**COMMONWEALTH OF AUSTRALIA**

**Copyright Regulation**

**WARNING**

This material has been reproduced and communicated to you by or on behalf of the University of Sydney pursuant to Part VB of the *Copyright Act* 1968 (**the Act**).

The material in this communication may be subject to copyright under the Act. Any further reproduction or communication of this material by you may be the subject of copyright protection under the Act.

Do not remove this notice

# Soft Matter: Onsager Theory and the Statistical Mechanics of Nematics

**Lecture 26**

Soft Matter: Introduction and Overview

Liquid Crystals

**Lecture 27**

Soft Matter:

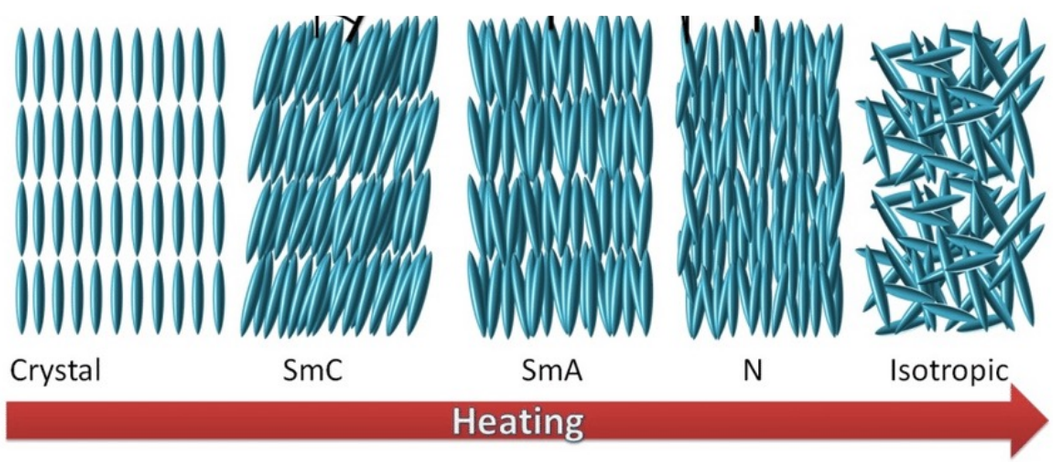
Onsager Theory of Nematics

**Lecture 28**

Soft Matter: Nematics – Properties and Applications

# Reminder: Mesophases: smectic, nematic, isotropic

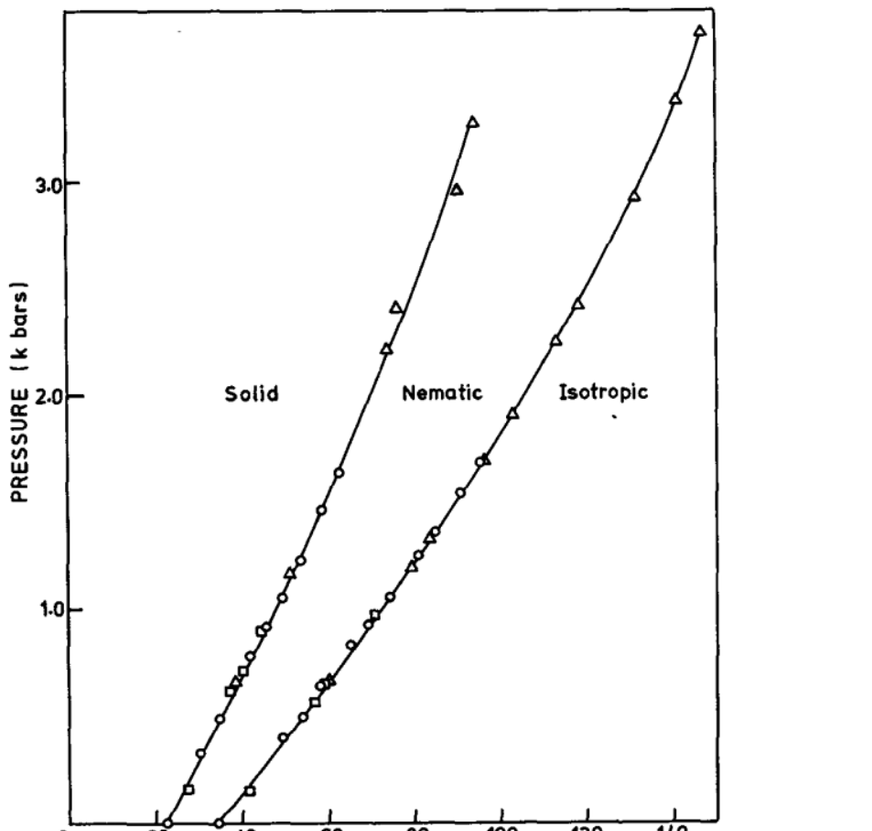
- The shape of a molecule, together with temperature and pressure, are the main factors determining whether it will act as a mesogen.

