Porous liquid phases of indented colloids with depletion interactions

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We study indented spherical colloids, interacting via depletion forces. These systems exhibit liquid-vapor phase transitions whose properties are determined by a combination of strong “lock-and-key” bonds and weaker non-specific interactions. As the propensity for lock-and-key binding increases, the critical point moves to significantly lower density, and the coexisting phases change their structure. In particular, the liquid phase is porous, exhibiting large percolating voids. The properties of this system depend strongly on the topological structure of an underlying bond network: we comment on the implications of this fact for the assembly of equilibrium states with controlled porous structures.

In colloidal systems, a wide range of structures can be self-assembled from a simple palette of components and interactions [1]. For example, anisotropic forces between particles can stabilise colloidal micelles or exotic crystals [2–9], which could form the basis of future materials and devices. Anisotropic attractions can be achieved experimentally via chemical patches [2, 6, 10–12], or through a combination of particle shape and depletion forces [4, 5, 13–16]. Depletion forces arise when colloids are dispersed in a solution of much smaller depletant particles, which induce an attractive interaction [17], whose properties can be tuned via the size and number density of the depletant. Here, we present Monte Carlo simulations of the assembly of indented (“lock-and-key”) colloidal particles [4, 18–23], in the presence of an ideal depletant [24]. We introduce an effective potential which captures quantitatively the effect of this depletant. This enables efficient simulation, and accurate characterisation of the liquid-vapor phase transitions that occur in this system. When the depletant particles are small in size compared to the colloids, the resulting liquid and vapor phases have unusual properties. In particular, the critical point for the phase transition occurs at a rather low density, and the liquid phases have a complex structure that includes a network of branched chains and large voids. Indeed, we find that the liquid phase is porous on a length scale comparable with the colloidal particles.

An indented colloidal particle is modelled as a sphere of diameter $\sigma$, from which we cut away its intersection with a second sphere of the same diameter [21, 22]. The distance between the sphere centres is taken as $d_c = 0.6\sigma$, so the depth of the indentation (measured from the lip) is $0.2\sigma$, comparable with experimentally realizable particles [4]. The orientation of particle $i$ is specified by a unit vector $n_i$ that points outwards through the centre of the indentation. The hard particle interactions between these particles are treated exactly in our model, but we parameterise the depletion interaction between the colloids through an effective potential, illustrated in Fig. 1. Specifically, when two colloids approach one another in the back-to-back configuration, they feel a square-well interaction potential of depth $\varepsilon_{BB}$ and range $r_{BB}$. When they approach in the lock-key configuration, the interaction range is $r_{LK}$, and the effective potential also depends on the angle $\phi$ between the particle directors. For perfect lock-key binding, the depth of the potential well is $\varepsilon_{LK}$. We fix the unit of energy by setting $\beta = 1/(k_B T) = 1$. The interaction ranges are fixed throughout this work according to $(r_{LK} - d_c) = (r_{BB} - \sigma) = 0.1\sigma$, comparable with the size of the depletant particles. (As for spherical particles, for perfect lock-key binding, the depth of the potential well is $\varepsilon_{LK}$. We fix the unit of energy by setting $\beta = 1/(k_B T) = 1$. The interaction ranges are fixed throughout this work according to $(r_{LK} - d_c) = (r_{BB} - \sigma) = 0.1\sigma$, comparable with the size of the depletant particles. (As for spherical particles, for perfect lock-key binding, the depth of the potential well is $\varepsilon_{LK}$.)

