

PAPER

Towards understanding the empty liquid of colloidal platelets: vapour–liquid phase coexistence of square-well oblate ellipsoids

Cite this: *Soft Matter*, 2013, 9, 5277

E. Meneses-Juárez,^a S. Varga,^b P. Orea^a and G. Odriozola^{*a}

We study the phase behaviour of hard oblate ellipsoids with superimposed short-ranged oblate-shaped square-well attractions using the replica exchange Monte Carlo method and a simple van der Waals type perturbation theory. By fixing the square-well range ($\lambda = 0.25\sigma_{\parallel}$), we examine the effect of varying the oblates aspect ratio, $k = \sigma_{\perp}/\sigma_{\parallel}$, on the density profiles, vapour–liquid and isotropic–nematic phase transitions. We observe that the formation of a liquid phase with vanishing density, an empty liquid, is possible with increasing aspect ratio. Surprisingly, the increasing shape anisotropy does not shift the stability region of the nematic phase to low densities, while the oblate-shaped square-well attraction favours disordered states. For $k > 1.5$, the critical temperature and packing fraction monotonically decrease with k , while the isotropic–nematic phase boundary moves towards higher packing fractions with decreasing temperature for all k . Simulations show that oblates preferably orientate their faces parallel to the vapour–liquid interface when located at the liquid side of the interface region and perpendicular when located at the vapour side.

Received 24th January 2013

Accepted 5th April 2013

DOI: 10.1039/c3sm50264c

www.rsc.org/softmatter

1 Introduction

Recent studies of colloidal suspensions have revealed that anisotropic attractive and repulsive interactions may give rise to some unexpected phase behaviours. These may include the formation of equilibrium gel structures, glasses, liquid phases with vanishing density, and phase transitions at extremely low densities.^{1,2} For example, reducing the coordination number of spherical patchy colloids substantially increases the stability region of the liquid state causing the critical density to be extremely low.³ The empty liquid, which corresponds to a liquid phase with a vanishing density, has been experimentally observed in laponite colloidal suspensions.⁴ Laponites are charged, plate-like colloidal particles with a diameter of approx. 25 nm and a thickness of 1 nm. To model such a complex system, it is convenient to take into account the effects of competing anisotropic hard body exclusions and attractions. In the present study we make an attempt to examine the low density phase behaviour of a new model system, which shows some resemblance with the phase behaviour of colloidal platelets.

It is widely accepted that spherical colloidal particles can, under certain conditions, be modelled as hard spheres (HS) to reproduce the structural and thermodynamic properties of colloidal suspensions. To include other effects such as

electrostatic interactions, van der Waals attractions, and depletion forces, the HS model is usually extended by adding soft repulsive and attractive contributions.^{5,6} Along this line, the simplest model is the HS potential with a superimposed spherical square-well (SW) interaction, which produces either soft repulsion or attraction between the particles within a given range of distances. For non-spherical colloidal particles, such as plate-like laponites² and rod-like halloysites,⁷ a natural extension of the HS + SW model would be the hard ellipsoid (HE) with a SW interaction. However, the thermodynamic properties of systems composed of particles interacting through ellipsoidal pair potentials are much less known than those with spherical symmetry. For instance, the phase diagram of hard ellipsoids of revolution has been recently revisited,^{8–11} whereas the HS phase behaviour was established a long time ago.^{12–14} In addition to this, there are several ways of producing a HE + SW potential: by superposing a spherical SW to the ellipsoidal hard core^{15–19} and by superposing an ellipsoidal SW to the ellipsoidal hard core are among them. Singh *et al.* used this last approach by defining a SW with an angular-dependent depth range.²⁰ It is also possible to define a Janus SW ellipsoid by partial enclosure of the HE.²¹

One of the most studied anisotropic pair potentials is the one given by Gay and Berne.²² It is based on the Berne and Pechukas (BP) closest approach distance²³ and has the advantage of being flexible enough to represent several molecular geometries. Additionally, it has a reasonable number of parameters to set the molecular aspect ratio and the ratio of side-by-side (face-to-face) to end-to-end (edge-to-edge) well depths. Arguably, its downside is the fact that the interacting

^aPrograma de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 Mexico, D.F., Mexico. E-mail: godriozola@imp.mx

^bInstitute of Physics and Mechatronics, University of Pannonia, PO Box 158, Veszprém, H-8201, Hungary

entities lack a clear shape, area, and volume. This is due to the fact that the BP expression produces results close to the exact HE closest approach distance only for non-T-shape like configurations. In these cases it leads to large overestimations. In order to deal with true ellipsoidal potentials, only time consuming numerical algorithms are available for detecting overlaps between the ellipsoids.^{24,25} The numerical surface-surface distance can then be employed to define a Lennard-Jones kind of ellipsoidal potential, such as that of Kihara²⁶ or Paramonov and Yaliraki.²⁷ In turn, the need of a numerical solution may explain why potentials with an ellipsoidal symmetry are not very popular. There is, however, a good analytic approximation to the exact ellipsoid closest approach distance. This was introduced by Rickayzen as a modification of the well-known BP approach, with the aim of fixing the BP T-shape mismatch, while keeping the original results practically unchanged for all other configurations.²⁸ With this modification, the equation of state of HE can be reproduced very accurately even for very anisotropic shapes.²⁹

In this work we employ this last approach to model the oblate hard core interaction. In addition, we superimpose an oblate-shaped SW attraction of constant depth and range to produce associations. This last choice, in contrast to the spherical SW attraction, favours the formation of isotropic low density liquids,^{3,4,30} instead of nematic or smectic phases.^{16–19} That is, house-of-cards arrangements are favoured against stacked ones. Using this pair potential, we focus our attention on the vapour-liquid coexistence. For this purpose, a short SW range is set and the simulations are carried out in a prism with a liquid slab at its centre defining two vapour-liquid interfaces. Simulations show that the critical density decreases with increasing shape anisotropy, which suggests that the occurrence of empty liquid states is quite feasible. This finding is then corroborated by means of the van der Waals perturbation theory, which allows the consideration of much larger anisotropies. Furthermore, the theory also shows the absence of nematic order at the liquid branch of the vapour-liquid coexistence, for all aspect ratios. Nonetheless, we have also observed that the liquid branch of the vapour-liquid phase coexistence extends over a large density range, which does not support the formation of equilibrium gels at very low temperatures and relatively high densities.⁴ Finally, despite obtaining isotropic vapour and liquid phases, particles at the vapour-liquid interface show some degree of orientational order.

