

COMMUNICATION

Empty liquid state and self-assembly of high valence non-spherical colloidal systems

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A vapour–liquid phase coexistence with vanishing critical volume fraction (empty liquid) is predicted in some model systems of attractive hard ellipsoids. The trends in critical density and temperature do not depend on the ellipsoid shape and the range of the square-well attraction. Our theoretical and simulation studies show transparently that the empty liquid limit is due to the competition between the anisotropic attractive and repulsive interactions. Additionally, the nematic phase is destabilized by the square-well attraction for both prolate and oblate shapes. The demand to maximize the number of bonds while keeping a relatively low excluded volume leads to special structures such as the cubatic and star-shaped cluster phases at low temperatures. The liquid branch of the vapour–liquid binodal is always isotropic for oblates, while it can be isotropic or cluster-like for prolates. Our results predict the occurrence of an empty liquid state in high valence anisotropic colloidal systems.

Recent advances made in the synthesis of colloidal particles with a controlled anisotropic shape, pattern and functionality have provided a great opportunity to study the role played by tunable anisotropic interactions in the self-assembly and phase transition properties of colloidal model systems.^{1–4} Among these, the ability to control the surface coverage of the particles by regions (patchy interactions) has opened a new avenue for the preparation of materials with desired properties. For instance, in model patchy hard spheres the reduction of the number of bond-sites has led to the prediction of the empty liquid (a liquid with vanishing density) and an equilibrium gel phase.⁵ On the other hand, recent long term experiments carried out on plate-like colloidal particles such as laponites and montmorillonites proved the existence of both empty liquids and equilibrium gels.^{6–8}

In the case of low valence patchy spheres, the low number of patches of the particles leads to low density liquids because the potential energy reaches its minimum with only a few neighbours. Hence, the vapour–liquid (VL) binodal shrinks and the critical volume fraction moves toward zero with a reducing number of patches.⁵ In the case of either rod-like or disk-like colloidal particles the situation is more diverse because there are several ways to dress up the reference hard bodies with attractive interaction sites. The aqueous suspension of laponite clays, where the particles' surfaces are negatively (positively) charged on the face (rim), was the first experimental system showing an empty liquid phase.⁶ This system belongs to the low valence kind, as the number of bonds between the particles is restricted by the preferred rim-to-face to the face-to-face and rim-to-rim configurations. When enclosing the anisotropic hard bodies with a homogeneous square-well (SW), a very subtle competition arises between the bond maximizing (energy minimizing) and the excluded volume minimizing (packing entropy maximizing) interactions. This type of pair potential can be a good approximation for colloidal (including some proteins⁹ and viruses¹⁰) systems where the potential range is short compared to the particle size.

In this communication we show that homogeneous short-range attractions can destabilize the formation of a nematic phase for either very long rod-like or flat disk-like shapes, *i.e.* the sufficiently anisotropic and rigid particle shape does not guarantee the self-assembly into a nematic phase, but the particles aggregate into star-shaped (or urchin-shaped) clusters for prolates and into orthogonally stacked columns (cubatic order) for oblate shapes. Curiously, the star-shaped and cubatic phases are preempted by an isotropic fluid phase for a sufficiently large volume fraction in a narrow temperature window, so that a nematic–isotropic–star-shaped/cubatic reentrance sequence is observed. The critical density of the VL phase coexistence curves moves into the direction of low densities with increasing shape anisotropy but the binodal curve becomes very wide.

We consider the system of hard uniaxial ellipsoids with dimensions $\sigma_{\parallel}$ and $\sigma_{\perp}$ along and perpendicular to the axis of

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revolution (with aspect ratio $k \equiv \sigma_{\perp}/\sigma_{\parallel}$). The particles are dressed up with a short-range SW attraction of variable range (λ) and constant depth (ε), which follows the shape of the hard body. The pair-wise interaction potential (u) is defined as

$$u = \begin{cases} \infty, & \text{for } r \leq \sigma, \\ -\varepsilon, & \text{for } \sigma < r \leq \sigma + \lambda, \\ 0, & \text{for } r > \sigma + \lambda, \end{cases}$$

where r is the distance between the centres of the particles, and σ is the distance of the closest approach between the ellipsoids. We set λ in the interval 0.25–1.0, in units of $\sigma_{\min} = \min(\sigma_{\parallel}, \sigma_{\perp})$. The attraction is not restricted to special orientations, *i.e.* there is no bond-selectivity in this SW hard ellipsoid (SWHE) model. Note that our interaction model is very different from the generalized Lennard-Jones models of mesogenic systems,¹¹ where the side-by-side arrangement between the particles is favoured.

