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# Phase behaviour of coarse-grained liquids with soft attractive-repulsive potentials

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We propose a new pairwise bounded interaction potential based on the Groot-Warren interaction[1] commonly used for mesoscopic Dissipative Particle Dynamics (DPD) simulations:

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

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

with repulsive parameters $A$ and $b$, power index $n$ and cutoff distance $r_c$ (equivalent to particle size $a_0$). This ***n*DPD** potential (as shown in Figure 1) includes both soft-core repulsion and attraction, enabling coexistence of multiple phases below the critical point, and reduces to 'standard DPD' when $b = 2$ and $n = 1$.

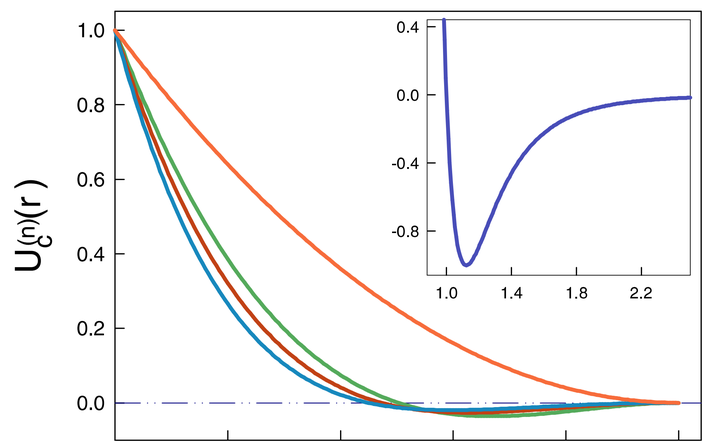


Figure 1: 'Standard DPD' Groot-Warren potential (orange), $n$DPD with $n = 2$ (green), $n = 3$ (red) and $n = 4$ (blue), and Lennard-Jones (purple, inset). Note attractive region for $\sigma \approx 0.5a_0 < r < a_0$

A modified version of DL_MESO[2,3] was used to carry out single-component DPD simulations with $n$DPD interactions, using a Langevin barostat[4] for constant pressure ensembles. Three integer power indices ($n$) – 2, 3 and 4 – were investigated with the corresponding values of $A$ and $b$ and resulting critical properties given in the table below.

| $n$ | $A$ | $b$ | $T_c$ | $p_c$ | $\rho_c$ |
|---|---|---|---|---|---|
| 2 | 25.0 | 3.02 | 1.025 | 0.2951 | 0.519 |
| 3 | 15.0 | 7.2 | 1.284 | 0.3979 | 0.504 |
| 4 | 10.0 | 15.0 | 1.286 | 0.4095 | 0.484 |

A simulation setup elongating the box in one dimension (Figure 2) and Maxwell constructions for states close to the critical point were used to obtain **gas-liquid coexistence curves** (Figure 3). While the gas branch is insensitive to $n$, variations in liquid behaviour occur from convex ($n = 2$) to realistic concave ($n = 4$) liquid branches. These variations can be eliminated by increasing the values of $b$ above the minimum values required for thermodynamic stability (Figure 4).

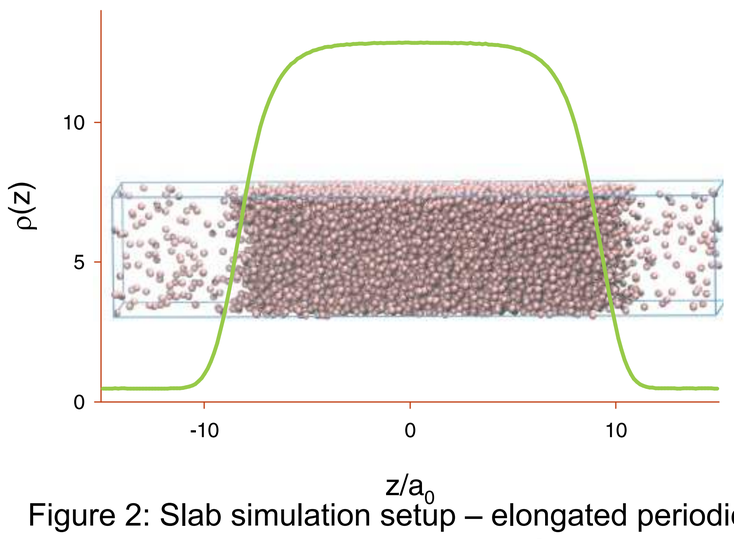


Figure 2: Slab simulation setup – elongated periodic boxes – used to estimate densities of coexisting gas and liquid states (density profile in green with phase interfaces at $z \approx \pm 10a_0$)

