Closed-loop liquid-vapor equilibrium in a one-component system

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We report Monte Carlo simulations that show closed-loop liquid-vapor equilibrium in a pure substance. As far as we know, this is the first time that such a topology of the phase diagram has been found for one-component systems.

This finding has been achieved on a two-dimensional lattice model for patchy particles that can form network fluids. We have considered related models with a slightly different patch distribution in the order to understand the features of the distribution of patches on the surface of the particles that make possible the presence of the closed-loop liquid-vapor equilibrium, and its relation with the phase diagram containing the so-called empty liquids.

Finally we discuss the likelihood of finding the closed-loop liquid-vapor equilibria on related models for three dimensional models of patchy particles in the continuum, and speculate on the possible relationship between the mechanism behind the closed-loop liquid vapor equilibrium of our simple lattice model and the salt-induced reentrant condensation found in complex systems.

The recent advances in the chemical synthesis of colloidal particles monodisperse in shape and size have attracted a lot of theoretical work to understand their collective behavior. These new particles can be thought as ‘colloidal molecules’ than can organize themselves by self-assembly into useful structures. Patchy colloids are very interesting because of the possibility of tuning the number, interaction, and local arrangements of their patches. The structure of the self-assembled clusters of the patchy colloids can produce therefore novel macroscopic behavior. On the other hand, primitive models of patchy particles have been used to represent the specific anisotropic interactions between globular proteins in solution. These systems present sometimes reentrant condensation induced by variations of salt concentration. This behavior is probably associated to effective charge inversion of proteins in the reentrant regime via binding of multivalent counterions. The mechanisms involved in the condensation and the dependence of the reentrant behavior with the temperature are not well understood, but it is likely that specific (patchy-like) interactions play an important role.

Given the complexity of both kinds of problems: self-assembling of patchy colloids, and phase behavior of protein solutions, it seems important the study of simple models of patchy particles, in order to understand the influence of the numbers of patches and their distribution on the surface of the macromolecules (or colloidal particles) on the phase behavior and aggregation mechanisms. Hopefully, understanding the phase behavior of simple models will be useful to gain insight in the behavior of those complex systems.

Recently it has been found that patchy models with two types of patches, A, and B in which only A − A, and A − B interactions are attractive can exhibit liquid-vapor equilibria (LVE) with liquid phases behaving as ‘empty liquids’. For these systems the term empty liquid refers to the fact that at low temperatures the density of the liquid phase, ρL on the binodal becomes very small at low. Actually ρL approaches zero in the limit T → 0. The empty liquid phenomenology has been found for hard sphere particles that carry on the surface two patches of type A located at opposite poles of the sphere, and several patches of type B elsewhere on the surface. The potential energy is defined as a sum of bonding interactions between pairs of patches belonging to different particles.

Within this interaction scheme, and assuming for simplicity that the interaction between two particles is zero if neither and AB nor an AA bond between them is formed, the phase diagram basically depends on the ratio between the bonding energies of the two types of possible bonds: \( y = \epsilon_{AB}/\epsilon_{AA} \). From both Monte Carlo Simulation and Wertheim’s perturbation theory it is known that the regime of empty liquid may occur for \( y < 1/2 \). Theoretical approximations predict also a lower limit of this ratio, namely \( y_l = 1/3 \). Simulation results are consistent with the existence of such a lower bound \( (y_l > 0) \) for the empty liquid regime. On the other hand, for \( y = 0 \), the systems at low temperature are expected to form linear chains, which, may give rise to orientational ordered (nematic) phases at moderate densities. This orientational order can also appear as a second phase transition for values of \( y < 0.5 \) where the liquid-vapor is present. The topology of the empty liquid phases is well understood. At low temperature (where the empty liquid regime occurs) and not too low density almost all the A-patches are participating in a bond, the liquid phases can be then described as a network fluid composed by (almost) straight chains of spheres linked by sequences of AA bonds. Each of the terminal spheres of the chains is connected to another straight chain, by an AB bond. In the empty liquid regime the reduction of the temperature implies an increase of the typical length of the AA chains, which in turn, produces a reduction of the density of the liquid.
phase. This is due to the fact that AA bonds for \( y < 1/2 \).

At this point, we can ask ourselves to what extent this physical picture remains valid if the nature of the colloid surface is changed, and the two \( A \)-patches are no longer located at opposite poles, but somewhat closer. We can define a bending angle, \( \theta_{ijk} \) for a triplet of particles, \( \{i, j, k\} \) in which \( j \) is linked through AA bonds to both \( i \), and \( k \), as:

\[
\cos \theta_{ijk} = \frac{\vec{r}_{ji} \cdot \vec{r}_{jk}}{|\vec{r}_{ji}| |\vec{r}_{jk}|}.
\]

Taking into account that the size of the patches is supposed to be small in order to preserve the conditions of only one bond per patch, the mean value of \( \cos \theta_{ijk} \) will fulfill: \( (\cos \theta_{ijk}) \approx \cos \alpha_{AA} \), where \( \alpha_{AA} \) is the angle between the vectors that connect the center of the sphere with the centers of its \( A \) patches. Notice that reducing the value of \( \alpha_{AA} \) from 180\(^\circ\) implies an increase the probability of forming rings of particles connected by AA-bonds, since the system can reduce its energy by forming cycles. Moreover, when one of these cycles is formed all the \( A \)-patches of its particles are bonded, and therefore these patches cannot bond other chains, which in turn can reduce the connectivity of different parts of the system, and eventually inhibit the appearance of LVE.