We use replica exchange Monte Carlo (REMC) simulations^{12,13} for both, obtaining VL coexistence properties and determining the temperature–density boundaries of the different mesophases. The replica exchange method helps to overcome free energy barriers by performing swap moves between adjacent replicas, which is useful in the vicinity of phase transitions. For accessing the VL coexistence we define $Q_{\text{ext}} = \prod_{i=1}^{n_r} Q_{NVT_i^*}$, where $T_i^* = k_B T_i / \varepsilon$ is the reduced temperature of ensemble i , V is the cell volume, $N = 800$ particles, and $n_r = 14$ replicas. The replicas are parallelepiped boxes containing a liquid slab at the centre, vapour at each side, and two interfaces.¹⁴ Details on this type of simulation are given in a previous work.¹⁵ For determining the temperature–density boundaries of the different fluid phases, we define $Q_{\text{ext}} = \prod_{i=1}^{n_r} Q_{NP_i T^*}$, where P_i is the pressure of the ensemble i .¹⁶ In these cases we are setting small system sizes, $N = 220$, while considering $n_r = 16$ cubic cells. Details on this implementation are given elsewhere.¹⁷

The critical temperature (T_c^*) and critical volume fraction (φ_c) of the VL phase coexistence for SWHEs with different λ values are presented in Fig. 1. Panel (a) shows that T_c^* monotonically decreases with the shape anisotropy for both prolates ($k < 1$) and oblates ($k > 1$). Moreover, the curves show the same trends for all λ , where the shift between the curves is due to the increasing strength of the cohesive energies. These results are in agreement with the well-known $T_c^*(\lambda)$ dependence for SW hard sphere (SWHS) fluids,¹⁸ which is indeed observed in Fig. 1(a) for $k = 1$. The decreasing trend remains for a constant λ and increasing anisotropy, since the hard body interactions become more dominant with respect to the attractive ones. φ_c shows a more interesting behaviour with k (see Fig. 1(b)). For $k \approx 1$, it increases with the anisotropy (for oblates and prolates), while it decreases monotonically for $k \ll 1$ and $k \gg 1$. As a result, two peaks appear in each curve in such a way that their position depends on λ .

The non-monotonic behaviour of φ_c can be understood from a mapping procedure which is performed between the actual SWHE system and an effective SWHS system having a σ_{HS} diameter and a square-well range λ^* . The second virial coefficients of the SWHS and SWHE pair potentials are given by $B_2^{\text{SWHS}} = 1/2\{V_{\text{exc}}^{\text{HS}} + [1 - e^{\beta\varepsilon}](V_{\text{exc}}^{\text{SWHS}} - V_{\text{exc}}^{\text{HS}})\}$ and $B_2^{\text{SWHE}} = 1/2$

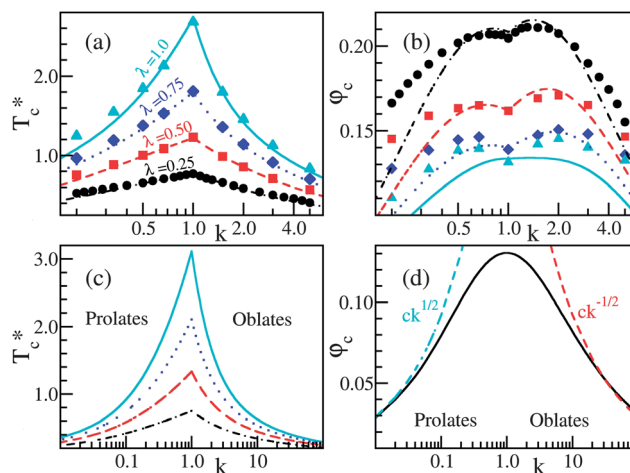


Fig. 1 Critical temperature (a) and critical volume fraction (b) as a function of aspect ratio for SWHEs of variable shape and potential range: MC data (symbols), mapping procedure (curves). The corresponding results of the vW theory are shown in (c) and (d). The dashed curves of (d) are the asymptotic formulas of the vW theory with $c = 2/\sqrt{15\pi}$.

