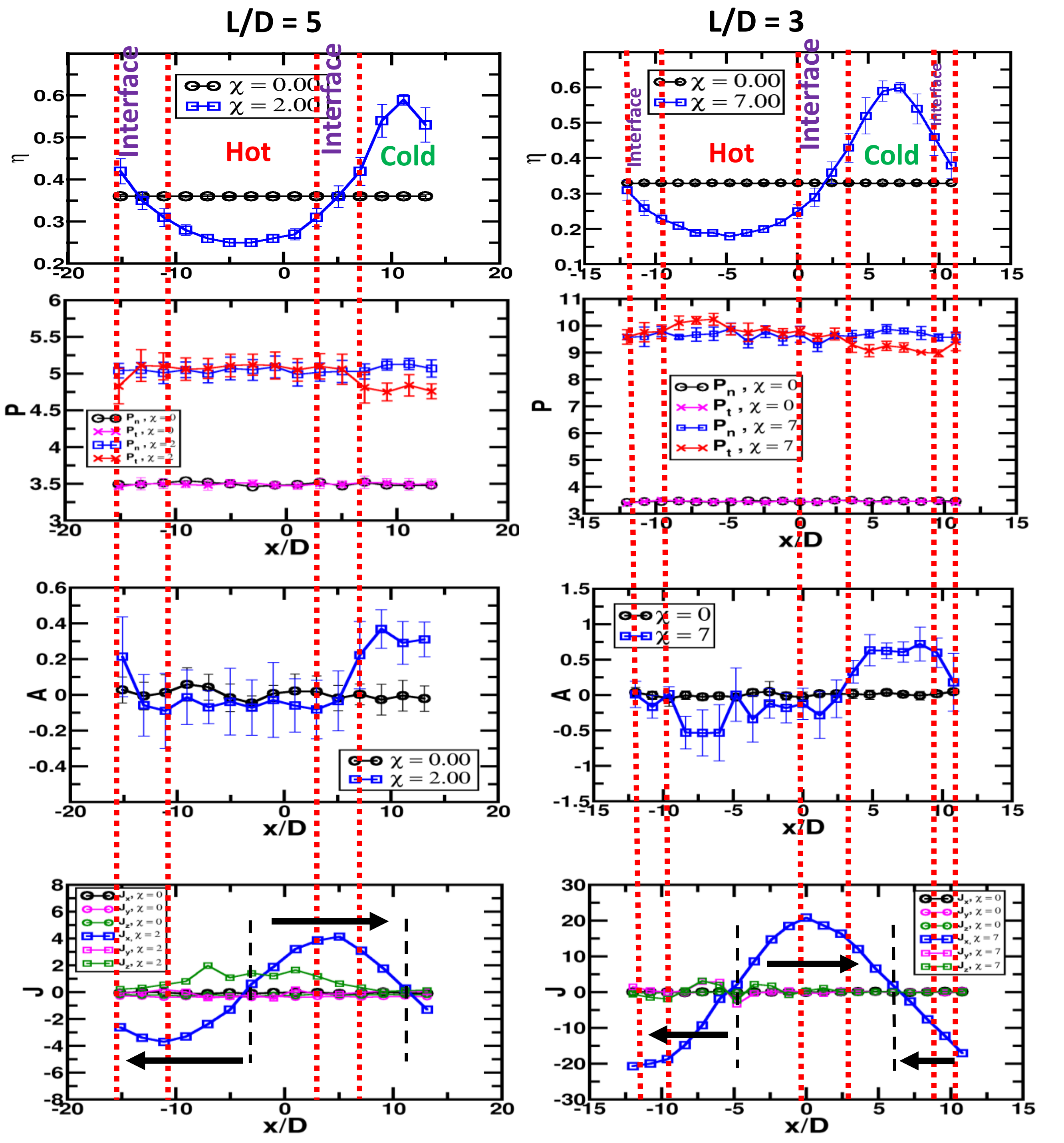
- The simple two temperature model can drive **phase separation and ordering transition.**
- **Liquid crystal ordering below Onsager's limit.**
- Ordering transition happens in order to **maintain pressure balance at the interface.**

- **Generalizing two-temperature model beyond spherical particles.**
- **This model may be useful in various experimental system like DNA organisation inside nucleus , liquid-liquid phase separation inside cell**

Heating leads to liquid-crystal and crystalline order in a two-temperature active fluid of rods, *J. Chattopadhyay, S. Pannir-Sivajothi, K. Varma, S. Ramaswamy, C. Dasgupta, and P. K. Maiti,* ***Phys. Rev. E,104, 054610 (2021).***

Thank You !

