

## Liquid-Vapor Transition Driven by Bond Disorder

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We report grand-canonical Monte Carlo simulations of an equimolar mixture of hard colloids coated with long polymers that have a complementary functionalization. Such systems have the potential to function as self-healing materials. Under conditions where the complementary polymer ends are strongly associated, we observe a first-order vapor-liquid transition from a dilute gas of colloidal dimers to a dense, liquidlike phase. This transition is driven exclusively by the increase in entropy associated with bond disorder—an effect that was predicted theoretically by Zilman *et al.* [Phys. Rev. Lett. **91**, 015901 (2003)]. Our simulations rationalize experimental observations by Schmatko *et al.* [Soft Matter **03** (2007) 703.]

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In 1957, Alder and Wood demonstrated in numerical simulations that hard spheres could freeze [1]. This work created quite a stir [2] because it showed a crystal phase could have a higher entropy than the liquid phase at the same density. This ran against the conventional wisdom that attraction was needed to cause crystallization of simple liquids [3]. Since then, many other “entropy-driven” phase transitions have been identified (see, e.g., [4]). For instance, a mixture of hard colloids and nonadsorbing polymers can undergo a liquid-vapor transition because, upon condensation, the loss in entropy of the colloids is compensated by the gain in entropy of the polymers [5,6]. Yet, this transition is not as surprising as it may seem because, to a first approximation, the polymers induce an attractive pair interaction between the colloids. This makes the mixture of purely repulsive polymers and colloids equivalent to an effective one-component system of colloids with mutual attraction. It is this effective attraction that drives the vapor-liquid condensation. More surprising was a theoretical study by Zilman *et al.* [7] that showed that a purely entropic condensation transition is possible in a system of inert droplets coated with strongly bound telechelic polymers [8]. In the system studied in Ref. [7], the telechelic polymers could redistribute over the droplets in such a way that they maximized their entropy. In the present Letter, we report numerical simulations that support the mean-field scenario of Ref. [7]. However, there are some differences in the underlying model. Most importantly, we consider a suspension of colloids grafted with long polymers that have “sticky” ends. These polymers can reversibly form bridges between the colloids. In this model, every colloid has a fixed number of linkers. A possible realization of the system that we study is a mixture of colloids, chemically coated with very long strands of double-stranded DNA (dsDNA), functionalized with a single-stranded (ssDNA) linker. These linkers can bind via complementary ssDNA linkers to other DNA-coated colloids [9,10]. These systems have the interesting property that individual bonds may be weak but, because of the

large number of bonds between two particles, the materials tend to be mechanically strong. Moreover, they should be “self-healing” [11]: if two blobs of a dense network of colloids coated with long DNA are brought into contact, they should be able to reconnect in such a way that the interface disappears. The time scale over which this happens depends on the binding strength between the complementary ssDNA fragments.

In what follows, we refer to the particles with complementary functionalization as *A* and *B*. Colloids type *A* and *B* are identical except that they are coated with complementary strands of ssDNA. We consider the situation where the radius of gyration of the polymer is comparable to the size of the colloids. In our simulations, we considered 1:1 mixtures of hard colloids coated with *n* sticky polymer arms. We consider the cases  $n = 2 - 8$ —the ratio of the radius of gyration of the polymer to the radius of the colloid was fixed at 0.3, which is a number that can easily be achieved in experiments on DNA-coated colloids [9,10]. We describe the individual polymer arms as soft colloids, using the approach of Ref. [12,13]. In particular, the work of Ref. [13] strongly suggests that the soft-colloid picture is to a good approximation transferable to the interaction between polymer moieties that are bound together. In the present Letter, we simply postulate that all polymer-polymer interaction are transferable and are of the form

$$\frac{V_{p-p}(r)}{k_B T} = 2 \exp\left[-0.7\left(\frac{r}{r_g}\right)^2\right]. \quad (1)$$

The effective interaction between a free polymer and a hard colloid is not known in closed form [12]. We therefore performed lattice simulation to compute the potential of mean force acting between a self-avoiding polymer and a hard colloid with a size ratio 1:3 (see caption of Fig. 2). We found that the repulsive interaction between polymer and colloid is again transferable (i.e., it is the same for bound and unbound polymers). As in Ref. [13], the attractive

interaction between a polymer and hard colloid is well described by a simple harmonic spring.

