Supporting Information for:

A many-body dissipative particle dynamics parametrisation scheme to study behaviour at air-water interfaces

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1 Surface tension fitting

1.1 Equation 14 and 15 - Molecules of single bead type

A parameter sweep varies the number of bonded beads N and their interaction parameter a_{ij}. Figure S1 shows the relationship between the calculated surface tension and N for different a_{ij} values. For each value of a_{ij}, a fit is obtained using equation

$$\gamma = \frac{-1.9}{\sqrt{N}} + \beta$$

fitting to the value of β.

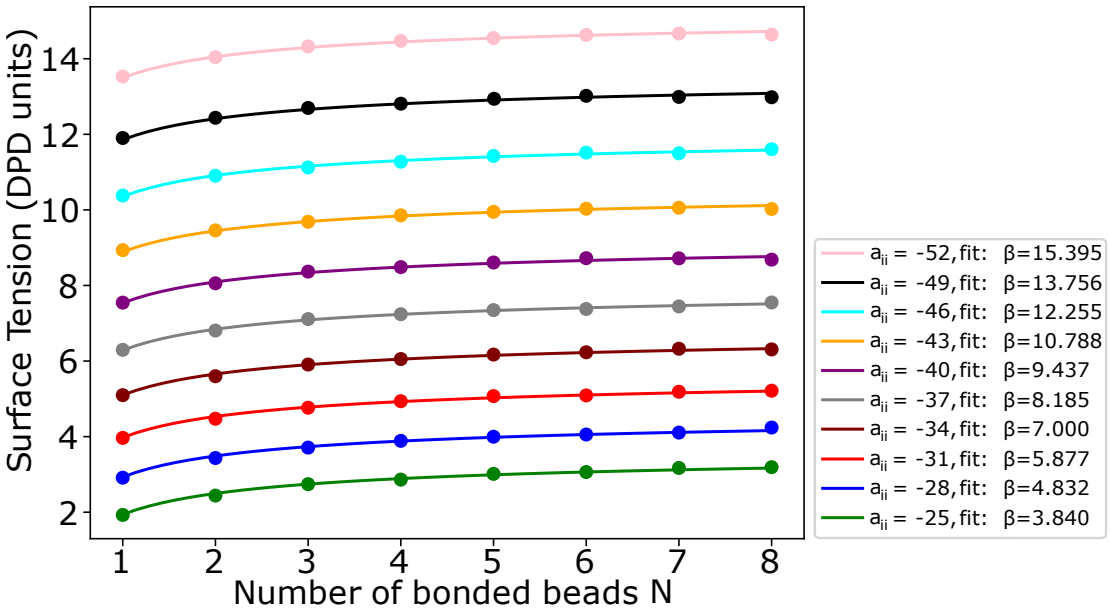

Fig. S1: Relationship between the surface tension and N for different values of a_{ij}.

The relationship between fitted β and a_{ij} is shown in Fig. S2. First and second order polynomial fits to β are shown, highlighting the improved fit when using a second order fit. The overall coefficient of determination R^2 value for the first order fit is $R^2 = 0.993566$, while for the second order fit $R^2 = 0.999885$.

1.2 Equation 22 - Molecules with two bead types

The coefficient values M, m_i, and c_i in Eq. 22 (main article) are obtained by fitting to raw data. This raw data is obtained via a parameter sweep through different values of a_{CC}, a_{DD} and a_{CD}. The quality of this fit is demonstrated in Fig. S3, in which the value of surface tension (obtained via Eq. 12), is plotted against the value obtained using Eq. 22.

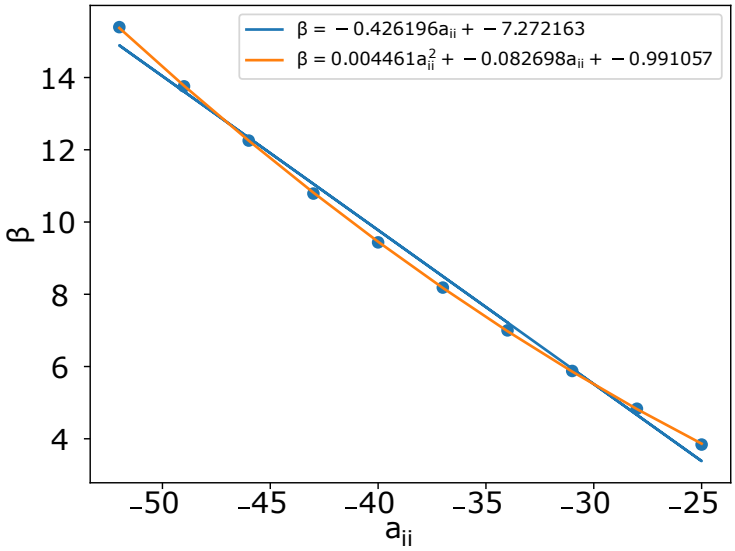

Fig. S2: Relationship between fitted β parameter and a_{ij}.