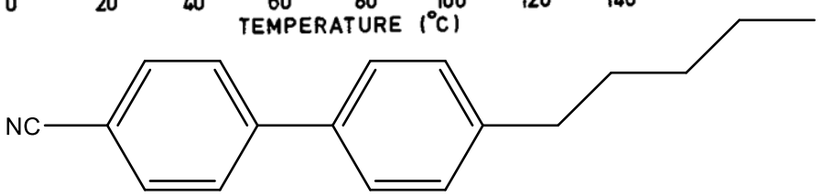


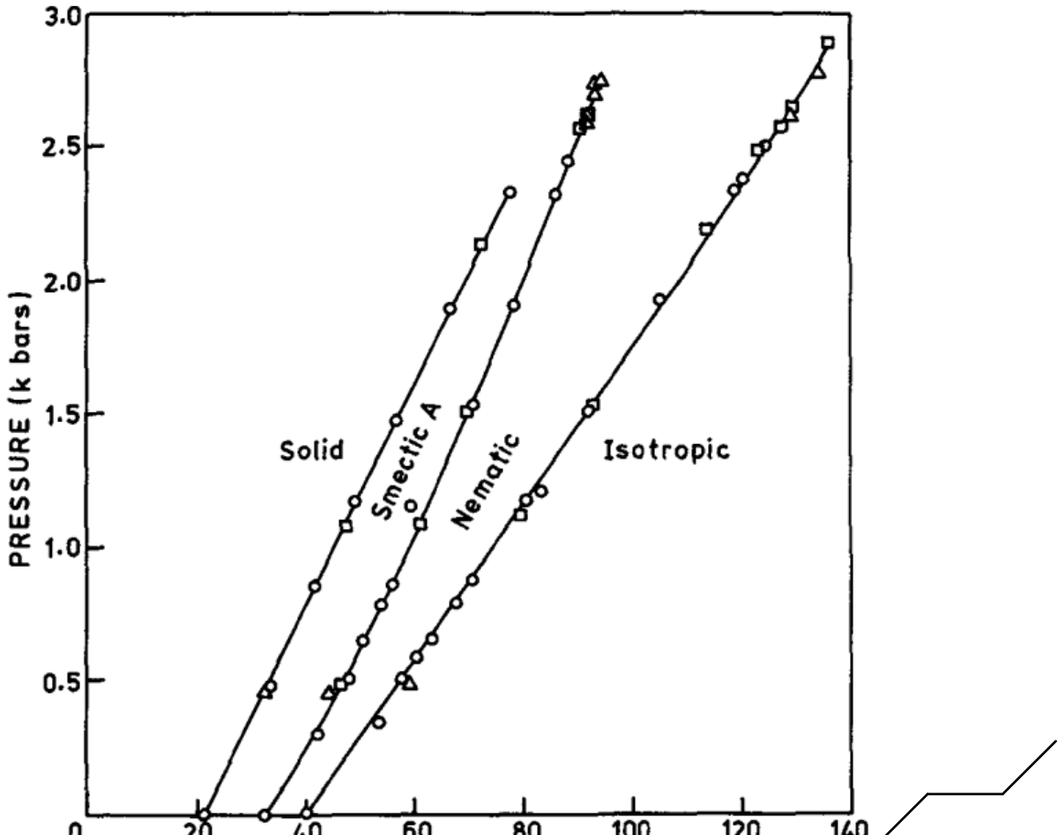

10.3390/nano7100305

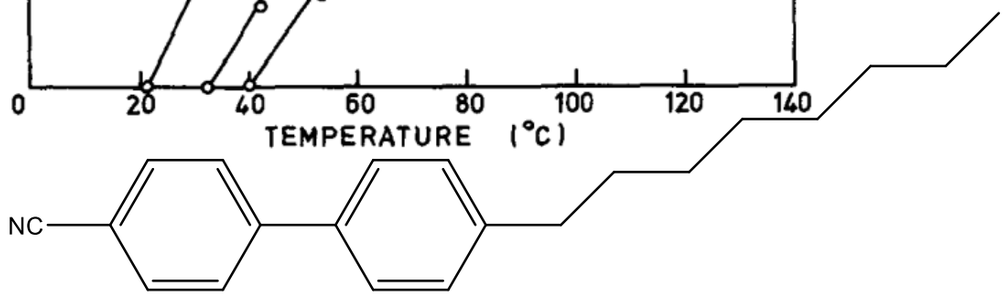
Two smectic phases  Nematic phase

# Two typical I-N-(S)-C phase diagrams



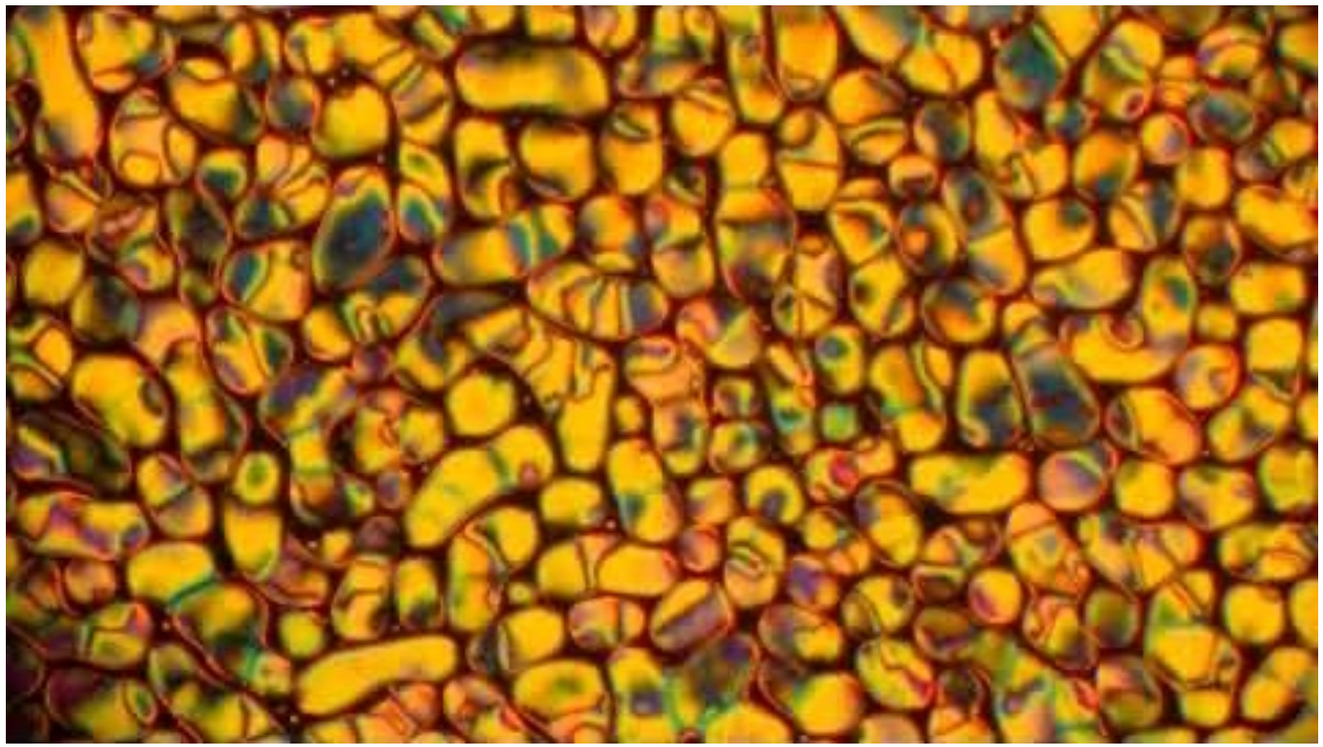




R. Shashidhar, G. Venkatesh. Journal de Physique Colloques, 1979, 40 (C3), pp.396-400. 10.1051/jphyscol

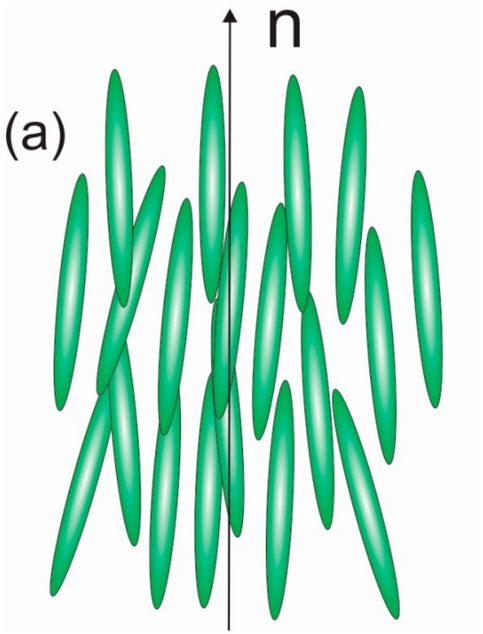
# Isotropic – Nematic transition: macroscopic



Phase transition from isotropic to nematic state of the nematic mixture MLC6816 (Merck) under cooling from ca. 78 to 73 degrees.
Full video: Alexey Bobrovsky https://www.youtube.com/watch?v=u1wqn7AL4yg

# Nematic – Isotropic Transition: microscopic

Q1




10.3390/ma11010024

Order parameter

$S = \frac{1}{2}\langle(3\cos^2\theta - 1)\rangle$

1 for perfect alignment
0 for isotropic

- θ is the angle between the long axis of a selected molecule and the average direction of the orientation, the director n.
- The brackets ⟨⟩ denote the average over all of the molecules in the sample.
- The order parameter, S, decreases when the temperature is increased. When the temperature is sufficiently high, the orientational order is suddenly and completely lost (now S=0) and there is a first-order phase transition into the isotropic state.

# Nematics: what is the simplest model?

- It turns out that molecular detail doesn't matter much (this is good news)
- Inflexible molecules and colloidal rods show similar behaviour
- So, perhaps we can simply consider a collection of hard rods…?
  - In a "hard particle" system, the particles are not allowed to overlap
  - No other particle interactions are considered
  - Increasing P or decreasing T is equivalent to increasing the density ρ
- Once we have solved a hard-particle problem, we can convert quasi-universally to the "macroscopic" energy, length, and time units:

$$e_0 = k_B T \qquad l_0 = \rho^{-1/3} \qquad t_0 = \rho^{-1/3}\sqrt{m/k_B T}$$

https://iopscience.iop.org/article/10.1088/0953-8984/28/32/323001

# Thermodynamics in "hard particle" systems

Q2

- To find the stable phase in an open system (with P and T set to the laboratory conditions), we need to minimise the Gibbs Free Energy