Now taking into account that for \( \alpha_{AA} = 180^\circ \) and appropriate values of \( y \) one can find the empty liquid regime at low temperatures, and that reducing the value of \( \alpha_{AA} \) might, in principle, destroy the LVE, it seems interesting to know what happens between the two scenarios. In order to investigate this issue, we have found convenient to analyze a simple lattice model whose results are expected to be representative of what can be found for models in the continuum, as it has been shown to occur in related models\[^{11,17}\]. The computation of phase diagrams is usually much cheaper in terms of CPU time in lattice models than in models defined on the continuum. In spite of their simplicity, lattice models can often capture the essential features of the phase diagrams of associating molecules and network fluids\[^{11,17,25}\].

We have considered models on the triangular lattice (See Fig. 1). Sites on the lattice can be either empty or occupied by one particle. Each particle carries two sites (of type A) that point to two of the nearest neighbor (NN) sites. Two particles, \( i, j \); being NN interact with an energy \( u_{ij} = -\epsilon \) if each one points to the other with one of its \( A \)-patches (AA bond); if only one of the particles points to the other with one of its \( A \) patches, we have \( u_{ij} = -\gamma \) (AB bond, with \( 0 < \gamma \leq 1/2 \)); and otherwise \( u_{ij} = 0 \).

We have studied three models (See FIG. 1), which will be denominated as o-, m- and p-2A4B models (by borrowing the prefixes from the organic chemistry nomenclature for the positions of the substituents in aromatic cyclic compounds: ortho, meta and para). The three models differ in the arrangements of the patches. In o-2A4B we have \( \alpha_{AA} = 60^\circ \), for m-2A4B \( \alpha_{AA} = 120^\circ \), and finally p-2A4B model considers \( \alpha_{AA} = 180^\circ \). Notice that the latest model is the natural translation of previous works for empty fluids into the triangular lattice. In the o-2A4B model cycles of AA bonds are easily formed, the smallest possible cycle contains just three particles, in the m-2A4B model we can find cycles of six AA-bonds, whereas in the p-2A4B models no cycles are possible. In order to compute the phase diagram we have made use of simulation strategies that were described in previous papers\[^{11,17,19}\]; namely Wang-Landau multicanonical simulations\[^{11,20}\] to locate critical points and some liquid-vapor coexistence points; and Gibbs-Duhem integration to trace the binodals. Some special techniques have been developed in the simulation procedures to improve the sampling, including efficient cluster algorithms for the p-2A4B model. Technical details will be published elsewhere\[^{27}\].

We have not found evidence of LVE for the o-2A4B model. This seems plausible, since at low temperature and moderate density the particles can easily arrange themselves in triplets that minimize the energy and block the development of an extended network of patch-patch bonds. Both m-2A4B and p-2A4B models show LVE for some range of values in the region \( y < 1/2 \). The p-2A4B model shows, as expected, a phase diagram (See FIG 2) that fully resembles those of the analogue models in the continuum\[^{9,10}\], and on the square lattice\[^{11}\]; i.e. it appears the regime of empty liquid.

The key result of this paper is, however, the phase diagram of the m-2A4B model (shown in Fig. 3). For \( y = 0.50 \) we get a similar behavior in m-2A4B and p-2A4B models.
2A4B models, i.e., we find typical LVE binodals. However, in the m-2A4B model we find that the LVE for some range of values of \( y \) (\( y_l < y < 1/2 \)), with \( y_l \approx 0.43 \), exhibits two critical points, that will be named, according to their critical temperature as lower critical point (LCP) and upper critical point (UCP). The LVE only occurs between these two temperatures, which of course depend on the value of \( y \). The critical points were determined through a finite-size scaling analysis on the multicanonical simulation similar to that explained in Ref. [11] considering typically system sizes in the range \( 12 \leq L \leq 48 \) for the m-2A4B model (with \( L^2 \) being the total number of sites). The scaling behavior was found to be fully consistent with the two-dimensional Ising criticality for both LCP and UCP.

The existence of reentrant phase equilibria is well known to appear in some binary mixtures. However, for one-component systems it is very unusual to find fluid-reentrant critical behavior. Roberts et al. [20] found such a behavior for a lattice model of network-forming fluids: However the closed-loop coexistence found in Ref. [20] involves liquid phases. In our case, the phase equilibria can be appropriately described as LVE, by considering that modifying the value of the interaction parameter \( y \) the reentrant phase diagrams can be connected continuously to typical LVE diagrams that appear for \( y \geq 1/2 \). Along this path the LVE envelope varies smoothly for \( T > 0 \).