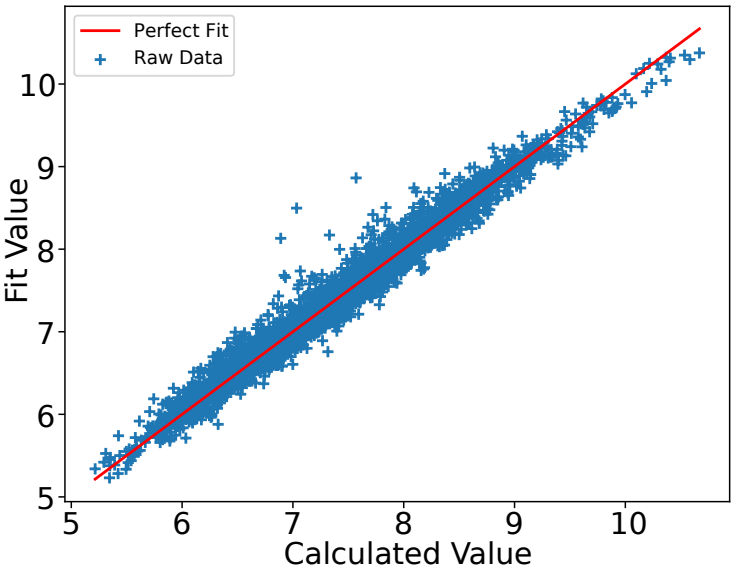

Fig. S3: The relationship between the 'fit' value of γ (using Eq. 22 in the main article) and the 'calculated' value (using Eq. 12 in the main article). Fit has $R^2 = 0.967053$.

2 Density fitting

Once again, a parameter sweep varies the number of bonded beads N and their interaction parameter a_{ij}. Figure S4 shows the relationship between the calculated density and N for different a_{ij} values. For each value of a_{ij}, a fit is obtained using equation

$$\rho = \frac{\alpha}{N} + \kappa$$

fitting to the values of α and κ. The relationships between fitted α and κ with a_{ij} are shown in Fig. S5. First order fits with a_{ij} produce Eq. 16 in the main article. The overall R^2 value for the fit for density against a_{ii} is $R^2 = 0.997421$.

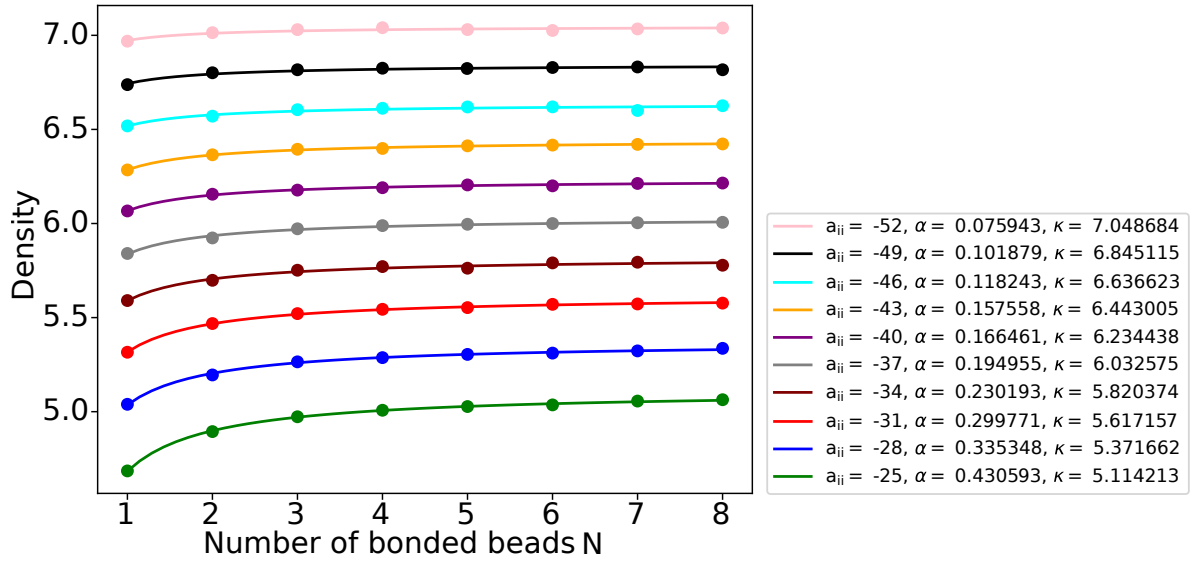

Fig. S4: Relationship between bead density and a_{ij}.

