



Mobile Linkers on DNA-Coated Colloids: Valency without Patches

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Colloids coated with single-stranded DNA (ssDNA) can bind selectively to other colloids coated with complementary ssDNA. The fact that DNA-coated colloids (DNACCs) can bind to specific partners opens the prospect of making colloidal “molecules.” However, in order to design DNACC-based molecules, we must be able to control the valency of the colloids, i.e., the number of partners to which a given DNACC can bind. One obvious, but not very simple approach is to decorate the colloidal surface with patches of single-stranded DNA that selectively bind those on other colloids. Here we propose a design principle that exploits many-body effects to control the valency of otherwise isotropic colloids. Using a combination of theory and simulation, we show that we can tune the valency of colloids coated with mobile ssDNA, simply by tuning the nonspecific repulsion between the particles. Our simulations show that the resulting effective interactions lead to low-valency colloids self-assembling in peculiar open structures, very different from those observed in DNACCs with immobile DNA linkers.

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During the past two decades there has been substantial progress in the functionalization of colloidal particles with various ligand-receptor pairs such as complementary single-stranded DNA (ssDNA) sequences [1,2]. ssDNA grafting makes it possible to control the specificity of interparticle interactions [3–5]: two grafted ssDNA sequences bearing complementary Watson-Crick sequences can hybridize to form a double-stranded DNA (dsDNA) bridge between two particles, thus generating an effective attraction. In contrast, particles coated with noncomplementary sequences do not attract. Exploiting this mechanism to tune colloidal interactions, DNA functionalization has enabled the design of a variety of self-assembling nanoparticle lattices [6–8], thus opening the way towards new functional materials [9]. However, at present our ability to design arbitrary structures is limited by the fact that it is not straightforward to control the coordination number (i.e., valency) in such colloidal structures. For instance, low-valency colloids can self-assemble into open structures [10] that do not form if interparticle interactions are pairwise additive and isotropic. On the atomic scale, carbon can form diamonds, where atoms are four-coordinated, because carbon atoms have a well-defined electronic valency. In contrast, noble gases interact through (nearly) pairwise additive interactions and only form dense structures, such as fcc and bcc.

If we wish colloidal particles to self-assemble into a diamond lattice, we need to control their valency. Colloidal diamond lattices are intensively studied because such crystals would facilitate production of photonics band gap materials [11,12]. However, their direct self-assembly is currently hampered by the lack of simple ways to control colloidal valency.

Considerable progress has been made in the (multistep) synthesis of colloids with a well-defined valency encoded through the careful positioning of ssDNA linkers in patches at specific positions. Wang *et al.* [13] have shown that it is possible to produce colloids with patches in precise locations; DNA can be grafted selectively onto these patches. In this Letter, we present calculations that indicate that it should be possible to enforce the valency of colloidal particles without “statically” encoding it in their structure. Instead, many-body effects naturally arising in DNA-coated colloids (DNACCs) with mobile linkers can be exploited to this purpose. Moreover, we show that valency control can be tuned by changing the grafting density of inert strands, temperature, or salt concentration.

As an illustration, we consider a binary system of colloids, *A* and *B* (see Fig. 1), covered with mobile n_α and n_β DNA strands. Each strand terminates in a short sequence of complementary ssDNA, α and β . Such colloids

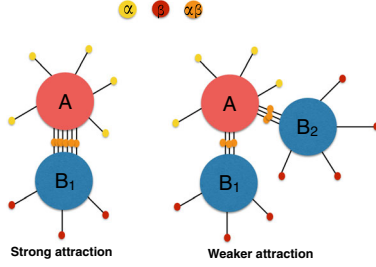


FIG. 1 (color online). Schematic representation of our system. Colloid A bears DNA sequences that are complementary to those on B . Given that a fixed number of linking DNA exists, when multiple possible partners are present the total number of bonds between colloids decreases, hence their binding free-energy. This is the basis of the multibody effect controlling valency.

have been previously synthesized in various ways, as described in Refs. [14,15]. When the suspension is cooled below a specific (sequence-dependent) temperature, the ssDNA will hybridize with its complement, forming bonds between the DNACCs. Reliable techniques exist [16,17] to predict the strength of attraction between A and B colloids as a function of temperature. Same-type colloids (i.e., A - A or B - B pairs) repel each other due to the steric repulsion between nonbinding ssDNA.