Extra



L/D = 5
L/D = 3
Interface
Hot
Cold
η
P
A
J
x/D

- Heat flux of a system (J) is defined by[1]:

$$\vec{J} = \frac{1}{V}\left\langle \sum_{i=1} \vec{v}_i e_i + \vec{Q} \right\rangle,$$

- $\vec{v_i}$ = Velocity of the i^{th} particle
- e_i = Total energy (kinectic + potential) of the i^{th} particle.
- $\vec{Q}$ = Virial contribution
- V = volume

- Molecular stress for pair interaction:

$$\sigma_i^{\text{pair}} = +\frac{1}{2}\sum_{j\neq i}^{N} \vec{r}_{ij} \otimes \vec{F}_{ij},$$

- $\overrightarrow{r_{ij}} = \vec{r_i} - \vec{r_j}$ = Distance between i^{th} and j^{th} particle
- $\overrightarrow{F_{ij}}$ = Interacting force between i^{th} and j^{th} particle

- Now, for pair interaction

$$\vec{Q}^{\text{pair}} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} \vec{r}_{ij}(\vec{F}_{ij}\cdot\vec{v}_i) = +\sum_{i=1}^{N} \sigma_i^{\text{pair}}\cdot\vec{v}_i,$$

- Then, local flux in volume Ω becomes,

$$\vec{J}^{\Omega} \approx \frac{1}{\Omega}\left\langle \sum_{i\in\Omega}^{N} \vec{v}_i e_i + \sum_{i\in\Omega}^{N} \sigma_i\cdot\vec{v}_i, \right\rangle,$$

*[1] PHYSICAL REVIEW E **99**, 051301(R) (2019)*
[2] Aging effects on thermal conductivity of glass-forming liquids, PHYSICAL REVIEW E 101, 022125 (2020)

- Local heat flux can also be computed from the relation:

$$J = \phi_q = -k\frac{dT(x)}{dx}$$

ϕ_q = heat flux

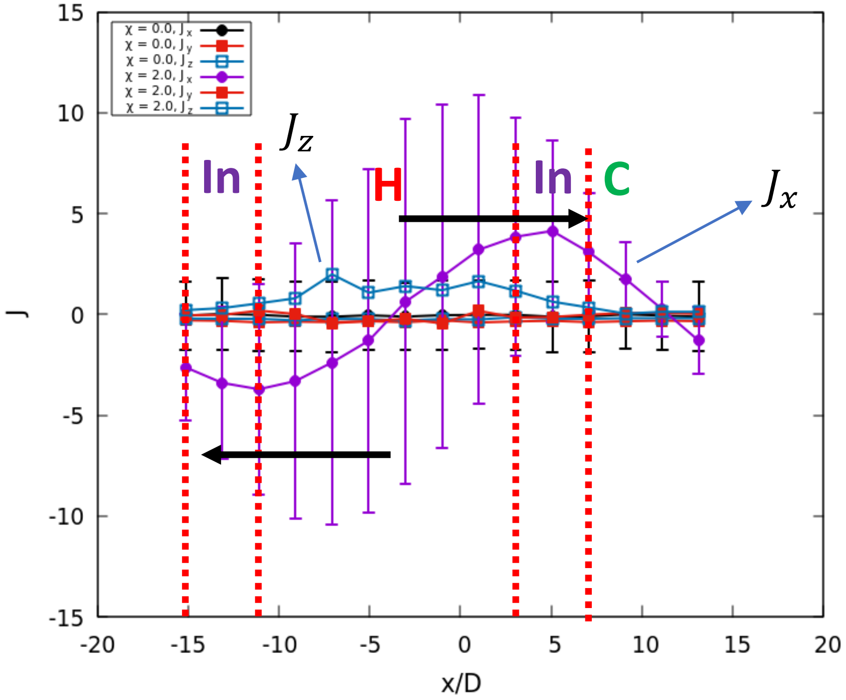
k = thermal conductivity

T = temperature

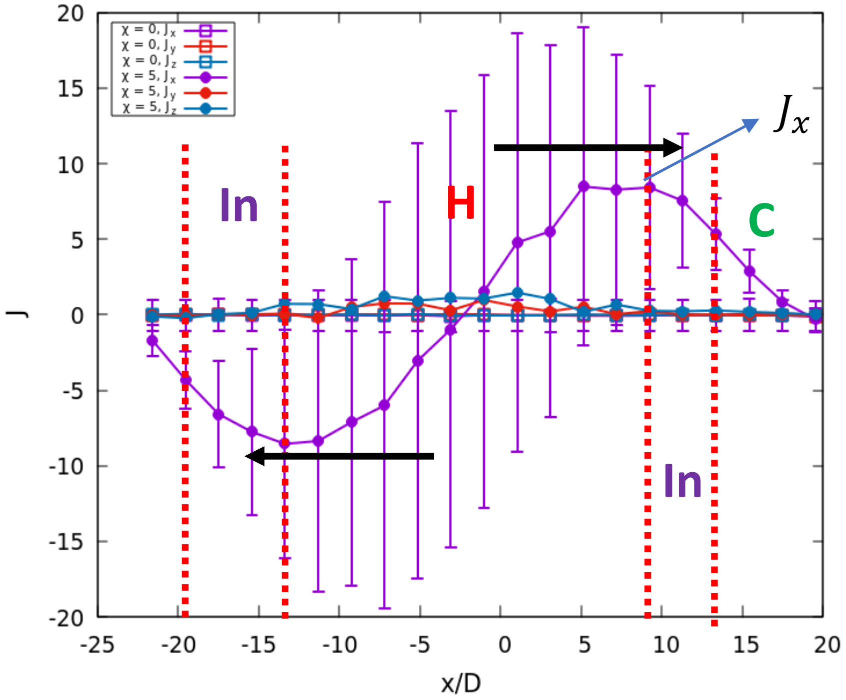
[3] J. P. Hansen and I. R. McDonald, Theory of Simple Liquids, 3rd ed. (Academic Press, London, 2006).