$$G = H - TS = U + PV - TS$$

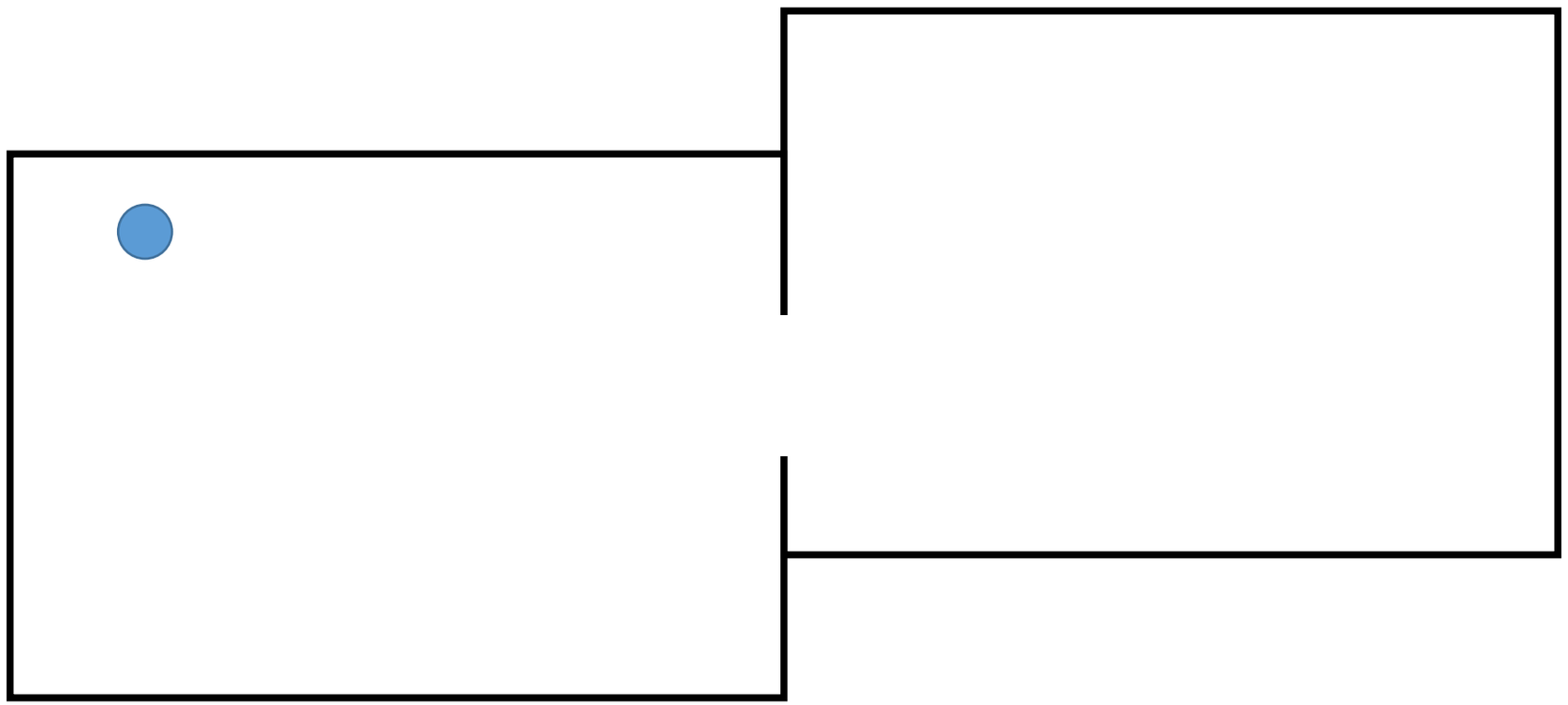
- If, instead, we consider a system with a fixed volume (i.e. fixed density), we need to minimise the Helmholtz Free Energy

$$F = U - TS$$

- "Hard particles" means no particle interactions, so U=0
- So, at the T of interest, we need to maximise S
- It is this feature that makes "hard particle" systems interesting

# Entropy and probability – one particle

Every microstate that satisfies the given constraints occurs with equal probability