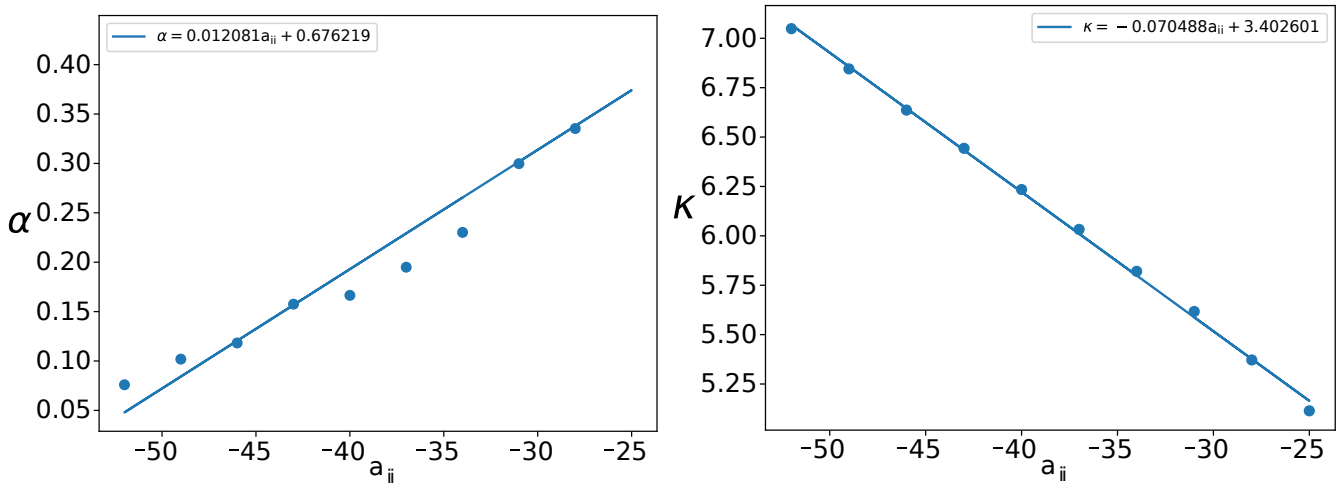

Fig. S5: Relationship between fitted α and κ with interaction parameter a_{ij}. For α vs. a_{ii} fit has $R^2 = 0.936001$, and for κ vs. a_{ii} fit has $R^2 = 0.998595$.

3 Cross interaction fitting

The coefficient values x_i in Eq. 21 (main article) are obtained by fitting to raw data. This raw data is obtained via a parameter sweep through different values of a_{AA}, a_{BB} and a_{AB}. The quality of this fit is demonstrated in Fig. S6, in which the value of $\ln(\gamma_A^\infty)$ (obtained via Eq. 20), is plotted against the value obtained using Eq. 21.

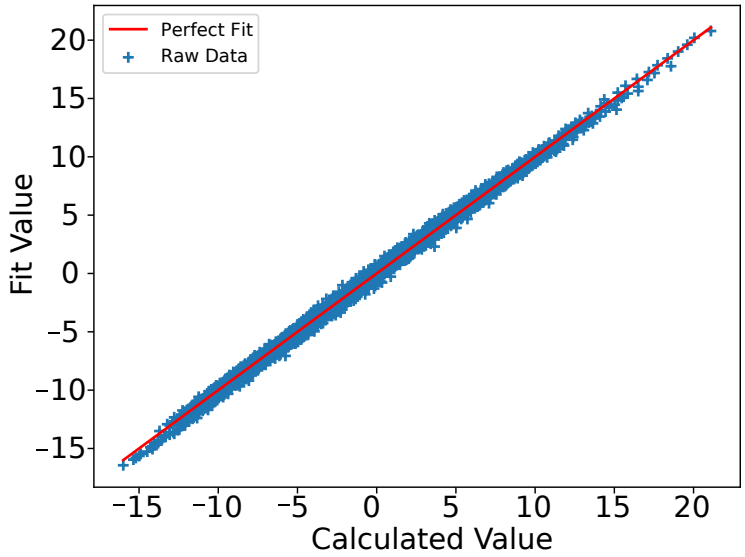

Fig. S6: The relationship between the 'fit' value of $\ln(\gamma_A^{\infty})$ (using Eq. 21 in the main article) and the 'calculated' value from widom insertion (using Eq. 20 in the main article). Fit has $R^2 = 0.996770$.