Heat flux for L/D = 5 at η= 0.36

N = 1024

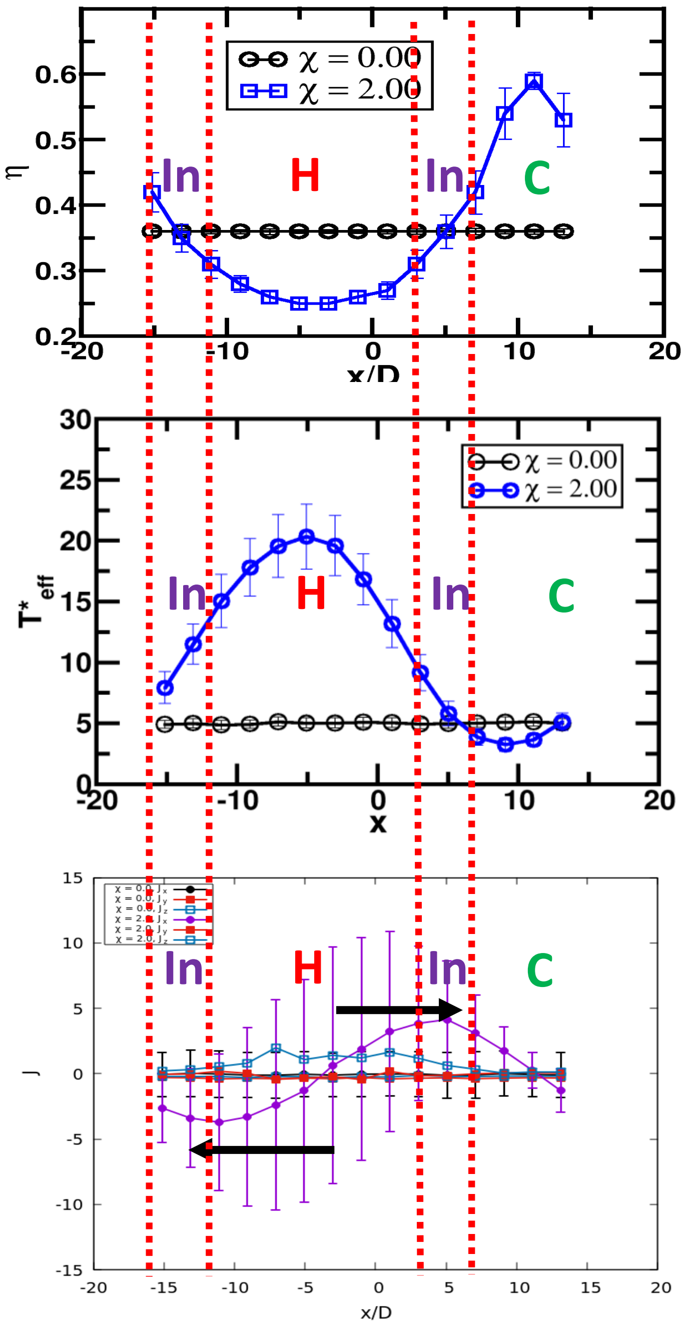


N = 4096



- For both system sizes we can see that, only the J_x component contributes to local heat flux across the interface.
- The black arrow shows the direction of heat flux calculated from the sign of J_x which tells heat flows from hot to cold region.
- The opposite sign of J_x towards the interfaces arise due to periodic boundary condition

