Self-assembly behaviour of hetero-nuclear Janus dumbbells†

Patrick O’Toole, b∗a Gianmarco Munaò, b,c Achille Giacometti d,c and Toby S. Hudson a,b

We investigate the fluid structure and self-assembly of a system of Janus dumbbells by means of aggregation-volume-bias Monte Carlo simulations and Simulated Annealing techniques. In our approach, Janus dumbbells model asymmetric colloidal particles constituted by two tangent (touching) spheres (labelled as h and s) of different sizes and interaction properties: specifically, the h spheres interact with all other spheres belonging to different dumbbells via hard-sphere potentials, whereas two s spheres interact via a square-well potential. By introducing a parameter \( x \in [0,2] \) that controls the size ratio between the h and s spheres, we are able to investigate the overall phase behaviour of Janus dumbbells as a function of \( x \).

In a previous paper (O’Toole et al., Soft Matter, 2017, 13, 803) we focused on the region where the s sphere is larger than the h sphere (\( x > 1 \)), documenting the presence of a variety of phase behaviours. Here we investigate a different regime of size ratios, predominantly where the hard sphere is larger than (or comparable to) the attractive one. Under these conditions, we observe the onset of many different self-assembled super-structures. Depending on the specific value of \( x \) we document the presence of spherical clusters (micelles) progressively evolving into more exotic structures including platelets, filaments, networks and percolating fluids, sponge structures and lamellar phases. We find no evidence of a gas–liquid phase separation for \( x \leq 1.1 \), since under these conditions it is pre-empted by the development of self-assembled phases.

1 Introduction

Recent advances in the study of colloidal particles have shown that anisotropies in their molecular geometry and in their interaction potential can give rise to a large variety of self-assembled structures.1–5 In particular, dumbbell-shaped particles have attracted a great volume of attention prompted by nascent innovation in colloidal synthetic techniques.6–8 These particles are typically constituted by two monomers, one of which is solvophilic and the other one is solvophobic; in essence, these colloids can be viewed as the molecular counterpart of Janus spheres9–17 and are also known as Janus dumbbells.18,19 These particles also can be conceived of as prototypical surfactants, given their amphiphilic surface character, molecular geometry, and their assembly behaviours.20 Very recently, theoretical and numerical studies of anisotropic colloids are arousing increasing interest; in particular, computer simulations of trimers,21,22 dumbbells20,23–30 and their mixtures31 have documented a large variety of super-structures including micelles, lamellae, vesicles, and tubes. Heteronuclear dumbbell shaped Janus colloids offer the ability to control the self-assembly via two routes: potential effects through surface chemistries; and packing through bead asymmetry and molecular geometry.

In a previous paper, that we shall refer to as ‘Paper I’, we report in detail how the phase behaviour of hetero-nuclear Janus dumbbells (HJD) is controlled by the relative size of the interaction sites.20 In order to properly account for their size ratios, we introduced a parameter \( x \in [0,2] \) (see the following eqn (1) for its mathematical definition), so that \( x = 2 \) and \( x = 0 \) correspond to the single square well spherical bead and the single hard spherical bead, respectively (see Fig. 1). In the region approaching the homo-nuclear Janus limit (\( x \rightarrow 1 \), where the interaction site cores have comparable sizes) we demonstrated that the gas–liquid phase separation becomes metastable with respect to the formation of bilayer structures. Under these conditions, curved structures tend to possess increasing characteristic length, beginning to flatten out into infinite planar lamellar structures which eventually dominate.

---

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7sm01401e
the phase diagram. Upon decreasing \( \alpha \) we observed three different regimes: a conventional gas–liquid phase separation (1.3 < \( \alpha < 2 \)); low temperature formation of inverse micelles (\( \alpha \approx 1.3 \)); and a competition between gas–liquid formation and the appearance of bilayer structures (1.1 \( \leq \alpha \leq 1.2 \)). Curved bilayer structures observed in this region range from vesicles to bi-continuous sponge-like structures.

In this paper we extend the analysis of Paper I to include the most interesting region corresponding to 0.25 < \( \alpha < 1.1 \), where self-assembled structures are expected to dominate the scene. Since no gas–liquid critical point has been found for \( \alpha < 1.1 \), the formation of a conventional liquid is not possible below this critical value. However, there is still a significant portion of the potential to engage in bonding. Our aim is to address the following important question: given that no conventional liquid is present here, and bonding is directed by the steric influence of the purely repulsive bead, what low temperature structures are expected to dominate the \( \alpha \) space region (0.25 < \( \alpha < 1.1 \))?

We perform our investigation by means of a combination of the Aggregation-Volume-Bias Monte Carlo (AVBMC) technique coupled with Simulated Annealing (SA) to study the structural variations of aggregates. We remark that while AVBMC was previously applied to perform extensive simulations of analogous systems with highly directional interactions, none of the previous studies have addressed the present model, nor underpinned the crucial role played by kinetic bottlenecks in the formation of aggregates, with the only notable exception of ref. 22.

Our study is then contrasted with other recent theoretical, as well as experimental studies on analogous systems in the last part of the paper. Before that, the paper is arranged as follows: in Section 1.1 we briefly discuss the model and the interaction potential; in Section 2 we introduce the AVBMC algorithm (Section 2.1) and the SA protocol (Section 2.2). The reader is referred to the previous Paper I for a more thorough description of both model and methods. In Section 3 we discuss the formation of self-assembled aggregates, characterise the differences between them, elucidate the effect of packing on continuous structures and present the phase diagrams. In Section 4 we compare our major findings with already existing experimental and theoretical works, finally drawing conclusions in Section 5.

The ESI contain a formulation to model packing constraints imposed on structures by the hard non-attractive bead and develop simple packing arguments that broadly predict the behaviour of layered structures as a function of \( \alpha \).