The interactions between colloids coated with mobile ssDNA are not pairwise additive. Consider two DNACCs, A and B_1 , brought to a distance where hybridization is possible. These two colloids will experience an attraction with a strength that increases with the number of bonds. If a second colloid of type B (here, B_2) is inserted in the system at the same distance from colloid A as colloid B_1 (Fig. 1), any of the mobile DNA strands on A can now hybridize with either B_1 or B_2 . The symmetry of the problem requires that on average the same number of bonds will form between A and B_1 and A and B_2 . Since the strength of the effective interparticle interaction is an increasing function of the number of bonds and given that there is a finite number of strands to form bonds, the presence of a third colloid lowers the effective attraction between two particles. This many-body effect is at the basis of the mechanism controlling valency in this class of colloids. However, and this is our key point, the decrease of the binding strength per bond with the number of neighbors is *not* enough to control the colloidal valency, as the maximum number of neighbors is determined by the total cluster interaction energy: each new bonding partner makes interparticle interactions weaker, but adds one more interacting pair. In the absence of nonspecific repulsions, the highest coordination numbers are most favorable. However, if we add nonspecific repulsions to the colloidal interactions, we can tune the optimal coordination number.

To make our argument quantitative, we calculate the effective interactions in different clusters. To this end, we need an expression for the interaction free-energy of a

cluster where the positions of the colloids are fixed at arbitrary positions. We then relax the fixed-positions' constraint and perform Monte Carlo (MC) simulations where the colloid positions are allowed to achieve their equilibrium distribution.

Our expression for the effective interaction between DNACCs is based on the mean-field approach developed in Refs. [16,17], and used to describe a variety of systems [18–21]. As shown in Ref. [17], this approach yields quantitative agreement with MC simulations.

Reference [17] showed that the attractive part of the effective interaction free-energy induced by a system of ligand-receptor pairs (e.g., complementary DNA strands) with bonding energies $\beta\Delta G_{ij}$ (where i and j label two specific binding partners) is approximated remarkably well by the following expression:

$$\beta F_{\text{att}} = \sum_i \ln p_i + \sum_{i<j} p_{ij}, \quad (1)$$

where p_i is the probability that linker i is unbound and p_{ij} is the probability that linkers i and j form a bond. These quantities are given by solving the following set of equations:

$$p_{ij} = p_i p_j e^{-\beta\Delta G_{ij}}, \quad (2)$$

$$p_i = 1 - \sum_j p_{ij}, \quad (3)$$

where $\Delta G_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ is the free energy for the formation of a single bond between the i - j pair. The latter can be rewritten in a more insightful form as [16,22]

$$\beta\Delta G_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \beta\Delta G_0 + \beta\Delta G_{\text{cnf}}(\mathbf{r}_i, \mathbf{r}_j), \quad (4)$$

where $\beta\Delta G_0$ is the hybridization free-energy for two DNA strands in solution. $\beta\Delta G_0$ depends only on the DNA sequence and is a function of temperature and salt concentration [23,24]. $\beta\Delta G_{\text{cnf}}(\mathbf{r}_i, \mathbf{r}_j)$, an explicit function of the grafting points $\mathbf{r}_i, \mathbf{r}_j$, is the configurational cost associated with the bond formation, and has been previously quantified both for single and double-stranded DNA [16,23].

For the case of mobile DNA, all strands with the same recognition sequence that reside on the same colloid are equivalent since they cannot be distinguished by their grafting position. In this case, the correct procedure is to replace $e^{-\beta\Delta G_{ij}(\mathbf{r}_i, \mathbf{r}_j)}$ by its average over all possible grafting points. Hence, the effective, single-bond strength between types α and β residing on colloids A and B , respectively, will be given by

$$\begin{aligned} \Xi_{\alpha\beta}(\mathbf{R}_A, \mathbf{R}_B) &= \langle \exp(-\beta\Delta G_{\alpha\beta}) \rangle_{|\mathbf{R}_A, \mathbf{R}_B} \\ &= \frac{\int_{S_A, S_B} \exp[-\beta\Delta G_{\alpha\beta}] d\mathbf{r}_\alpha d\mathbf{r}_\beta}{S_A S_B}, \end{aligned} \quad (5)$$