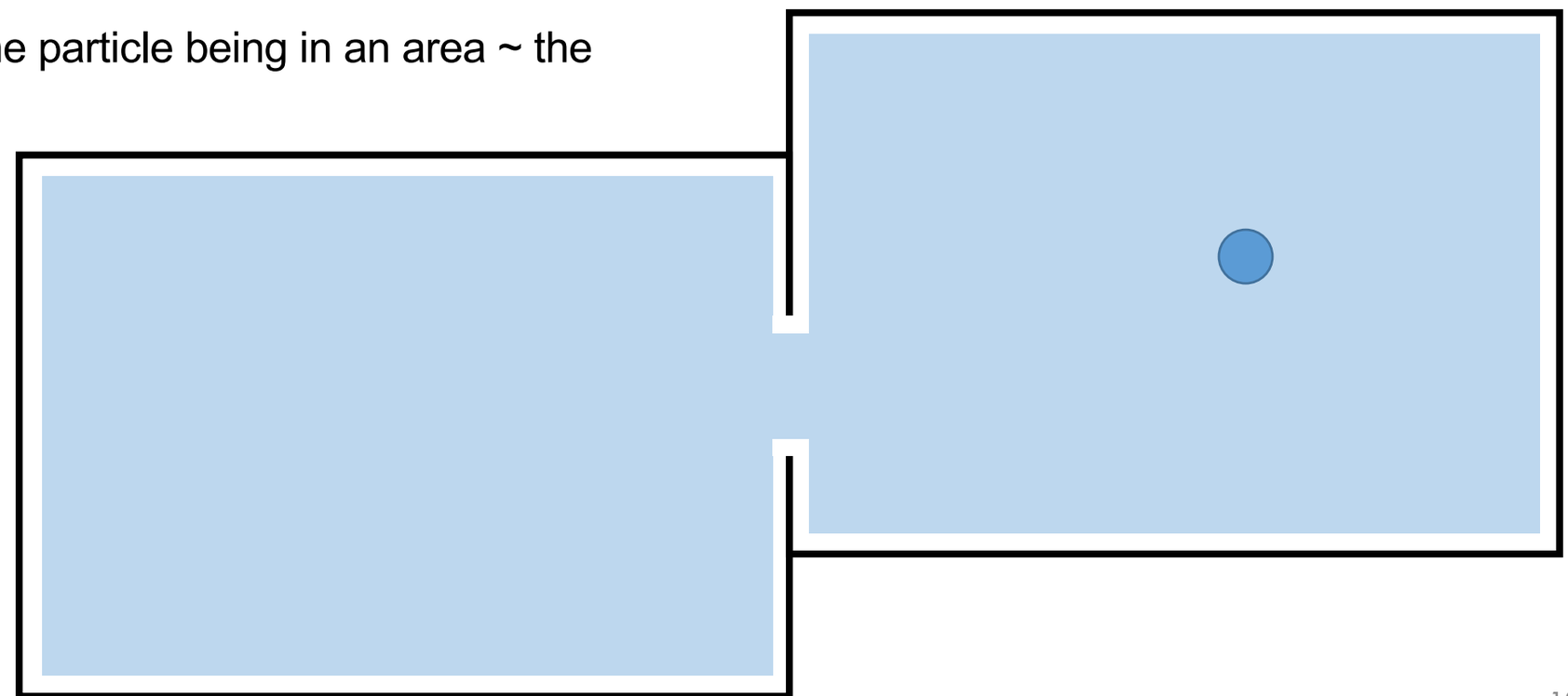


# The concept of Accessible Volume

The blue area (3d: “volume”) is accessible to the centre of the particle.

The area on the right is equal to that on the left, so the particle is equally likely to be on either side of the partition.

In general, the probability of the particle being in an area ~ the accessible volume



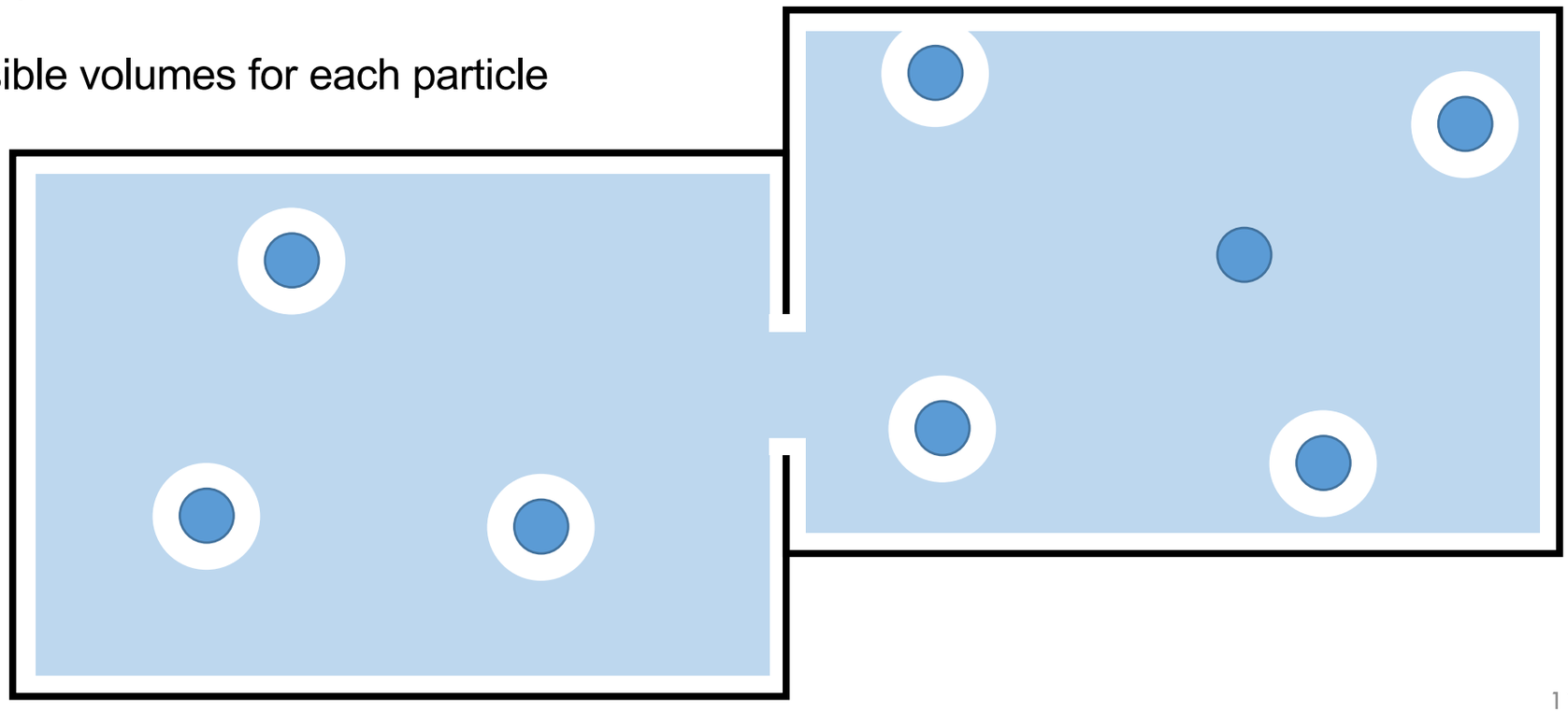
# Excluded volume – multiple particles

The blue area (3d: “volume”) is accessible to the centre of the particle.

