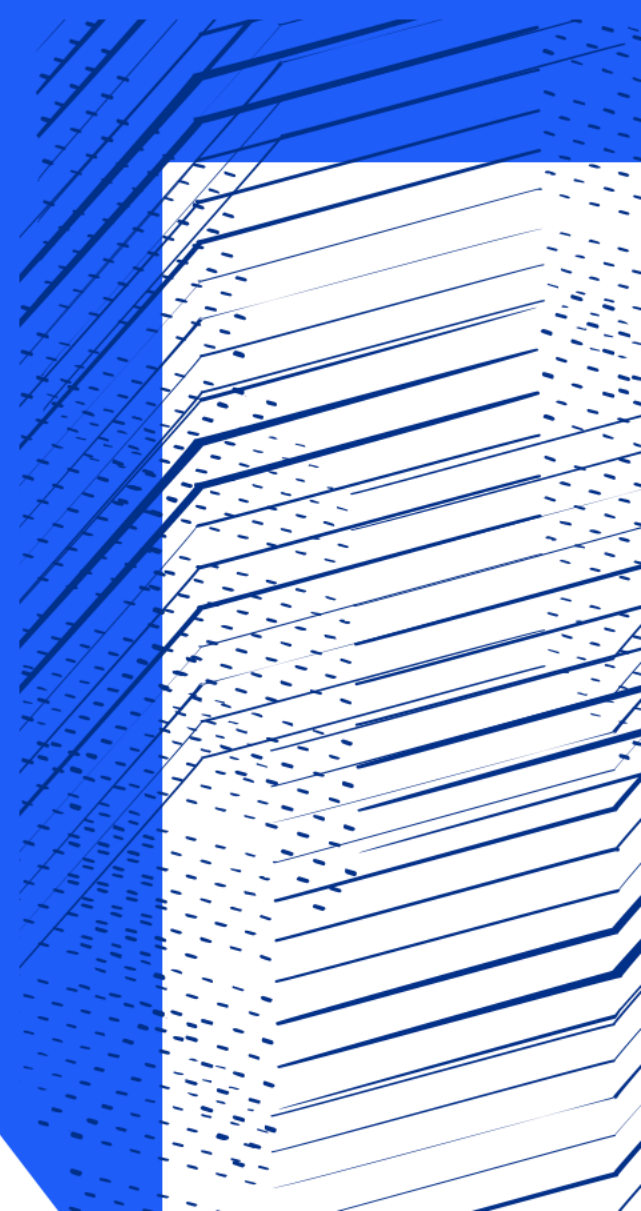
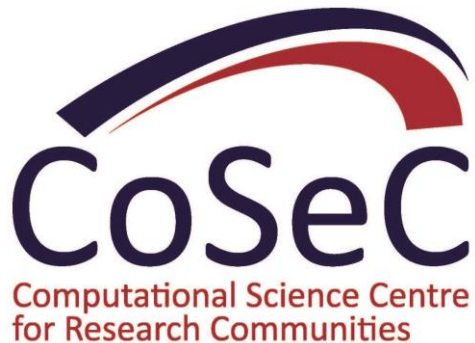




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# Thermodynamically consistent multi-phase DPD

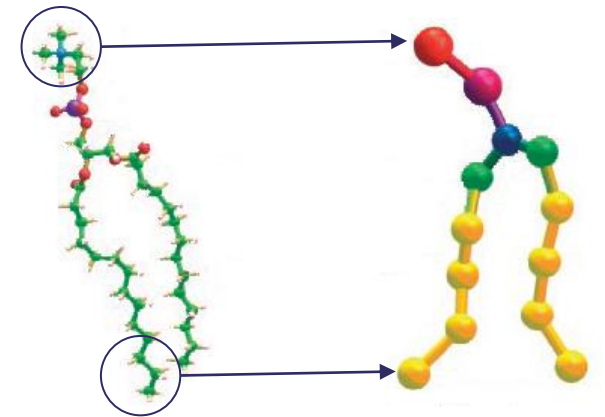
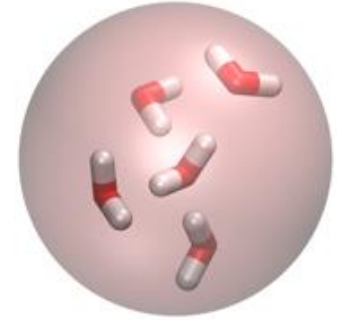
Michael Seaton, Vlad Sokhan, Ilian Todorov  
UKRI STFC Daresbury Laboratory