II Methods

In this section we summarise the methodology followed to access the phase coexistence properties of the system of square-well oblate ellipsoids. The section is split into three parts. The first one describes the employed interaction potential, the second gives details of the simulation method and the third presents the applied van der Waals perturbation theory.

A Interaction potential

We employ a pairwise additive interaction potential, $u(r)$, which consists of a HE exclusion volume plus a SW attractive term, *i.e.*,

a square-well hard-ellipsoid (SWHE) potential. We are, however, restricting this study to the oblate case. It is given by

$$u(r) = \begin{cases} \infty, & \text{for } r \leq \sigma_{\text{RBP}}, \\ -\varepsilon, & \text{for } \sigma_{\text{RBP}} < r \leq \sigma_{\text{RBP}} + \lambda, \\ 0, & \text{for } r > \sigma_{\text{RBP}} + \lambda, \end{cases} \quad (1)$$

where σ_{RBP} is the distance between the geometric centres of the ellipsoids when the particles are in contact, and ε and $\lambda = 0.25\sigma_{\parallel}$ are the well depth and width respectively ($\sigma_{\parallel}$ is the oblate diameter parallel to the axis of revolution, which is taken as the unit of length). As mentioned in the Introduction, we are using a modification of the BP²³ (or the hard Gaussian overlap) closest approach distance. This modification was introduced to fix the T-shape mismatch of the BP formula and to yield a better approximation to the exact solution of the closest approach distance. The Rickayzen–Berne–Pechukas (RBP) expression reads²⁸

$$\sigma_{\text{RBP}} = \sigma_{\perp} \left(1 - \frac{1}{2} \chi [A^{+} + A^{-}] + (1 - \chi) \chi' [A^{+} A^{-}]^{\gamma} \right)^{-1/2} \quad (2)$$

being

$$A^{\pm} = \frac{(\hat{r} \cdot \hat{u}_i \pm \hat{r} \cdot \hat{u}_j)^2}{1 \pm \chi \hat{u}_i \cdot \hat{u}_j}, \quad (3)$$

$$\chi = \frac{\sigma_{\parallel}^2 - \sigma_{\perp}^2}{\sigma_{\parallel}^2 + \sigma_{\perp}^2}, \quad (4)$$

and

$$\chi' = \left(\frac{\sigma_{\parallel} - \sigma_{\perp}}{\sigma_{\parallel} + \sigma_{\perp}} \right)^2. \quad (5)$$

Here, $\sigma_{\perp}$ is the perpendicular diameter with respect to the ellipsoid axis of revolution (spheroid). $\hat{u}_i$ and $\hat{u}_j$ are the unit vectors along the axis of revolution of each particle and $\hat{r}$ is the unit vector along the line joining the geometric centres. Furthermore, γ is introduced²⁹ as a free adjusting parameter to approach even closer the exact numerical solution. The values of γ are given in ref. 29. For example, for $1/5 \leq k \equiv \sigma_{\perp}/\sigma_{\parallel} \leq 5$ the average difference between RBP and the exact numerical solution for a collection of 10^8 random configurations (varying $\hat{r}$, $\hat{u}_i$, and $\hat{u}_j$) is always below 0.8%. The equations of state corresponding to RBP with $k = 5$ and hard ellipsoids were also compared showing no significant differences.²⁹ To the best of our knowledge, despite the simplicity of our model potential (eqn (1)), it has not been previously examined.

B Replica exchange method and simulation details

We are combining the replica exchange Monte Carlo method^{31–33} with the slab technique.³⁴ The general idea is to simulate M replicas of the system of interest, being each replica at a different temperature, so that their exchange is allowed (swap moves). In this way, replicas at high temperatures travel long distances in configuration space, whereas low temperature systems perform precise sampling at local

regions of configuration space. Hence, by introducing these swap trials, a particular replica travels through many temperatures allowing it to overcome free energy barriers. Particular ensembles are not disturbed but enriched by the different contributions of the M replicas. This technique enhances sampling the low temperature coexistence regions. It is based on the definition of an extended ensemble as follows

$$Q_{\text{extended}} = \prod_{i=1}^M Q_{NVT_i}, \quad (6)$$

where Q_{NVT_i} is the partition function of the canonical ensemble of the system at temperature T_i , volume V , with N particles. M is the considered number of replicas of the system, which equals the number of different temperatures defining the extended ensemble. To fulfil the detailed balance, the acceptance probability for swap trials (performed between adjacent replicas only) is

$$P_{\text{acc}} = \min(1, \exp[(\beta_j - \beta_i)(U_i - U_j)]), \quad (7)$$

where $U_i - U_j$ is the potential energy difference between replicas i and j , and $\beta_i - \beta_j$ is the difference between reciprocal temperatures i and j . Adjacent temperatures should be close enough to provide large exchange acceptance rates between neighboring ensembles.

We employed parallelepiped boxes with sides fulfilling $L_x = L_y = L_z/3$ for simulating the vapour–liquid coexistence of the SWHE fluid. Each simulation cell is initially set with all particles ($N = 800$) randomly placed and oriented within a slab, surrounded by vacuum,³⁴ such that the total volume fraction is $\phi = \rho v_e = 0.23$, being ρ the number density and $v_e = \pi \sigma_{\parallel} \sigma_{\perp}^2/6$ the ellipsoid volume. The centre of mass is placed at the cell centre. Periodic boundary conditions are set in the three directions. Verlet lists are implemented to improve performance.³⁵ Simulations were carried out for capturing the vapour–liquid region, so the highest temperature is set below the critical temperature. Other temperatures are fixed by following a geometrically decreasing trend.³⁶ Firstly, the replicas perform approximately 1×10^7 MC steps, while maximum displacements are varied to yield acceptance rates close to 30%. Long displacement trials are also considered. These displacements are important to improve sampling since they allow large jumps in the vapour phase with relatively large acceptance rates while naturally performing particle transference trials between liquid and vapour phases. The thermodynamic properties are calculated by discarding the first 1×10^7 MC steps and considering additional 2×10^7 configurations. Snapshots of configurations at equilibrium for different temperatures and for SWHE systems with $k = 3.0$ are shown in Fig. 1.