$\{ \langle V_{\text{exc}}^{\text{HE}} \rangle + [1 - e^{\beta\varepsilon}](\langle V_{\text{exc}}^{\text{SWHE}} \rangle - \langle V_{\text{exc}}^{\text{HE}} \rangle) \}$, respectively. Here $\beta = 1/k_B T$, $V_{\text{exc}}^{\text{HS}} = 4\pi\sigma_{\text{HS}}^3/3$, $V_{\text{exc}}^{\text{SWHS}} = V_{\text{exc}}^{\text{HS}}(1 + \lambda^*)^3$, $\langle V_{\text{exc}}^{\text{HE}} \rangle$ is the average excluded volume of the ellipsoid, and $\langle V_{\text{exc}}^{\text{SWHE}} \rangle$ is the average excluded volume of the imaginary SWHE having a contact distance of $\sigma + \lambda$. $B_2^{\text{SWHE}} = B_2^{\text{SWHS}}$ is assumed to determine σ_{HS} and λ^* . From the given relationships one obtains $4\pi\sigma_{\text{HS}}^3/3 = \langle V_{\text{exc}}^{\text{HE}} \rangle$ and $(1 + \lambda^*)^3 = \langle V_{\text{exc}}^{\text{SWHE}} \rangle / \langle V_{\text{exc}}^{\text{HE}} \rangle$. The volume fractions of the effective HS and the actual HE bodies are given by $\varphi^{\text{SWHS}} = \rho\nu_{\text{HS}}$ and $\varphi = \rho\nu_{\text{HE}}$, where $\nu_{\text{HS}} = \pi\sigma_{\text{HS}}^3/6$, $\nu_{\text{HE}} = \pi\sigma_{\parallel}\sigma_{\perp}^2/6$, and ρ is the number density. Assuming ρ holds the same for both systems, then $\varphi = \varphi^{\text{SWHS}} 8\nu_{\text{HE}} / \langle V_{\text{exc}}^{\text{HE}} \rangle$. We apply this equation for the critical point. In this last expression $\langle V_{\text{exc}}^{\text{HE}} \rangle$ is determined numerically and we use a third order polynomial fitting with λ^* for φ_c^{SWHS} and T_c^{SWHS} from MC data of Largo *et al.*¹⁸ Finally, we also use $T_c^{\text{SWHE}} = T_c^{\text{SWHS}}$.

Panels (a) and (b) of Fig. 1 show that the mapping procedure quite accurately reproduces the MC results for both T_c^* and φ_c . In light of this agreement one can easily explain the observed critical behaviours. λ^* must decrease for both $k < 1$ and $k > 1$, because λ is kept constant and $\langle V_{\text{exc}}^{\text{SWHE}} \rangle / \langle V_{\text{exc}}^{\text{HE}} \rangle$ decreases. Hence the weakening contribution of the SW interaction with respect to hard excluded volume interactions manifest in T_c^* . Regarding φ_c , it should rise with weakening attractions as happens in SWHS fluids.¹⁸ The reason why this does not happen in SWHE systems is that the average excluded volume of the ellipsoid increases with the shape anisotropy and the particles are not forced to get closer to each other by the constant λ , *i.e.* there is more room around the ellipsoid particles. As a result of the competition between attractive and repulsive interactions, a maximum takes place in φ_c for all λ . We also employ a simple van der Waals (vW) perturbation theory,¹⁹ which uses the well-known Parsons–Lee decoupling approximation for the excluded volume interactions, while the contribution of the attractive interactions is treated on the level of a second virial approximation. In this theory the free energy per particle can be written