# Mesoscale modelling

**Challenge: representing materials at larger-than-atomic scales (10nm and larger, nanoseconds and longer)**

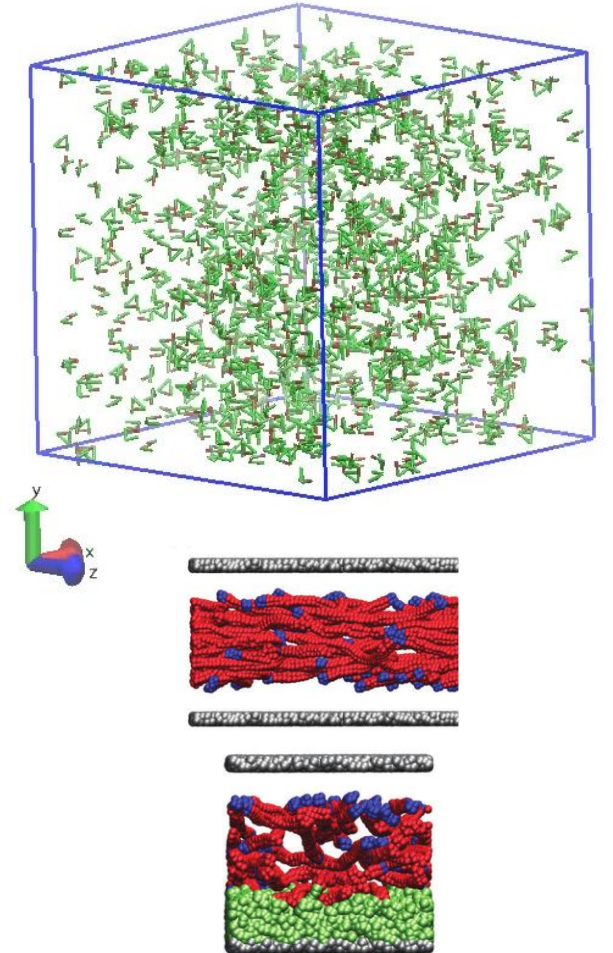
- Often requires coarse-graining
  - Collect together atoms/molecules/molecular segments into larger particles ('beads')
  - Work out interactions (potentials, forces) between beads to collectively match up with those between original atoms
- Interactions between beads tend to be soft and (mostly) repulsive
  - Hard-core atomistic interaction types (e.g. Lennard-Jones) not the most realistic at these length and time scales



# Dissipative particle dynamics (DPD)

## Enhanced molecular dynamics for mesoscale

- Includes additional pairwise forces as momentum-conserving thermostat<sup>[1,2]</sup>
  - Controls temperature without disrupting hydrodynamics
- Often used in combination with soft interactions between beads to use larger time steps
  - Rapid equilibration compared with atomistic MD
- Has been applied to many soft matter systems involving formation of large-scale structures (e.g. vesicles<sup>[3]</sup>) and/or flows<sup>[4]</sup>



1. Hoogerbrugge and Koelman, *EPL* **19** (3), 155–160 (1992)
2. Groot and Warren, *J Chem Phys* **107** (11), 4423–4435 (1997)
3. Yamamoto *et al.*, *J Chem Phys* **116** (13), 5842–5849 (2002)
4. Posel *et al.*, *Soft Matter* **13** (8), 1634–1645 (2017)

# DPD bead interactions

Default: soft repulsive (Groot-Warren, 'standard DPD') pairwise potential<sup>[1]</sup>

$$U(r_{ij}) = \begin{cases} \frac{1}{2}Ar_c \left(1 - \frac{r_{ij}}{r_c}\right)^2, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c \end{cases}$$

- Finite at zero separation (bounded), zero beyond cutoff (no long-range corrections)
- Similar to potential obtained by coarse-graining polymer melts<sup>[2]</sup>
- Leads to **quadratic equation of state** with bead density  $\rho$ :

$$p \approx \rho k_B T + 0.101 Ar_c^4 \rho^2$$

- Can vary  $A$  between different species to match e.g. required energy of mixing
- Single species cannot separate into rarefied/dense (e.g. vapour/liquid) phases

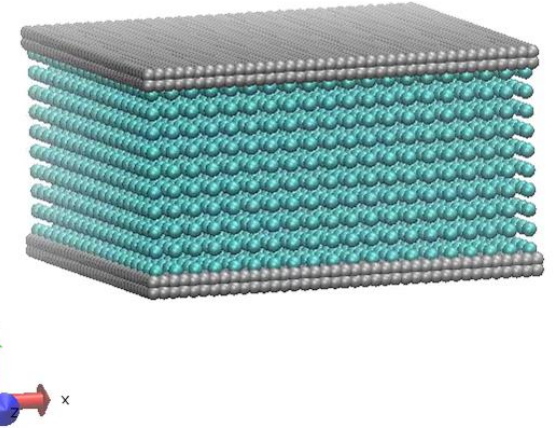
# DPD with improved thermodynamics?