The critical volume fraction, ϕ_c , and temperature, T_c^* , were calculated by using the rectilinear diameter law and the universal value of $\beta = 0.325$ (ref. 37 and 38) for low anisotropy ($k \leq 1.3$) and $\beta = 0.333$ for high anisotropy ($k > 1.3$).³⁹ Results are given in dimensionless units as follows: $r^* = r/\sigma_{\parallel}$ and $z^* = z/\sigma_{\parallel}$ for distance, and $T^* = k_B T/\epsilon$ for temperature.

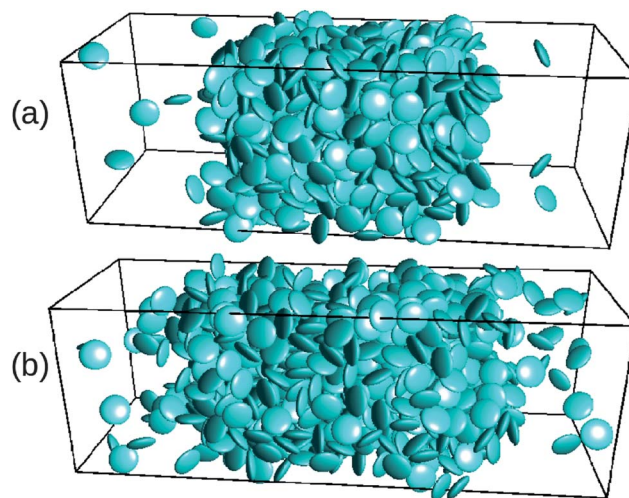


Fig. 1 Snapshots showing configurations of simulation cells at equilibrium containing 800 oblates with $k = 3$ for $T^* = 0.37$ (a), and $T^* = 0.48$ (b).

C Theory

To study the orientationally disordered and ordered phases of the SWHE we use the well-known Parsons–Lee decoupling approximation for the free energy contribution of the anisotropic hard body interactions, while the effect of anisotropic attraction is included by the second-virial approximation.^{15,16} On the level of the approximation, the free energy density can be written as

$$\frac{\beta F}{N} = \ln \rho - 1 + \sigma[f] + \frac{\beta F_{\text{exc}}^{\text{hs}}}{N} \left\langle \left\langle \frac{v_{\text{exc}}}{8v_e} \right\rangle \right\rangle + \rho B_2^{\text{sw}}. \quad (8)$$

The orientational entropy of eqn (8) is given by

$$\sigma[f] = \int d\hat{\mathbf{u}} f(\hat{\mathbf{u}}) \ln(4\pi f(\hat{\mathbf{u}})), \quad (9)$$

where f is the orientational distribution function and the integration is performed over the surface of the unit sphere. The prefactor of the hard body contribution of eqn (8) is chosen to be the Carnahan–Starling excess free energy of the HS fluid, *i.e.*

$$\frac{\beta F_{\text{exc}}^{\text{hs}}}{N} = \frac{4\phi - 3\phi^2}{(1 - \phi)^2}. \quad (10)$$

With this choice our theory incorporates the well-known Carnahan–Starling equation of state for HS and the Onsager theory of non-spherical particles. The weighted average of the dimensionless excluded volume is obtained from

$$\left\langle \left\langle \frac{v_{\text{exc}}}{8v_e} \right\rangle \right\rangle = \int d\hat{\mathbf{u}}_i f(\hat{\mathbf{u}}_i) \int d\hat{\mathbf{u}}_j f(\hat{\mathbf{u}}_j) \frac{v_{\text{exc}}(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j)}{8v_e}, \quad (11)$$

where the excluded volume is related to the contact distance of the geometric centres through

$$v_{\text{exc}}(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = \frac{1}{3} \int d\mathbf{r} \sigma_{\text{RBP}}^3. \quad (12)$$

The last term of eqn (8) includes the contribution of the attractive forces and takes the following form for our pair potential (eqn (1))

$$B_2^{\text{sw}} = \frac{(1 - \exp(\beta\epsilon))}{2} \int d\hat{\mathbf{u}}_i f(\hat{\mathbf{u}}_i) \int d\hat{\mathbf{u}}_j f(\hat{\mathbf{u}}_j) v_{\text{sw}}(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j), \quad (13)$$

where $v_{\text{sw}}(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j) = \frac{1}{3} \int d\hat{\mathbf{r}} [(\sigma_{\text{RBP}} + \lambda)^3 - \sigma_{\text{RBP}}^3]$. In isotropic phases, which include vapour and liquid phases, the free energy density can be easily obtained at a given volume fraction by the substitution of the isotropic orientational distribution function ($f = 1/4\pi$) in eqn (8). In the nematic phase we must search for that $f(\hat{\mathbf{u}})$ which minimises the free energy (eqn (8)). To determine an approximate border between the isotropic and nematic phases, it is customary to perform a bifurcation analysis between the two phases (see the review⁴⁰ for the details of the method). In the present case it can be shown that the bifurcation volume fraction (ϕ_B) of the isotropic–nematic phase transition is given by

$$1 + \frac{2}{5} \left\{ \frac{4\phi_B - 3\phi_B^2}{(1 - \phi_B)^2} v_2 + \frac{\phi_B}{2} k_2 (1 - \exp(\beta\epsilon)) \right\} = 0, \quad (14)$$

where $v_2 = \frac{5}{2} \int_0^\pi d\theta \sin \theta \frac{v_{\text{exc}}(\theta)}{8v_e} P_2(\theta)$, $k_2 = \frac{5}{2} \int_0^\pi d\theta \sin \theta \frac{v_{\text{sw}}(\theta)}{v_e} P_2(\theta)$,

and $P_2(\theta) = \frac{3}{2} \cos^2 \theta - \frac{1}{2}$ is the second Legendre polynomial. In addition to the isotropic–nematic bifurcation, we determine the vapour–liquid coexistence curve, the critical volume fraction and temperature from eqn (8) using the standard thermodynamic relations. Solid phases are not considered.