To obtain the interaction strengths $\varepsilon_{LK}$ and $\varepsilon_{BB}$ as a function of depletant parameters, we used the geometric cluster algorithm (GCA) [27, 28] to simulate systems of two colloidal particles interacting with a depletant of penetrable spheres [24]. The size ratio between colloids and depletant particles is $q$ (the depletant diameter is $q\sigma$), and the
FIG. 2. (a) Summary of phase behaviour, as a function of $\varepsilon_{\text{LK}}, \varepsilon_{\text{BB}}$. In the shaded region, coexistence of liquid and vapor phases can occur, for suitable colloid densities $\rho$. The stars indicate the positions of critical points. The dotted lines show how the effective interaction strengths ($\varepsilon_{\text{LK}}, \varepsilon_{\text{BB}}$) depend on the depletant size ratio $q$ (the depletant volume fraction $\eta_s$ varies along these lines). (b,c) Representative configurations from the coexisting liquid and vapor phases at the indicated state point, which phases can occur, for suitable colloid densities $\rho$. The solid line in Fig. 2(a) indicates how the parameters of the effective model are related to depletant parameters ($q, \eta_s$): for smaller $q$, lock-key binding is more favorable than back-to-back binding. Increasing $\eta_s$ at constant $q$ leads to an increase in both $\varepsilon_{\text{LK}}$ and $\varepsilon_{\text{BB}}$, along the dotted lines. To assess the accuracy of the effective potential, we used the GCA within a restricted Gibbs ensemble [31] to locate the critical point in a system of indented colloids with explicit depletant, for $q = 0.2$. We find that the critical parameters lie within 10% of the results obtained with the effective potential. This confirms the effectiveness of our coarse-graining scheme, which being based on virial coefficient matching is expected to hold for more general colloid and depletant interactions than the idealised ones considered here. However, with explicit depletant, it is not generally possible to investigate the structure of liquid and vapor phases, nor the behavior for smaller $q$, due to the computational cost required. Hence our use of the effective potential in this work.

The binodal curves associated with liquid-vapor phase coexistence are shown in Fig. 2(d), as a function of the depletant volume fraction $\eta_s$, for three values of $q$. As the depletant particles get smaller (decreasing $q$ at fixed depletant volume fraction is $\eta_s$. Full details of the effective potential and the parameterisation of ($\varepsilon_{\text{LK}}, \varepsilon_{\text{BB}}$) are given in Supplementary Material (SM) [25].

We employed grand canonical Monte Carlo (GCMC) simulation to study the phase behaviour of the colloids, interacting through the effective potential, in cubic boxes of sizes between $(12\sigma)^3$ and $(20\sigma)^3$. Smaller boxes sufficed for large $q$, where the size of bound clusters is typically small; bigger boxes were needed to accommodate the larger clusters that form at small $q$. Our GCMC method uses the usual particle updates (insertions, deletions, displacements and rotations), combined with biased insertions and deletions, which attempt to add (or remove) a colloid in a lock-key bound state, subject to satisfying detailed balance. This innovation, (described further in the SM [25]), increases the efficiency of the simulation by up to 4 orders of magnitude.

Fig. 2(a) summarises the phase behavior of the indented colloids. The state point of the system is specified by three parameters ($\rho, \varepsilon_{\text{LK}}, \varepsilon_{\text{BB}}$) where $\rho$ is the number density of colloids. The solid line in Fig. 2(a) indicates values of ($\varepsilon_{\text{LK}}, \varepsilon_{\text{BB}}$) for which a liquid-vapour critical point exists, at some critical density $\rho^c$. For values of ($\varepsilon_{\text{LK}}, \varepsilon_{\text{BB}}$) above this line, there exist values of the density for which liquid-vapor phase coexistence occurs: see for example Figs. 2(b,c). The structure of these phases is discussed further below. Dotted lines in Fig. 2(a) show how the parameters of the effective model are related to depletant parameters ($q, \eta_s$); for smaller $q$, lock-key binding is more favorable than back-to-back binding. Increasing $\eta_s$ at constant $q$ leads to an increase in both $\varepsilon_{\text{LK}}$ and $\varepsilon_{\text{BB}}$, along the dotted lines. To assess the accuracy of the effective potential, we used the GCA within a restricted Gibbs ensemble [31] to locate the critical point in a system of indented colloids with explicit depletant, for $q = 0.2$. We find that the critical parameters lie within 10% of the results obtained with the effective potential. This confirms the effectiveness of our coarse-graining scheme, which being based on virial coefficient matching is expected to hold for more general colloid and depletant interactions than the idealised ones considered here. However, with explicit depletant, it is not generally possible to investigate the structure of liquid and vapor phases, nor the behavior for smaller $q$, due to the computational cost required. Hence our use of the effective potential in this work.

