Sterically stabilized lock and key colloids: A self-consistent field theory study

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Abstract

A self-consistent field theory study of lock and key type interactions between sterically stabilized colloids in polymer solution is performed. Both the key particle and the lock cavity are assumed to have cylindrical shape, and their surfaces are uniformly grafted with polymer chains. The lock-key potential of mean force is computed for various model parameters, such as length of free and grafted chains, lock and key size matching, free chain volume fraction, grafting density, and various enthalpic interactions present in the system. The lock-key interaction is found to be highly tunable, which is important in the rapidly developing field of particle self-assembly.

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I. INTRODUCTION

Self-assembly of colloidal particles into desired structures, which is driven by selective and directional interparticle interactions, can provide a promising route for fabrication of novel materials.\(^1\) One particularly promising approach in this research area is based on utilizing “lock and key” colloidal systems.\(^2, 3\) As such, these model systems have recently received substantial attention both experimentally\(^2, 3\) and theoretically.\(^4, 5\)

In a recent experimental study,\(^2\) an efficient method has been developed to produce colloidal lock particles containing a spherically shaped cavity. The interaction between these lock particles and complementary spherical key particles is comprised of two major contributions: Coulomb repulsion arising due to charge stabilization, and depletion attraction\(^4\) due to the presence of the polymeric depletants in solution. The depletion attraction is the strongest when the radius of the key particle exactly matches that of the cavity due to the fact that the overlap of excluded volumes associated with lock and key particles is maximized in this case. As a result, this key-lock binding is highly specific, which is one of the crucial requirements for developing a successful self-assembly process. In addition to geometric considerations, the strength of depletion attraction can be controlled either by varying the depletant concentration or by adjusting temperature, thereby changing the polymeric depletant size.\(^2\) Hence, the key-lock interaction is not only selective, but also reversible and tunable, which is equally important for controlling self-assembly. In this regard, it was found that the binding-unbinding transition in the key-lock system is significantly sharper when steric stabilization (arising due to the presence of grafted polymer layers on both key and lock surfaces) is used instead of charge stabilization.\(^2\) The sharpness of the binding-unbinding transition is determined by considering the fraction of occupied lock cavities as a function of depletant concentration. Experimental data show that for charge stabilized key-lock systems this function grows gradually, while for sterically stabilized systems it approaches a step function, i.e. the binding-unbinding transition becomes much sharper.\(^2\)

On the theoretical side, key-lock interactions in colloidal systems have been studied using integral equation theory,\(^4\) density functional theory,\(^6\) and molecular simulation techniques.\(^7\) Very recently, a highly efficient hybrid approach to study key-lock model systems (among other multidimensional problems) has been developed, which combines Monte Carlo simulation for obtaining microscopic configurations of the depletant particles and density functional theory for calculating the free energy.\(^8\) All these previous studies employed microscopic models based exclusively on hard-sphere excluded volume interactions, whereby the depletion attraction between lock and key particles is driven by the entropic solvent contribution. In agreement with experimental observations and geometric arguments based on excluded volume overlaps, it has been found that the strongest binding interaction occurs for the systems where the size of the key exactly matches the size of the lock cavity. However, it was also found that a simple Asakura-Oosawa type treatment\(^9\) based exclusively on considering excluded volume overlaps is not always sufficient. In particular, these studies have highlighted the importance of employing a realistic microscopic model for the solvent (depletant) by showing that the Asakura-Oosawa approach, which assumes ideality of the solvent, can significantly underestimate the selectivity of key-lock interactions.\(^4\)

While earlier theoretical studies of lock and key model systems have considered several different geometric shapes of key particles and lock cavities, the depletant has always been treated as a simple hard sphere solvent, thereby limiting the key-lock interaction to purely entropic depletion attraction. At the same time, in the experimental work the strength of key-lock binding has been tuned by changing the effective size of polymeric depletant via temperature changes, which indicates the potential importance of enthalpic effects in these systems.\(^2\) Furthermore, the fact that the sharpness of binding-unbinding transition can be increased in the presence of steric stabilization,\(^2\) points to the necessity of developing a microscopic model of lock and key systems that would explicitly include grafted chains on the surfaces of lock and key particles. The central goal of the present work is to develop such a model.