1.1 Model

In our approach, HJDs (with characteristic length parameter \( \sigma_i \)), are composed by two spherical interaction sites, referred to as beads \( s \) and \( h \), with diameters, \( \sigma_s \) and \( \sigma_h \), each modified through a size ratio parameter \( \alpha \in [0,2] \). This parameter defines the relative size of each bead core by

\[
\begin{align*}
\sigma_s &= \begin{cases} 
\frac{2\alpha}{\alpha - 1} & \alpha < 1 \\
\sigma & \alpha > 1
\end{cases} \\
\sigma_h &= \begin{cases} 
\sigma & \alpha < 1 \\
(2 - \alpha)\sigma & \alpha > 1
\end{cases}
\end{align*}
\]

where \( \sigma_h \) is the diameter of a purely repulsive hard-sphere (HS), denoted \( h \), and \( \sigma_s \) is the diameter of the core of a square-well (SW) sphere, denoted \( s \), with interaction range in addition to its hard-core, parametrised as \( \lambda (= 0.5) \), such that the resultant interaction range is

\[
\gamma = \sigma_s + \lambda \sigma_s.
\]

Neighbouring particles whose \( s \) sphere’s centre comes within \( \gamma \) of the \( s \) sphere centre have a bonding energy of \( -\varepsilon \). The total site-wise interaction potential between two particles is defined as

\[
V_{\text{total}} = V_{\text{SW}}(r_{ss}) + V_{\text{HS}}(r_{hs}) + V_{\text{HS}}(r_{sh}) + V_{\text{HS}}(r_{hh}),
\]

i.e. as the sum of contributions from the \( s \) and \( h \) beads, where the potentials \( V_{\text{SW}} \) and \( V_{\text{HS}} \) are defined by

\[
V_{\text{SW}}(r_{ss}) = \begin{cases}
\infty & r_{ss} < \sigma_s \\
-\varepsilon & \sigma_s < r_{ss} \leq \gamma \\
0 & r_{ss} > \gamma
\end{cases}
\]

\[
V_{\text{HS}}(r_{ab}) = \begin{cases}
\infty & r_{ab} < (\sigma_a + \sigma_b)/2 \\
0 & r_{ab} > (\sigma_a + \sigma_b)/2
\end{cases}
\]

where \( a \) and \( b \) correspond to the interaction sites along with the corresponding particle diameters. Therefore, in the case

\[
(a, b) \in \{(s, h), (h, s), (h, h)\},
\]
corresponding to \( \sigma_s = \sigma_h \) (the Janus limit), particles take the form denoted in panel d) of Fig. 1. The interaction energy parameter \( \varepsilon \) (set to unity for all \( \sigma \)) provides the unit of energy, in terms of which we define the reduced temperature \( T^* \equiv k_B T / e \). We also make use of the reduced number density \( \rho^* \equiv (N/V) \sigma^3 \), where \( N \) is the total number of particles and \( V \) the volume of the simulation box.

## 2 Methods

### 2.1 Aggregation-volume-bias Monte Carlo

In our study we make use of a suitable version of the Aggregation Volume Bias Monte Carlo (AVBMC) algorithm. The implementation can be found in Paper I that focused on the region \( x > 1 \). Where \( x < 1 \) the smaller \( \sigma_s \) sphere forces assembled clusters to generally have a closed topology (with the sticky components facing toward a centroid (either point, or for elongated structures toward a centroid ‘line’ or plane section, depending on the geometry of the cluster, i.e. a globe or filament or a plane). These inward facing cluster topologies often cause relaxation to an ‘equilibrium’ structure to be slow, and percolation to depend upon the diffusion of clusters through the simulation box. Cluster structures at low temperature are long-lived and thus using naïve particle move algorithms requires long simulation times to adequately sample cluster configurations. In order to facilitate the relatively quick sampling of cluster size distributions and geometries an implementation of the AVBMC algorithm is employed to increase equilibrium relaxation rates and also improve the gathering of cluster related statistics. AVBMC moves are attempted 50% of the time, with the remaining attempts split equally between rotations and translations.

### 2.2 Simulated annealing

Since \( T^* \) must be sufficiently low to encourage an aggregation process, and in order to traverse the large length-scale variation in a sensible manner, the parameter \( x \), which determines \( \sigma_s \) and thus \( \sigma_{\text{eff}} \), the interaction range, implies that the corresponding \( T^* \) that encourages an aggregation process will also vary with \( x \) (consider Fig. 2). In this context, particle systems of \( N = 1000 \) with \( x < 1.3 \) are subjected to Monte Carlo (MC) simulations in the canonical ensemble incorporating an annealing process with initial temperature, \( T_{\text{init}}^* \) above the corresponding Boyle temperature, \( T_B(x) \). The latter is defined as the temperature where the second virial coefficient \( B_2 \) vanishes, thus indicating that attractive interactions become prevailing. A \( (T^*) \) descent algorithm was chosen such that the progression was linear in \( \beta = (kT^*)^{-1} \) and the length of each simulation chosen such that the descent rate was approximately consistent between simulations run at different \( T_{\text{final}}^* \). Once the systems have reached the desired temperature, the resulting structures were allowed to locally equilibrate for another \( 10^7 \) Monte Carlo steps (MCS) before sampling over another \( 10^7 \) MCS commenced. Total simulation lengths varied between \( 10^8 \) and \( 2 \times 10^8 \) MCS. This process was applied across the range \( 0.25 \leq x \leq 1.3 \). The total set of \( T^* \) and \( x \) explored is depicted in Fig. 3. We note that the method of annealing here is consistent with a slow cool rate and should yield reasonable approximations to the global thermodynamic minima at the corresponding densities. The highest density considered here is \( \rho^* = 0.3 \), the volume fraction, \( \phi^* = \pi \rho (\sigma_s^3 + \sigma_h^3) / 6 \), naturally varies across \( x \) consistent with the variation in bead volume sum. Restricting the maximum number density \( \rho^* \) has the effect of probing liquid and low \( \rho^* \) aggregation behaviour. Dense liquid \( (\phi^* \to 0.454, \rho^* = 0.454) \), the corresponding first point of crystallisation for pure hard spheres) and dense crystalline

![Proposed \( T^* - x \) phase diagram demonstrating the high density phases observed in this work. Regions bound by solid lines are obtained in this paper and Paper I, while regions bound by dashed lines indicate likely behaviour for low temperature structures based on packing arguments for \( x > 1.3 \). FCCoct indicates an FCC crystal structure of \( s \) beads with octahedral site interstitial spaces occupied by the \( h \) bead. Likewise, the “oct-tet” indicates substitutional disorder over the octahedral and tetrahedral interstices.](image)

![Summary of all \( T^* \) examined at each \( x \) by SA employing the AVBMC algorithm (black squares). Coloured circles around each square indicate the degree of structure developed in assemblies at each \( (x,T^*) \) point. Also located here for reference, various temperatures considered when determining the temperature descent protocol: \( T_{\text{ref}}, T_{\text{ref}} - \text{scaled to } T_{\text{ref}}^*(x = 2), T_{\text{ref}}^*(x) \) as obtained by SUS technique. The right legend indicates the degree of structure in the bonding networks of \( s \) beads.](image)
phases ($\phi^* \rightarrow 0.545$, the last point of fluid order in the same system) require special methods to elucidate their structure and thermodynamic properties and cannot be obtained meaningfully from the present methodology. Nevertheless, structures that are observed to have long range order or a consistent dominant environment, as measured by certain metrics (see Section 2.3), are termed crystalline in the corresponding sense.