To bring out the entropic nature of the phase transitions, we consider the case where the binding constant is very large, implying that there are no free  $A$  or  $B$  ends [14]. However, we do assume that bonds can switch, such that the topology of a resulting network can change. In Fig. 3, we illustrate how two pairs of colloids can be reconnected by a switching of the bonds between complementary DNA's on colloids of type  $A$  and  $B$ . The acceptance of the trial moves is determined by the ratio of the partition functions of the bridging DNA (approximated as harmonic springs). We performed Grand-Canonical Monte Carlo simulations [15] on such a system of functionalized colloids [16]. In our simulations, we chose the thermal energy  $k_B T$  as the unit of energy and  $\sigma$ , the diameter of the colloid, as the unit of length. We considered a system with a volume  $V = 1000\sigma^3$ . At very low densities, this system will form a gas of  $AB$  dimers. The reason is that, because the polymers are very long, all polymers on an  $A$  colloid can bind to a complementary polymer on a  $B$  colloid. In contrast to the model considered in Ref. [7], loop formation and, more importantly, polymer fractionation, cannot occur. The resulting dimers are “inert” as they have no unsatisfied bonds.

Upon increasing the chemical potential of the system, we find that the colloids undergo a very sudden transition from a low-density “dimer” phase to a uniform, high-density phase where almost all colloids belong to a single, system-spanning cluster (see Fig. 1). We stress that, as the degree of association of the polymers is 100%, independent of density, there is no change in the binding energy of the system upon condensation. The condensation transition is completely driven by the gain in entropy associated with an increase of the number of allowed network topologies. In Fig. 4, we plot the density of the system against fugacity of dimers  $f_D \equiv \exp(\beta\mu)$ .  $f_D$  can be interpreted as the density of a gas of noninteracting dimers that is in osmotic equilibrium with the interacting system, and  $\mu$  is the

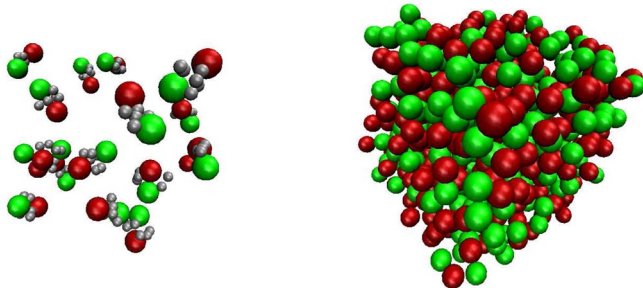


FIG. 1 (color online). Snapshot of a low-density (left) and high-density (right) system of a 1:1 mixture of hard colloids (shown as big dark and light spheres, respectively) coated with complementary sticky polymers (shown as small spheres in left snapshot).

chemical potential of dimers. Figure 4 shows that at very low densities, the dimer concentrations in the system are equal to the fugacity  $f_D$ , as it should be. The location and magnitude of the density jump depend on the number of polymers per colloid. For the case where we have only two arms per colloids, the magnitude of the density jump is very small (possibly zero): it could not be resolved in our simulations. It is not surprising that particles with two arms should exhibit qualitatively different behavior because particles linked to at most two neighbors cannot form percolating clusters. Nevertheless, there still is an entropic advantage associated with the formation of a dense phase, as a single configuration can be decorated in many distinct ways by polymer bridges.

The discontinuous transition from vapor to the dense phase is also reflected in the behavior of  $N_c$ , the average number of distinct connected neighbors per particle, shown in Fig. 5. At low densities, where all colloids form dimers,  $N_c = 1$ . With increasing chemical potential,  $N_c$  appears to undergo a sudden, possibly discontinuous change, except for the case  $n = 2$  where there is no percolation in the dense phase.

In order to bring out the essential features of the entropy-driven condensation reaction, we constructed a simple cubic (and therefore unfrustrated) lattice-gas model of our continuous system. We performed Grand-Canonical