III Results and discussion

In this section we start with the presentation of the volume fraction profiles, $\phi(z^*)$, uniaxial order parameter profiles, $c(z^*) = \langle P_2(\theta_z) \rangle$ (being θ_z the angle between the z axis of the simulation box and the particle's axis of revolution under consideration), and vapour–liquid coexistence curves for SWHE systems with $\lambda = 0.25\sigma_{\parallel}$. That is, we keep fixed the potential range of the SW while the oblates aspect ratio is increased. In particular, for $k = 3$, Fig. 2(a) shows the obtained volume fraction profiles, $\phi(z^*)$, for temperatures below T_c^* . By construction, the liquid phase, with volume fraction ϕ_l , is located at the centre of the simulation box, whereas the vapour phase, with volume fraction ϕ_v , is contiguous to both sides of the liquid slab. Thus, profiles show a high volume fraction plateau at the box centre, a low volume fraction flatness at the box sides, and an intermediate region corresponding to the interfaces. The profile corresponding to the highest temperature produces the lowest ϕ_l value and the highest ϕ_v value, whereas the one for the lowest temperature yields the highest ϕ_l value and the lowest ϕ_v value. Other profiles correspond to intermediate temperatures. The width of the interface increases with temperature, which is related to a decrease taking place in the surface tension.

Panel (b) of the same figure shows the corresponding uniaxial order parameter profiles, $c(z^*)$. For temperatures close to T_c^* , $c(z^*)$ is practically zero for all z^* , which points out an isotropic structure for vapour, liquid, and interfaces. This is also corroborated by radial distribution functions at the liquid slab, where no long range angular and positional order are detected (not shown). The isotropic nature of vapour and liquid

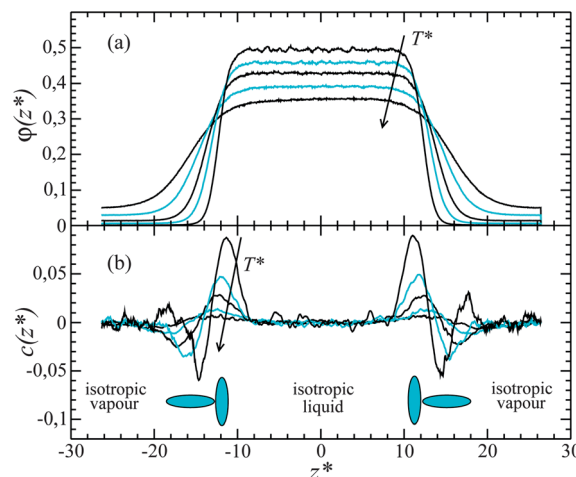


Fig. 2 (a) Volume fraction profiles, $\phi(z^*)$, for a SWHE system with $k = 3.0$ for different temperatures. (b) The corresponding uniaxial order parameter profiles, $c(z^*)$, and a cartoon of the low temperature simulation cell structure. Different colours are used for easy visualisation. Arrows indicate the increasing temperature direction ($T^* = 0.3700, 0.4137, 0.4405, 0.4634$, and 0.4800). For this system $T_c^* = 0.5056$.

phases persists for all temperatures. This is in contrast with the spherical-SW-HE model, where the preferred face-to-face interactions stabilise the nematic and smectic structures.^{16–19} Nonetheless, positive and negative $c(z^*)$ peaks grow at the interfaces with decreasing temperature. The positive peaks locate at the liquid side of the interfaces, whereas the negative peaks develop at the vapour side of the interfaces. This points out a preference for oblates to maximise their contact area with the liquid slab, when located at the liquid side of the interface, and a preference for those oblates at the vapour side of the interface to form a T-shaped structure with the first ones. This picture is schematised in the inset of Fig. 2(b). The corresponding snapshot for a low temperature simulation cell is shown in Fig. 1(a). There, the orientational arrangement at the interface is not evident (note that the largest $c(z^*)$ peak at the interface is close to 0.1). The height of these peaks increases for decreasing temperature and increasing aspect ratio, k . In fact, as expected, peaks vanish for $k \rightarrow 1$ for all temperatures.

Now we continue with the presentation of the vapour–liquid phase coexistence curves obtained from simulations and theory (see Fig. 3). Panel (a) is obtained from averaging the volume fraction profiles at the vapour and liquid regions of the simulation cells for different aspect ratios, k . This yields ϕ_v and ϕ_l , respectively. From each dataset the critical point is obtained using the rectilinear diameter law with a given β value, as explained at the end of section II B. The corresponding critical points are given in Table 1 and are included in Fig. 3(a). This figure shows the SW spherical case ($k = 1$) for $\lambda = 0.25\sigma_{\parallel}$, appearing at the highest temperatures. This coexistence, as well as its critical point, is in agreement with data from previous works.^{41–43} On the other hand, the curve located at the lowest temperatures corresponds to the highest anisotropy, $k = 5$. Note the narrower temperature window at which the coexistence is captured. Intermediate aspect ratios produce the other curves,

