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The Self-Assembly of Particles with Isotropic Interactions: Using DNA Coated Colloids to Create Designer Nanomaterials

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Abstract. Self-consistent field theory equations are presented that are suitable for use as a coarse-grained model for DNA coated colloids, polymer-grafted nanoparticles and other systems with approximately isotropic interactions. The equations are generalized for arbitrary numbers of chemically distinct colloids. The advantages and limitations of such a coarse-grained approach for DNA coated colloids are discussed, as are similarities with block copolymer self-assembly. In particular, preliminary results for three species self-assembly are presented that parallel results from a two dimensional ABC triblock copolymer phase. The possibility of incorporating crystallization, dynamics, inverse statistical mechanics and multiscale modelling techniques are discussed.

Keywords: self-consistent field theory, DNA, colloids, self-assembly

PACS: 81.16.Dn, 64.70.pv, 64.75.Yz, 81.16.Rf

INTRODUCTION

Self-consistent field theory (SCFT) has a long track record of significant contributions to the understanding of block copolymer self-assembly [1, 2, 3]. Block copolymers are an archetypal self-assembling system, but research continues to explore other methods of developing nanometre length-scale structures through self-assembly. DNA-mediated colloidal organization, first introduced in 1996 by Mirkin et al. [4] and Alivisatos et al. [5], held the promise of allowing the self-assembly of pre-determined three dimensional nanometre and micron length-scale structures. Enthusiasm has faded however due to limitations of the approach and complications of design [6]. In DNA coated colloid (DNACC) systems, colloids are covered with DNA molecules such that selective and mutually exclusive interactions can take place depending on the coatings. For desired structures to be formed however, many different and mutually exclusive interactions are required. It is not presently possible to predict which structures will be formed from given surface treatments, nor if target structures will ultimately be the stable equilibrium. This is related to further complications concerning kinetic traps due to strong bonding [6].

In this perspective, we review the possibility of using SCFT to predict the morphologies of DNACCs and related systems. To a first approximation, DNA-mediated

colloids have isotropic interactions [7] and are thus just one example of a class of selectively and isotropically interacting potentials that also includes single species colloids with two length-scale interactions [8, 9] and self-assembling polymer stabilized colloids [10, 11]. SCFT has been successful in block copolymer self-assembly due to its coarse-grained approach which allows for numerical tractability, so a similar approach is followed here. Specifically, we regard the colloids as particles that interact isotropically and selectively through effective pair potentials. We provide very simple generalized SCFT equations for an arbitrary number of species of DNACCs and we outline the advantages and limitations of viewing complicated DNACC systems in this simple way. Our preliminary work on this topic revealed parallels with block copolymer self-assembly despite significant differences in architecture and microscopic physics between copolymers and DNACCs [12]. In this perspective we provide further evidence that deepens this correspondence. Lastly, we suggest ways in which this approach can be extended to include dynamics, crystallization, inverse statistical mechanics and multiscale simulations.

FORMALISMS

We wish to represent mathematically, in the spirit of SCFT, a system of particles in a suspension. Equations for the case of a single particle type in suspension were given in reference [12]. The generalization of these formulae for multiple particle types, $i = 0, 1 \dots N$ in a vol-

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ume V is

$$\varphi_i(\mathbf{r}) = \frac{f_i V}{v_r Q_i} e^{-\alpha_i w_i(\mathbf{r})} \quad (1)$$

$$w_i(\mathbf{r}) = \int \frac{d\mathbf{r}'}{v_r} \sum_{\substack{j=0 \\ j \neq i}}^N \varphi_j(\mathbf{r}') \frac{U_{ij}(|\mathbf{r} - \mathbf{r}'|)}{\alpha_i \alpha_j k_B T} + \kappa \left(\sum_{i=0}^N \varphi_i(\mathbf{r}) - 1 \right). \quad (2)$$