where the average is taken keeping the center of colloid $A(B)$ at $\mathbf{R}_{A(B)}$ fixed and $S_{A(B)}$ is the area of the colloid. In Eq. (5) we use Greek subscripts to label a strand type [rather than *specific* strands as in Eqs. (3), (2)]. We follow this convention from now on. Using Eqs. (2), (3) to replace p_{ij} in Eq. (1), and considering that strands of the same type are equivalent and, hence, have the same value for Ξ , we obtain

$$p_\alpha + \sum_{\gamma=1}^{N_{\text{types}}} n_\gamma p_\alpha p_\gamma \Xi_{\alpha\gamma}(\mathbf{R}_\alpha, \mathbf{R}_\gamma) = 1, \\ \dots \\ p_{N_{\text{types}}} + \sum_{\gamma=1}^{N_{\text{types}}} n_\gamma p_{N_{\text{types}}} p_\gamma \Xi_{N_{\text{types}}\gamma}(\mathbf{R}_{N_{\text{types}}}, \mathbf{R}_\gamma) = 1, \quad (6)$$

and

$$\beta F = \sum_\gamma n_\gamma [\ln p_\gamma + 1/2(1 - p_\gamma)]. \quad (7)$$

Equation (6) is a system of N_{types} equations, one for each possible nonequivalent strand in the system: its solution is an explicit function of all colloidal positions $\{\mathbf{R}\}$. Hence, if two strands cannot bind because they are grafted on distant colloids, $\Xi = 0$ and the sum over γ in Eq. (6) effectively runs only on strand types on neighboring colloids. Equations (6), (7) are key results of this Letter. They allow us to calculate the bond-mediated binding energy for any two generic objects interacting via mobile linkers. We show in the Supplemental Material [25] that for mobile linkers these formulas become exact in the limit of large numbers of linkers.

Let us first consider clusters made of 1 colloid of type A surrounded by N_B colloids of type B at equivalent positions (by symmetry only two types of strands are present, α and β) for which Eqs. (6), (7) become

$$p_\alpha + N_B n_\beta p_\alpha p_\beta \Xi = 1, \\ p_\beta + n_\alpha p_\alpha p_\beta \Xi = 1, \quad (8)$$

and

$$\beta F_{\text{clus}}^{\text{bond}} = n_\alpha (\ln p_\alpha + 1/2 - p_\alpha/2) \\ + N_B n_\beta (\ln p_\beta + 1/2 - p_\beta/2). \quad (9)$$

Equation (9) (closed-form solution in the Supplemental Material [25]) gives only the contribution due to bond formation between ligands, and is purely attractive. For typical DNACCs realizations, other terms due to van der Waals forces or electrostatic interactions are negligible at the binding distance between colloids of a few nanometers imposed by the DNA length [22]. Hence, their effect can be safely disregarded. However, other terms due, for example, to the presence of inert DNA strands or other polymers can still be relevant. These polymers act as

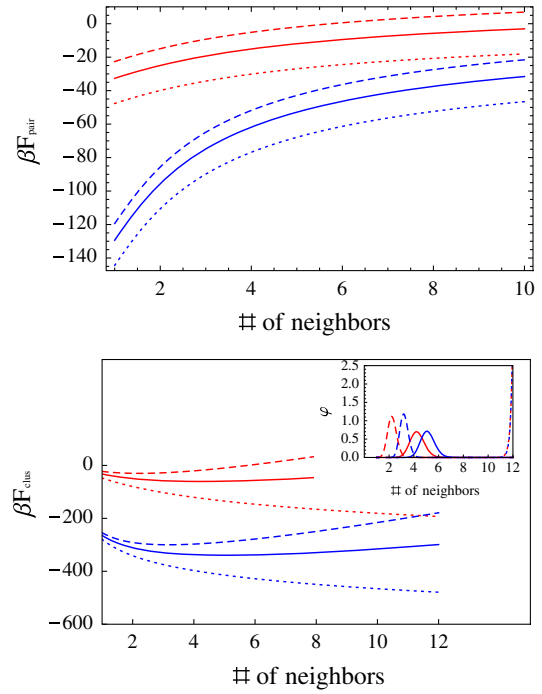


FIG. 2 (color online). Energy per pair (βF_{pair} , above) and cluster energy (βF_{clus} , below) for a cluster in our system of DNACCs with mobile strands. Same color (online version) means the same value of ΔG_0 . Lines of different styles represent different values of $\beta F_{\text{rep}}^{\text{min}}$ (0, 15, and 25 for dotted, continuous, and dashed lines, respectively). Lines of different colors have been shifted by an irrelevant constant to facilitate comparison. The inset shows the valency probability distributions φ , which peak at low valency if $F_{\text{rep}}^{\text{min}} > 0$.