4 Surface tension and interface size

Fig. S7 shows the surface tension calculated as a function of the number of beads in the molecule and the value of a_{ii}. We vary the size of the box, where one has dimensions $10r_C \times 10r_C \times 100r_C$ and is conducted using 10,000 beads. Another, larger box, has dimensions $22r_C \times 22r_C \times 100r_C$ and contains 100,000 beads. We show that the surface tension results between the two box sizes are virtually identical, for molecules of various lengths and different a_{ii} values.

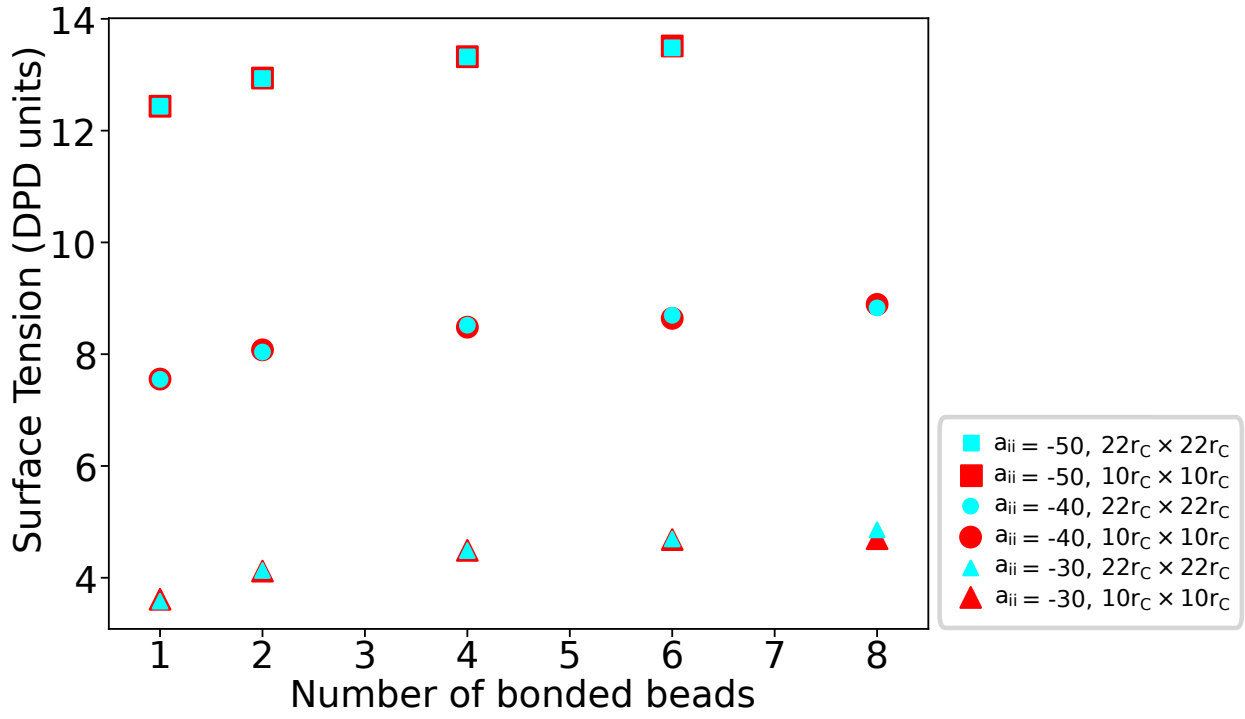

Fig. S7: Relationship between the surface tension and the number of bonded beads, for different values of a_{ii} and interface surface areas.

5 Surface tension and equilibrium bond length

Fig. S8 shows the surface tension calculated for a molecule of length $N = 4$, as a function of a_{ii}. We vary the equilibrium bond length chosen, comparing $l_0 = 0.5$ and $l_0 = 0.45$. We show that the

surface tension results between the two are virtually identical, meaning that the choice of bond length is critically important to the parametrisation scheme.