as $\beta F/N = \ln \rho - 1 + (4\phi - 3\phi^2)\langle V_{\text{exc}}^{\text{HE}} \rangle / [(1 - \phi)^2 8\nu_{\text{HE}}] + \rho(1 - e^{\beta\epsilon}) - (\langle V_{\text{exc}}^{\text{SWHE}} \rangle - \langle V_{\text{exc}}^{\text{HE}} \rangle)/2$. This simple perturbation theory is capable of reproducing the k dependence of T_c^* for any λ (Fig. 1(c)) while it fails to reproduce the peculiar behaviour of ϕ_c for weak shape anisotropies (Fig. 1(d)). Thorough examination of the theory using the critical conditions ($\delta^2 F/\delta V^2 = 0$ and $\delta^3 F/\delta V^3 = 0$) shows that ϕ_c does not depend on λ , but is only a function of the average excluded volume, *i.e.* $\phi_c^2(5 - \phi_c)/(1 - \phi_c)^5 = 4\nu_{\text{HE}}/3\langle V_{\text{exc}}^{\text{HE}} \rangle$. Our calculations show that $\langle V_{\text{exc}}^{\text{HE}} \rangle/\nu_{\text{HE}} = \pi k$ for $k \rightarrow \infty$ and $\langle V_{\text{exc}}^{\text{HE}} \rangle/\nu_{\text{HE}} = \pi/k$ for $k \rightarrow 0$, thus ϕ_c of very flat (long) ellipsoids does really vanish with k as follows: $\phi_c = c/\sqrt{k}$ ($\phi_c = c\sqrt{k}$), where $c = 2/\sqrt{15\pi}$ (see Fig. 1(d)). Even though the perturbation theory does not reproduce the simulation trends for weak shape anisotropies, it shows the right ϕ_c dependence for strong shape anisotropies. From these results we can conclude that an empty liquid can form in a system of very anisotropic prolate or oblate particles.

It may happen, however, that other transitions, such as isotropic–nematic, preempt vapour–liquid.¹⁹ For example, the system of very long hard rods undergoes an isotropic–nematic phase transition with a transition density dependence of $\phi \sim k$, which goes to zero faster than ϕ_c does.²⁰ This would give rise to a vapour–nematic phase equilibrium. Therefore it is necessary to examine the stability of other mesophases in our system. The isotropic–nematic bifurcation analysis of the extended vW theory¹⁵ shows that the attractive SW interaction does work efficiently against the nematic ordering to such an extent that the isotropic–nematic phase boundary does not interfere with the vapour–liquid coexistence, and it shifts in the direction of higher densities with decreasing temperature for any shape and λ . Our REMC simulations confirm this theoretical result.

Fig. 2 highlights the typical positional ($g(r)$) and orientational distribution functions ($\langle P_2(r) \rangle$ and $\langle P_4(r) \rangle$) (ref. 21) observed at high and low T^* . Three different structures can be identified for both oblates (Fig. 2(a)) and prolates (Fig. 2(b)). These structures are isotropic, nematic and cubatic, and isotropic, nematic and star-shaped, respectively. At high T^* the role of attraction is marginal with respect to the excluded volume interactions, *i.e.* $g(r)$, $\langle P_2(r) \rangle$ and $\langle P_4(r) \rangle$ show the typical features of the isotropic and nematic phases at low and large ϕ , respectively. This behaviour has been observed for hard ellipsoids.^{17,22} However, at low T^* and large ϕ , where the SW contribution becomes dominant, $g(r)$ peaks at face-to-face and rim-to-rim contact distances ($\sim \sigma_{\text{min}}$ and $5\sigma_{\text{min}}$), while $\langle P_2(r) \rangle \sim 0$ and $\langle P_4(r) \rangle$ is positive for all r , pointing toward a cubatic order for oblates. The prolates' case is more complicated since these correlation functions do not provide clear information on the possible particle aggregation at low T^* and large ϕ . From the behaviours of $g(r)$, $\langle P_2(r) \rangle$ and $\langle P_4(r) \rangle$ one can see that there are only short-range positional and orientational orderings. The observed star-shaped cluster structure manifests only in the damped oscillatory behaviour of $\langle P_2(r) \rangle$ and $\langle P_4(r) \rangle$.

Further information on the nature of the cubatic order and cluster formation is gained from the equation of state $Z(\phi)$, isothermal compressibility χ , internal energy $\langle u \rangle$, order parameters S_2 , S_4 , and a cluster size analysis (see Fig. 3). The flatness of Z , large density fluctuations, $S_2 \sim 0$ (nematic order