2.3 Metrics

In order to analyse our simulations we employ a group of metrics. As some of these metrics rely on a concept of a ‘bond’ we define two particles to be connected by a bond if the distance between their s beads is less than the interaction range i.e. $\delta(r_i - r_j) < \gamma$ (eqn (2)). Firstly the radial distribution function $g_{ij}(r) = g(r)_{ij}$, taken separately over each of: the particle centroids; the s beads; and the h beads. For instance the s–s radial distribution function is defined as

$$g_{ss}(r) = \frac{1}{4\pi r^2 \rho N} \sum_{i=1}^{N_s} \sum_{j=1}^{N_s} \delta(r - r_{ij})$$

where $i_s$, $j_s$ are all the particle pairs in the system, and $r_{ij} = |r_i - r_j|$. Similar definitions hold true for $g_{sh}(r)$, and $g_{hh}(r) = g_{hh}(r)$. These correlation functions can be inspected for each state-point to identify persistent structure in any of the liquid or self-assembled phases.

Secondly we obtain the radius of gyration computed as:

$$R_g^2 = \frac{1}{N_s} \sum_{i=1}^{N_s} (r_i - C)^2$$

where $C$ is the cluster centroid. This value can then be compared to the cluster sizes to find the fractal dimension of the system (see Section 3.4.2).

Thirdly, we collect values of bond-orientation over each particle in a state-point via distributions of $q_0(N_b)^{36}$ where $N_b$ is the number of bonds per particle. This is the $l = 6$ case of the general bond-orientation order parameters

$$q_l = \sqrt{\frac{4\pi}{2l+1}} \sum_{m=-l}^{l} \left| \frac{1}{N_b \sum_{b \in \text{bonds}} Y_{lm}(\Omega)} \right|^2$$

that is routinely used to identify close-packing crystalline structures. Here $N_b$ is the number of bonds and $Y_{lm}(\Omega)$ are the usual spherical harmonics. We also monitor the corresponding distributions of bonds ($P(N_b)$) and of $q_6$.

Fourthly, distributions $P(N_s)$ of cluster sizes $N_s$ are collected and presented for some state-points with finite structures, to identify morphological characteristics associated with each cluster. It is possible to carry out an analysis of the complexity of aggregates by using a relation between the number of particles in a cluster, $N_s$, and the gyration radius of the cluster, $R_g$. The resulting relation can be expressed as a power law:

$$N_s = k_I \left( \frac{R_g}{z_0} \right)^{D_I}$$

Eqn (8) gives a method to find what is usually called the fractal dimension, $D_I$. The log–log plot of $N_s$ against $R_g$ can be fit linearly, to give the slope, $D_I$, and the fractal pre-factor $k_I$. The scaling factor $z_0$ is simply the average diameter of each monomer in the cluster calculated as $(\sigma_s + \sigma_h)/2$, but is not used to scale the data during processing. The slope is then

$$\frac{d \log N_s}{d \log R_g} = D_I$$

In addition to the above structural order parameters, we will also monitor the system average energy to identify equilibrium configurations.

3 Results

3.1 The $T^* - \alpha$ phase diagram

It is convenient to introduce a general phase diagram in the $\alpha$, $T^*$ plane, as schematically presented in Fig. 2. This diagram presents the higher density ($\rho^* > 0.2$) phases observed in the entire range $0 < \alpha < 2$ corresponding to all possible morphological asymmetry variation of the dumbbells (see Fig. 1). For more detailed information about the specific location in the density axis at each of the points in the $\alpha - T^*$ space, the reader is directed to the phase diagrams in the ESI.*

The region corresponding to $1.3 \leq \alpha \leq 2$ displays conventional gas and liquid phases at intermediate temperatures, as well as several crystalline phases at lower temperatures. We analysed the former in Paper I,† whereas the latter can be expected due to analogy with a system of hard asymmetric dumbbells, considering that the h bead diameter is subsumed by the length of the interaction range and can pack into the interstices of the fcc crystal lattice: i.e. tetrahedral/ octahedral substitutional disorder where $\sigma_h < 0.225$, and octahedral interstitial occupancy where $0.225 < \sigma_h < 0.414$. Of course, these assumptions can be inspected, but this is outside the scope of this paper. The region corresponding to $1.1 < \alpha < 1.3$ was also discussed in Paper I and will be extended here in terms of coverage. Finally, the region with $\alpha < 1.1$ pertains to the self-assembly domain and will be the focus of the present study. As further discussed below, a rich polymorphism is found, as a function of both temperature and $\alpha$, that include lamellae, filaments, platelets, micelles, and polypotes.

Note that in Fig. 2, regions bonded by solid lines are resulting from actual calculations reported below, whereas regions bonded by dashed lines are qualitative expectation, as referred to earlier.

3.2 Amorphous and structured assembly

Fig. 3 summarizes the results of the present study, via the metrics illustrated in Section 2.3, in the aforementioned relevant range of the $T^* - \alpha$ plane. We observe a temperature dependence of the internal structure of aggregates that can be measured via the radial distribution function $g(r)$ and distributions of bond-orientation order parameter, $q_6$. In general, evidence of structural motifs emerge for temperatures below a certain $T^*$ value. Where self assembled structures form for $\alpha < 1.1$ we refer to this structuring...
temperature as $T_c^\ast$. This value varies over $z$ due to structure specific variations.