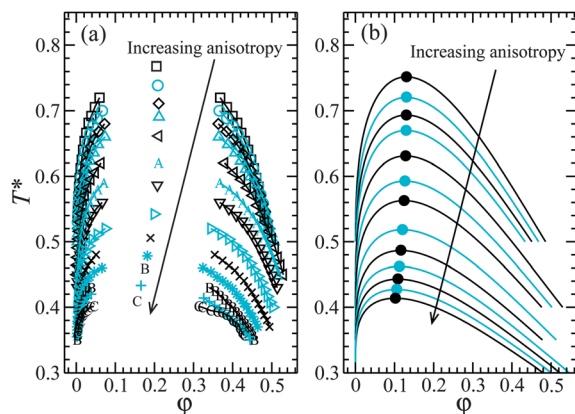


Fig. 3 Vapour-liquid coexistence curves for different aspect ratios, k (aspect ratios are given in Table 1): (a) simulation results, (b) perturbation theory. Light and dark lines and symbols are used for easy visualisation. The curve at higher temperatures corresponds to $k = 1$ and the one at lower temperatures to $k = 5$. Thus, particles' anisotropy increases as shown by the arrow. Critical points are also included.

such that increasing k leads to a monotonic decrease of T_c^* . All these features, including the monotonic decrease of T_c^* with k , are well captured by our perturbation theory (see Fig. 3(b)). For increasing k , T_c^* decreases due to the relative decrease of the square-well range as compared to the particle size (this is a well known effect of SW systems^{43,44}). This critical temperature decrease, when large, *i.e.* for sufficiently large aspect ratios, implies the occurrence of large bond lifetimes inside the binodal. Hence, the establishment of the vapour-liquid phase separation may be preempted by the formation of a gel state (an arrested and low density percolating network). This arrested gel state evolves, in case of laponites, in the year time-scale.^{2,4} The trend found for the critical volume fraction, ϕ_c , is non-monotonic, according to simulations. As shown in panel (a), ϕ_c increases with k for $k < 1.3$, and decreases with k for $k > 1.5$, producing a ϕ_c maximum near $k = 1.5$. This maximum is not captured by the theory (panel (b)), which predicts a monotonic decreasing trend. Nonetheless, the decreasing trend is practically a plateau for $k < 1.3$.

The non-monotonic behaviour of ϕ_c with k from simulations is clearly observed in the inset at the bottom of Fig. 4(a). The main panel shows ϕ_c as a function of the critical temperature, T_c^* , and the upper inset shows the T_c^* dependence with the aspect ratio, k . The maximum of ϕ_c is observed at $T_c^* \approx 0.67$ and at $k \approx 1.5$, respectively. For low anisotropy, the increase of ϕ_c with the aspect ratio, k , can be understood from the opposite effects of

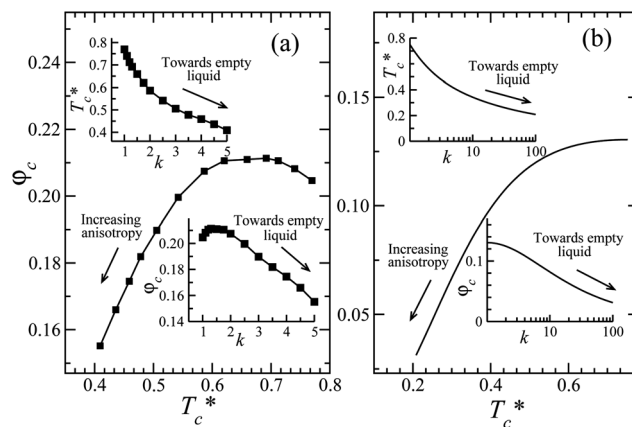


Fig. 4 Critical volume fraction, ϕ_c , as a function of the critical temperature, T_c^* . The arrows indicate the direction towards the empty liquid or the increasing shape anisotropy. The insets show the aspect ratio, k , dependence of the critical temperature, T_c^* , and the volume fraction, ϕ_c . Panel (a) shows the simulation data, while panel (b) presents the results of the van der Waals perturbation theory.

the excluded volume and the SW attractions on the liquid volume fraction. As mentioned in the previous paragraph, as k increases, the relative SW range, in terms of the particle size, shortens. This shortening produces a decreasing effect on the particle-particle distances, *i.e.* it increases the critical volume fraction (another well-known effect for the spherical SW). Conversely, the excluded volume increases with k giving rise to larger average particle-particle distances with the consequent lowering of the volume fraction. For low anisotropy, the SW attraction effect is stronger which results in the increasing trend of the critical volume fraction, whereas the excluded volume becomes dominant for $k > 1.5$. The two competing effects produce a maximum in the critical volume fraction at $k \approx 1.5$. Very low critical densities are reported in systems with tendency to form house-of-cards structures, such as clays, where T-shape and parallel, partially overlapped (also called overlapping coins^{45,46}) configurations are dominant.^{2,45-47} In particular, laponites and patchy colloids with a small number of sticky sites, both systems showing a common tendency to produce low coordination numbers (low-valence systems), are known to form liquids with vanishing density, referred to as empty liquids.²⁻⁴ Our $\phi_c(k)$ and $\phi_c(T_c^*)$ trends obtained from simulations suggest a probable empty liquid limit for large anisotropies. Accordingly, the SWHE potential would be another example of anisotropic potential capable of producing empty liquids. Fig. 4(b) expands over much larger k values, corroborating that the monotonic decrease of $\phi_c(k)$ holds over a very

Table 1 Critical temperature, T_c^* , and volume fraction, ϕ_c , as a function of the oblates aspect ratio, k , as obtained from MC simulations and van der Waals perturbation theory (PT). Estimated MC errors are less than 1.0% and 2.0% for T_c^* and ϕ_c , respectively

	k	1.00	1.10	1.20	1.30	1.50	1.75	2.00	2.50	3.00	3.50	4.00	4.50	5.00
MC	T_c^*	0.7696	0.7402	0.7122	0.6918	0.6593	0.6204	0.5863	0.5421	0.5056	0.4783	0.4589	0.4359	0.4093
PT	T_c^*	0.7519	0.7204	0.6934	0.6698	0.6308	0.5928	0.5628	0.5183	0.4865	0.4622	0.4430	0.4272	0.4139
MC	ϕ_c	0.2046	0.2082	0.2106	0.2113	0.2109	0.2105	0.2074	0.1996	0.1898	0.1819	0.1745	0.1659	0.1551
PT	ϕ_c	0.1304	0.1303	0.1300	0.1295	0.1283	0.1265	0.1244	0.1202	0.1160	0.1122	0.1086	0.1053	0.1022