In the previous paragraph we have indicated that the closed-loop LVE occurs for any value of \( y \) in the range \((y_l, 1/2)\), however our simulation results only support, in principle, the reentrance for \( y_l < y \leq 0.46 \). As \( y \) approaches 1/2 it becomes a very hard task to compute the LCP using Monte Carlo simulation, since it occurs at very low temperatures. However, we can make use of the scaling criteria introduced in Ref. [11]. At very low temperature, the probability of finding non-bonded A patches becomes negligible small, therefore we can consider as a good approximation to analyze the phase equilibria considering only those configurations in which each patch A forms either an AA or an AB bond. Under this assumption the potential energy of the model can be written as: [11] \( U/\epsilon = -N + N_{AB} (1/2 - y) \), where \( N \) is the number of occupied sites and \( N_{AB} \) the number of AB bonds. Therefore the phase behavior at low temperature, \( T \), will basically depend on the ratio \((1/2 - y)\epsilon/k_BT\) (with \( k_B \) being the Boltzmann constant). Then the temperature at the LCP is expected to scale for \((1/2 - y) \to 0^+\) as: \( T_{LC} \propto (1/2 - y) \). The low temperature phase diagram of the m-2A4B model has been found to fulfill very well this scaling at low temperature (See FIG. 3). Of course the reliability of this prediction depends on the absence of additional possible phase transitions that could occur in the model. Notice that the p-2A4B model is expected to exhibit and order-disorder transition [11] [14–16]. Such a transition will merge with the LV transition as \( T \to 0 \). In the case of the m-2A4B model we have not found any signature of a second phase transition at the temperature range where the close-loop LVE occurs. The origin of the different topologies of the LVE phase diagrams of p- and m-2A4B models can be explained by looking at representative configurations of both models at low temperature (FIGS 5–7). In the p-2A4B model the end particles of each chain are bonded via AB-bonds to two other chains on the system, then on average each chain is bonded to four neighbor chains \( (N_{AB} = 2N_{chains} \text{ at low } T) \). At very low temperature in the m-2A4B model we can see (FIG 6) the formation of rings with different number of particles, and the existence of AB intra-chain bonds. As a consequence the number of available A patches to form interchain bonds is reduced, and the bonds do not produce a macroscopic bond network. Notice that as one increases the temperature (See FIG 7) there is a reduction of the number of rings due to en-
tropic effects. This enhances the connectivity and the phase separation can take place, by a mechanism similar to that present in the $p$-$2A4B$ model.

It has to be emphasized that the origin of the reentrance of the LVE is not just the angle between patches in the colloidal particles, but the fact that at low temperature the particles have the trend to self-assemble forming small aggregates (usually rings) in which most of their sticky spots are saturated by intra-aggregate interactions. This process might produce a reduction of the effective valence of the aggregates with respect to that of the independent particles, which in turns reduces the possibility of bond network formation and subsequently hinders the ability of the system to condense.

The mechanism underlying the reentrance of the LVE is rather different to that appearing in binary liquid mixtures, in which the reentrant solubility at low temperature is attributed to the effects of large anisotropic interactions (hydrogen bonding) between the two components, whereas the demixing at intermediate temperatures is due to Wan der Waals interactions, which favor the interaction between pairs of particles of the same species.

Notice that the results presented in this communication resemble, to some extent, those reported by Sciortino et al. for a system of Janus particles, and by Reinhardt et al. for systems with competition between phase separation and self-assembly. In both cases, at low temperature, the vapor density at LVE increases on cooling. However in these systems no LCP appears, due to the presence of crystalline phases that make both liquid and vapor metastable prior the possible presence of the LCP.

The question that arises after having found the closed-loop LVE in the lattice model for systems with two A-patches with $\alpha_{AA} = 120^\circ$, is to what extent these results can be extrapolated to models in the continuum, either in two or three dimensions. In principle, one can expect
that for 2D-models the formation of rings, which in turn may produce the closed-loop LVE, will be enhanced for models with angles $\alpha_{AA}$ that fit those of regular polygons $\alpha_{AA} \approx \frac{n-2}{n} \pi$, with $n = 4, 5, 6, \cdots$. For 3D models one can also expect the formation of rings, in this case the presence of additional degrees of freedom in the chains will give the systems more flexibility for the formation of rings, however, on the other side, the larger space dimensionality of the system will favor the presence of open chains due to entropy effects. In any case the pursue of the conditions whether closed-loop LVE will be obviously not so straightforward as in the current lattice models. We plan to work on these issues in the future.

As a summary, we have shown how patchy models on the triangular lattice can exhibit closed-loop LVE on one-component systems. The basic physics underlying this behavior is the reduction of valence at low temperature by the formation of compact structures at low and moderate densities that reduce the amount of connectivity between different parts of the systems. The phase diagram depends dramatically on the angle between the A patches. As far as we know, the work presented here constitutes the first model exhibiting closed-loop LVE on a one-component system. Finally, self assembling mechanisms similar to those appearing in the simple models presented in this paper, might play some role in the reentrant condensation phenomena of globular proteins\cite{8} and polyelectrolytes \cite{34}.

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