Local thermodynamic quantities for L/D = 5 at η= 0.36 and χ = 2



Packing fraction

Temperature

Heat flux

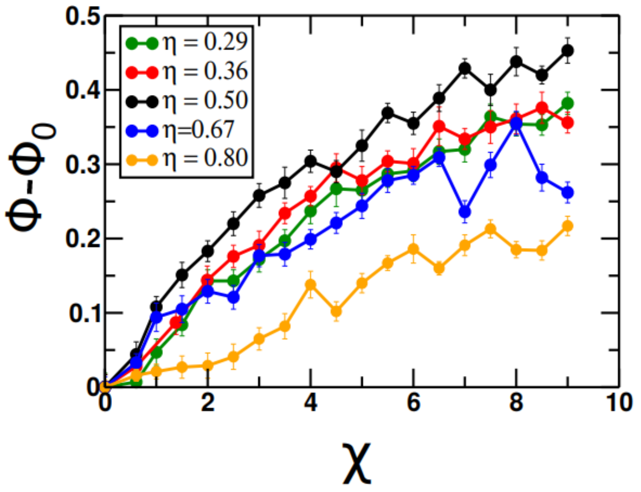
- C – Cold zone
- I – Interfacial zone
- H-Hot zone

Phase separation and critical activity

$$\phi = \frac{1}{N_{box}} \sum_{i=1}^{N_{box}} \left| \frac{\left(n_{hot}^{i} - n_{cold}^{i}\right)}{n_{tot}^{i}} \right|$$

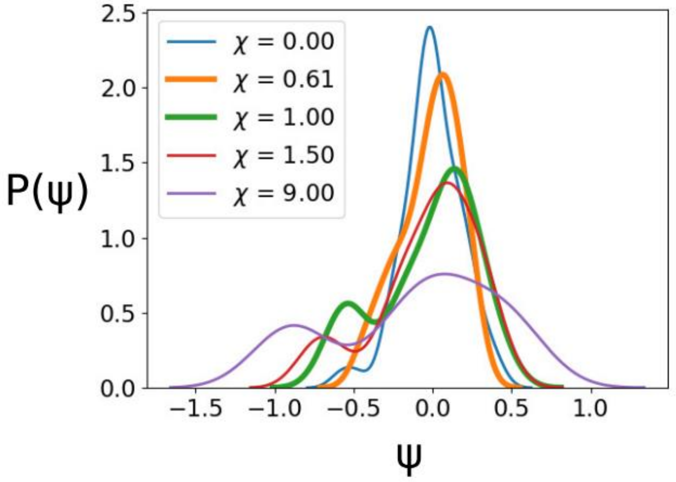
- n_{hot}^{i} and n_{cold}^{i} are the number of hot and cold particles in the i^{th} sub-box.
- $n_{tot}^{i} = n_{hot}^{i} + n_{cold}^{i}$
- N_{box} is the total number of sub-boxes.
- ϕ_0 is the initial value of density order parameter. As $\phi_0 \neq 0$ at $\chi = 0$ so we offset ϕ by its initial value ϕ_0.

Density order parameter ϕ versus activity χ at different packing fractions η.



- ➢ **Phase separation increases monotonically with χ for all the packing fractions.**
- ➢ **The amount of phase separation increases with η up to Nematic phase then decreases in the smectic and crystal phase.**

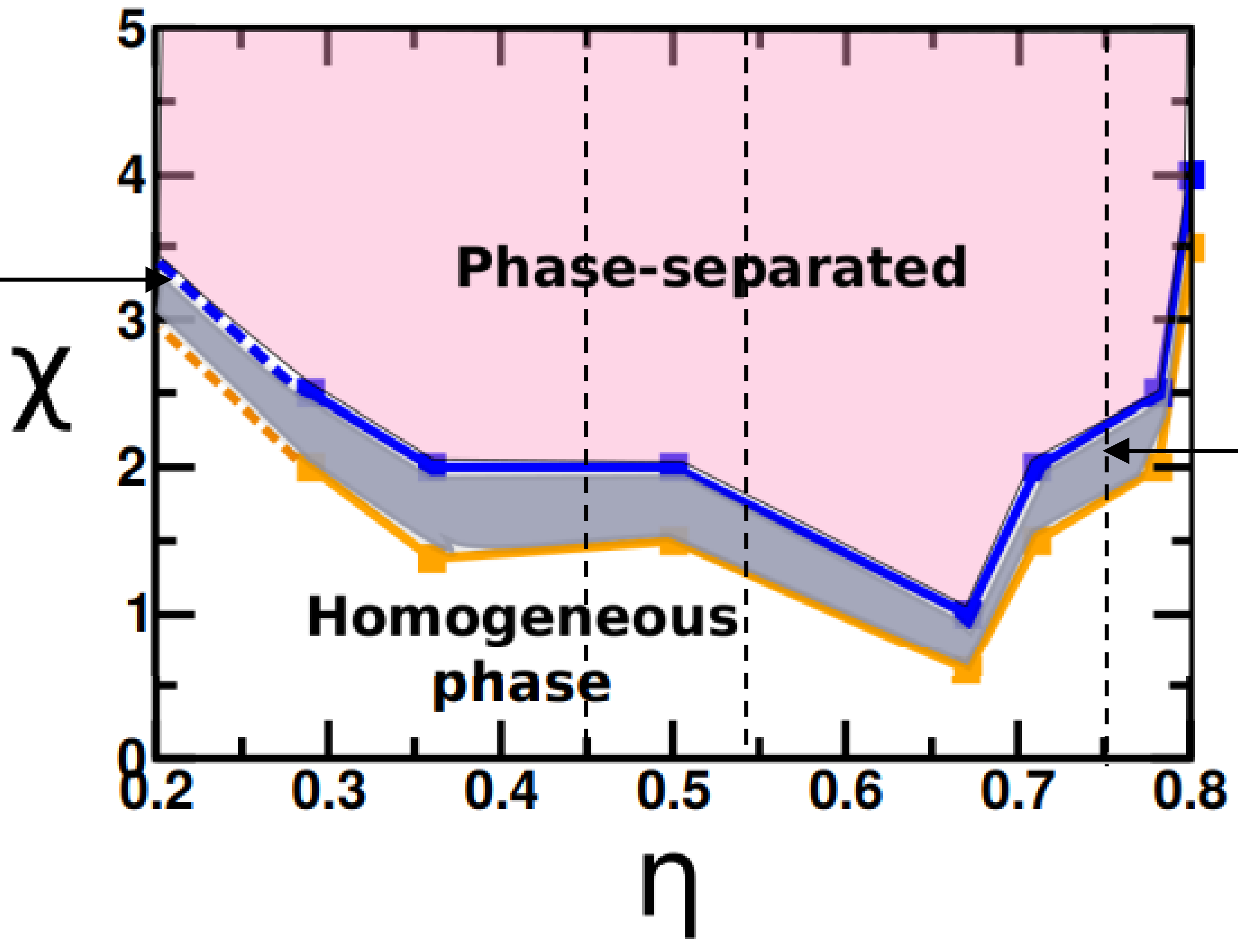
Probability distribution of Ψ at η = 0.67 for different activities χ.