We might assign $i = 0$ to be the suspension molecules and $i = 1 \dots N$ to be the various colloids. Equations (1) and (2) give the position dependent volume fractions $\varphi_i(\mathbf{r})$ and position dependent chemical potential fields $w_i(\mathbf{r})$ for species i , respectively. α_i is the ratio of the volume of the i th species to a reference volume v_r , f_i is the overall volume fraction of the i th species, k_B is Boltzmann's constant and T is the temperature. Partition functions for each species i are given by

$$Q_i = \int \frac{d\mathbf{r}}{v_r} e^{-\alpha_i w_i(\mathbf{r})}. \quad (3)$$

Equations (1), (2) and (3) are non-linear and coupled, and so are solved numerically through iteration. The result is the position dependent volume fractions $\varphi_i(\mathbf{r})$, which is the predicted morphology for the system. It may be that multiple competing morphologies can be found for separate numerical iterations depending on starting conditions. In order to discriminate the stable phase from meta-stable phases, the morphology with the lowest free energy is selected. This free energy is given by²

$$\begin{aligned} \frac{v_r F}{k_B T V} = & - \sum_{i=0}^N \frac{f_i}{\alpha_i} \ln \left(\frac{v_r Q_i}{V} \right) + \frac{v_r}{V} \int \frac{d\mathbf{r}}{v_r} \left\{ \int \frac{d\mathbf{r}'}{v_r} \frac{1}{2} \right. \\ & \times \sum_{\substack{i=0 \\ j \neq i}}^N \sum_{\substack{j=0 \\ j \neq i}}^N [\varphi_i(\mathbf{r}) - f_i] \frac{U_{ij}(|\mathbf{r} - \mathbf{r}'|)}{\alpha_i \alpha_j k_B T} [\varphi_j(\mathbf{r}') - f_j] \\ & \left. - \sum_{i=0}^N w_i(\mathbf{r}) \varphi_i(\mathbf{r}) + \frac{\kappa}{2} \left(\sum_{i=0}^N \varphi_i(\mathbf{r}) - 1 \right)^2 \right\}. \quad (4) \end{aligned}$$

In equations (2) and (4), κ is a numerical parameter that is chosen sufficiently large so as to enforce incompressibility. The resulting overall constant volume of the mixture provides an ensemble average excluded volume. Since the excluded volume is not enforced at the particle level, the details of colloidal packing are lost – see figure 1. On the other hand, the formalism is greatly simplified

² Equation (4) is a generalization of equation (1) of reference [12]. Note the typo there, in that the factor of 1/2 in equation (1) of [12] should be inside the curly brackets. That is, it compensates for double counting only on the first term inside the curly brackets. We have also chosen a different zero of free energy for (4), thus some factors of α_i and f_j are different from reference [12].

and the essential larger scale morphological details are preserved.

There are many possible choices for the potentials $U_{ij}(r)$. We choose them to be isotropic, differentiable over their domains, and to be short range repulsive and longer range attractive. Specifically, we use simple piecewise functions – see for example equation (8) of reference [12].³ Another common choice involves using a combination of exponentials [13, 14]. The use of short range repulsive and longer range attractive potentials for modelling DNACCs can be justified as follows. First, there is a shortest range repulsion from the excluded volume of the colloids or the compression of DNA coatings, but this is not part of the potentials $U_{ij}(r)$. Rather, excluded volume is enforced in an average way through the incompressibility condition as previously mentioned. The short range repulsions in $U_{ij}(r)$ correspond to DNA mediated *attractions* between DNA coated colloids of the same type ($i = j$), which gives rise to effective *repulsions* for DNACCs of different types ($i \neq j$), for which $U_{ij}(r)$ are defined. The longer range attractions corresponds to the saturation of complementary ends between like DNA coated colloids, and therefore effective attractions between unlike DNACCs. The overall pair potentials as described can give a rough, phenomenological, effective pair interaction, consistent with the level of detail of the coarse-grained model.