In our earlier work, we have employed mean-field type theoretical methods (density functional theory and self-consistent field (SCF) theory)\(^10\) to study interactions between sterically stabilized colloidal particles in polymer melts and solutions.\(^11, 12\) By comparing theoretical results with computer simulations, it was shown that theory yields accurate density profiles of both free and grafted chains,\(^12\) as well as potentials of mean force (PMF) between sterically stabilized colloids.\(^11\) In the present work, we employ mean-field techniques to study interactions between sterically stabilized lock and key particles in the presence of polymeric depletants. We compute the corresponding PMFs and study their dependence on the geometric matching between the sizes of key particle and lock cavity, which is the crucial parameter governing the strength of lock-key interactions.\(^2\) In addition, we study the dependence of PMF on several other model parameters, which are known to play an important role in governing the microstructure of sterically stabilized colloids in polymer melts and solutions, such as the ratio of free and grafted chain lengths,\(^11, 13–16\) grafting density,\(^11, 13\) and enthalpic interactions of free chains with grafted chains\(^12\) and with the surface of lock and key particles.

The remainder of the paper is organized as follows. In Section II we introduce our microscopic model and describe SCF-based approach for calculating PMF between sterically stabilized lock and key particles. The results of our calculations of PMFs for a wide range of model parameters are presented in Section III. Section IV concludes the
FIG. 1. A schematic side-view of the microscopic model. The key particle (shown in red) is a cylinder of height \( H \) and radius \( R_k \); the lock cavity (shown in black) is a cylinder of height \( D \) and radius \( R_l \). Both particles are uniformly grafted with polymer chains of length \( N \) (shown in blue) at grafting density \( \sigma_g \) and immersed in a solution of polymer chains of length \( P \) (shown in green) with bulk volume fraction \( \phi_b \).

II. MICROSCOPIC MODEL AND THEORY

Previous studies of lock-key interactions have considered various geometries for the particles, including spherical and ellipsoidal shapes.\cite{4-8} In the present work, we assume cylindrical shape both for the key particle and for the lock cavity. In particular, the key particle is assumed to be a cylinder of radius \( R_k \) and height \( H \), while the lock cavity is characterized by radius \( R_l \) and depth \( D \). The conditions \( R_k = R_l \) and \( H = D \) correspond to the perfect size matching between lock and key. The particles are immersed in a solution of polymer chains of length \( P \) with bulk volume fraction \( \phi_b \). In addition, the surfaces of the particles are uniformly grafted with chains of length \( N \) at grafting density \( \sigma_g \). In what follows, we consider only coaxial arrangements of the cylinders describing key particle and lock cavity, both of which are aligned along the \( z \) axis. As a result, the lock-key PMF is a function of a single coordinate \( z \). A schematic side-view of our microscopic model is presented in Fig. 1.

We use SCF theory to obtain the PMF between sterically stabilized lock and key particles in a polymer solution. The central quantity in the SCF approach is mean-field free energy, which is expressed as a functional of the volume fraction profiles and SCF potentials for all components in the system. Minimization of this free energy under the incompressibility constraint and appropriate boundary conditions yields equilibrium density distributions of various components. For most problems of interest, SCF equations need to be solved iteratively and numerically, which necessarily involves space discretization, i.e. use of a lattice. Here we employ the method of Scheutjens and Fleer,\cite{10} which uses the segment diameter \( \sigma \) as the size of the cell; throughout this work all the distances are reported in units of the cell size \( \sigma \).