## Need to add attraction to interactions to get phase separation

- Could do this by using many-body DPD<sup>[1,2]</sup> to impose specific equation of state
  - Additional pairwise calculations of localised bead densities
  - Harder to vary interactions between different species<sup>[3,4]</sup>
  - Not easy to ensure thermodynamic stability
- Alternatively, could borrow approach from Mie potential<sup>[5]</sup>:

$$U(r_{ij}) = \left(\frac{n}{n-m}\right) \left(\frac{n}{m}\right)^{\frac{m}{n-m}} \epsilon \left[ \left(\frac{\sigma}{r_{ij}}\right)^n - \left(\frac{\sigma}{r_{ij}}\right)^m \right]$$

Control repulsion with  $n$ , attraction with  $m$ : standard Lennard-Jones interaction when  $n = 12$  and  $m = 6$



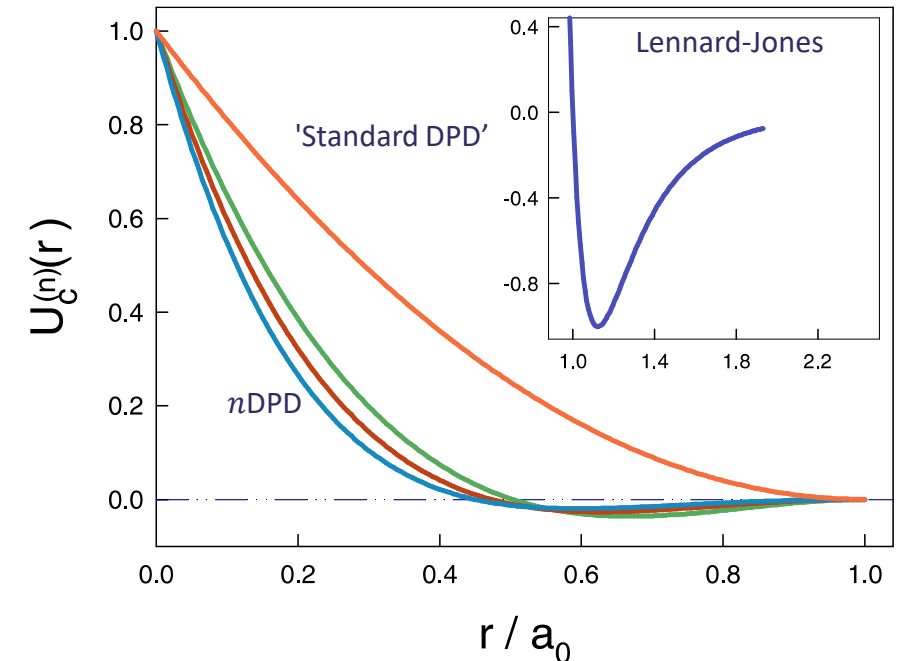
# $n$ DPD: extended Groot-Warren interactions<sup>[1]</sup>

- Force and potential for bead pairs within cutoff distance  $r_c$ :

$$\mathbf{F}^C(\mathbf{r}_{ij}) = A \left[ b \left( 1 - \frac{r_{ij}}{r_c} \right)^n - \left( 1 - \frac{r_{ij}}{r_c} \right) \right] \frac{\mathbf{r}_{ij}}{r_{ij}}$$

$$U(r_{ij}) = \frac{Abr_c}{n+1} \left( 1 - \frac{r_{ij}}{r_c} \right)^{n+1} - \frac{Ar_c}{2} \left( 1 - \frac{r_{ij}}{r_c} \right)^2$$

- Includes form of original interaction as attractive part (similar to many-body DPD model<sup>[2]</sup>)
- Additional control on repulsion with  $b$  and  $n$
- Reduces to 'standard DPD' when  $b = 2, n = 1$



Length scale defined as distance where  $U = 0$  ( $b > \frac{n+1}{2}, n \neq 1$ ):

$$\frac{\sigma}{r_c} = 1 - \left( \frac{n+1}{2b} \right)^{\frac{1}{n-1}}$$

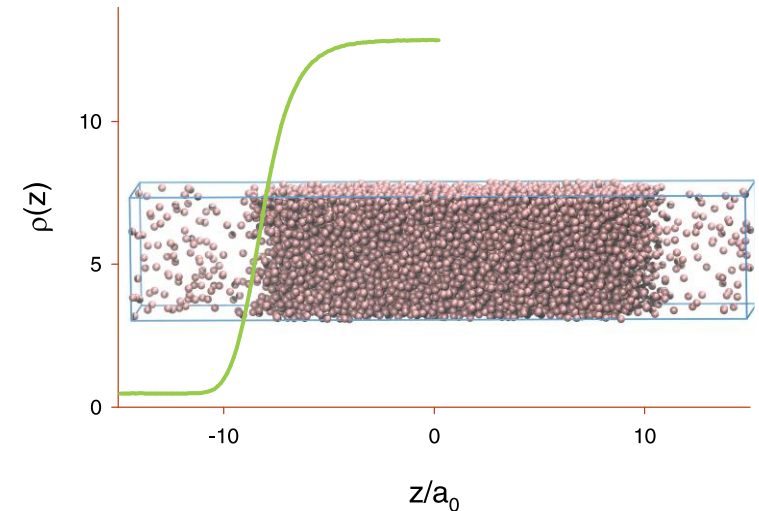
- Sokhan *et al.*, *Soft Matter* **19** (30), 5824–5834 (2023)
- Warren, *Phys Rev E* **68** (6), 066702 (2003)