steric stabilizers via excluded volume interactions, giving a repulsive energy of general form

$$\beta F_{\text{rep}} = -k_B T \ln \left(\frac{\Omega(\{\mathbf{r}_i\})}{\Omega_{\text{free}}} \right), \quad (10)$$

where $\Omega(\{\mathbf{r}_i\})$ is the partition function counting all accessible states of the polymers given the positions of the colloids $\{\mathbf{R}\}$ and Ω_{free} is the same partition function when the colloids are at infinite separation. As for $\beta \Delta G_{\text{cnf}}$, the contribution due to Eq. (10) can be calculated exactly for selected polymeric architectures or otherwise computed with MC simulations [16].

To illustrate the effect of nonspecific repulsion, first consider the case that F_{rep} between two colloids has a constant value $F_{\text{rep}}^{\text{min}}$. The total energy of a $1A + N_B B$ cluster then has an additional term $N_B F_{\text{rep}}^{\text{min}}$. Added to Eq. (9), we obtain a closed analytical expression for the free-energy of a cluster $F_{\text{clus}}(n_\alpha, n_\beta, N_B, \Xi, F_{\text{rep}}^{\text{min}})$. If we divide F_{clus} by the number of neighbors, we obtain the total energy per bonding pair $F_{\text{pair}} = F_{\text{clus}}/N_B$ [Eqs. (18)–(22) in the Supplemental Material [25]].

Figure 2 confirms that F_{pair} is *always* an increasing function of the number of colloids; hence, attraction in an

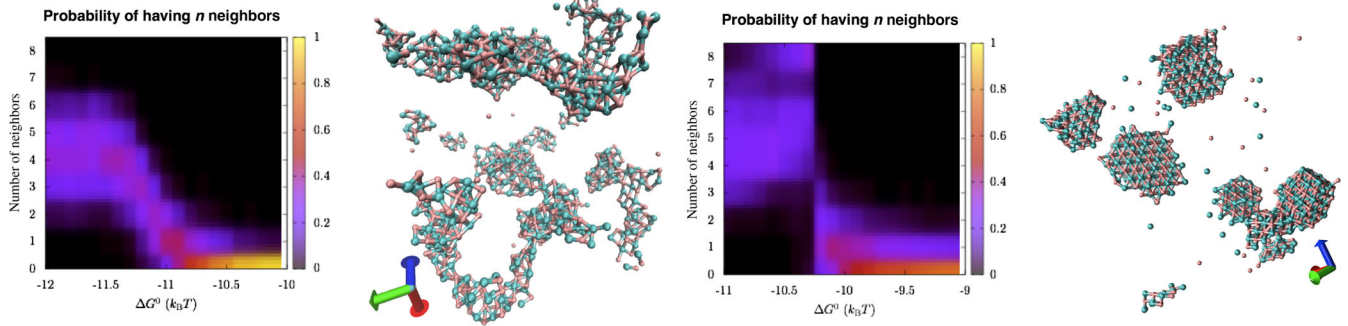


FIG. 3 (color online). Valency distribution as a function of $\beta\Delta G_0$ for colloids with (left) and without (right) inert strands. The repulsive free-energy at the equilibrium distance between colloids has an appreciable value only when inert strands are present, and is basically zero otherwise. The snapshots show typical configurations found at low $\beta\Delta G_0$ in the two cases, where the system either assembles open structures of tetrahedral coordination (left, with inert strands) or a more compact NaCl structure (right, no inert strands).