Particles reduce the accessible volume of other particles

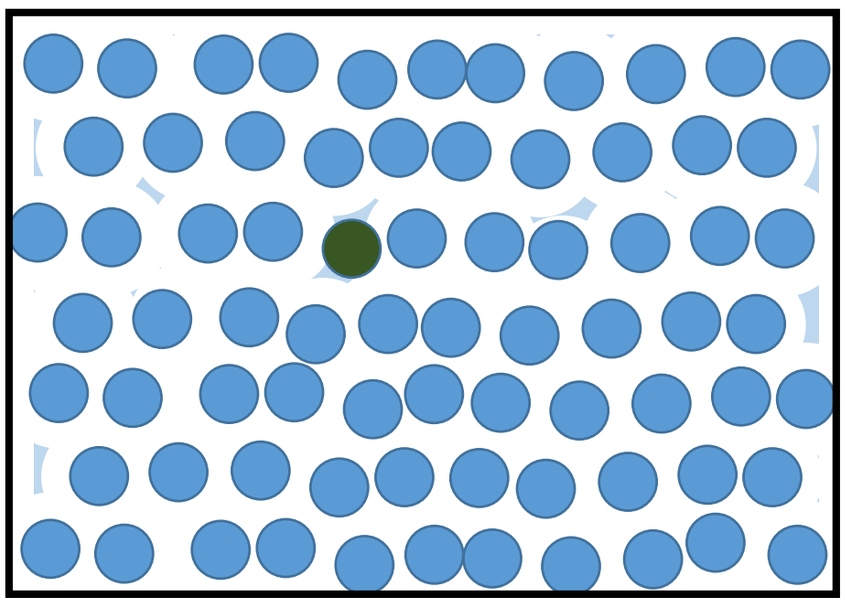
Overall, the translational entropy of the particles is $S = k_B \ln W$

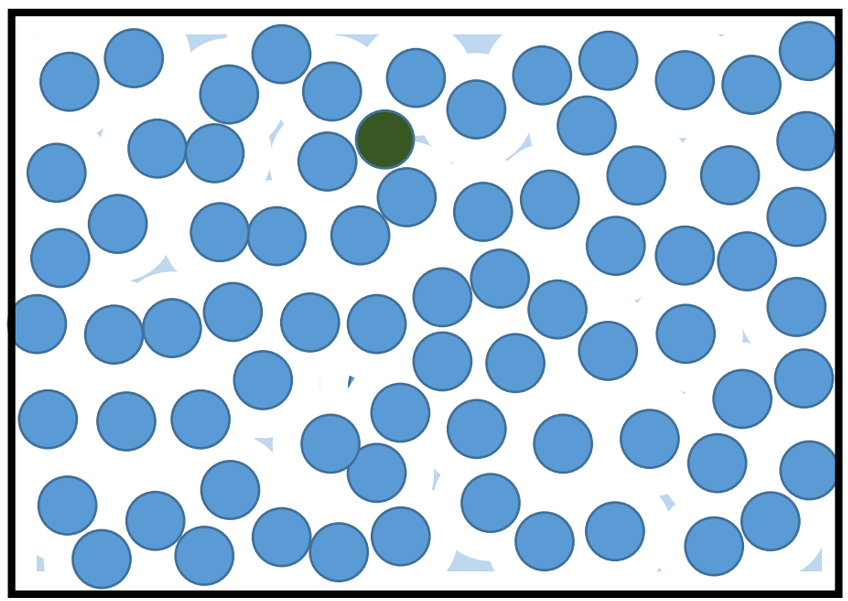
W ~ The product of the accessible volumes for each particle



# Entropy can drive order

- At high densities, all configurations have much lower accessible volumes.
- In the crystalline phase, the accessible volume is shared equally between particles.
- In disordered configurations, the accessible volume is shared unequally.
- W is maximised if the particles share the accessible volume equally.
- Therefore, the crystalline phase has higher entropy!