- ➢ **P(Ψ) is unimodal in homogeneous phase where hot and cold particles are mixed (χ = 0) and bimodal in phase separated state.**
- ➢ **Bimodality appears at χ = 1.00. So, the range of critical activity, $\chi_c = 0.61 - 1.00$.**

The phase diagram of the active-passive SRS system

Dotted line is the extrapolation of calculated data

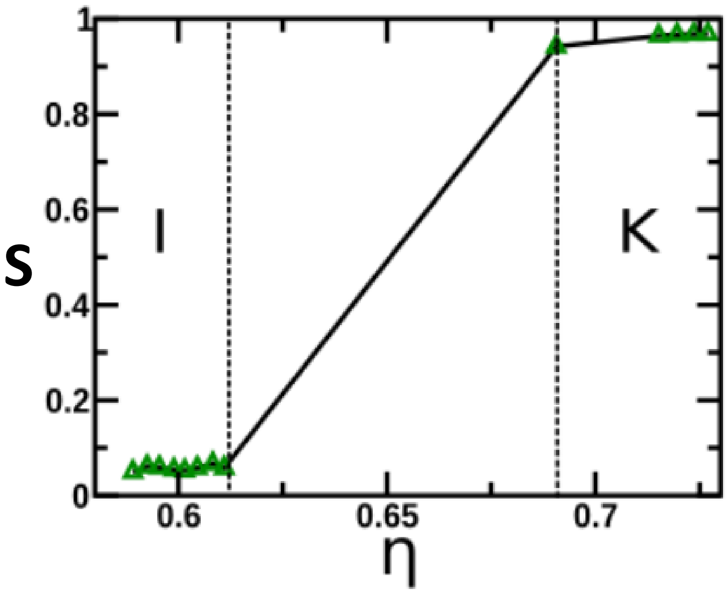


Region of possible values of critical activity χ_c

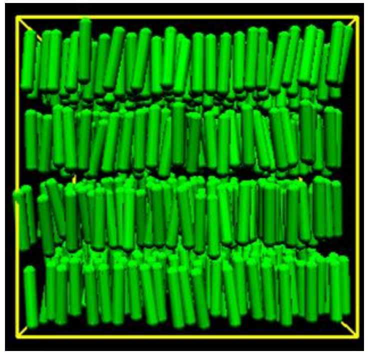
- **Critical activity decreases with density in the liquid regime and increases again in the crystal regime.**