A few solid lines have been drawn because they are convenient to identify some characteristic regions. The top (red) line, labelled with $T_B$, represents the Boyle temperature separating attraction-dominated regions (below the line) from a region where repulsion dominates (above the line).$^{25,26}$ When scaled to meet the $z = 2$ critical point, corresponding to the single bead square-well gas–liquid critical point, the (yellow) line $T_B$-scaled is obtained as a reasonable approximation to the gas–liquid critical points (in blue) as previously computed by the successive umbrella sampling (SUS) technique.$^{20}$ Around the point where self-assembled phases begin to appear on the phase diagrams this approximation breaks down, observable as the divergence of the blue and yellow lines. For $z < 1.1$, the gas–liquid critical temperature line (blue) seems to yield to the location of the onset of structured aggregates.

Black squares with coloured coronas also appear in Fig. 3. Above the Boyle temperature line $T_B$, the corresponding computed state points (with red coronas) are found to show no sign of assembly, as expected. For the other points, we divide them in two different classes: in the case of assemblies where the local environment around each particle is amorphous, $g(r)$ is consistent with a fluid phase; these state points will be denoted as amorphous and appear in Fig. 3 with yellow coronas. The alternative case corresponds to state points where peaks resolve in $g(r)$ and strong peaks also develop in bond-wise distributions of $q_6$. These points will be denoted as structured and appear in Fig. 3 as black squares with green coronas. Notice that both amorphous and structured state points display a non-monotonic behaviour as a function of $z$ prompting that care must be exercised in their interpretation.

Let us first consider amorphous structures (yellow points). They appear both for $z < 1$ and $z > 1$. In the $z < 1$ case, it is evident that they roughly lay above a continuation of the projected gas–liquid critical temperature curve (the blue $T_c$ line in Fig. 3) indicating these state points to be of a gas phase that is eventually driven to a metastable condensed phase upon cooling, the occurrence of this phase being pre-empted by the onset of other, energetically favoured, self-assembled phases. In the $z > 1$ case, they also appear below the stable gas–liquid critical line, indicating these to be part of a stable liquid having a strong tendency to self-assembly, however.

Next we consider structured (green) state points, also appearing above and below $z = 1$. In the $z < 1$ case, these points are the counterparts of the previous case, as they lay below the projected gas–liquid critical temperature. As no stable liquid is present here, as remarked, we suggest these to be “crystalline” structures driven by a self-assembly process. In the $z > 1$ case, the interpretation is not quite as simple, as we shall see next.

3.3 Structures for $z > 1$

From Fig. 3 it is apparent that in the region $1.1 \leq z \leq 1.3$ there is a gas–liquid transition at $T^\ast \approx 0.4$ (whose detailed value depends on $z$) and an additional structural transition on cooling from $T^\ast \approx 0.3$ to $T^\ast \approx 0.2$ where the structures change from amorphous (yellow coronas) to structured (green coronas). This can be explicitly checked by our metrics.

Fig. 4 demonstrates long range order developing in $g_{ss}(r)$ on cooling $T^\ast: 0.3 \rightarrow 0.2$ across the region $1.05 \leq z \leq 1.3$. Some snapshots of typical structures obtained can be viewed in Fig. 5: bilayer structures observed at $T^\ast = 0.3$ (top two panels of Fig. 5), demonstrate a $g(r)$ similar to the liquid (compare the first panel of Fig. 4 with the $g(r)$ for liquid state reported in Fig. 9 of Paper$^1$). Conversely, corresponding state-points at $T^\ast = 0.2$ for the same $\rho^\ast$ (bottom panels of Fig. 5), show the development of a consistent long range order (second panel of Fig. 4).

Further insights can be obtained by identifying the local environment around the dominant bonding structure via bond-wise distributions of $q_6$ taken over the \textit{s} beads, as in Fig. 6. These distributions are selected from $z = 1.2, \rho^\ast = 0.3$ and various $T^\ast$. The left-most two panels ($T^\ast = 0.4$ and 0.3) correspond to bond distributions consistent with liquid structure around each particle, whereas the right-most two panels ($T^\ast = 0.2$ and 0.1), where the presence of a few local environments is signalled by the development of a strong peak in the distributions of $q_{6}$, indicate the onset of a dominant local environments with $N_o \in (13,16)$.

In the snapshots of the bottom two panels of Fig. 5, distributions corresponding to the “crystalline” local order are seen as the 16, 15, and 14 coordinate systems, which correspond to different environments on the curved bilayer. Where $N_o = 16$ the local environment is consistent with a flat section of the bilayer structure, and where $N_o < 16$, the particle resides on a portion of the bilayer with higher curvature.

Further interesting continuous structures are observed in this region (as indicated in Fig. 7), the left-most a “liquid-like” configuration from $z = 1.15$, and the right-most a “crystalline-like” configuration from $z = 1.2$. These high curvature structures can be interpreted via simple geometric arguments (see ESI†).
As anticipated in Fig. 2, a plethora of different morphologies are found where \( \alpha > 1 \), whose detailed properties strongly depend on the specific \( \alpha \) value. In order to facilitate the discussion, we will illustrate our findings below by grouping them by common characteristics rather than by specific values of \( \alpha \). A correspondence between morphologies and \( \alpha \) values can be read off from Fig. 2. While finite size effects were considered as a major factor in the systems that form structures that percolate across the simulation cell, we did not perform a thorough study of finite size effects here. We expect that finite size effects—which are discussed at length in Paper 1—don’t allow us to pin the exact values for the percolation loci, in fact the study here was kept to the relatively low density results in order to observe low density aggregation and how the small scale structures might build to larger structures. In our opinion there is scope for a large scale stand-alone finite-size effects study, especially for regions where the fractal dimension is either low dimensional (filaments) or perhaps non-integer (networks and sponges).

### 3.4 Structures for \( \alpha < 1 \)

As anticipated in Fig. 2, a plethora of different morphologies are found where \( \alpha < 1 \), whose detailed properties strongly depend on the specific \( \alpha \) value. In order to facilitate the discussion, we will illustrate our findings below by grouping them by common characteristics rather than by specific values of \( \alpha \). A correspondence between morphologies and \( \alpha \) values can be read off from Fig. 2. While finite size effects were considered

![Fig. 5](image5.png)

**Fig. 5** Snapshots of bilayer structures obtained for \( \rho^* = 0.3 \) and different values of \( \alpha \) and \(-T^*\). Top panels: \( \alpha = 1.1, T^* = 0.3 \) (left) and \( \alpha = 1.2, T^* = 0.3 \) (right); bottom panels: \( \alpha = 1.1, T^* = 0.2 \) (left) and \( \alpha = 1.2, T^* = 0.2 \) (right).