For the present problem, the SCF equations are set up on a cylindrical lattice and solved using two-gradient approach, where the density profiles vary both radially and laterally.\cite{17-19} The lattice layers along the axis of the cylinder are numbered according to \( z = 1, 2, \cdots, N_z \), while circular arrangements of the lattice sites within each \( z \)-layer are numbered as \( r = 1, 2, \cdots, N_r \). Due to the azimuthal symmetry of the problem, there are \( L(r) = \pi[r^2 - (r - 1)^2] \) indistinguishable sites at each coordinate \((z, r)\). In order to implement SCF formalism, one needs to define \textit{a priori} step probabilities, which are determined by the fractions of sites in neighboring layers adjacent to a given site on a
lattice. In the r-direction, these probabilities follow from geometric considerations:

\[
\Lambda(r|r - 1) = \frac{S(r - 1)}{3L(r)}, \quad \Lambda(r|r + 1) = \frac{S(r)}{3L(r)},
\]

\[
\Lambda(r|r) = 1 - \Lambda(r|r - 1) - \Lambda(r|r + 1),
\]

where \( S(r) = 2\pi r \) is the surface area between the two cylinders of unit height and radii \( r \) and \( r + 1 \). The transition probabilities along the z-direction are given by: \[ \Lambda(z, z') = 1/3, \text{ where } z' = z - 1, z, z + 1. \] Overall, for each lattice site \((z, r)\), there are nine transition probabilities given by:

\[
\Lambda(z, r|z', r') = \Lambda(z, z')\Lambda(r, r') = \frac{1}{3}\Lambda(r, r'),
\]

where \((z', r') = (z + \alpha, r + \beta)\), with \( \alpha, \beta = -1, 0, 1 \). The transition probabilities thus defined are properly normalized, with their sum equal to unity.

In our model, both lock and key particle are assumed to be uniformly composed of a fixed number of segments of type \( p \) that fill the corresponding geometrical forms discussed above. Accordingly, the particles are impenetrable to any other segment types present in the system, i.e., the volume fraction \( \phi_p(z, r) \) = 1 for all the lattice sites located inside the particles and \( \phi_p(z, r) \) = 0 otherwise. In addition to the particles, there are three other segment types in our model, those of free chains \((f)\), grafted chains \((g)\), and solvent \((w)\). The latter fill all the remaining vacancies on the lattice, thereby ensuring the incompressibility condition.

The SCF equation for the volume fraction of grafted chains is written in terms of propagators as follows:

\[
\phi_g(z, r) = C_g \sum_{s=1}^{N} \frac{G_g(z, r, s|1) G_g(z, r, s|N)}{G_g(z, r)},
\]

where the sum runs over all the segments of the grafted chain, the normalization constant \( C_g \) is determined by the grafting density \( \sigma_g \), and \( G_g(z, r) \) is given in terms of the potential \( u_g(z, r) \):

\[
G_g(z, r) = \exp(-\beta u_g(z, r)),
\]

where \( \beta = 1/k_B T \).

The potential \( u_g(z, r) \) is comprised of two terms:

\[
u_g(z, r) = u^{hc}(z, r) + u^{int}(z, r),
\]

where the hard-core potential \( u^{hc}(z, r) \) is independent of the segment type and serves as a Lagrange multiplier enforcing the incompressibility condition, while the interaction potential is given by:

\[
\beta u^{int}_g(z, r) = \frac{1}{2} \sum_{i \neq g} \chi_{ig} < \phi_i(z, r) >,
\]

where the sum runs over all the segment types other than \( g \), \( \chi_{ig} \) are the corresponding Flory-Huggins interaction parameters, and the step-weighted volume fractions are defined as follows:

\[
< \phi_i(z, r) > = \sum_{z', r'} \lambda(z, r|z', r') \phi_i(z', r').
\]

As our boundary condition for the grafted chains, we pin their end-segments to the surfaces of lock and key particles as depicted in Fig. 1.