Equilibrium phases of different aspect ratios

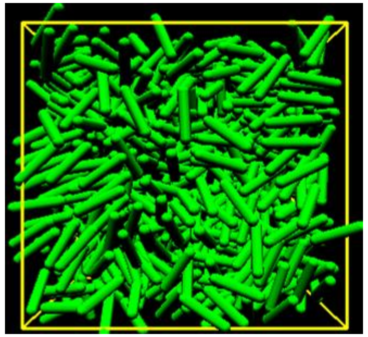
L/D = 2



Crystal



Isotropic

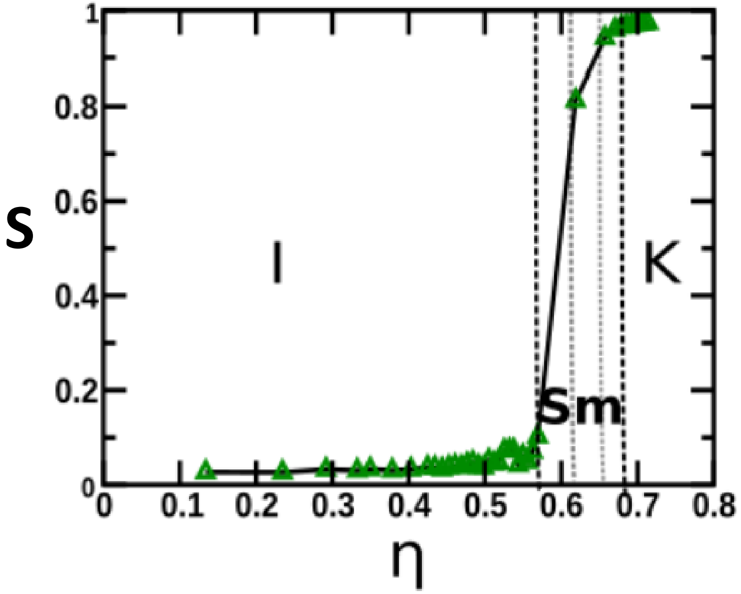


- **In equilibrium we see two phases for L/D = 2.**

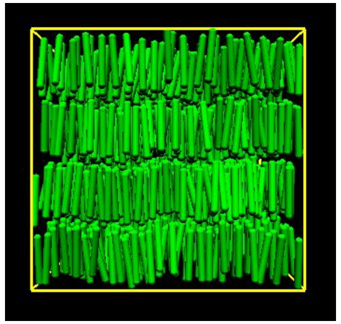
(1) Isotropic (I)
(2) Crystal (K)

S – Nematic Order parameter
η –Packing fraction

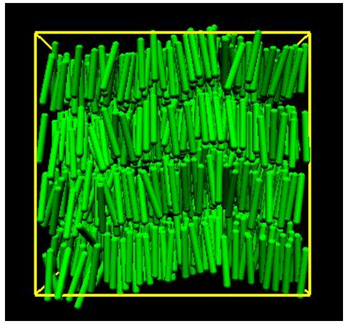
L/D = 3



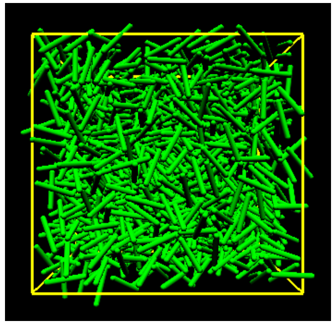
Crystal



Smectic



Isotropic



- **In equilibrium we see three phases for L/D = 3.**

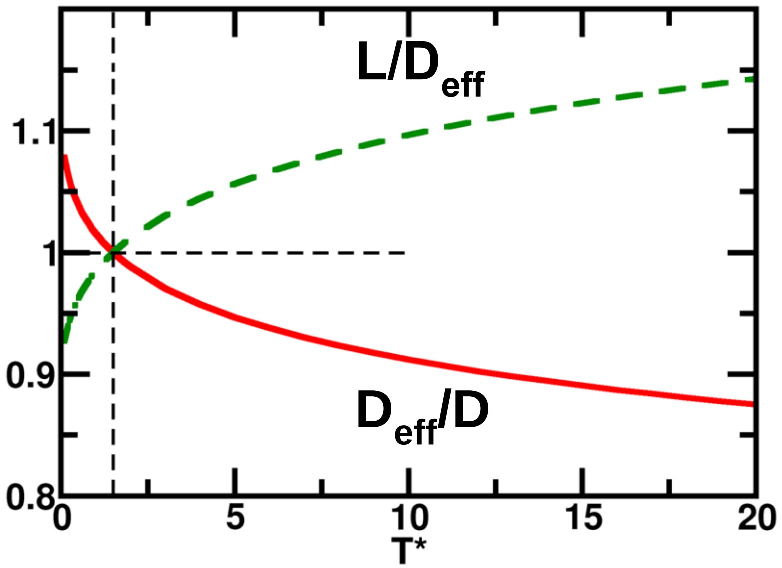
(1) Isotropic (I)
(2) Smectic
(2) Crystal (K)