large k range (note the logarithmic k -scales of the insets). Besides, it also shows a more pronounced decreasing trend for $\varphi_c(k)$ than for $T_c^*(k)$. Note that the general qualitative agreement between simulations and theory is satisfactory. In fact, the agreement between the critical temperatures is quantitatively good (see Table 1). Nonetheless, the theory underestimates the critical volume fractions. The main reason for this failure is that the SW perturbation term (last term of eqn (8)) is a good approximation only for very low densities, which is not the case in the vicinity of the spherical case, $k = 1$. In order to get a closer agreement between theory and simulation, higher order perturbation terms of the SW attraction must be included. For high shape anisotropies, the success of the theory is due to the fact that the critical volume fraction decreases ($\varphi_c \rightarrow 0$), *i.e.* the higher order terms of the perturbation theory become negligible. This feature of the perturbation theory was also reported in the study of spherical patchy colloids.³

The reduced vapour–liquid coexistence curves for $1.0 \leq k \leq 5.0$ are shown in Fig. 5. Here, the reduced volume fraction and temperature are given by $\varphi_r = \varphi/\varphi_c$ and $T_r^* = T^*/T_c^*$, respectively. It is observed how the gap between the vapour and liquid branches monotonically widens for increasing anisotropy. As a consequence, the corresponding states law is not fulfilled. More importantly, since the widening is quite large for $k = 5$ oblates, the liquid branch of the vapour–liquid coexistence curve covers a wide density range. Hence, empty liquids are only expected to be formed close to (and at the right of) the critical point. On the other hand, for intermediate densities, a sufficient temperature drop would produce a dynamically arrested network showing density inhomogeneities. This kind of behaviour is driven by an underlying phase separation process and shown to exist in spherical short-range attractive colloids.¹ This contrasts with the laponites and patchy colloids behaviour, where an empty liquid could be quenched to produce a percolation driven homogeneous gel state, which slowly evolves towards a stable network.^{2,4} This is due to the fact that the phase separation region, for these last cases, shrinks to very low densities and

temperatures, and so, gel states can be accessed in equilibrium, because particles are able to form macroscopic bonded networks with large bond lifetimes without intervening the phase separation.² Finally, it should be noted that for $k = 5$ the liquid density is even above that of the isotropic–nematic transition of hard oblates, which occurs at $\varphi = 0.348$.¹¹ Hence, the SWHE is clearly hindering the nematic phase in favour of an isotropic liquid, and an isotropic–nematic transition should occur at higher temperature and/or pressure.

To confirm the absence of a nematic–liquid phase in coexistence with a vapour phase, we built Fig. 6 from data obtained by means of the perturbation theory. There we show the phase diagram of SWHE for $k = 25$ and for $k = 5$ as an inset. We can see that the isotropic–nematic phase transition is shifted towards higher densities such an extent that the vapour–liquid phase transition is not affected by the ordering transition even at very strong shape anisotropies. This happens for $k = 25$, which corresponds to the shape anisotropy of laponites, where the excluded volume interactions are strong enough to give rise to the formation of a nematic phase at very low volume fractions in the high temperature limit. This is evidently due to the fact that the orientational ordering is energetically not favourable as fewer particles can get in SW contact (bond) with a parallel ordering, *i.e.* the orientational ordering produces low-valence liquid crystal phases. Hence, the SW attraction works very efficiently against orientational ordering even though the excluded volume interactions produce vanishing densities for the isotropic–nematic phase transition for $T \rightarrow \infty$ and $k \rightarrow \infty$. Something similar occurs in fluids of SW rod-like spherocylinders, where a destabilisation of the nematic phase with respect to the isotropic phase occurs as the temperature is decreased.⁴⁸ Thus, when the role of the attractive anisotropic interaction is increased (through, for instance, a temperature decrease), the isotropic liquid phase is favoured.

Fig. 7 shows, for the most asymmetric case considered by simulations, *i.e.* for $k = 5$, the centre–centre radial distribution functions, $g(r^*)$, their integrals, $n(r^*) = 4\pi \int r^{*2} g(r^*) \rho dr^*$, and

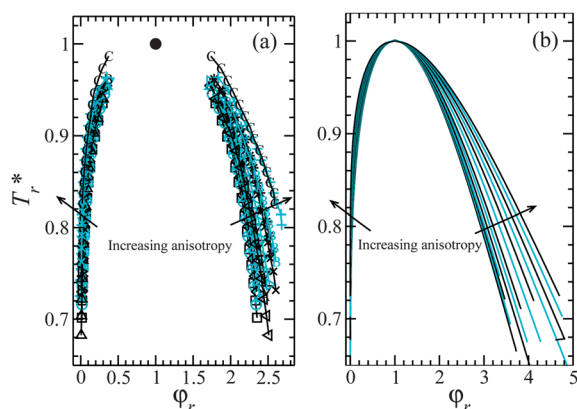


Fig. 5 Reduced vapour–liquid coexistence curves for all aspect ratios. Colours and symbols correspond to those shown in Fig. 3. It is shown how the gap between the vapour and liquid branches widens for increasing aspect ratio. Panel (a) shows the simulation data, while panel (b) presents the results of the van der Waals perturbation theory.

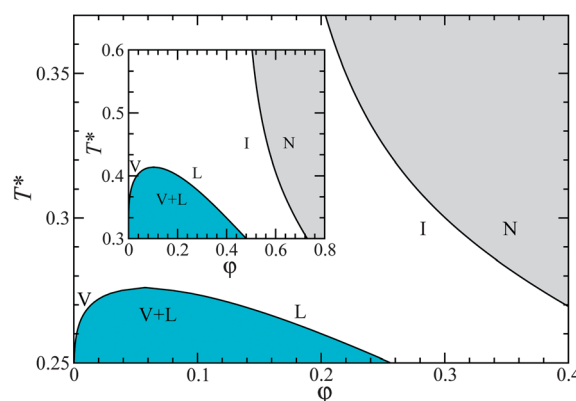


Fig. 6 Phase diagram of SWHE (oblates) for $k = 25$. The inset presents the phase diagram for $k = 5$. Vapour–liquid phase coexistence and isotropic–nematic bifurcation curves are shown. The labels I, N, V, and L denote isotropic, nematic, vapour, and liquid (isotropic) phases. The curves are the results of the van der Waals perturbation theory (solid phases are not considered).