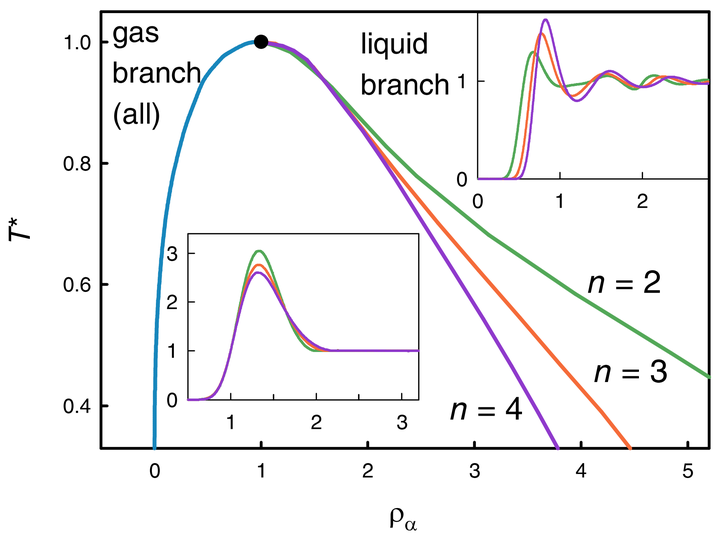


Figure 3: Coexistence curves for $n$DPD using $n = 2,3,4$ with gas and liquid branches (note variation in concavity in latter with $n$). Black dot denotes critical point (curves rescaled to $T^* = 1$), radial distribution functions (liquid branches at $T^* = 0.4$) in insets.

*NPT* simulations starting with solid and liquid phases joined together were used to find the **solid-liquid transition** (Figure 5). **Unusual properties** observed for $n = 4$ include:

- A low freezing point ($T^* \approx 0.092$) compared with real fluids (e.g. triple point of water at $T^* = 0.577$)
- Temperature of maximum density (TMD) just above the freezing point ($T^* \approx 0.11$)
- Negative thermal expansion (NTE) of solid phase (contraction upon heating), as observed in ice[5], a few elemental metals/metalloids (e.g. gallium, silicon) and more complex soft matter

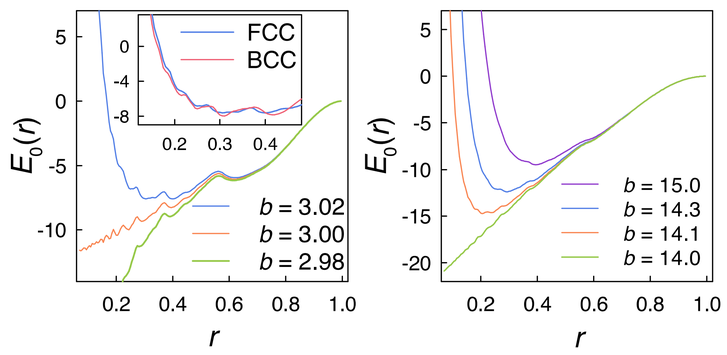


Figure 4: Potential energies per particle calculated for different values of $b$ for $n = 2$ (left) and $n = 4$ (right). Minimum values of $b$ are required to ensure thermodynamic stability and prevent high density singularities. Multiple energy minima – particularly noticeable for $n = 2$ – could result in polymorphic solids (e.g. fcc and bcc phases as shown in inset).

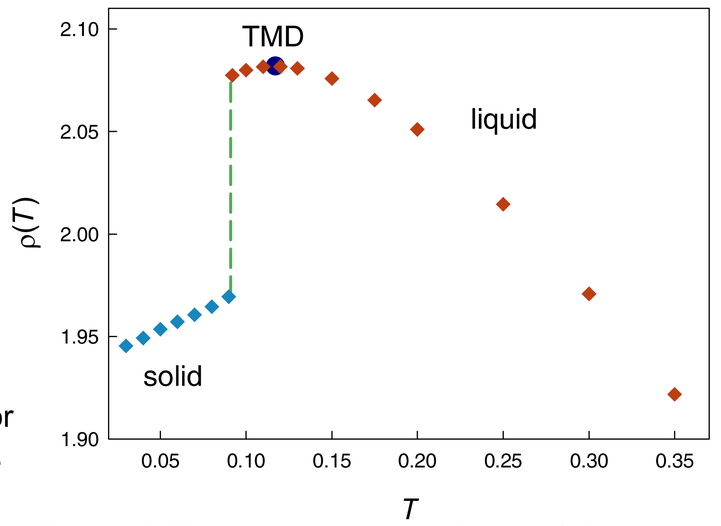


Figure 5: Temperature dependence of density around solid-liquid phase transition, including NTE of solid phase. Green line shows transition temperature, black dot gives temperature of maximum density (TMD)

**References:**

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