![Fig. 7](image7.png)

**Fig. 7** Orthographic snapshots of continuous phases obtained at liquid densities at \( \alpha = 1.15 \) (left) \( \alpha = 1.2 \) (right). 2nd nearest images are included for clarity with simulation box overlay. The right panel takes edge on in the 110 plane; due to the orthographic camera the tubes through the structure appear linear, but are in fact curved.

![Fig. 8](image8.png)

**Fig. 8** Radial distribution functions for \( \alpha = 2/3 \), reporting the formation of finite structures as a function of the temperature (indicated in the legend): at low \( T^* \), platelet develop as indicated by the peaks that resolve for \( sso \) or \( sorr \). Also developing here are peaks corresponding to the h beads on neighbouring particles pushing against one another (third panel), and also neighbouring s beads (last panel).
observed, with a progressive development of additional peaks at larger \( r/\sigma \) that are indicators of the onset of long-range spatial ordering. Fig. 9 displays snapshots of representative configurations corresponding to \( T^* = 0.3 \) (left) and \( T^* = 0.1 \) (right), where a gradual transition from a less structured, amorphous to a highly structured, crystalline-like configuration, is clearly visible. It is worth emphasizing that this region is studied fairly extensively in experiments, in terms of asymmetry between the \( h \) (representing the solvophobic moiety) and the \( s \) (representing the solvophilic). However certain differences in the modelled potential and the scales at which the experiments are carried out limit direct comparison, in particular in terms of the range of interactions that is of the order of 10% of \( \sigma \) in experiments, as compared with the values of 50% used here. A similar issue is also present in Janus fluids, and it is due to the numerical difficulties associated with a very short range attraction (and hence very low temperatures), albeit some special techniques have been implemented to cope with this problem.

It has been observed elsewhere that equal diameter spheres \( (x = 1) \) yield only lamellar structures at moderate and higher \( \rho^* \), whereas at lower densities micelles and platelets form due to systems residing below the percolation locus. Moving away from this limit we observe a progression of the structural variation that proceeds by limiting the spacial extent of bilayer structures. Where \( x \approx 1 \) bilayers adopt continuous two-dimensional lamellar topologies, whereas at the other end of this progression \( (x = 2/3) \) structures are topologically compact. On decreasing \( x \) between these points the \( h \) beads of each contiguous co-planar particles eventually enforce a limit on the spacial extent of a cluster in at least one dimension. This behaviour has effects on the structure of aggregates, such as to restrict packing in one to three dimensions, depending on the particular \( x \) (see the ESI† for more details). In a similar fashion to the \( x > 1 \) cases (with the appearance of “structured” patterns) in this case we document the onset of platelets and micelles, demonstrated by peaks resolving in \( g_{oo}(r) \). At the end of the progression mentioned above, where \( x \approx 2/3 \), we observe that \( g(r) \) develops peaks consistent with the formation of finite structures (see the large dip in all \( g_{oo}(r) \) at \( r \approx 2.5 \) for all \( T^* \), in the second panel of Fig. 8). These features are also visible in the relative snapshots of micelles and platelets at \( x = 2/3 \) from above and below the structuring transition depicted in Fig. 9.

3.4.2 Onset of fractal aggregates for \( 1/2 \leq x < 1 \). In the region \( 2/3 < x < 1 \), the progression from continuous bilayer structures to finite micelles and platelets is preceded by two different major regions of aggregate formation, due to densification and packing constraints (see ESI†). To explore the effects on the structure of aggregates we make use of the gyration radius \( R_g \), defined in eqn (6).

Additional insights can be obtained from the calculation of the fractal dimension \( D_f \) of the aggregates, as discussed in Section 2.3.

From this formulation we presume that linear clusters will have a \( D_f \approx 1 \), lamellar structures will have \( D_f \approx 2 \), approximately spherical clusters and networks will have a \( D_f \approx 3 \), presumably (but not necessarily) with different fractal pre-factor \( k_f \). If \( D_f \) takes integer values the system is characterized by a relatively simple geometry; on the other hand, if \( D_f \) attains non-integer values, the geometry is more difficult to rationalise. Cases of \( D_f \) close to integer values imply that the proximal dimension dominates. This means that a system composed of one-dimensional filaments that have some curvature in the long axis will have fractional \( D_f \). If that curvature lies in one additional dimension, \( D_f \) lies in \((1,2]\), if it lies in two additional dimensions, the cluster system will have \( 2 < D_f < 3 \). A system that possesses some 2D structure that bends will have \( 2 < D_f < 3 \).

Fig. 10 compiles histograms of \( R_g \) indexed by \( N_s \) collected over all structures observed in every simulation for all \( x \in (0.5,1.0) \). Structures that have percolated across the cell are omitted from the diagram as these may have \( D_f \) that are not representative of the primitive cluster. Clusters can have an \( R_g > L_{box}/2 \) and still not have “percolated”, in the sense that the cluster connects to its next periodic image, so as an added precaution structures with \( R_g \gg L_{box}/2 \) are also omitted. This does introduce the limitation that legitimately compact 1D structures that align along the space diagonal of the simulation.
Analysing Fig. 10 we see that structures between 2/3 ≤ α ≤ 1 cross several regions with differing $D_l$. At small cluster sizes ($N_b < 20$) aggregates have $D_l \approx 3$ regardless the specific value of $r$. As aggregates grow larger ($N_b > 20$), $D_l$ depends strongly on $r$. For 0.65 ≤ $r$ ≤ 0.775 most aggregates have $D_l \approx 1$, consistently with elongation in a single dimension, and we will refer to these structures as elongated micelles and filaments (see the Section 3.4.4). For 0.775 ≤ $r$ ≤ 0.90 most aggregates are formed by merging curved filaments into branching networks (for $r < 0.85$), or by merging platelets into sponge-like structures (for $r \geq 0.85$). For $r \to 1$ all aggregates have $D_l \approx 2$, consistent with platelets and lamellar structures. All these different regions are schematically summarized in the phase diagram of Fig. 2 and further detailed below.