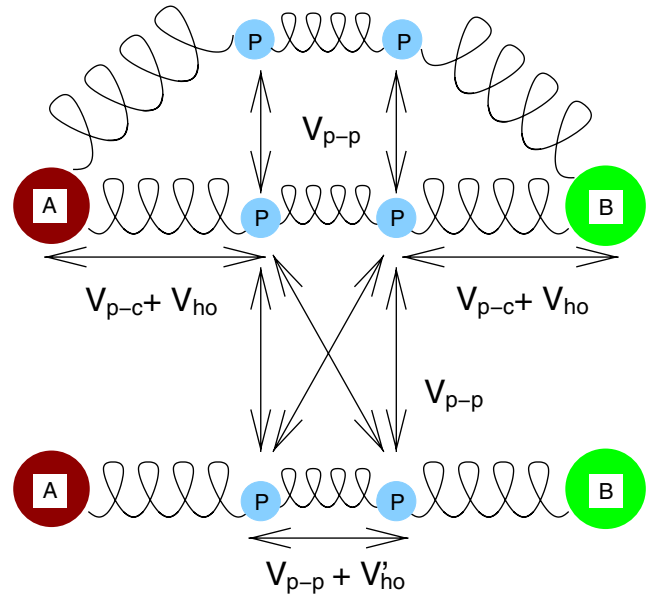


FIG. 2 (color online). Pair-potentials: The transferable repulsive potential between two polymers,  $V_{p-p}$ , has the form given by Eqn. (1). The transferable potential between polymer and colloid is repulsive and has the form  $V_{p-c}(r) = 580 k_B T \exp[-(r/r_{col})^2/0.23]$ . An harmonic spring [ $V_{ho}(x) = k_B T x^2 / (2R_g^2)$ ] is assumed to tether the center of mass of each polymer to “its” colloid. When two complementary DNA's are bound, they are assumed to be connected by a harmonic spring ( $V'_{ho}$ ) that is half as stiff as  $V_{ho}$ .

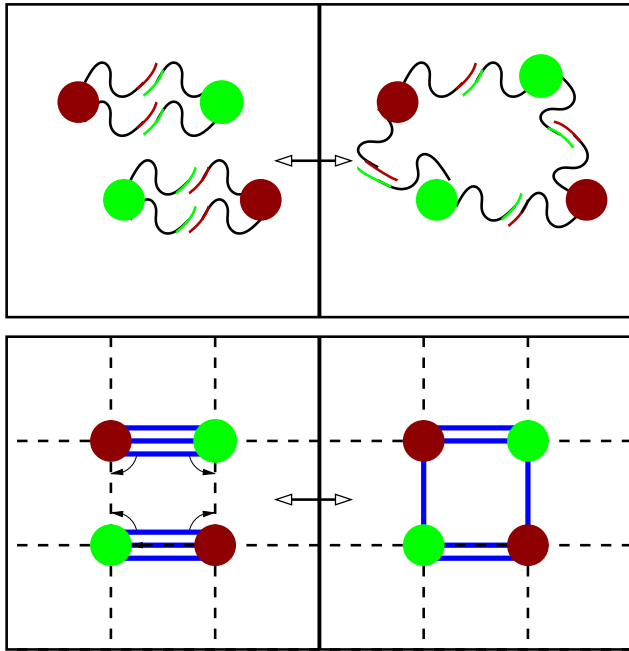


FIG. 3 (color online). Bond-switch trial moves in off-lattice (top) and lattice (bottom) models. In the lattice simulation, bond switches (if possible) are always accepted. In the off-lattice case, the acceptance is dictated by the change in the free energy of the polymers “springs” upon reconnecting.

MC simulations on the 3D lattice model that has the following features: 1. A lattice site is either empty, or occupied by an  $A$  or a  $B$  particle 2. There are equal numbers of  $A$  and  $B$  particles 3. Every  $A(B)$  particle is connected with exactly  $n$  bonds to nearest neighbor  $B(A)$  particles. In addition to dimer insertion or removal moves, we perform bond switches that conserve the total number of bonds per particle (see Fig. 3). In this way, we ensure that there are no unsatisfied bonds. Figure 6 shows the relation between the

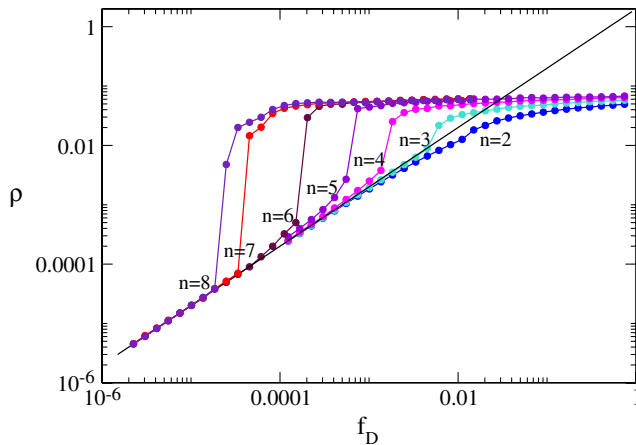


FIG. 4 (color online). Off-lattice grand-canonical simulation; Number density  $\rho$  versus the dimer fugacity  $f_D$ . The straight line indicates the ideal gas behavior.