# Simulations to explore phase behaviour

Modified DL\_MESO\_DPD<sup>[1]</sup> and DL\_POLY<sup>[2]</sup> to include new  $n$ DPD potential/force

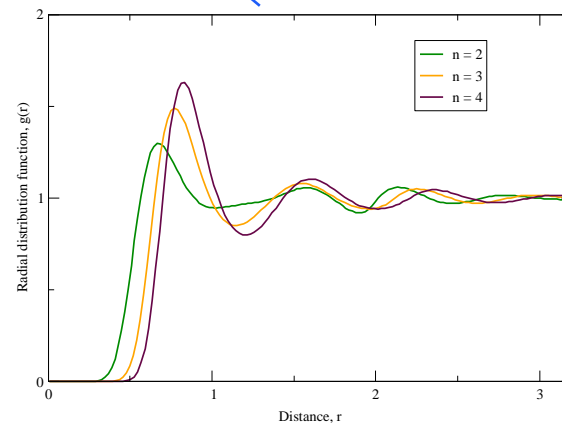
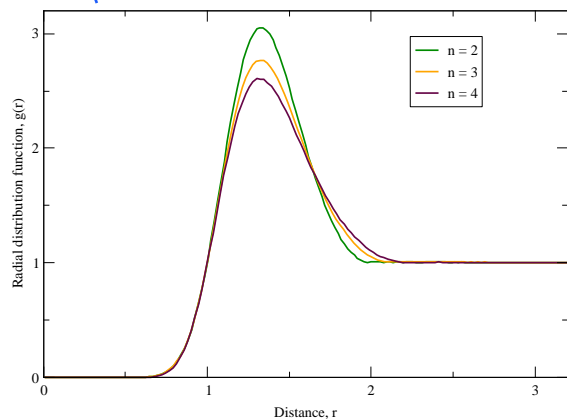
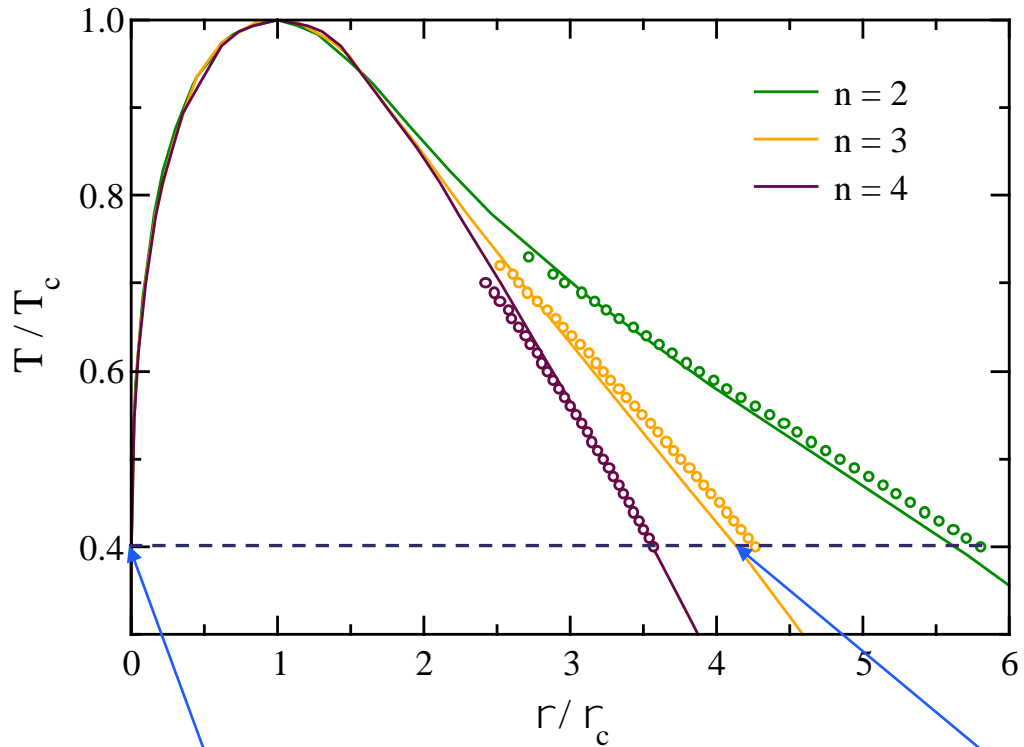
- Used elongated boxes to favour separation into vapour and liquid, to determine phase densities, pressure and surface tension at given temperatures
- Found solid phase structures by annealing (heating and cooling around melting point)
- Simulations confirmed theoretically-determined condition for thermodynamic stability<sup>[3]</sup>:

$$b > \frac{(n + 1)(n + 2)(n + 3)(n + 4)}{120}$$



$n$	$A$	$b$	$\sigma/r_c$	$T_c$	$p_c$	$\rho_c$
2	25.0	3.02	0.5033	1.025	0.2951	0.519
3	15.0	7.2	0.4730	1.284	0.3979	0.504
4	10.0	15.0	0.4497	1.286	0.4095	0.484