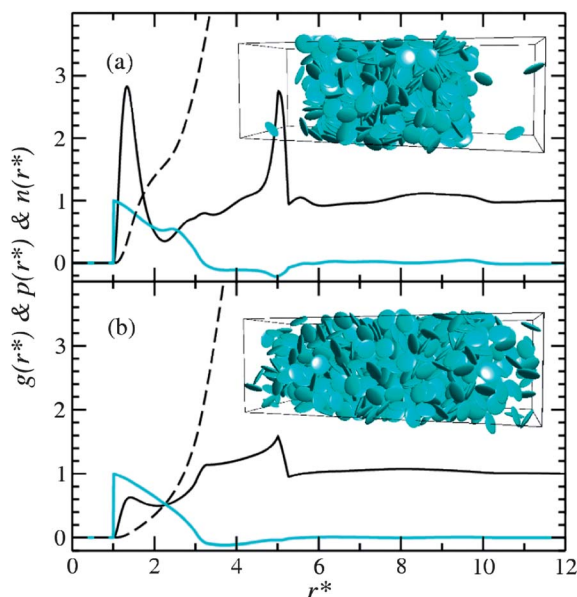


Fig. 7 Radial distribution functions (dark lines), $g(r^*)$, their integrals (dashed lines), $n(r^*)$, and angular distribution functions (light lines), $p(r^*)$, for the liquid phase of oblates with $k = 5$, and for $T^* = 0.353$ (a) and $T^* = 0.405$ (b). The insets show the corresponding snapshots.

angular distribution functions, $p(r^*) = \langle P_2(\theta(r^*)) \rangle$ being $\theta(r^*)$ the angle between vectors $\hat{u}_i$ and $\hat{u}_j$ of particles at a distance r^* , for a temperature close to T_c^* and for the lowest temperature.⁴⁹ All these functions are built within the liquid slab, excluding interfaces. This figure highlights the strong density change of the liquid phase with temperature. It shows how two $g(r^*)$ peaks develop at $r^* \approx \sigma_{\parallel}$ and $r^* \approx \sigma_{\perp}$, the first one corresponding to parallel configurations and the second to (mostly) T-shaped configurations, as pointed out by the $p(r^*)$ sign, at low temperatures, whereas both peaks practically vanish at temperatures close to T_c^* . Consequently, $n(r^*)$ reaches much larger values at low temperatures, signalling an increase of the coordination number. This increase is gradually produced, according to the way $n(r^*)$ changes with temperature (not shown). The snapshots of Fig. 7 show the obtained structures at both temperatures, where the density increase with decreasing temperature is found to be clearly related to an increase of $n(r^*)$. That is, Fig. 7(a) shows local semi-parallel fan-shaped structures surrounding small groups of stacked particles, whereas in Fig. 7(b) T-shaped configurations are dominant. Hence, asymmetric SWHE-systems show an intermediate behaviour when compared to attractive spherical particles and laponites (or patchy particles). That is, they present low critical temperatures and volume fractions, as empty liquid formers, but also produce relatively dense liquids in coexistence with vapour phases at lower temperatures. Thus, a sufficient temperature decrease at relatively large volume fractions may lead to the formation of arrested networks by means of an underlying phase separation process, similar to the particles interacting through potentials with spherical symmetry.¹ To further approach a laponite (or patchy colloid) behaviour, one must somehow restrict the oblates coordination number³ to avoid the fan-shaped

structures. This, we guess, can be done by superposing a repulsive, short-range, and spherical SW to the SWHE studied here, which would roughly capture the face-to-face repulsion and edge-to-face attraction of laponites.

IV Conclusions

Properties of the vapour-liquid coexistence of systems composed of hard ellipsoids (oblates) plus an attractive ellipsoidal-shaped square-well (SWHE) were studied by means of replica exchange Monte Carlo simulations and perturbation theory. For this purpose, we fixed the depth and range of the square-well anisotropic interaction whereas the oblates aspect ratio, k , was varied. This potential, in contrast to hard ellipsoids with spherical attractive interactions, promotes T-shaped configurations instead of face-to-face arrangements. Consequently, isotropic liquid phases are favoured over nematic and smectic ones. We found a monotonically decreasing trend for the critical temperature with k . The trend of the critical density with k , however, is non-monotonic. For nearly symmetric particles ($1.0 \leq k \leq 1.3$), we found an increase of the critical density with k followed by a linear decreasing trend for large aspect ratios, defining a maximum at approx. $k = 1.5$. The existence of this maximum is a consequence of the competition between the attractive square-well and the repulsive excluded volume interactions. Whereas the square-well attraction favours the high density structures, the excluded volume repulsion prefers the low density liquid states. For high anisotropy, the SWHE systems form empty liquids close to the critical point, but relatively dense liquids are in coexistence with vapour phases at lower temperatures, *i.e.* the vapour-liquid binodal is wide. The empty liquid behaviour is in line with laponites and patchy colloids with a small number of sticky sites, both systems showing a common tendency to produce low coordination numbers. The wide vapour-liquid binodal is typical of attractive, spherically symmetric potentials, with tendency to produce much larger coordination numbers.

Acknowledgements

EMJ thanks the Ph.D. scholarships granted by IMP and CONACyT. SV acknowledges the financial support of the Hungarian State and the European Union under the TAMOP-4.2.2.A-11/1/KONV-2012-0071. PO thanks Programa de Ingeniería Molecular. GO acknowledges CONACyT financial support through Project no. 169125.