The SCF equation for the volume fraction of free chains is similar to Eq. (3), except that the normalization constant is obtained from the value of the bulk volume fraction of free chains \( \phi_b \) (instead of the grafting density), and no pinning of the end-segments is performed. Finally, the equation for the solvent is straightforward:

\[
\phi_w(z, r) = \exp(-\beta u_w(z, r)).
\]

By imposing the incompressibility constraint, we solve SCF equations simultaneously and iteratively to obtain the equilibrium volume fractions of all the components present in the system.
From the resulting volume fractions, one can compute the Helmholtz free energy of the system as follows:

$$\beta A = \sum_{i=1}^{m} \sum_{z=1}^{N_x} \sum_{r=1}^{N_y} L(r) \phi_i(z,r) \left\{ \frac{\ln \phi_i}{N_i} + \ln G_i(z,r) + \sum_{j>i}^{m} \chi_{ij} \phi_j(z,r) \right\},$$

(9)

where the summation index \( i \) runs over all the segment types present in the system; \( N_i = 1, N, \) and \( P \) for \( i = w, g, \) and \( f, \) respectively; \( \phi_i^0 \) is equal to the bulk volume fraction \( \phi_b \) for the free chains, while for the grafted chains

$$\phi_i^0 = \frac{nN}{\sum_{z=1}^{N_x} \sum_{r=1}^{N_y} L(r) G_i(z,r, N[1])},$$

(10)

where \( n \) is the number of grafted molecules in the system determined by the grafting density. We note that the total Helmholtz energy can be split into the contribution due to the grafted chains, \( \beta A_g \) (given by the term \( i = g \) in the sum over \( i \) in Eq. (9)), and the contribution due to the mobile species, i.e. free chains and the solvent, \( \beta A_{wf} \) (given by the terms \( i = w, f \) in the sum over \( i \) in Eq. (9)).

The dimensionless lock-key PMF as a function of lock-key separation \( z \) is given by the difference of the Helmholtz free energy at the particle separation \( z \) and at infinite separation.

$$\beta W(z) = \beta A(z) - \beta A(\infty).$$

(11)

By splitting the free energy into contributions from grafted and mobile species, the PMF can be decomposed into the term due to grafted chains and the term due to mobile species:[13, 20]

$$\beta W(z) = \beta W_g(z) + \beta W_{wf}(z).$$

(12)

Note that here we focus exclusively on the polymer- and solvent-mediated part of the PMF, i.e. we do not consider the bare interaction between lock and key particles, the latter term can always be added separately to the PMF.

III. RESULTS

As discussed in the Introduction, prior experimental studies of lock and key colloids have shown that the sharpness of binding-unbinding transition can be increased by grafting polymeric chains on the surfaces of lock and key particles. Furthermore, recent experimental results in the field of polymer nanocomposites indicate that the interaction between sterically stabilized colloids in polymer melts and solutions can be tuned from repulsive to attractive by varying the ratio of free and grafted chain lengths.[1, 13–16] Hence, we begin by studying the effect of the ratio \( P/N \) on the PMF between sterically stabilized lock and key particles.

The corresponding results are presented in Fig. where we plot dimensionless PMF as a function of the lock-key separation for several values of the free polymer volume fraction. In our lattice model, the surface of the bottom of the lock cavity corresponds to the surface layer \( z = 1, \) and the lock-key separation is measured from the leading edge of the key particle, i.e. \( z = 2 \) on the graph corresponds to lock and key being in contact. Throughout this study, we fix the height of the key and the depth of the lock at \( H = D = 4, \) the radius of the lock cavity at \( R_l = 6, \) and the length of the grafted chains at \( N = 10. \) In the upper panel, we set \( P/N = 5, \) and in the lower panel, \( P/N = 0.5. \) In both cases, the grafting density is fixed at \( \sigma_g = 0.01 \) and the key particle radius is taken to be \( R_k = 6, \) i.e. the lock and key sizes match perfectly. One sees that in the case when the length of the free chains is smaller than that of the grafted chains, the polymer-induced component is repulsive for all values of the free polymer volume fraction considered, which is similar to the behavior of sterically stabilized colloidal particles.[1, 13–16] By decomposing the total PMF into contributions due to mobile species and grafted polymers (not shown), one finds that the repulsion is primarily due to the overlap of the grafted chains, which outweighs the attractive term coming from the osmotic pressure of the mobile species in solution (again in analogy to sterically stabilized colloids).