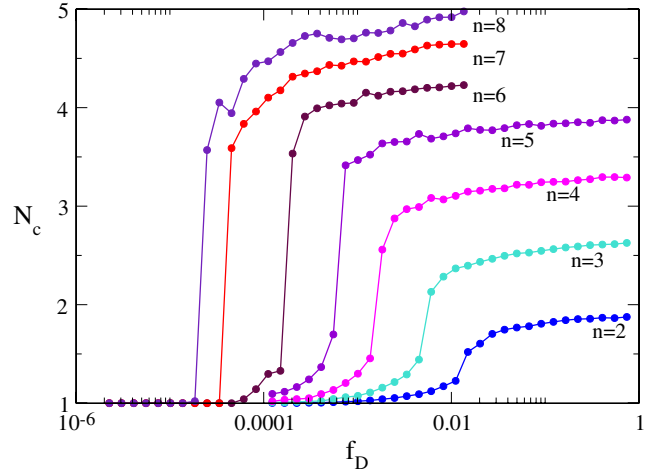


FIG. 5 (color online). Off-lattice grand-canonical simulation; The average number of distinct connected neighbors versus  $f_D$ .

occupation of the lattice and the fugacity of dimers. The behavior shown in Fig. 6 is qualitatively very similar to that of the colloid-polymer system.

One of the characteristic features of a first-order transition is occurrence of hysteresis. As the lattice simulations are much faster than their off-lattice counterparts, it is easier to probe the hysteretic behavior in lattice simulations. We studied hysteresis by initializing the system in the cluster phase and lowering the chemical potential. We do not observe hysteresis for systems with three bonds per colloid. However, systems with a larger number of bonds per colloid show clear hysteresis loops. This is hardly surprising as networks of multiply-bonded particles are relatively “immune” to the fluctuations that are needed for cluster breakup [17].

Unfortunately, we cannot compare our results directly with the mean-field predictions of Ref. [7] because that work considers colloids coated by telechelic polymers where the number of polymers bound to any given colloid

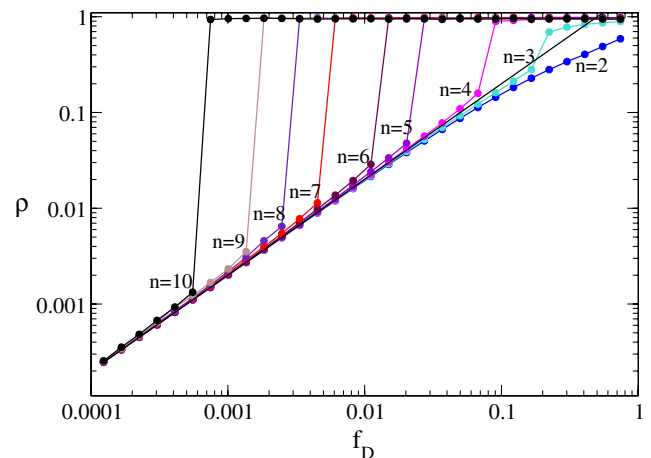


FIG. 6 (color online). Lattice grand-canonical simulation;  $\rho$  versus  $f_D$ . The straight line indicates the ideal gas behavior.

is not fixed: due to fractionation, it will be higher in the dense phase than in the dilute phase. In contrast, the linkers in the system studied here cannot fractionate, nor can they loop back onto the same particle. If we consider the limit of the mean-field predictions of Ref. [7] for the case where telechelics can only form bridges and no loops, the phase diagram that is predicted by Ref. [7] shows some similarity to the one that we observe. However, the finite-density dimer phase that we observe before condensation is not found in Ref. [7], presumably because it is preempted by polymer fractionation.

Thus far, our discussion of models for polymer-coated colloid system focused on the case where the polymer endpoint are always bound to complementary polymers. This allowed us to show unambiguously that the condensation transition is of entropic nature. However, in real systems of DNA-coated colloids, the binding strength is finite. Using Grand-Canonical Monte Carlo simulations, we have verified that lowering of the polymer-polymer association constant does not qualitatively change the scenario that we have observed, as long as the binding strength is above a critical value below which the first-order transition disappears. We therefore expect that the entropic condensation should be observable in real DNA-coated colloid systems, provided that the polymers are long enough to allow  $n$  of them to bridge the same pair of colloids. Clearly, this condition is not fulfilled for polymers that have a radius of gyration that is much smaller than the radius of the colloids [18]. Coating colloids by long polymers is feasible: Schmatko *et al.* [9] reported confocal microscopy studies of colloids coated with  $\lambda$ -DNA with a radius of gyration equal to 1.6 times the colloid radius. These experiments observed strong clustering of the colloids, followed by structural arrest. This is due to the strong DNA hybridization under the experimental conditions studied in Ref. [9]. In order to observe the underlying phase transition predicted here, the experiments would have to be carried out under conditions where the DNA network is able to rearrange on experimental time scales.

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