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\( \eta_s \), the attractive forces between colloids get stronger, so phase separation occurs for smaller values of \( \eta_s \). However, the most striking effect in Fig. 2(d) is the strong decrease (by more than a factor of 2) in the critical density of the colloids \( \rho_c \). The origin of this effect is the very strong lock-key binding that occurs when \( q \) is small which leads to chain formation. Similar properties have also been found in model polymer liquids [32–34] and in the empty liquids that occur in patchy-particle models [35–40]. In our case, however, the emergence of chains and their condensation into a liquid occurs in a system which is not inherently patchy.

Figs. 2(b,c) illustrate the unusual structures of the coexisting phases for \( q = 0.126 \), corresponding to strong lock-key binding. There are large void spaces within the liquid: we identify these by inserting spherical “ghost particles” of size \( \sigma_g \) into the system, wherever this is possible without overlapping an existing colloid (ghost particles may overlap with each other). We take \( \sigma_g = \sigma \) except where otherwise stated, in which case the ghost particles are the same size as the colloids. The ghost particles, shown in Fig. 2(c), highlight the existence of the voids. At this state point, the depletant volume fraction is 5% greater than its critical value \( \eta_c^{vp} \), so the system is significantly outside the critical regime: these voids are not associated with critical fluctuations, but are intrinsic to the liquid states that occur for small \( q \).

Figs. 2(e,f) show the largest voids in two single-phase liquid configurations, at \( q = 0.2 \) and \( q = 0.126 \). To ensure that the configurations are directly comparable, they are both sampled at phase coexistence, with depletant volume fraction \( \eta_s = 1.05 \eta_c^{vp} \). For the larger depletant \( (q = 0.2) \), all voids in the system are relatively small, and the state is similar to a conventional colloidal liquid. For the smaller depletant \( (q = 0.126) \), there is a single large void which spans the entire system (Fig. 2f), so we expect that a test particle of a size comparable with a colloid can travel freely through the liquid: the state is porous on this scale.

The ghost particles allow this effect to be analysed quantitatively. Fig. 3 shows the fraction \( f_{\text{void}} \) of the system volume that is accessible to ghost particles of varying diameters. For \( \sigma_g = \sigma \), this fraction changes by more than two orders of magnitude, as \( q \) is decreased from 0.2 to 0.126. To provide a clear distinction between the porous states at small \( q \) and the more conventional colloidal liquids at larger \( q \), we analysed the \( (\eta_s, \text{dependent}) \) colloid densities \( \rho^{vp} \) for which the ghost particles percolate the system. Dashed lines in Fig. 2(c) indicate the boundaries between percolating and non-percolating void spaces, for \( q = 0.126 \) and \( q = 0.2 \). The lines extend through the super-critical fluid \( (\eta_s < \eta_c^{vp}) \) and into the liquid \( (\eta_s > \eta_c^{vp}) \). We propose that a porous liquid be defined as a state with \( \eta > \eta_c^{vp} \) for which the void space percolates, \( \rho < \rho^{vp} \). We expect that some empty liquids [35, 36, 39] will also fall into this class. Shaded regions in Fig. 2(d) indicate regions where porous liquid states are found, either as pure phases or in coexistence with colloidal vapor. Clearly the single-phase porous liquid can exist only in a density range of width \( \Delta \rho = \rho^{vp} - \rho^{c} \). For \( q = 0.2 \), one has \( \Delta \rho \approx 0.3 \) so porous liquids exist only very close to criticality. However, for \( q = 0.126 \) one has \( \Delta \rho \approx 0.7 \), so there is a significant density window in which porous liquids can be found. We expect this window to expand further at smaller \( q \), indicating that small depletant particles would be most appropriate in experimental searches for such states.