On the other hand, when free chains are longer than the grafted ones, the polymer mediated PMF is strongly attractive at low polymer volume fraction (\( \phi_b = 0.3, \) moderately attractive at intermediate volume fraction (\( \phi_b = 0.7, \) and repulsive at high volume fraction (\( \phi_b = 0.9). \) We note here that in the case of flat polymer brushes, the phenomenon of autophobic dewetting would lead to an attractive PMF in the regime \( P/N > 1 \) for all values of free polymer volume fractions.[1, 13–16] However, for highly curved brushes (grafted on spherical or cylindrical surfaces), melt-brush interpenetration and wetting is strongly enhanced. Indeed, recent SCF calculations have shown that wetting-dewetting transition is shifted to much larger values of \( P/N \) ratio for highly curved sterically stabilized nanoparticles.[21]

This change in the nature of the lock-key PMF from attractive to repulsive with increasing volume fraction (when \( P > N \)) provides one possible way for tuning interactions in sterically stabilized lock-key colloidal systems.
Hence, it would be of interest to decompose the total polymer-induced PMF according to Eq. (12) into two separate contributions arising due to mobile species and grafted chains. This decomposition is shown in Fig. 3, where the contribution due to grafted chains is given in the upper panel, and the contribution due to mobile species in the lower panel. Compared to the case when $P < N$, the situation is reversed in that the term due to grafted chains is predominantly attractive, except for a weak repulsive barrier at intermediate lock-key separations at the lowest volume fraction considered. The term coming from osmotic pressure due to mobile species is attractive at the low volume fraction, weakly repulsive at the intermediate $\phi_b$, and strongly repulsive at the highest value of $\phi_b$ studied. Once again, this behavior is qualitatively similar to sterically stabilized colloids, where it was rationalized by arguing that mixing of grafted chains from two particles is more favorable than mixing of short grafted chains and long free chains.[13]

As a next step, we study the effect of the size matching between the lock and key particles on the PMF. To this end, we set the grafting density at $\sigma_g = 0.05$, the length of the free chains at $P = 50$, and compute the lock-key PMF for two sizes of the key particle: $R_k = 6$ (perfect size matching), and $R_k = 3$ (key is half the size of the lock cavity). Our results are shown in the upper panel of Fig. 4 for the smaller key, and in the lower panel for the larger key. First of all, one immediately notices that the lock-key interaction is substantially weaker in the absence of perfect geometric
matching, in agreement with earlier theoretical and simulation studies.\textsuperscript{4, 7, 8} In addition, while the lock-key PMF for the smaller key is weakly attractive at all values of free polymer volume fraction, for the larger key it changes from strongly attractive at low volume fraction to repulsive at higher values of $\phi_b$, similarly to what was seen earlier in the upper panel of Fig. 2. By comparing the lower panel of Fig. 4 with the upper panel of Fig. 2 one can see the effect of the grafting density on the lock-key PMF (all other model parameters being equal in these two panels). The most pronounced difference is the abrupt change in the slope of the PMF at short lock-key separations in the case of higher grafting density, which leads to a well-defined minimum in the PMF at the low free polymer volume fraction.

In all the calculations reported so far, the Flory-Huggins parameters between all the components present in the system (free and grafted polymer chains, solvent, and particles) have been set equal to zero, i.e. all the effects observed in the lock-key PMFs have been purely entropic. It would be also of interest to consider the role of enthalpic effects in tuning lock-key interactions. To this end, we study the effect of specific interactions between free chains and segments comprising key and lock particles (by varying the Flory-Huggins interaction parameter between particle segments and free chains, $\chi_{pf}$), and between free and grafted chains (by varying the Flory-Huggins interaction parameter between free and grafted chains, $\chi_{gf}$). The former results are shown in the lower panel of Fig. 5, and the latter results in the upper panel. In these calculations, we have set the free polymer volume fraction at $\phi_b = 0.5$, the length of free chains at $P = 50$, the grafting density at $\sigma_g = 0.05$, and the sizes of key particle and lock cavity are perfectly matched.