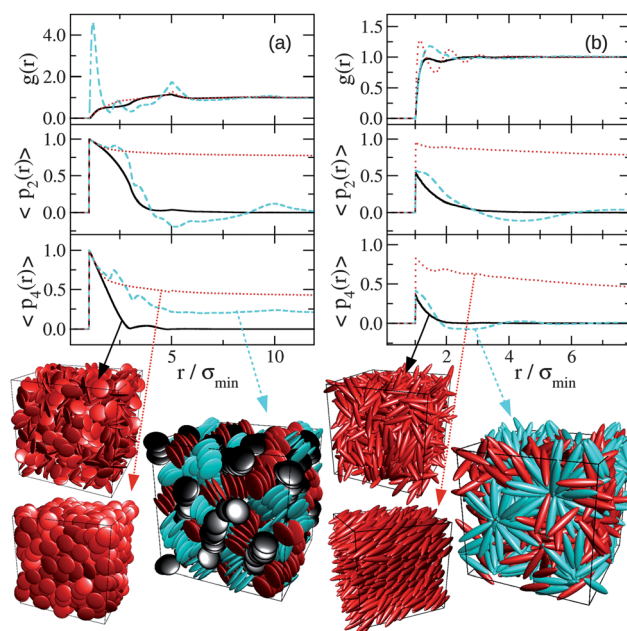


Fig. 2 Positional ($g(r)$) and orientational ($\langle P_2(r) \rangle$, $\langle P_4(r) \rangle$) radial distribution functions as a function of distance with $k = 5$ for oblates (a) and $k = 1/5$ for prolates (b), with $\lambda = 1.0$. Solely in this case, data are obtained from standard NPT* simulations with $N = 800$, and setting P and T^* well inside the stable region of the phases. The observed phases are: isotropic (solid line), nematic (dotted line) and cubatic/aggregate (dashed lines). Snapshots are connected by arrows with the corresponding curves.

parameter)²¹ and the sudden increase of S_4 (cubatic order parameter),²³ together imply that the oblate particles undergo a first order isotropic–cubatic phase transition at $\phi_{\text{IC}} \sim 0.47$. The monotonically increasing $\langle u \rangle$ (absolute value of potential energy per particle) indicates that the stabilization of the cubatic phase

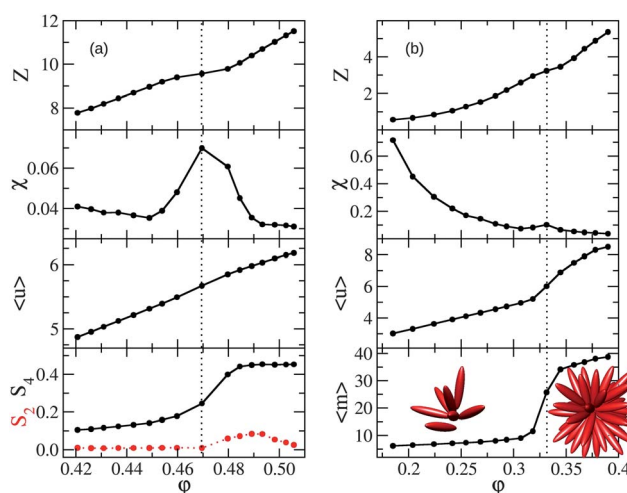


Fig. 3 Compressibility factor ($Z = \beta P/\rho$), isothermal compressibility ($\chi = (\langle \rho^2 \rangle - \langle \rho \rangle^2)/\langle \rho \rangle^2$), absolute value of potential energy per particle ($\langle u \rangle$), orientational order parameters (S_2 , S_4) and the average of the largest cluster-size ($\langle m \rangle$) for oblates (a) and prolates (b). Oblate parameters: $\lambda = 1$, $k = 5$, and $T^* = 1.1$. Prolate parameters: $\lambda = 1$, $k = 1/5$, and $T^* = 1.4$. The snapshots highlight the typical largest clusters found in small and large ϕ phases.

is due to the high valence nature of the attractive interactions, since bonds can take place in any orientation including face-to-face, rim-to-rim, and rim-to-face configurations. In the fluid of hard platelets with $k = 5$, an isotropic–columnar phase transition takes place, but a metastable cubatic order retards it.²⁴ A short-range attraction changes the situation, because the columnar order restricts the number of possible bonds (not including the manifold rim-to-face configurations). The cubatic phase still allows for a very efficient packing while making it possible to reach a large number of bonds. Regarding the prolate particles, the non-monotonic behaviour of Z and χ indicates a first order transition between two isotropic phases (Fig. 3(b)). The sudden increase of $\langle u \rangle$ and $\langle m \rangle$ shows that a cluster formation takes place at increasing ϕ . The average size of the largest cluster $\langle m \rangle$ is typically around 40 particles in the cluster phase, while it is close to 7 for the low density fluid (see the insets of Fig. 3). The cluster-size is defined by the number of ends of the ellipsoids not being further than $1.2\sigma_{\min}$ apart from the centre of the cluster. Due to the short-range nature of the attraction, not all particles of a cluster are bonded and there are many particles which are not part of any cluster (see the cluster phase snapshot in Fig. 2). This explains why the growth of $\langle u \rangle$ is not proportional to $\langle m \rangle$. Note that the star-shaped cluster phase spontaneously develops in our up-down symmetric potential model. To bring about aggregation it is customary to use dissimilar pair interaction models like the hard partial surface model of contact lens-like particles²⁵ and the partial coverage of Janus particles.²⁶ Decorating the prolates at their tips with a patchy attraction should further enhance a star-shaped cluster arrangement.