# Vapour/liquid phase diagram



Plots of temperature against vapour and liquid densities (rescaled by critical values)

- Consistent vapour branch for all  $n$
- Concavity of liquid branch dependent on  $n$  and  $b$
- Liquid branches confirmed for  $T < 0.7T_c$  using HNC with  $n$ DPD potential<sup>[1]</sup> (circles)
- RDFs indicate whether a phase is vapour or liquid

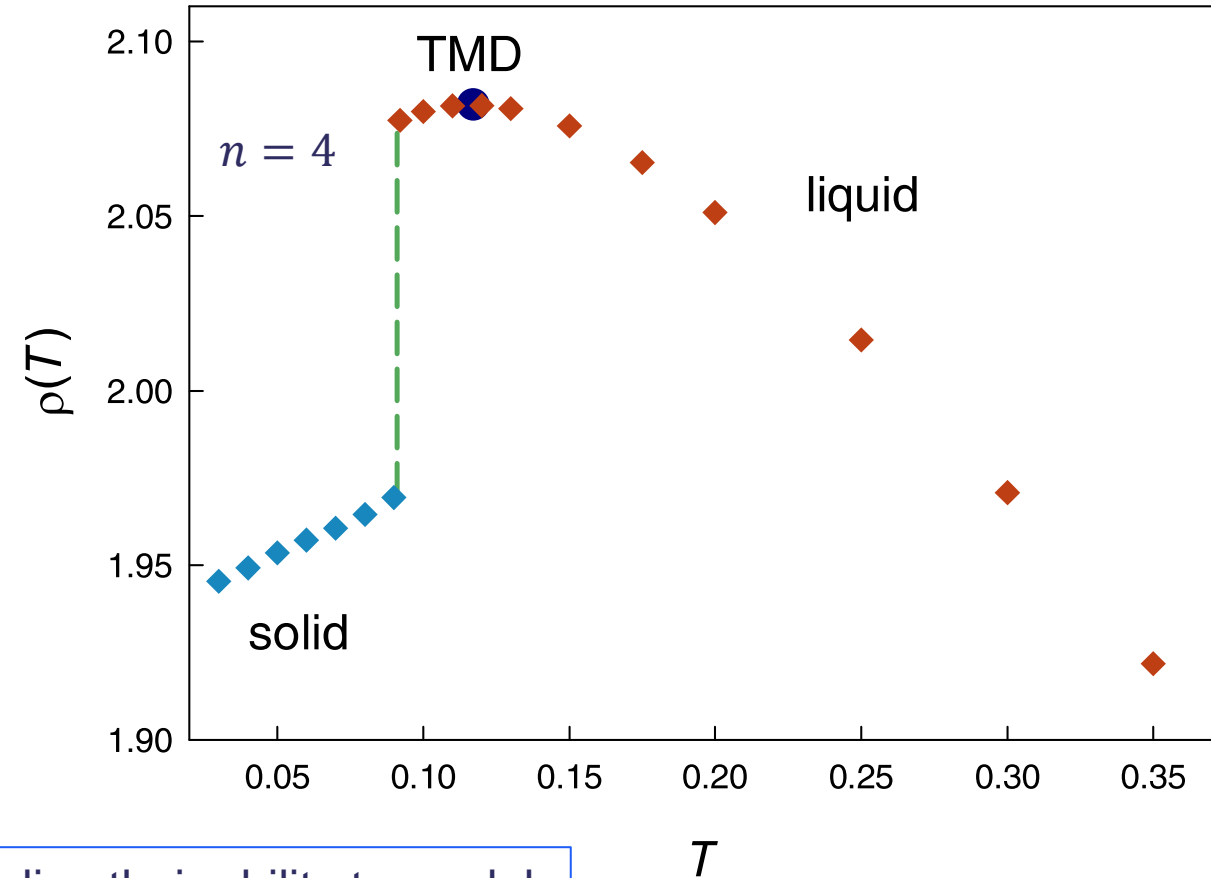
1. <https://github.com/patrickbwarren/SunlightHNC>