One can choose to solve equations (1), (2) and (3) numerically, as we have done [12], or one might consider re-phrasing the equations to remove the chemical potential fields $w_i(\mathbf{r})$. Since the particles have no connectivity, these chemical potential fields can be removed from the free energy (4) by solving equations (1) for the $w_i(\mathbf{r})$ and substituting these back into (4). This algebra gives

$$\begin{aligned} \frac{v_r F}{k_B T V} = & \frac{v_r}{V} \int \frac{d\mathbf{r}}{v_r} \left\{ \sum_{i=0}^N \frac{\varphi_i(\mathbf{r})}{\alpha_i} \left[\ln \left(\frac{\varphi_i(\mathbf{r})}{f_i} \right) - 1 \right] \right. \\ & + \frac{1}{2} \int \frac{d\mathbf{r}'}{v_r} \sum_{i=0}^N \sum_{\substack{j=0 \\ j \neq i}}^N [\varphi_i(\mathbf{r}) - f_i] \frac{U_{ij}(|\mathbf{r} - \mathbf{r}'|)}{\alpha_i \alpha_j k_B T} [\varphi_j(\mathbf{r}') - f_j] \\ & \left. + \frac{\kappa}{2} \left(\sum_{i=0}^N \varphi_i(\mathbf{r}) - 1 \right)^2 \right\}. \quad (5) \end{aligned}$$

The formalism now has the character of a classical density functional theory (DFT). The -1 in the first term on the right hand side of (5) has been added and changes the zero of free energy but has no physical effect. It makes

³ Equation (8) of reference [12] is reversed, that is, short range attractive and longer range repulsive due to a difference of convention. The physical type of interaction is however the same.

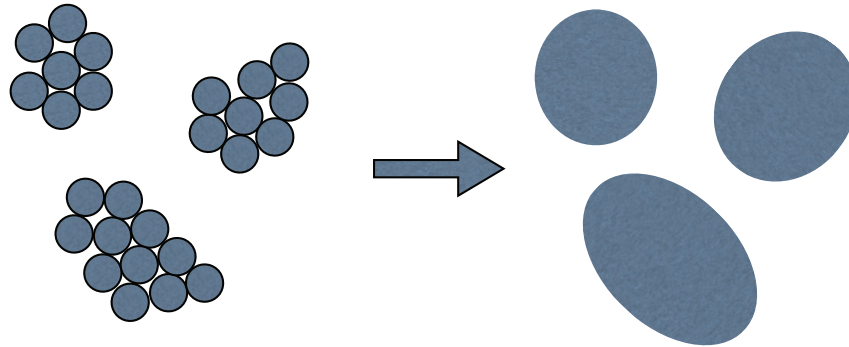


FIGURE 1. A schematic showing the loss of packing information resulting from using an incompressibility constraint to enforce excluded volume. Note that although colloidal detail is lost, morphological detail should be approximately retained.

this term recognizable as the translational entropy of the particles. The second term on the right hand side is the mean field effective pair potentials. In most expressions of classical DFT, there would normally be a term F_{ex} in the energy (5) to account for excluded volume. Instead, we have, in the third term, the incompressibility condition to account for ensemble averaged excluded volume. Obviously the formalism could be changed to a more traditional excluded volume if packing effects were of interest, but this would also reduce the simplicity of form and complicate the numerical solution.