The simulation results for the phase diagram of the SWHE system are collected in Fig. 4. It is a common feature of oblates and prolates that the nematic phase is destabilized in favour of an isotropic phase at decreasing T^* . The stability region of the nematic phase moves into higher densities with increasing λ . These results can be attributed to the fact that the nematic order strongly decreases the possible number of bonds with respect to the isotropic fluid, *i.e.* the nematic ordering switches the system from high to low valence. Finally, both prolates and oblates show a second transition when T^* is further decreased. The prolate–oblate symmetry breaks here, due to the appearance of a cubatic ordering for oblates and a star-shaped aggregate phase for prolates. Nonetheless, both phases enhance the bond capabilities of the particles at the expense of decreasing the available free volume. Therefore the stabilization of these phases is the result of the victory of the cohesive energy over the packing entropy. Consequently, a nematic–isotropic–cubatic/cluster reentrance behaviour takes place with lowering T^* . The prolate–oblate symmetry breaking manifests with two other important differences. First, the high density cluster phase of prolates exists only for not very short λ values. Second, star shaped aggregates are stable over a wide ϕ range and they constitute the liquid side of the VL coexistence (see the snapshot in Fig. 4(b)). This contrasts with the VL coexistence of oblates whose liquid side is isotropic for all studied conditions (see the snapshot in Fig. 4(a)).

In brief, our results show that enclosing oblate (prolate) hard bodies with oblate-shaped (prolate-shaped) square-well

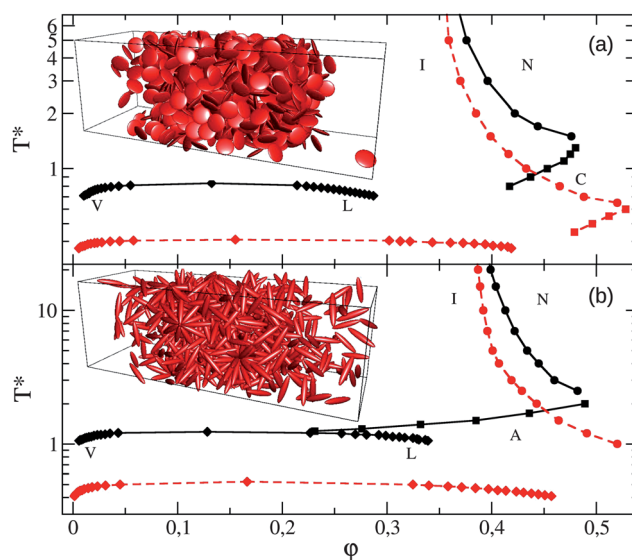


Fig. 4 Phase diagrams for $k = 5$ (a) and for $k = 1/5$ (b). SWHE system for $\lambda = 1$ (solid line) and 0.25 (dashed line). Labels V, L, I, N, C, and A denote vapour, liquid, isotropic, nematic, cubatic and aggregate phases, respectively. Snapshots of the VL phase coexistence at lowest (a) and highest (b) examined temperatures are depicted for $\lambda = 1$.

attractions has a dramatic effect on the phase behaviour of the system. On the one hand it gives rise to a rich phase behaviour at high densities where nematic, isotropic, cubatic and star-shaped cluster ordering appear. All these are the result of a delicate energy–entropy interplay. On the other hand, empty liquids may arise in the limits of large anisotropies for both oblates and prolates, which is a common feature of our high valence and the low valence patchy systems. However the gap of the VL binodals is very wide (see Fig. 4) and widens further with increasing shape anisotropy, while the patchy colloids show a shrinking biphasic gap. The consequence of this manifests in gel formation, which arises from the dynamical arrest during phase separation,²⁷ and is homogeneous and percolation driven (without crossing the binodal) in low valence systems.⁶

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