# Solid/liquid transitions

## Interesting behaviours at low temperatures

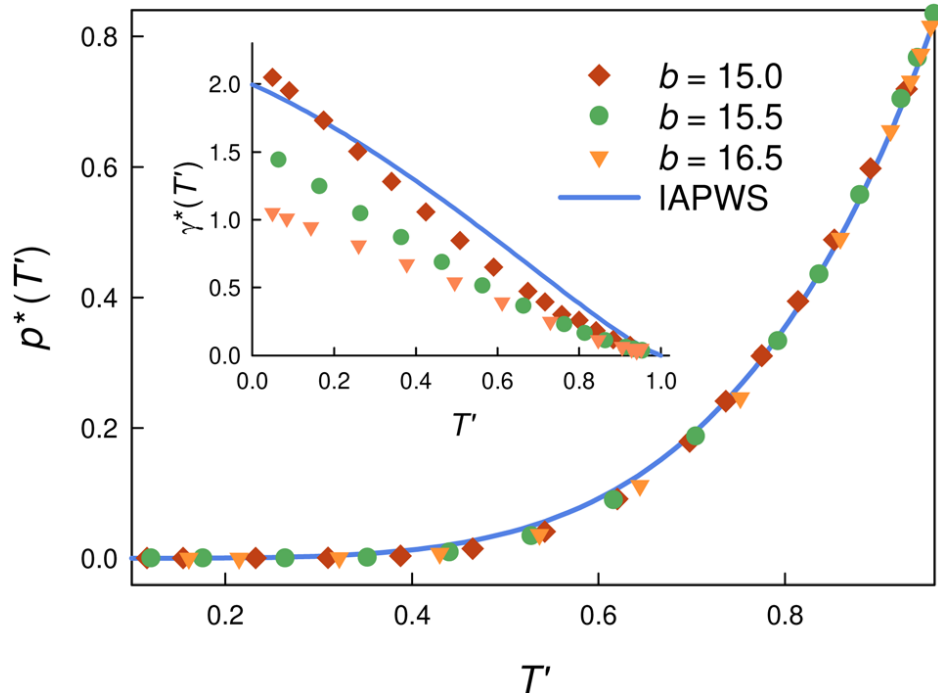
- Low melting point ( $T_0 \approx 0.07T_c$ )
- FCC solid favoured over BCC
- Temperature of maximum (liquid) density (TMD) slightly above melting point
- Solid contracts when heated: **negative thermal expansion**
- Increasing pressure reduces melting point: **pressure-induced melting**



Simplicity of  $n$ DPD interactions belies their ability to model richly complex thermodynamics: many of above effects likely to originate from medium-range (mesoscopic) structure rather than e.g. hydrogen bonding

# Parameterising $n$ DPD for simple liquid

## Assuming single beads for e.g. water



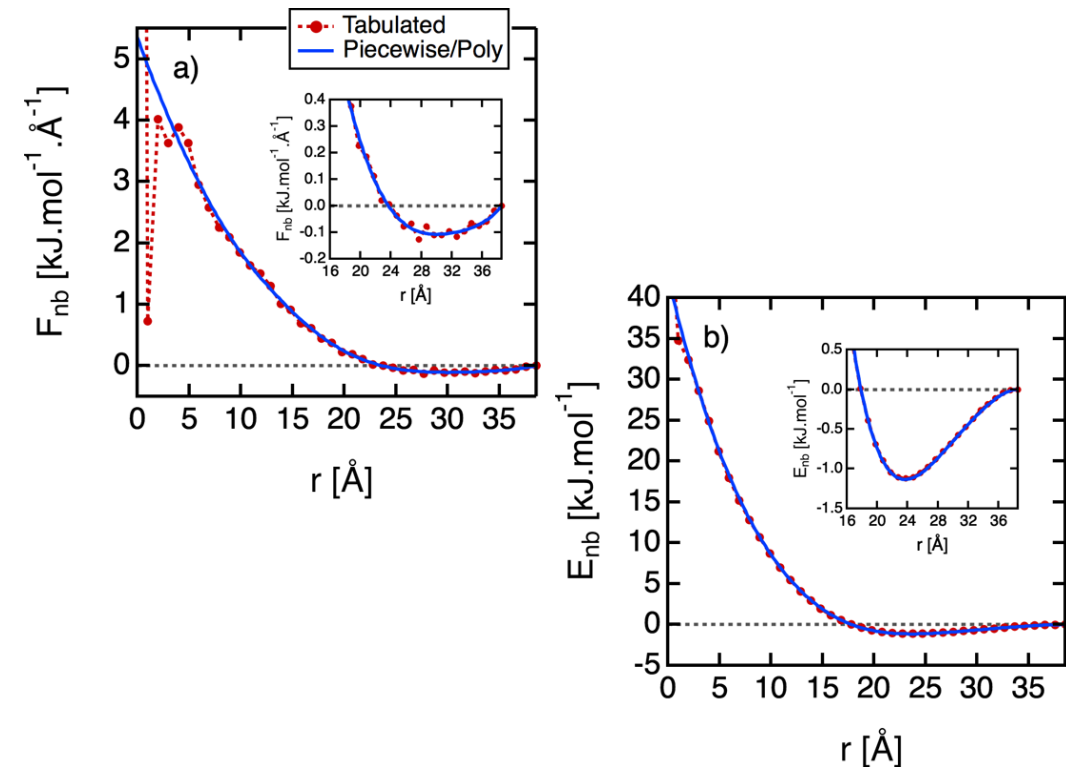
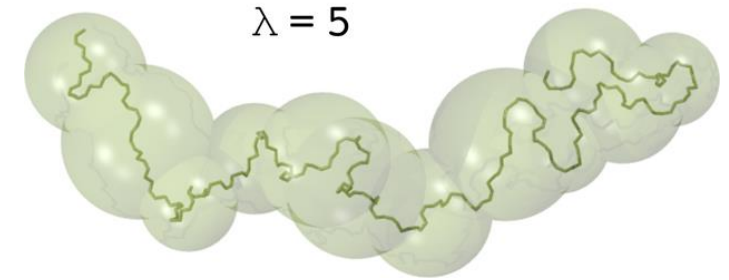
Variation of saturated vapour pressure (inset: surface tension) with temperature scaled to melting point  $T_0$ ,  $T' = \frac{T-T_0}{T_c-T_0}$  (compared with reference equation of state<sup>[1]</sup>)