3.4.3 Branching networks and sponge-like structures for 0.85 < $r$ < 0.95. Network structure and sponge-like structures can be distinguished by the lengths of component pieces. While the characteristic substructures in each type are determined by the interplay of packing and potential effects, network structures have smaller minimum diameter, which we describe as merged filaments, whereas a sponges appear as merged platelets. Snapshots demonstrating the substructures in the branching network and the sponge can be viewed in Fig. 11.

3.4.4 Filaments and networks for 0.75 < $r$ < 0.85. While one-dimensional aggregates are found across 0.7 < $r$ < 0.9, they are most readily identifiable where $r \approx 3/4$ (due to packing effects, see the ESI†). Their formation below $T^*_s$ can be inferred by looking at the behaviour of $g(r)$ reported in Fig. 12: we observe that long-range filament order develops on cooling, as signalled by the resolution of peaks at $r = w_{\text{filament}}$, where $w_{\text{filament}}$ corresponds to the filament width. Snapshots of full isotherms of the fluid and self-assembled phases can be viewed in Fig. 13. The increase in filament formation upon increasing the density is accompanied by a consistent bond-orientation signature in $q_6$ (Fig. 14), corresponding to a progression from platelet-dominated state points, with $\rho^* \leq 0.15$, to filament dominated state-points, with $\rho^* \geq 0.15$. Interestingly, the appearance of similar structures has been documented also in patchy models with patch coverage fraction slightly less than the Janus case.44 Differences between micelles, platelets and filaments in the distributions of $N_b$ can be viewed in Fig. 15.

The increase of the number of stripes, made by close-packed (cp) particles with $N_b \geq 14$, 13, 12, 10, 8, indicates that particles can pack finitely due to the steric effect of the h bead, but can stack together (on a diagonal) infinitely in one dimension, engaging in bonding between $i$ and $i + 1$ successive stacking layers (consistently with the bond-limited (bl) case in packing model in the ESI†). On the other hand, a decrease in $N_b$ corresponds to a particle location further from the centroid of the aggregate. Distances between filament bonding environments can be viewed by the location of the cp ↔ bl distances at $r \gtrsim \sigma_b$ and $r \lesssim \gamma$ for nearest neighbours.

For $r \in (0.775, 0.85)$, the additional volume of the potential available for bonding allows filaments to tolerate twisting and more curvature (see the ESI†). Structures at moderate densities in this region have $D_l \approx 1$, however depending upon the extent of twisting and filament curvature, separate nucleation sites can merge to form branched structures with $D_l \in (1, 3)$. Percolating branching filament structures are referred to as networks, and are found across this region at the higher $\rho^*$ studied. An example

![Fig. 11 Snapshots of configurations with a branching network at $\rho^* = 0.15$ and $T^* < T^*_s$ (top) and a sponge structure at $\rho^* = 0.875$ (bottom) for the same $\rho^*$.](image-url)
of twisted filaments, a branching filament and a network configuration obtained for \( \kappa = 0.825 \) can be seen in Fig. 16.

### 3.4.5 Platelet formation for 0.65 < \( \kappa \) < 0.75

Platelets form across values of \( \kappa \in (0.5,1) \), although are mostly common in the range 0.65 < \( \kappa \) < 0.75. For \( \kappa = 1/2 \), platelets that engage in bl=cp bond length splitting internal structure are both finite and highly ordered. As \( \kappa \) increases, the restrictions on the bonding behaviour, imposed by the presence of the h bead, are reduced; as a consequence, platelets tend to be characterised by larger values of characteristic length and gyration radius, assuming a more fluid internal structure. For \( \kappa > 0.85 \) the relaxation of the packing restrictions allow platelets to merge via edge defects, giving rise to sponge like structures; for \( \kappa > 0.95 \) percolated platelets are turned into lamellar structures, observed for progressively lower densities upon increasing \( \kappa \). Examples of platelet structures are found in Fig. 17.

### 3.4.6 Polytopes and micelles for 0 < \( \kappa \) < 1/2

Ordered structures observed for \( \kappa < 1/2 \) can be classified into several broad categories based on the structure of s bead bonds: simple polytopes, face-capped polytopes and roughly spherical micelles. Here ‘polytope’ refers to any regular or irregular polyhedron, including prisms and antiprisms, and face-capped refers to the coordination of another particle to any facet of these polyhedra comprised of at least three cyclic s bead bonds. From \( \kappa \approx 0.056624 \), below which only pairs may form, the location of maximally bonded structures—where all particles make bonds with all others in the cluster—can be predicted based on simple geometric considerations, see Table 1. Relaxing the condition of maximal bonding allows a larger number of HJDs to delete bonds with some particles and maximise others. Table 2 collects \( \kappa \) limits on structures comprised of simple anti-prisms. Of course, other exotic geometries are expected to occur where \( \kappa \) is larger than the...
corresponding limit, allowing a sufficient volume of micro-states available to that structure to be thermodynamically stable. This is demonstrated via the fact that, while the limit for a pentagonal anti-prism, which allows another particle to face-cap one of the constituent pentagonal faces where $\alpha < 0.25$, the structure is not obtained (Fig. 18) in simulations until $\alpha \approx 1/3$ (Fig. 19). This indicates that while structures may be thermodynamically stable at low $\rho^*$, they may not be mechanically stable upon compression, where additional packing effects will play a significant role. For short range potentials a structure that can maximise the total number of contacts between particles in the cluster might be favoured and, away from the regular polytope limits, structures that can distort to achieve this maximum are more likely to dominate. This behaviour presents the problem of many possible nearby minima in the potential energy surface of a cluster.

**Table 1** Summary of small polytope structure limits imposed by the presence of the h bead. The values of $\alpha$ for which these structures are possible are reported. Only maximally bonded structures are considered. Face-capping of distorted structures where $\alpha$ is larger than the corresponding limit is expected.