References

- 1 P. J. Lu, E. Zaccarelli, F. Ciulla, A. B. Schofield, F. Sciortino and D. A. Weitz, *Nature*, 2008, **453**, 499.
- 2 B. Ruzicka and E. Zaccarelli, *Soft Matter*, 2011, **7**, 1268.
- 3 E. Bianchi, J. Largo, P. Tartaglia, E. Zaccarelli and F. Sciortino, *Phys. Rev. Lett.*, 2006, **97**, 168301.
- 4 B. Ruzicka, E. Zaccarelli, L. Zulian, R. Angelini, M. Sztucki, A. Moussad, T. Narayanan and F. Sciortino, *Nat. Mater.*, 2011, **10**, 56.

- 5 H. Chen, Z. Ye, C. Peng, H. Liu and Y. Hu, *J. Chem. Phys.*, 2006, **125**, 204708.
- 6 H. Chen, Z. Ye, J. Cai, H. Liu, Y. Hu and J. Jiang, *J. Phys. Chem. B*, 2007, **111**, 5927.
- 7 E. Joussein, S. Petit, J. Churchman, B. Theng, D. Righi and B. Delvaux, *Clay Miner.*, 2005, **40**, 383.
- 8 A. Donev, F. H. Stillinger, P. M. Chaikin and S. Torquato, *Phys. Rev. Lett.*, 2004, **92**, 255506.
- 9 P. Pfleiderer and T. Schilling, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, **75**, 020402.
- 10 M. Radu, P. Pfleiderer and T. Schilling, *J. Chem. Phys.*, 2009, **131**, 164513.
- 11 G. Odriozola, *J. Chem. Phys.*, 2012, **136**, 134505.
- 12 M. N. Rosenbluth and A. W. Rosenbluth, *J. Chem. Phys.*, 1954, **22**, 881.
- 13 W. W. Wood and J. D. Jacobson, *J. Chem. Phys.*, 1957, **27**, 1207.
- 14 B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, 1957, **27**, 1208.
- 15 S. Varga and I. Szalai, *Mol. Phys.*, 1998, **95**, 515.
- 16 S. Varga, D. C. Williamson and I. Szalai, *Mol. Phys.*, 1999, **96**, 1695.
- 17 E. M. Del Río, A. Galindo and E. De Miguel, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2005, **72**, 051707.
- 18 E. M. Del Río and E. De Miguel, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2005, **71**, 051710.
- 19 E. De Miguel and E. M. Del Río, *Phys. Rev. Lett.*, 2005, **95**, 217802.
- 20 A. Singh, T. Dey and S. Sinha, *Pramana*, 1990, **34**, 123.
- 21 W. Li, Y. Liu, G. Brett and J. Gunton, *Soft Matter*, 2012, **8**, 6027.
- 22 J. G. Gay and B. J. Berne, *J. Chem. Phys.*, 1981, **74**, 3316.
- 23 B. J. Berne and P. Pechukas, *J. Chem. Phys.*, 1972, **56**, 4195.
- 24 J. W. Perram and M. S. Wertheim, *J. Comput. Phys.*, 1985, **58**, 409.
- 25 X. Zheng, W. Iglesias and P. Palfy-Muhoray, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2009, **79**, 057702.
- 26 T. Kihara, *J. Phys. Soc. Jpn.*, 1951, **6**, 289.
- 27 L. Paramonov and S. N. Yaliraki, *J. Chem. Phys.*, 2005, **123**, 194111.
- 28 G. Rickayzen, *Mol. Phys.*, 1998, **95**, 393.
- 29 F. de J. Guevara-Rodríguez and G. Odriozola, *J. Chem. Phys.*, 2011, **135**, 084508.
- 30 N. G. Almarza, J. M. Tavares, M. Simes and M. M. Telo da Gama, *J. Chem. Phys.*, 2011, **135**, 174903.
- 31 A. P. Lyubartsev, A. A. Martinovski, S. V. Shevkunov and P. N. Vorontsov-Velyaminov, *J. Chem. Phys.*, 1992, **96**, 1776.
- 32 E. Marinari and G. Parisi, *Europhys. Lett.*, 1992, **19**, 451.
- 33 K. Hukushima and K. Nemoto, *J. Phys. Soc. Jpn.*, 1996, **65**, 1604.
- 34 G. A. Chapela, G. Saville, S. M. Thompson and J. S. Rowlinson, *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 1133.
- 35 A. Donev, S. Torquato and F. H. Stillinger, *J. Comput. Phys.*, 2005, **202**, 737.
- 36 N. Rathore, M. Chopra and J. J. de Pablo, *J. Chem. Phys.*, 2005, **122**, 024111.
- 37 D. Frenkel and B. Smit, *Understanding molecular simulation*, Academic, New York, 1996.
- 38 M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon, Oxford, 1986.
- 39 J. T. Brown, M. P. Allen, E. M. Del Río and E. De Miguel, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1998, **57**, 6685.
- 40 G. Vroege and H. Lekkerkerker, *Rep. Prog. Phys.*, 1992, **55**, 1241.
- 41 L. Vega, E. De Miguel, L. F. Rull, G. Jackson and I. A. McLure, *J. Chem. Phys.*, 1992, **96**, 2296.
- 42 E. Schöll-Paschinger, A. L. Benavides and R. Castañeda-Priego, *J. Chem. Phys.*, 2005, **123**, 234513.
- 43 R. López-Rendón, Y. Reyes and P. Orea, *J. Chem. Phys.*, 2006, **125**, 084508.
- 44 F. Del Río, E. Ávalos, R. Espíndola, L. F. Rull, G. Jackson and S. Lago, *Mol. Phys.*, 2002, **100**, 2531.
- 45 B. Jönsson, C. Labbez and B. Cabane, *Langmuir*, 2008, **24**, 11406.
- 46 M. Delhorme, B. Jönsson and C. Labbez, *Soft Matter*, 2012, **8**, 9691.
- 47 G. Odriozola, M. Romero-Bastida and F. de J. Guevara-Rodríguez, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2004, **70**, 021405.
- 48 D. C. Williamson and F. Del Río, *J. Chem. Phys.*, 1998, **109**, 4675.
- 49 R. Eppenga and D. Frenkel, *Mol. Phys.*, 1984, **52**, 1303.