- Start by setting  $n$  (e.g.  $n = 4$ )
- Energy scale set by  $A$ , based on temperature we wish to use compared to  $T_c$
- Length scale set by  $r_c$ , based on coarse-graining level (molecules per bead)
  - 5 H<sub>2</sub>O molecules per bead,  $r_c \approx 13.88 \text{ \AA}$
- Value of  $b$  sets thermodynamic behaviour, can be based on variation of surface tension with temperature

# Fitting $n$ DPD parameters from coarse-graining

## CG/DPD model for *cis*-1,4-polybutadiene<sup>[1]</sup>

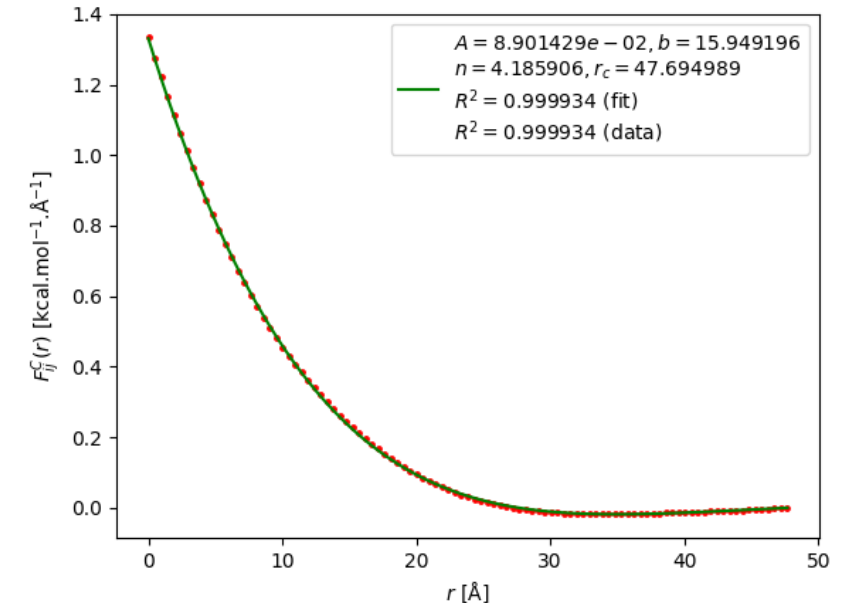
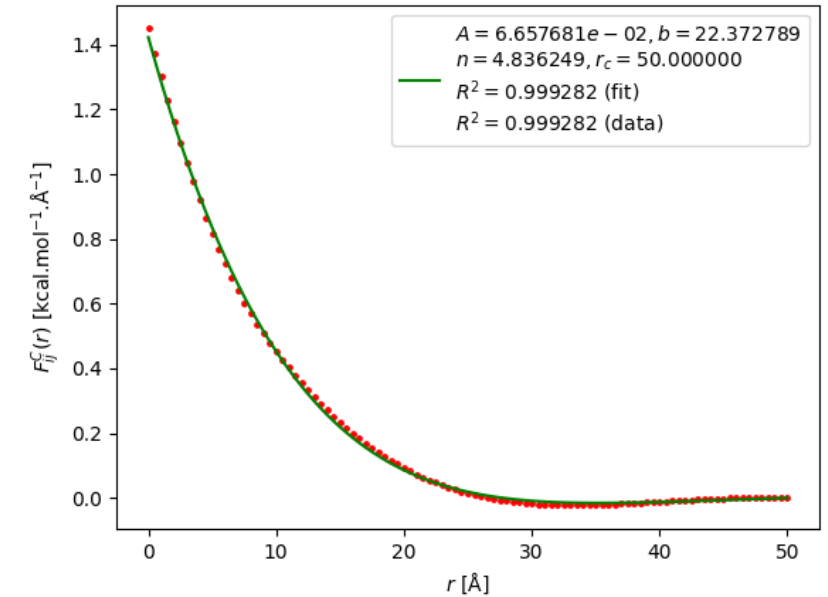
- Applied trajectory matching technique from MD simulations of cPB with united atom force field
- Devised van der Waals (non-bonded) pairwise forces and potentials for various CG levels
  - $\lambda$  monomers of 4 C atoms per bead
  - Bond and angle potentials also applied between beads
- Originally fitted CG forces to piecewise polynomial functions of  $r$  for DPD calculations
- Force/potential looks rather like  $n$ DPD ...