A - B pair becomes weaker by increasing the number of neighbors. However, it is F_{clus} that controls the valency distribution function. Without a local minimum in F_{clus} , the latter peaks at the highest possible coordination number (i.e., 12 for equal-sized spheres). A minimum in F_{clus} appears only if a finite repulsion $\beta F_{\text{rep}}^{\text{min}}$ is present, in which case the valency distribution peaks at a lower value dependent on $\beta F_{\text{rep}}^{\text{min}}$ (dashed and continuous curves in the inset), suggesting a viable route to tune DNACCs' valency. In practice, the repulsive energy at the equilibrium distance can be controlled by coating colloids with inert DNA strands or other polymers that are somewhat longer than the “sticky” DNA strands [19]. Based on these results, we expect that in a realistic system of DNACCs with mobile linkers one can control the average valency by varying temperature or salt concentration. We also expect, based on Eqs. (5), (10), that the specific value of ΔG_0 at which a particular valency is stabilized will depend on the grafting density and the size of the colloids, since both these parameters enter in our equations.

To demonstrate this, we performed MC simulations of an equimolar $A:B$ mixture of colloids that can move freely. βF_{rep} was calculated by using Eq. (10) and considering the case of mobile strands (details of its calculation are reported in the Supplemental Material [25]). We stress that our outcomes are insensitive to the precise choice of F_{rep} . We take two specific realizations of the system, differing in the presence or absence of long inert strands. Each colloid is modeled as a hard sphere with a radius $R = 100$ nm on which 70 rigid, double-stranded DNA of length $L = 20$ nm terminating with a short single-stranded DNA sequence are grafted (as in the plots for Fig. 2). In the system with inert strands, 40 additional strands of dsDNA of length 60 nm are added. Since $L \ll \xi_p$, the persistence length of dsDNA, linkers can be described as rigid rods [22], for which both the contribution to the repulsive energy as well as DG^{conf} for mobile linkers can be calculated analytically given the colloids' positions (see the Supplemental Material [25]). This model for the DNA construct corresponds to the

experimental realization described in [22,26–28]. In each run, 10^5 MC sweeps *per* particle are made, starting with 100 colloids in random positions at packing fraction 0.05 and at various values of ΔG_0 . Each trial move consists of a random displacement $\mathbf{r} \in [-0.25L, 0.25L]^3$, and the total free-energy recalculated using Eqs. (6), (7) under periodic boundary conditions. The analysis was performed every 100 sweeps *per* particle, and the valency distribution function (φ in the inset of Fig. 2) was calculated using the maximum bonding distance, i.e., $2L$ for rigid rods.

Results are presented in Fig. 3, for the case with (left) and without (right) inert strands, corresponding to $F_{\text{rep}}^{\text{min}} > 0$ and $F_{\text{rep}}^{\text{min}} = 0$, respectively. These results support the conclusions based on the simpler analytical model derived for the quenched-cluster system: repulsion plays an important role in stabilizing low-valency structures. In particular, higher repulsion shifts the average valency to lower values. As predicted by our simplified model, the valency probability distribution can be tuned by changing ΔG_0 , i.e., temperature or salt concentration. The observed valency distribution for colloids without inert strands is relatively broad, which can mainly be attributed to finite size effects in our system. Although we did not calculate the equilibrium phase diagram for this system, all observed structures assemble quickly and spontaneously from a random configuration and remain stable, suggesting at least metastability. Without inert strands a compact and well-ordered crystal forms, whereas the open structures observed in their presence lack long-range order. This is not necessarily required to achieve interesting functional properties: low valency was shown to be enough to obtain structures with a proper, three-dimensional photonic band gap [29].

Finally, we note that Feng *et al.* [15] have reported the experimental observation of low-valency structures of deformable, micron-sized oil droplets coated with mobile DNA. In this system, the repulsion mechanism is droplet deformation. As we have not applied our theory to this case, we cannot yet conclude whether droplet deformation alone can limit valency.

To conclude, in this Letter we have studied the collective behavior of suspensions of binary *isotropic* colloids functionalized by mobile linkers. We showed how the interaction parameters can be tuned to induce the self-assembly of aggregates exhibiting a desired number of neighbors. Our model indicates that such a valency control can be achieved by changing the nonspecific repulsion between colloids and is a function of temperature and salt concentration. We also derive an explicit formula for the bonding energy of a system of mobile linkers, provide the set of self-consistent equations needed to calculate it, and show how they can be used to drive an MC algorithm to efficiently sample the DNA-mediated free-energy. Hence, beyond motivating experimental work towards the design of low valency structures, we provide tools to model other systems interacting via reversible mobile binders: an obvious example is the interaction between lipid vesicles [30], or functionalized particles with cell membranes, whose interaction strongly depends on ligand-receptor bond formation [31].

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