<table>
<thead>
<tr>
<th>$N_s$</th>
<th>Geometry</th>
<th>$\alpha$</th>
<th>$N_{\text{bonds}}$</th>
<th>$N_{\text{bonds/}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>$\frac{1}{\sqrt{3}} \cdot \frac{1}{\frac{1}{1+\alpha}}$</td>
<td>$&lt; 0.056624$</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Equilateral triangle</td>
<td>$\frac{1}{\sqrt{3}} \cdot \frac{1}{\frac{1}{1+\alpha}}$</td>
<td>$\approx 0.056624$</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedron</td>
<td>$\frac{\sqrt{3}}{8} \cdot \frac{1}{\frac{1}{\sqrt{3}+\frac{1}{1+\alpha}}}$</td>
<td>$\approx 0.079216$</td>
<td>6</td>
</tr>
<tr>
<td>4, 5, 6</td>
<td>Square, Sq. base pyramid, octahedron</td>
<td>$\frac{1}{\sqrt{2\lambda + \sqrt{2} + 1}}$</td>
<td>$\approx 0.132705$</td>
<td>6, 10, 15</td>
</tr>
</tbody>
</table>

**Table 2** Summary of anti-prism structure limits. The values of $\alpha$ for which these structures are possible are reported. Face-capping of the open sites is likewise expected for these structures. Numbers greater than five in each layer are better described as platelets.

<table>
<thead>
<tr>
<th>$N_s$</th>
<th>Geometry</th>
<th>$\alpha$</th>
<th>$N_{\text{bonds}}$</th>
<th>$N_{\text{bonds/}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Triangle</td>
<td>$\approx 0.132704$</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>8 (9, 10)</td>
<td>Square (facecapped × 2)</td>
<td>$\approx 0.186081$</td>
<td>16(24)</td>
<td>4(5,4)</td>
</tr>
<tr>
<td>10 (11, 12)</td>
<td>Pentagon (facecapped × 2)</td>
<td>$\approx 0.234122$</td>
<td>20(30)</td>
<td>4(5)</td>
</tr>
</tbody>
</table>

**Fig. 17** Platelet structures obtained across $\alpha$ indicated underneath each platelet. In general platelets diameters increase with $\alpha$.  

**Fig. 18** Variation in structures for $\alpha = 1/4$, with $N_s \in 4, 5, 6, 7, 8, 9$ (from left to right). The most common structures for the lowest $T^* (=0.1)$, are distorted octahedron, distorted square anti-prism, and a 7-member structure. The largest aggregate is a monoface-capped distorted square antiprism (right-most).

**Fig. 19** Variation in structures for $\alpha = 1/3$, with $N_s \in 6, 7, 8, 9, 10, 11, 12$ (from left to right). The most common structure for the lowest $T^* (=0.1)$ is a face-capped square antiprism. The largest structure is an axially compressed icosahedron (right-most).
undergoing reorganisation, and it is likely to be a source of kinetic trapping in experiments of Janus particles at the larger scales (≈ μm) where assembly is driven by size exclusion effects via depletion.

4 Comparison with other simulation and experimental studies

The current findings bear comparison to similar systems which have attracted some attention recently.

4.1 Simulation studies

Whitelam et al.23 explore an essentially similar model (of peanuts) by a method that approximates the dynamical evolution of assembly via a Monte Carlo process. The authors provide a kinetic phase diagram, exploring the effect of size ratio and site separation. The most relevant difference between their model and the one adopted in the present study is the use of a continuous attractive interaction (unlike the discrete potential and the one adopted in the present study is the use of a kinetic phase diagram, exploring the effect of size ratio and site separation. The most relevant difference between their model and the one adopted in the present study is the use of a continuous attractive interaction (unlike the discrete potential employed here). Despite differences in model and approach, several key features are found to agree with the present work. For thermodynamic states categorised by site separation δ(R₁ + R₀) = (σ₁ + σ₀)/2, attraction strength ε ∝ T⁻¹ and size ratio range 0.2 ≤ R₀/R₁ ≤ 2 (where R₁ and R₀ correspond to the radii of the solvophilic and solvophobic particles, respectively, whence 0.5 ≤ z ≤ 1.8) broad agreement about the low density micellisation is found. Micelle polydispersity is observed to vary with lobe size ratio, even if different structural properties are observed: for instance, cluster size distributions calculated by Whitelam et al. are distinctly smaller than those obtained in the present work. Broadly, they observe crystalline clusters and faceted polyhedra, in addition to micelles and bilayers; it may be worth noting that for the first two identified structures the site separation is too small to warrant a valid comparison with the present work, and a better point of reference is the work of Avvisati et al.28 Nonetheless, the formation of similar phases for site separations equivalent to ours is an encouraging result. The authors also note that a longer square-well attraction, that they used for exploratory simulations, allowed the formation of structures not realised by adopting the relatively short range interactions presented in the paper and that it is likely that smaller particles may therefore have structures available to them that their larger counterparts do not. We agree with this intuition, and recommend any experimental work that wishes to test these predictions do so with as small a particle as possible—in Whitelam et al. they suggest a particle size of around σ ≈ 5 nm, however it is likely that double that might be sufficient. We also note that functionalising a dumbbell-shaped particle to be amphiphilic at that scale may prove difficult, though some promising results from AuPS (gold–polystyrene) nano-scale particles may pave the way to probe these length scales (admittedly with inverted hydrophilicity for comparison to z < 1), however proper choice of solvent conditions can mitigate this.4

Other theoretical studies of similar systems, including “Mickey-Mouse” particles (constituted by trimers with two h lobes per s) and patchy dumbbells can be found, respectively, in ref. 21 and 28. In the trimer case they identify essentially similar behaviour with respect to the variation in critical parameters on increasing the particle shape anisotropy (the h–s lobe distance), as described in our previous Paper I.20 In ref. 28, the authors explore the effect of site separation, parametrized as l = 2d(σ₁ + σ₀), in the range 0.07 ≤ l ≤ 0.5 (at maximum, half of ours [l = (σ₁ + σ₀)/2]), and lobe size ratios q = σ₀/σ₁ = 0.95, 1.035, 1.25, equivalent to our z = 1.05, ≈ 0.966, 0.8. Due to the incorporation of non-tangent bead separations, the Kern–Frenkel model45 is employed to restrict the potential evaluation to only those interactions that do not directly pass through the h bead. For the tangent configuration, an extremum of the parameter space included in the model but not explored in their study, accounting for the mutual orientation component is unnecessary due to the geometry of the particle. State diagrams are presented in the volume fraction (φ) and sphere separation for the three diameter ratios explored. In particular, for q = 1.035 (z ≈ 0.966) they increase the site separation from a system that resembles the Janus sphere (l ≤ 0.05 with patch coverage ζ ≈ 0.4) up to a more conventional dumbbell shape (l ≈ 0.5, z ≈ 0.5). In the limit of large sphere separation, for this q value, their model provides lamellar structures agreeing in trend with the extension to tangent systems; however, upon reducing the internuclear separation, they observe compact aggregates with high curvature, such as vesicles (l ≈ 0.2) and micelles of elongated and spherical shape. For q = 1.25 (related to our point z = 0.8), the observation of elongated micelles for all l ≥ 0.3, except for high volume fractions (where bilayer structures are found) seems to agree, at least in principle, with the formation of filament like structures. The authors present neither diagrams of structures, nor structural properties of these elongated micelles, and hence a more rigorous comparison can hardly be performed. We also note that the attraction strength used in their study (T* ≈ 0.28) is slightly higher than the corresponding T*₂₅ (≤ 0.25) for this particular size ratio; this implies that the highly structured filaments may have just been missed, although we acknowledge that the packing behaviour is slightly different do to the intra-particle s–h inter-nuclear distance (see ESIF).