The unusual structure of these porous liquid states originates from a hierarchy of energy scales – the system supports strong lock-key bonds, and weaker back-to-back binding. To illustrate this effect, imagine that the colloids form linear chains, connected by strong lock-key bonds [21]. For large \( \varepsilon_{LK} \), almost all of the available lock-sites are participating in binding – the weaker back-to-back binding then provides both inter-chain and intra-chain interactions, which can cause the chains to aggregate or collapse, as happens in solutions of polymers [32–34, 41]. However, chains of colloids linked by depletion forces are in fact akin to living polymers [42], in that they are continuously breaking and re-forming in the equilibrium state. One can associate the liquid state with an aggregated state of many polymers, while the unusual vapor phase contains polymeric chains that tend to collapse into compact states [recall Fig. 2(b)]. In fact, Fig. 2(d) closely resembles the behaviour of polymers in solution, interacting via a relatively weak non-specific attraction [32–34]. As the polymer length increases in that
FIG. 4. (a) Network motifs for lock-key bonds. Circles indicate particles and arrows indicate lock-key bonds, directed from the lock to the key. The most important local environments are linear chains (one outward and one inward bond) and branching points (two inward and one outward bond). The converse branching case (one inward and two outward bonds) is not possible, due to the particle shape. (b) Clusters of particles can be characterised by networks of arrows. Once a connected cluster of particles includes a single loop, it can grow further only by forming inward bonds (some possible locations for additional bonds are shown with dotted arrows). It follows that each connected cluster can include at most one loop.

system, the critical point moves to lower polymer density and weaker non-specific interactions. The unusual liquid structure also affects critical properties (particularly field-mixing effects), as discussed in SM [25].

This analogy with polymers leads to a prediction for the colloidal system: in the limit of long polymers, one expects the liquid-vapor critical point to occur at the Θ-temperature of the polymer [32–34], where the chain statistics are those of a simple random walk. This requires a weak non-specific attraction, to overcome the excluded volume interactions that cause the polymer to swell. For the colloidal system, the long-polymer limit corresponds to $\varepsilon_{\text{LK}} \to \infty$, in which case one would expect the liquid-vapor critical point to occur when the non-specific (back-to-back) interaction $\varepsilon_{\text{BB}}$ balances the excluded volume swelling effect [43]. This implies that the line of critical points in Fig. 2(a) should tend to a non-zero value of $\varepsilon_{\text{BB}}$, as $\varepsilon_{\text{LK}} \to \infty$, consistent with our results.

However, while this analogy between chains of indented colloids and linear living polymers is appealing, it misses an important feature of the colloidal system. For the particle shape considered here, these colloids readily form \textit{branched} chains. In simple patchy-particle models (with a single type of attractive patch), the presence of branching is sufficient to drive a liquid-vapor phase transition [35–39, 43, 44], but this is not the case for lock-and-key colloids. The reason is the directed nature of the lock-key bond. In Fig. 4, we illustrate different local structures in these systems, and the construction of a bond network. Lock-key bonds are indicated by arrows that point from the lock particle to the key. In this representation, the crucial feature is that a particle may have several inward bonds, but at most one outward bond. It follows that a cluster of particles connected by lock-key bonds may contain at most one loop, as illustrated in Fig. 4(b). In patchy particle models, directed bonds can be realized by introducing more than one kind of bond, which can lead to similar phase behavior to that reported here [43, 44]. This effect can be illustrated using Wertheim’s theory of associating fluids [21, 35, 36, 45], as discussed in SM [25].

These results illustrate the subtle role of the bonding topology in hierarchical fluids. Loops are essential for condensation – they may arise either from undirected branching [35, 36] or from non-specific interactions [32–34]. Yet another point of reference is provided by dipolar fluids [46–48], where formation of ring (or loop) structures acts to suppress condensation, due to the absence of non-specific interactions between closed rings, and the low probability of branching. Thus, while the formation of colloidal polymers can occur for several kinds of particle, the energy scales associated with liquid-vapor phase separation can be quite different, as can the properties of the coexisting phases.

In conclusion, indented colloids with depletion interactions support unusual liquid and vapor phases, which arise from a hierarchy of energy scales for lock-key and back-to-back binding. In particular, for small $q$, liquid phases of indented colloids are porous, characterised by large percolating voids. As shown in Figs. 2 and 3, the volumes associated with these voids can be tuned over several orders of magnitude by varying the properties of the depletant fluid. Indented colloids share some properties with empty liquids [35, 36, 39, 44] and dipolar fluids [46–48]. These similarities indicate that porous liquids might be accessible in those systems too. However, the fine experimental control that can be achieved by manipulation of particle shape and depletant properties [17] makes indented colloids ideal for further experimental study in this direction, offering the potential for preparation of equilibrium gels [35, 39, 49] with controllable properties.

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