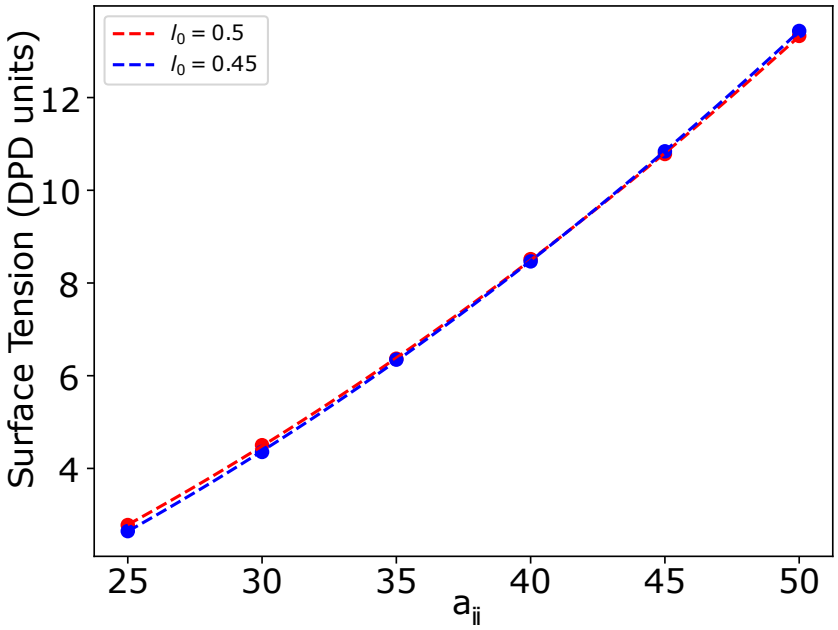

Fig. S8: Relationship between surface tension (for a molecule of length $N = 4$) and interaction parameter a_{ii} when the equilibrium bond length l_0 is varied.

6 Mixtures in larger simulation boxes

As discussed in the main article, we also tested increasing the bulk size for aqueous mixtures of polyethylene glycol to investigate the impact this has on the surface tension calculated. This was motivated by the preference for solute molecules to gather at the interface, influencing the bulk concentration.

Fig. S9 shows the surface tension calculated for two different box sizes. One is the domain size which is presented in the main article and is conducted in a simulation box with $22r_C \times 22r_C \times 100r_C$ using $n = 100,000$ simulation beads. For comparison, we also show a larger box size, which has $22r_C \times 22r_C \times 300r_C$ using $n = 300,000$ simulation beads. We observe that the results from the larger domain size are slightly closer to the experimental results, likely because the bulk concentration in this case is closer to the experimental bulk concentration. However, the difference is negligible, and the results are fairly similar.

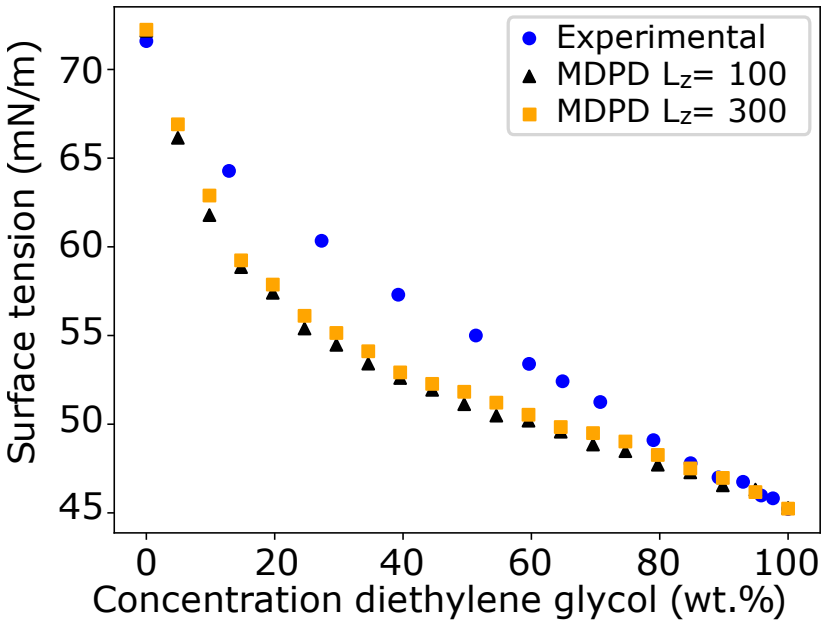

Fig. S9: Surface tension of aqueous diethylene glycol mixtures as a function of concentration, for two different box sizes.