DISCUSSION

There are advantages to using an incompressibility constraint to enforce an averaged excluded volume rather than using a DFT prescription for F_{ex} , or other simulation methods such as Monte Carlo or molecular dynamics, to model complicated DNACC systems. To engineer desired three dimensional nanostructures using DNACCs, it is assumed to be necessary to have many component mixtures of mutually exclusive interactions [15]. The DFT formalism for such many component mixtures would be more involved than equations (1), (2) and (3). More importantly, much of the computational bur-

den in a DFT approach would be devoted to how the colloids crystallize. This would limit the simulation size of the calculation and would provide, as primary information, packing results that are not necessarily of interest. Rather, it is the gross morphological patterns that are of concern for much of nanotechnology, and it is this data that SCFT is ideally suited to providing at relatively low computational cost – see the schematic in figure 1. Monte Carlo simulations and molecular dynamics type simulations, such as Brownian dynamics and dissipative particle dynamics, are both more complicated than the SCFT described here and cannot obtain the equilibrium structure as readily and simply as does SCFT. Frenkel and Wales suggest design rules for useful DNACC self-assembly, the first of which is that a target structure needs to be thermodynamically the most stable among all possible arrangements [16]. SCFT is perfectly suited to checking this condition. Of course, the simplicity of the SCFT approach described here is also its limitation. It will always be a complementary approach to DFT and simulations, in that DFT can provide crystallization data and simulations can describe the dynamic evolution of systems. The second design rule of Frenkel and Wales is that a target morphology should be kinetically accessible in order to avoid getting trapped in unwanted, metastable structures [16]. The SCFT described has no dy-

dynamic information at all. On the other hand, SCFT is remarkably scalable. One can add dynamics to SCFT, for example using the dynamic density functional theory approach [17], or one can add packing effects by directly incorporating DFT terms in the SCFT free energy.

A present disadvantage of using an incompressibility constraint to incorporate an ensemble average excluded volume is the size asymmetry between DNA coated colloids and the surrounding suspension molecules. For example, Mirkin et al. used colloids of a 13 nm diameter in water [4]. A rough value for the diameter of a water molecule is 2.74Å. A quantitatively realistic value for the α_i volume ratio between a suspension molecule and a reference colloid for the SCFT equations for the Mirkin et al. case should then be about 10^{-6} . This is not computationally feasible. One obvious approximation that can be used to get around this is to treat the suspension molecules as an implicit solvent. This however means that an incompressibility constraint cannot be used, and that another form of excluded volume must be included. One arrives back therefore at standard DFT. If one wants complementary information to DFT methods, or indeed any other method that uses implicit solvents, then one must keep the explicit solvent. After all, one of the advantages of SCFT in complementing other approaches is that it keeps the translational entropy information of the solvent. In the future, new approximations or computational techniques can be explored to find ways of approaching realistic solvent volumes, and therefore, correct solvent entropies. Anderson mixing techniques could be helpful in this regard [18, 19, 20, 21].

Even without realistic solvent volumes, the SCFT method described here holds promise in other areas outside of DNACCs. For the case of only two species of equal molecular size, it was found that upon varying volume fractions, the range of phases produced is exactly the same as a diblock copolymer, namely, lamellar, gyroid, hexagonally packed cylinders and body-centered cubic spheres [12]. If one examines three species, again of equal size, preliminary results show phases matching those of an ABC triblock copolymer system. An example of this is shown in figure 2. The majority species form hexagonal tiles in a two dimensional calculation, matching the results of Fredrickson et al. [2]. Given the simplicity of the present SCFT equations, it may be possible to perform inverse statistical mechanics. That is, one could choose a morphology of interest, assume a number of chemical components, and then iterate the SCFT equations to seek the potentials $U_{ij}(r)$ necessary to self-assemble the chosen morphology. One could then attempt to map the discovered pair potentials onto block copolymer architectures, and then run the true block copolymer SCFT equations for that architecture to see if something similar to the desired morphology will self-assemble.

As the volume of one species is made smaller, so that it starts to behave more like a solvent, the morphologies become different from block copolymer phases. Although realistic volumes for suspension molecules cannot yet be reached, the trend shown in reference [12] hints at what one might expect to find. As solvent molecules become smaller, phases become more defected and distinct from diblock phases. In particular, the sheets and cylinders formed begin to resemble more those self-assembled by polymer coated nanoparticles in suspension [10]. This is not surprising since, to an approximation, polymer grafted nanoparticles are also a system with isotropic interactions.