# Fitting $n$ DPD for CG polymer

## Two CG models available for 5-monomer cPB: fitted $n$ DPD parameters using least squares regression

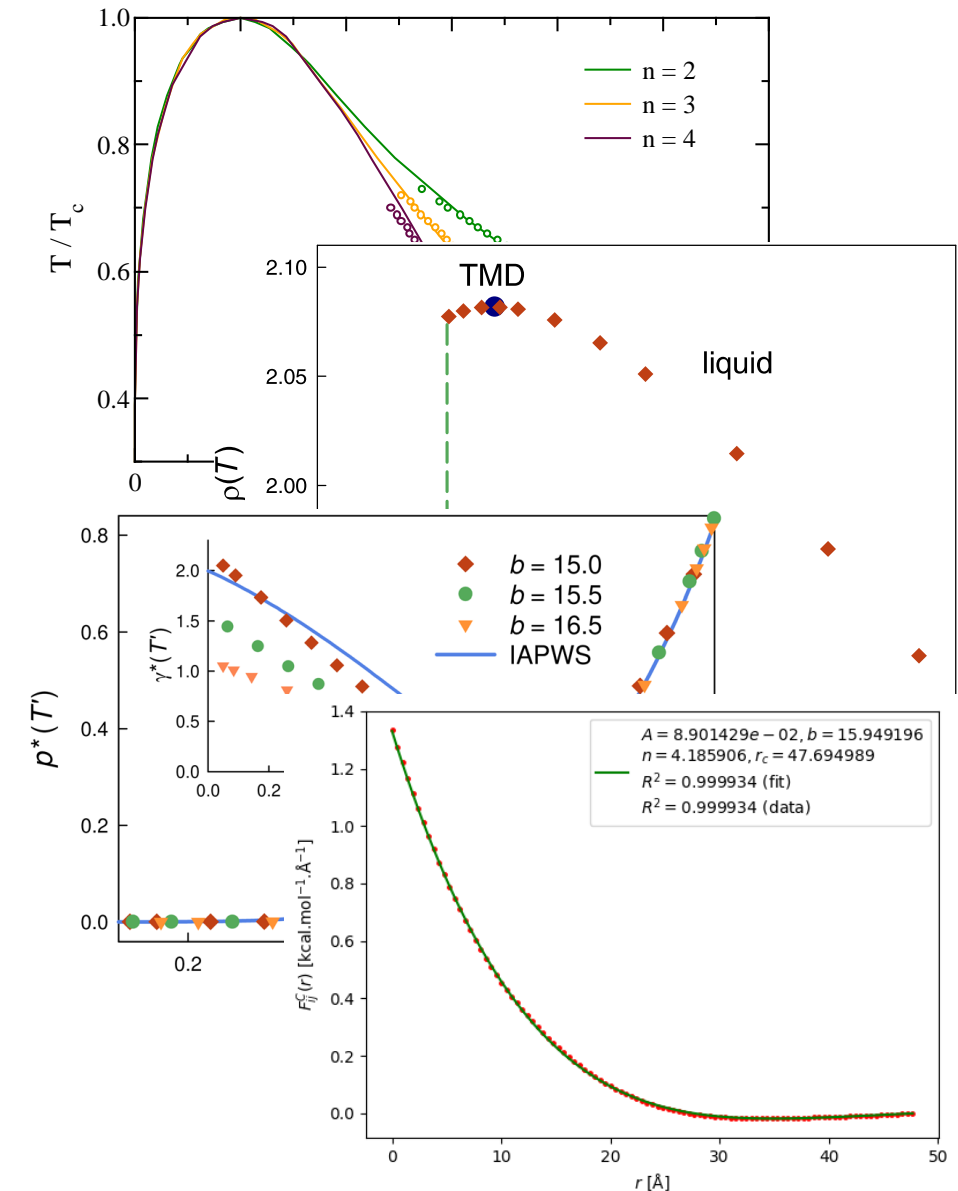
- One based on best likelihood to fit MD trajectories (via Bayesian matching)
  - $b \approx 22.372$  smaller than minimum (23.022) for thermodynamic stability based on  $n = 4.836$
- Other based on best match to actual cPB densities
  - $b \approx 15.949$  thermodynamically stable ( $n = 4.186$ )
  - Matched pressure and RDFs using fitted  $n$ DPD interactions in DL\_MESO\_DPD and DL\_POLY NVT calculations (cf. LAMMPS from original study)



# Conclusions

## New interaction model ( $n$ DPD) for CG/mesoscale modelling

- Added attraction and more control on repulsion to Groot-Warren ('standard DPD') interactions
- Enables vapour/liquid phase coexistence below critical point
- Interesting solid/liquid behaviour around melting point despite simplicity of interaction
- Straightforward to parameterise for simple fluids
- Matches interactions obtained by coarse-graining more complex materials (e.g. polymers)



# Acknowledgements

- CoSeC
  - MCC for computing time on ARCHER2
  - UKCOMES for supporting development of DL\_MESO
- STFC
  - Innovation and Development Programme (IDP)
  - Computing time on SCARF
- Patrick Warren (Hartree Centre) and Andrew Masters (University of Manchester) for discussions, ongoing HNC and RPA calculations
- Alain Dequidt (Université Clermont Auvergne) for supplying original data from cPB studies



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