Mapping of SRS on Hard Spherocylinder

- ➢ The SRS fluid can be mapped onto an Hard spherocylinder (HSC) fluid with an effective diameter (D_{eff}) and correspondingly, an effective aspect ratio $A_{eff} = \frac{L}{D_{eff}}$ by using following equation:

$$D_{eff}(T) = \int_0^{\infty} (1 - exp[-\beta U_{SRS}(d_m)]d(d_m)$$

Temperature dependence of the effective Molecular diameter

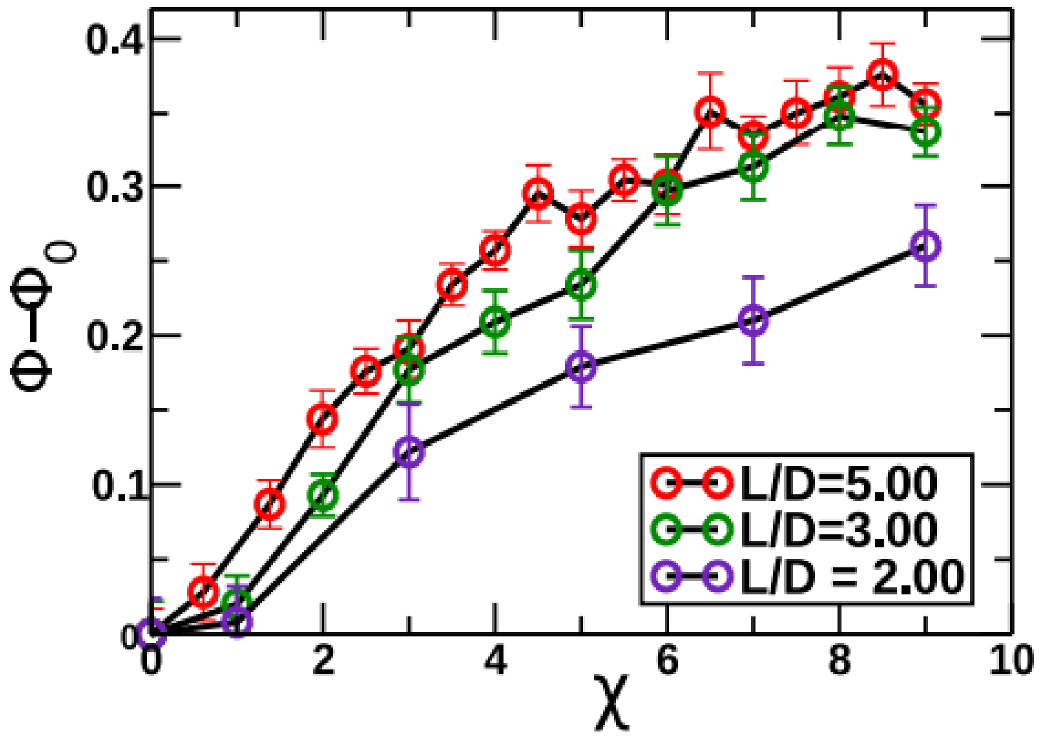


A^{SRS}	$A_{eff}^{HSC}(T^*)$
5	5.28
3.52	**3.70**
3	3.20
2	2.11

➢ Onsager's limit for SRS is $\frac{L}{D_{eff}} = 3.52$ at T* = 5

- *A. Cuetos and B. Mart́ ınez-Haya, Molecular Physics113,1137 (2015).*
- *T. Boublık, Molecular Physics32, 1737 (1976).*

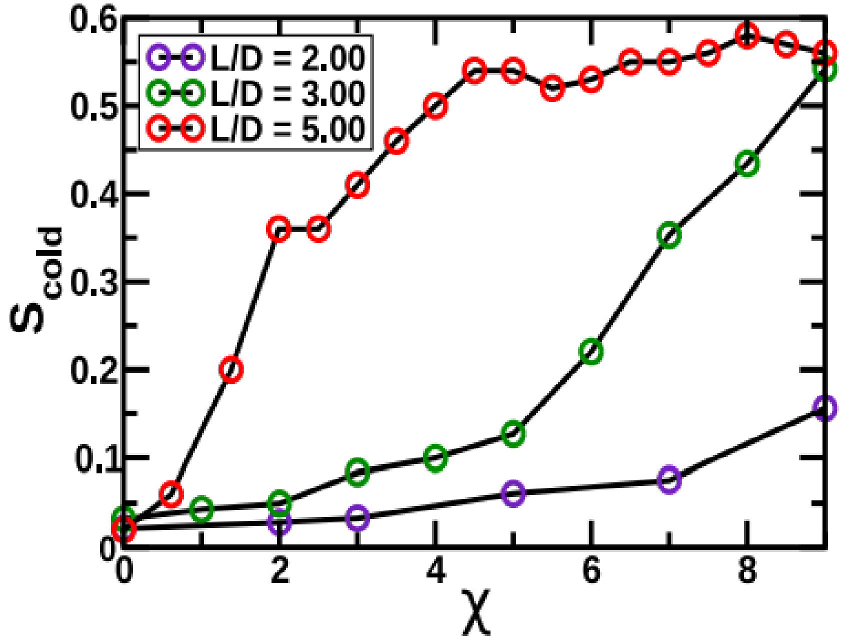
Phase separation in different aspect ratios