Finally, Hatch et al.22 study a model system of trimer colloids models by means of AVBMC technique and Configurational Bias Monte Carlo simulations to explore a set of models upon varying lobe diameters and distribution lobe angles. We note that, despite the differences in models, similar structural behaviours are found for certain combinations of their parameters, including filament structures, micelles, and vesicles. The occurrence of similar structures and behaviours in models resembling the one investigated in the present study suggests the existence of some overarching rules concerning the nature of self-assembled phases for these simple colloids.

As a further interesting consideration, dynamical studies of soft Janus dimers in the bulk30 or confined between plates46 document the presence of density driven clustering behaviour and diffusion anomaly, this resembling some water-like properties. Confined in cylindrical pores,27 a related model of Janus dumbbells
studied via Langevin dynamics demonstrates formation into micelles with dispersity controlled by density, and the formation of lamellar structures and elongated micelles. The potential employed in their work makes comparison difficult, especially given the depiction of the repulsive lobe in the family of models they explore.

4.2 Experimental studies
Kraft et al. experimentally investigate a system of rough-surface lobe Janus particles at the sub-μm scale, with particle geometry and lobe amphiphilicity similar to those considered in the present work. In their study the amphiphilicity is induced asymmetrically via surface roughness, with the interaction strength controlled by depletant concentration. Such a prescription implies that the interaction range is on the order of $R_g$ of the polymeric depletant and thus, for lobe diameters of roughly 0.1 μm, $\gamma \lesssim 0.05\pi$, hence yielding an interaction range corresponding to approximately 10% of the one considered here. The structures obtained in their experiments are subject to different potential constraints, yet close packing behaviour should be unaffected, provided that the s–h lobe interaction is sufficiently passivated. Indeed for the system equivalent in size and number of bonds does not exceed an average value of just $N_s$ per particle of cluster sizes up to 15 (see Fig. 2 panel C of the work at issue), a possible mechanism for this re-organisation to relax to equilibrium structures on increasing $t$. We also note that, given the observed tendency of the h beads to break down here. We agree with this analysis and add that, as above, it is likely that a kinetic trapping mechanism prevents local cluster re-organisation to relax to equilibrium structures on increasing attraction strength. The authors note that upon sufficiently large densities of depletant the interaction asymmetry is reduced, so we expect packing constraints based around the maintenance of only the s–s bonds also to break down here. We also note that, given the observed tendency of the h beads in our simulations to push against the neighbouring s beads (see Fig. 4, 8, and Paper F), a possible mechanism for this kinetic trapping is due to the lack of microstates available to the system to re-organise under pressure. Such a phenomenon appears related to the bond nature, and hence a softer or longer interaction range might be necessary to overcome these kinetic products for particles with this geometry.

Patchy dumbbell-shaped colloids consisting of a smaller sticky and a larger non-sticky lobe has been studied via essentially the same experimental technique in a recent study. By tuning the depletant concentration, the authors found a transition from micelles to random aggregates.

5 Conclusions
In this study, we have used Aggregation-Volume-Bias Monte Carlo (AVBMC) and Simulated Annealing (SA) techniques to study the self-assembly properties of a system of Janus dumbbells modelled as two tangent asymmetric spheres having different sizes and interaction properties. While the h sphere bears only steric interaction, the s sphere has an additional attractive square-well tail with width equal to 50% of the s sphere diameter. The size ratio of the two spheres has been taken into account by introducing a parameter $z$. We show that this simple model of Janus dumbbells demonstrates a very wide array of emergent aggregation behaviour controlled by the lobe diameter $z$.

The present work complements previous work by us by analysing the regime where the size of the h sphere is larger than the size of the s sphere ($z < 1$). Under these conditions, the attractive portion of the dumbbells are not sufficiently extended to drive a gas–liquid transition, and the aggregation properties are dominated by self-assembly.

By a careful analysis of the phase diagram in the temperature–$z$ plane, we find a rich polymorphism as summarized in Fig. 2 and detailed in Section 3. Different structures were identified by a combination of metrics including the radial distribution functions $g(r)$, the radius of gyration $R_g$, the fractal dimension $D_\phi$, the bond-orientation order parameter $q_o$, and the cluster size distribution $P(N_c)$.

The present work highlights four main findings. Firstly, it confirms the termination of the gas–liquid critical point due to liquid meta-stability to the formation of low-energy bilayer structures at $z \approx 1.1$, before the case of equal bead diameter. Secondly, we observe a variation in bilayer interfacial topology upon approaching the Janus limit ($z = 1$), from highly curved structures such as vesicles and tubes ($1.1 < z < 1.3$) eventually flattening out to lamellar structures ($z \to 1$). Thirdly, we document a progressive variation of structure dimensionality in percolating self assembled structures with diminishing sticky bead diameters via a combination of packing and potential effects. Finally, the formation of compact topologies where $z < 2/3$ is detected.

While we manage to match experimental conditions in terms of size asymmetry, our simulations have been carried out at a much greater interaction range than typical experiments, but in line with other similar studies (see Section 4). Although this limits the possibility of a direct comparison with experiments, we believe that the results presented here, complemented by those reported in our previous paper, represent the first detailed study of the structural and thermodynamic behaviour of the Janus dumbbells in the entire asymmetry range. We highlight the conditions that may enable our predictions to be tested (Section 4) and we believe the methods employed here may be useful for the exploration of other anisotropic nanoparticle systems.
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We would like to thank the Sydney Informatics Hub at the University of Sydney for providing access to HPC facility Artemis.

References