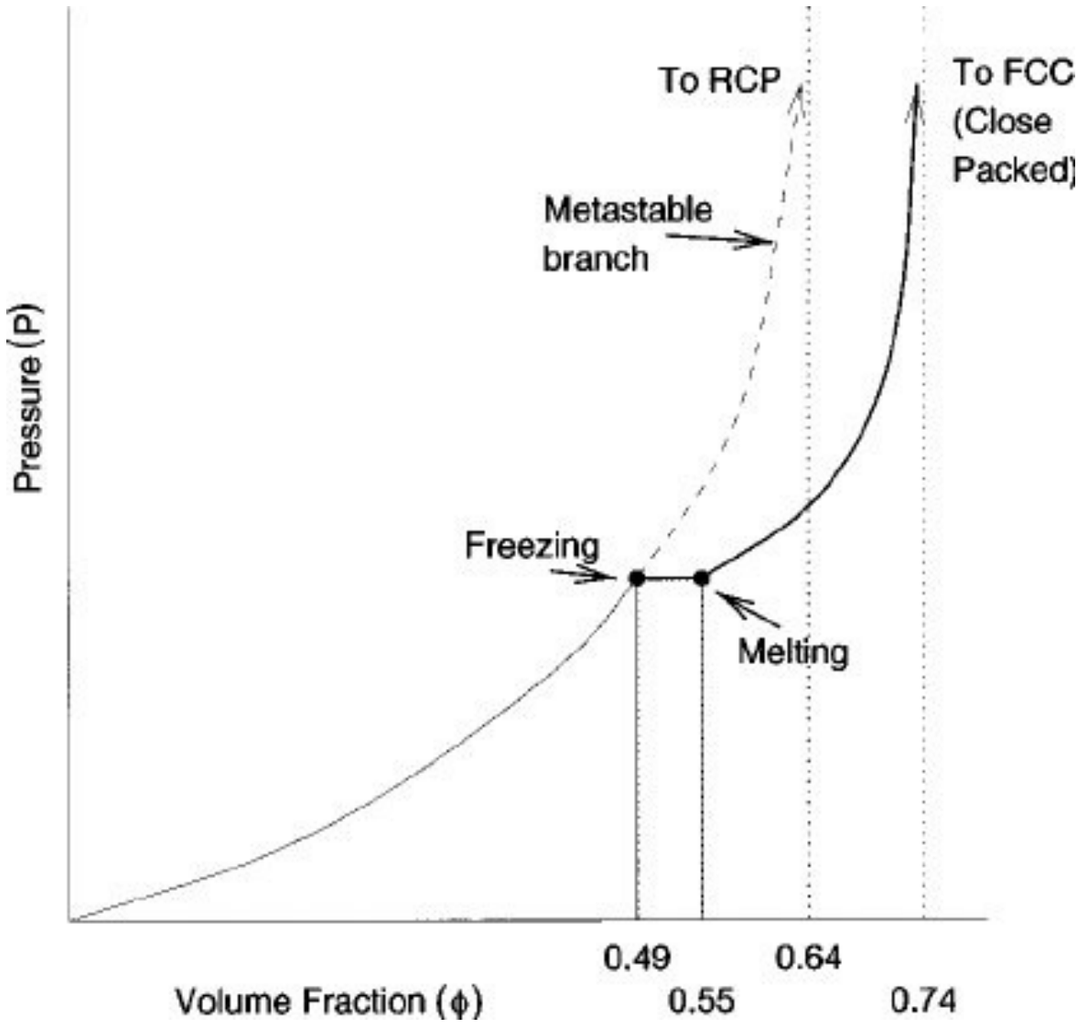




# Hard-sphere phase diagram

Q3

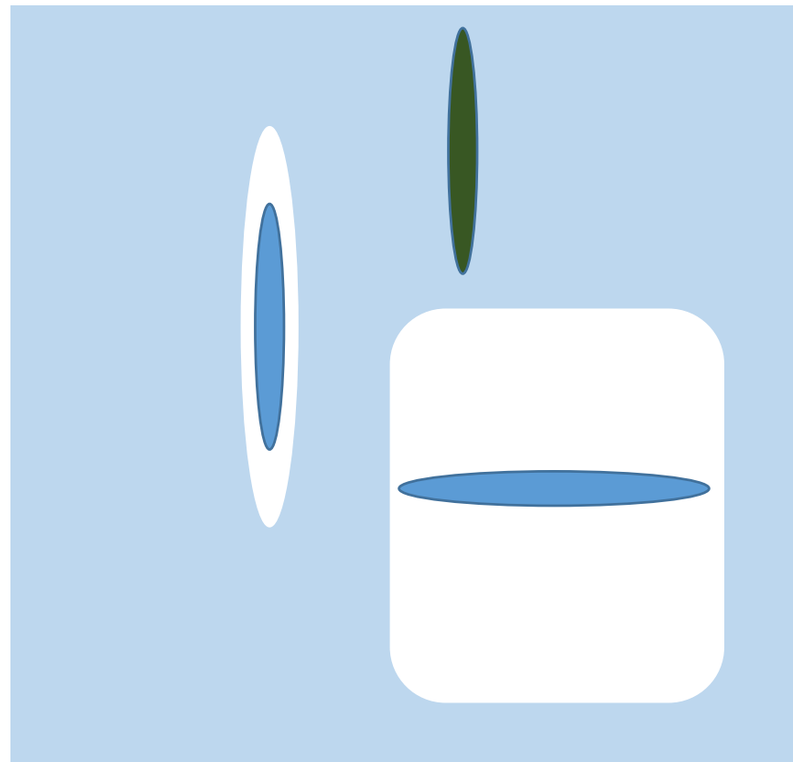
- In the diagram on the right, RCP stands for Random Close Packed
- At high densities, the crystalline (FCC) phase has higher entropy than the amorphous (RCP) phase
- So, at high densities, the crystal becomes the more stable phase, and we get a phase transition




10.1103/PhysRevE.58.532

# Excluded volume for long particles

- Rod like (length L, diameter D) particles have orientational freedom and, thus, orientational entropy.
- At **low concentrations**, they exploit this and form an **isotropic** phase.
- However, excluded volume now depends on their relative orientations.
  - For isotropic orientations, the average excluded volume is much larger than the volume of the rod ($\sim DL^2$).
  - For aligned rods, the excluded volume is about 4x the volume of the rod ($\sim D^2L$).
- As with spheres, these exclusions increase linearly with concentration.
- At **high concentrations**, the accessible volume, and hence translational entropy is far greater in the **nematic** than in the isotropic phase.
- To maximise total entropy, the nematic phase sacrifices orientational entropy for translational entropy.