All the Flory-Huggins parameters other than those specified in the legend of Fig. 5 are set equal to zero. Hence,
FIG. 4. The lock-key PMF for a cylindrical cavity of radius $R_l=6$ and for two values of the key particle radius: $R_k=3$ (upper panel) and $R_k=6$ (lower panel).

the PMF corresponding to $\chi_{pf}=0$ in the lower panel of Fig. 4 can be regarded as that of the reference system in the absence of enthalpic effects. This reference PMF displays weak lock-key repulsion at contact and a weak attractive minimum at short lock-key separations. In the presence of favorable enthalpic interactions between free chains and particles ($\chi_{pf}=-1.5$), free chains absorb on particle surfaces, thereby penetrating inside the grafted chains and making the lock-key PMF uniformly repulsive. When this interaction is unfavorable ($\chi_{pf}=1.5$), free chains are expelled from surfaces, which makes the PMF strongly attractive.

Similar behavior is observed in the upper panel of Fig. 4 where we vary the enthalpic interaction between free and grafted chains. When this interaction is favorable ($\chi_{gf}=-0.5$), the free chains wet the brushes, which produces a strongly repulsive lock-key PMF. In the opposite case ($\chi_{gf}>0$), the mixing between free and grafted chains is unfavorable, which results in a uniformly attractive lock-key PMF, with a deep minimum at short separations. One can also note that the range of the PMF in the upper panel is somewhat larger compared to the lower panel, which could be due to the changes in the extension of the grafted chains promoted by varying the $\chi_{gf}$ parameter.
FIG. 5. The lock-key PMF between a cylindrical key of radius $R_k = 6$ and a cylindrical cavity of radius $R_l = 6$. The length of the grafted chains is $N = 10$ and their grafting density is $\sigma_g = 0.01$; the length of free chains is $P = 50$ and their bulk volume fraction is $\phi_b = 0.5$. Upper panel: PMF for three different values of the Flory-Huggins interaction parameter between free and grafted chains; lower panel: PMF for three different values of the Flory-Huggins interaction parameter between free chains and particles.

IV. CONCLUSION

In this work, we have carried out a mean-field theoretical study of lock-key interactions between sterically stabilized particles in a polymer solution. Both the key particle and the lock cavity were assumed to have cylindrical shape, and their surfaces were uniformly grafted with polymer chains. A two-dimensional version of lattice-based SCF theory was employed to compute the PMF between lock and key particles. In analogy with earlier studies of interactions between sterically stabilized colloids, it was found that PMF is quite sensitive to several model parameters, making lock-key interactions easily tunable. In particular, it was shown that when the free chains are shorter than the grafted ones, the PMF is repulsive at all conditions studied, while in the opposite case the lock-key interaction can be tuned from attractive to repulsive by increasing the volume fraction of free polymer chains. Likewise, the behavior of the PMF, including its range, can be changed by varying the enthalpic interactions between free chains and grafted ones or between free chains and particles. Finally, in agreement with earlier experimental and theoretical studies, it was observed that the strongest lock-key interaction occurs in the case of perfect size matching between the lock and the key; decreasing the size of the key relative to that of the cavity weakens the interaction dramatically.

It would be of interest to extend the present study to other geometrical shapes of lock and key particles and to
go beyond the one-dimensional representation of the PMF by considering different trajectories of the key approaching the lock cavity. In addition, it would be of interest to compare the sharpness of binding-unbinding transition (as determined by the fraction of occupied lock cavities as a function of free chain concentration) between sterically stabilized and charge stabilized systems. This will be the subject of future research.

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