Although SCFT holds promise for modelling self-assembly with isotropic interactions, there are some aspects in which it is unlikely to succeed. The details for the polymer grafts for polymer coated nanoparticles, for example, could be represented, but this might be clumsy. Similarly, the DNA bondings for DNACCs would not be easily represented in SCFT. On the other hand, the effective pair potentials in the present formalism are amenable to multi-scale modelling. For example, one could simulate, calculate or measure, as Rogers and Crocker have done [22], the potential of mean force between DNACCs, and input this into SCFT. Strong bonding effects would still be difficult to model, but then again, stronger DNA binding that prevents kinetic evolution to predictable equilibrium morphologies is not desirable in any case. Experimental techniques such as lower density DNA coatings or using nanoparticles instead of micron sized particles are experimental attempts to avoid stronger bonding [6]. Even SCFT itself, phrased with more detail and studying only pair potentials, could be used as the input for this larger scale SCFT.

OUTLOOK

There is a good prospect for SCFT models of isotropically interacting particles to find a niche in the soft matter theory landscape as a complementary tool to DFT and simulations. The natural inclusion of solution molecule translational entropy, morphological free energies, and larger scale phases beyond the crystallization level are all advantages of the SCFT method. The simplicity of the equations and iterative algorithm are also attractive. Nonetheless, difficulties with molecular volume asymmetries and potential algorithmic complications that might arise in numerically solving highly asymmetric systems are present limitations. Still, the possibility of performing inverse statistical mechanics as a supplement to traditional block copolymer SCFT is intriguing. Also, extra DFT terms can be included if packing effects are of interest, and the techniques of dynamic density functional theory or other dynamics can be eas-

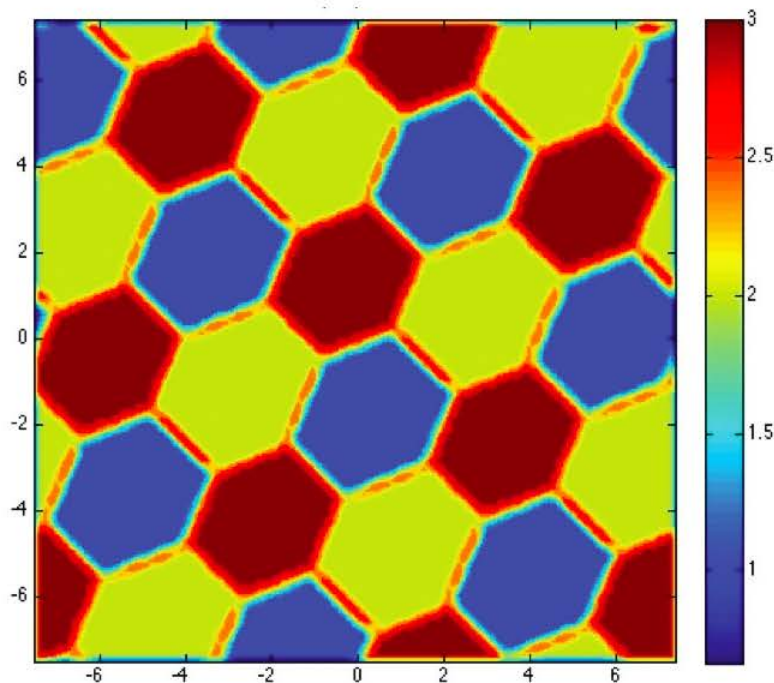


FIGURE 2. Hex pattern predicted to self-assemble from a three component, symmetric mixture of particles with isotropic interactions. The different shades correspond to the majority components of each species. The reader may note that this is the same pattern found by Fredrickson *et al.* for symmetric ABC triblock copolymers [2].

ily transferred to this formalism. Lastly, multiscale modelling through the effective pair potentials can link this approach with more detailed methods.

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