# Onsager's prediction of the I-N phase boundary

- Lars Onsager captured these qualitative arguments in a quantitative description, predicting the phase boundary entirely theoretically:
  - Assumed the distribution $f(\theta)$ of angles $\theta$ between each rod and the nematic director.
  - Then, at each concentration, minimised the free energy with respect to variations in the distribution function $f(\theta)$

- This predicted that:
  - Isotropic phase stable at concentrations $< 4.2/DL^2$
  - Nematic phase stable at concentrations $> 7.0/DL^2$
  - Phase coexistence in between

Since the volume of a rod is $D^2L\,\pi/4$, the packing fraction at which these transitions occur decreases as L/D increases

D. Fennel Evans, H. Wennerström. *The Colloidal Domain: Where physics, chemistry and biology meet*. Wiley, 1999. pp 526-530

# I-N phase boundary: theory vs simulation

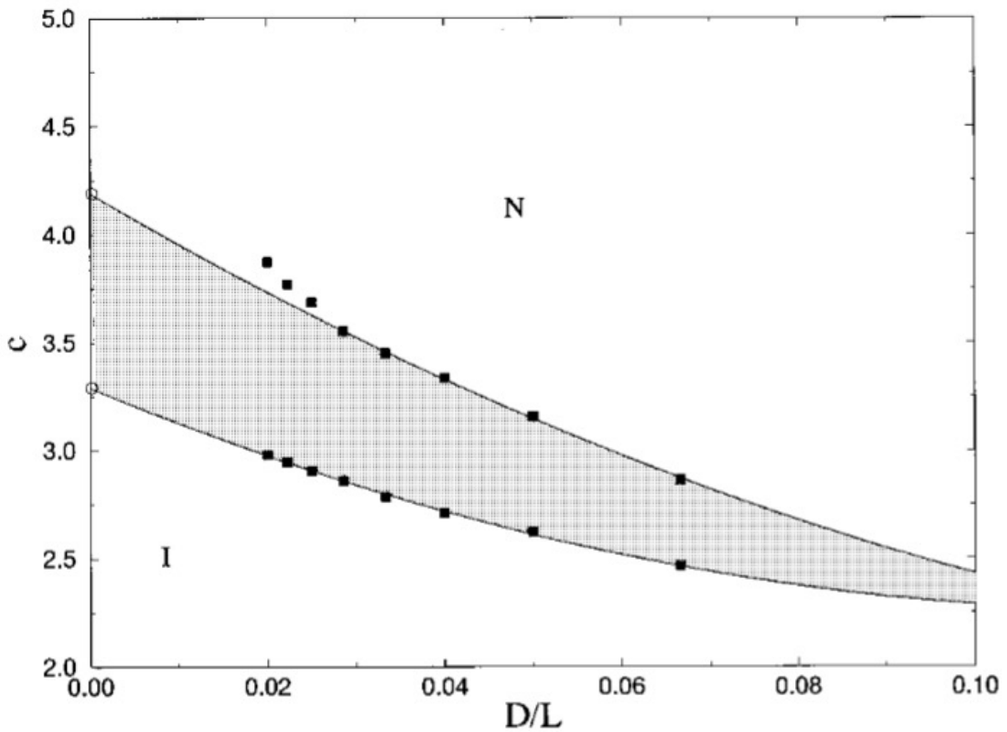



FIG. 12. Isotropic-nematic transition of spherocylinders in the large $L/D$ limit. In order to facilitate comparison with the Onsager limit, all densities are expressed in units $c=\frac{1}{4}\pi L^2 D\rho$. On the $x$ axis, we plot $D/L$ rather than $L/D$. Hence, the Onsager limit corresponds to the value $D/L=0$. Note that our simulation results approach smoothly towards the exact solution of the Onsager model, except for a few points at low D/L.

Bolhuis and Frenkel, J. Chem. Phys. 106 (1997) 10.1063/1.473404

# Learning outcomes

After this lecture you should be able to

- Describe the approximations made when treating particles as “hard”
- Recognise the role of an order parameter as a simple measure of a complex distribution that distinguishes clearly between phases
- Understand and utilise the concepts of accessible and excluded volume
- Explain the thermodynamic reasons for the occurrence of nematic phases
- Identify common features of molecules that promote the occurrence of nematic phases
- Recognize the role of theory in the science of complex phenomena

# Further Reading

- D. Fennel Evans, H. Wennerström. *The Colloidal Domain: Where physics, chemistry and biology meet*. Wiley, 1999. pp 526-530
- Configurational integral: https://link.springer.com/content/pdf/10.1007%2F978-3-319-46401-5_28.pdf