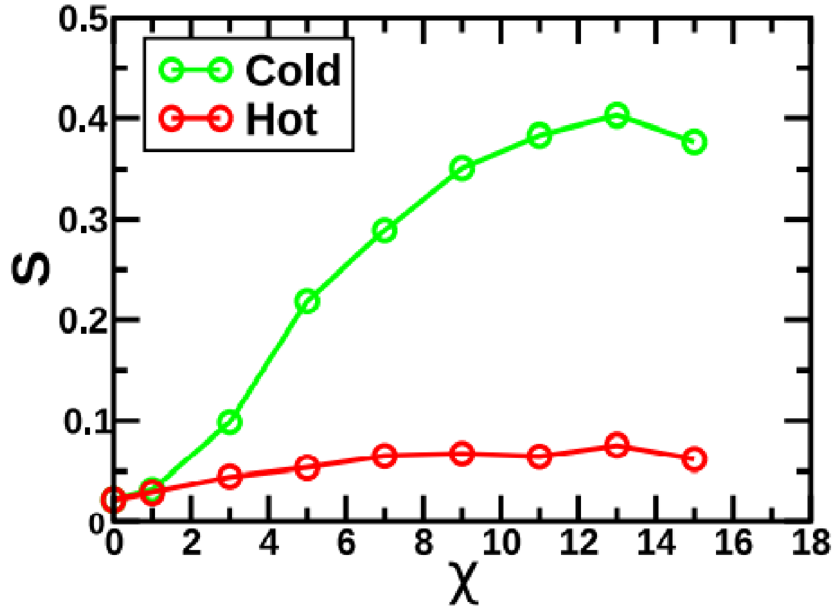
- Plot of order parameter ϕ versus activity χ at the same packing fraction η = 0.34 for different aspect ratios.
- As χ increases, the value of ϕ increases and finally saturates.
- Phase separation starts at a lower activities for higher aspect ratios
- The amount of phase separation (value of ϕ) at a given χ is higher for higher aspect ratios.

Isotropic-Nematic transition for different aspect ratios

Nematic order parameter of cold particles S_{cold} vs activity χ at η = 0.34 for different aspect ratios L/D



Nematic order parameter of hot and cold particles vs activity χ at η = 0.43 for L/D = 2



- The value of activity χ for ordering transition decreases for higher L/D.
- L/D = 2 shows ordering transition at higher packing fraction η = 0.43 than that of L/D = 3 and 5.

Vector and Scalar Active systems

- Conventionally activity is vectorial in nature due to the forces of self-propulsion.

- Examples of vector active matter model:
- Vicsek model : Flocking of birds, schools of fish
- Run and Tumble Particles (RTP): Dynamics of motile *E-coli* bacteria, *Chamydomonas algae*
- Active Brownian Particles (ABP): Bacterial colony, spherical janus particles

<u>Activity ∝ Self-propulsive force</u>

- Many physical and biological processes such as chromatin separation, phase separation in colloidal systems happens due to the differences in the level of activity which does not have any preferred direction.

- These heterogeneous activity can be modeled by assigning different temperatures between the components of the system.
- In the recent literature, this simple two-temperature model has been used to study phase-separation and other non-equilibrium behaviours.

<u>Activity ∝ effective temperature difference</u>

Ref.: T. Vicsek and A. Zafeiris, Phys. Reports 517, 71 (2012)

•*Ganai et al, Nucleic Acids Res. 42, 4145 – 4159 (2014).*

Scalar Active systems

- Many physical and biological processes such as chromatin separation, phase separation in colloidal systems happens due to the differences in the level of activity which does not have any preferred direction.

- These heterogeneous activity can be modeled by assigning different temperatures between the components of the system.
- In the recent literature, this simple two-temperature model has been used to study phase-separation and other non-equilibrium behaviours.
- In experiment, it is shown that non-reciprocal interactions yield two different temperatures in many systems like dusty plasma ,diffusiophoretic colloids .

activity $\propto$ effective temperature difference

- *Ganai et al, Nucleic Acids Res. 42, 4145 – 4159 (2014).*
- *A. Y. Grosberg and J.-F. Joanny, Phys. Rev. E 92, 032118 (2015).*
- *J. Smrek and K. Kremer, Phys. Rev. Lett. 118, 098002, (2017).*
- *Frey et al, Phys. Rev. Lett. 116, 058301 (2016)*
- *J. Bartnick, A. Kaiser, H. L¨owen, and A. V. Ivlev, The Journal of chemical physics 144, 224901 (2016).*
- *A. V. Ivlev, J. Bartnick, M. Heinen, C.-R. Du,V. Nosenko, and H. L¨owen, Phys. Rev. X 5, 011035 (2015).*
- *R. Soto and R. Golestanian, Phys. Rev. Lett. 112, 068301 (2014).*