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## Modeling Self-Assembly of Nanoparticle Structures: Simulation of Nanoparticle Chemical Potentials in Polymer-Nanoparticle Mixtures

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### ABSTRACT

The expanded ensemble Monte Carlo (EEMC) simulation method has been applied to calculation of the chemical potential of nanocolloidal particles in the presence of polymeric surface modifiers. Two general classes of surface modifiers have been studied – nonadsorbing and freely-adsorbing. For both systems, the infinite dilution colloid chemical potential was calculated as a function of the colloid diameter and the modifier chain length. The colloid chemical potential was found to decrease with increasing modifier chain length for both types of modifiers, albeit for different reasons. Empirical power-law scaling relationships were found to represent the simulation results well. A physical interpretation was proposed for the power law exponents obtained in the case of adsorbing modifiers.

### INTRODUCTION

Nanoscale colloidal dispersions play an important role in most synthesis and processing steps for nanoscale structural materials. Applications include catalysts, adsorbents, polymer nanocomposites for high-strength barrier and flame resistant materials, and nanocrystals for photonics and electronics. These nanostructures can be prepared not only via nucleation and arrested growth processes, but also as equilibrium products, allowing thermodynamic control of crystal lattice structure and feature size. Many experimental approaches utilize short-chain organic modifiers to promote nanoparticle stability and to influence the lattice structure and size. Examples of common organically-modified nanocolloids include noble metal nanoparticles stabilized with poly (2-hydroxyl methacrylates) [1], two- and three-dimensional arrays of Pd or CdSe nanocrystals modified with alkanethiols [2, 3], and polymer-silica nanocomposites that mimic natural organic-inorganic materials. [4, 5] Unfortunately, the present knowledge of organically-modified nanoparticle self-assembly is inadequate for precise thermodynamic control of these structures. A breakthrough in rational predictive strategies for nanoscale structural material synthesis would be the development of molecular-models that account for the effect of surfactants on the thermodynamic and transport properties of nanoparticles.

Towards this goal, we have recently developed a novel application of the expanded ensemble Monte Carlo (EEMC) simulation method, which allows accurate calculation of the chemical potentials of organically-modified nanoparticles. Chemical potential ( $\mu$ ) is the free energy of inserting a molecule (collection of molecules in the case of a nanoparticle) into a system of interest relative to a reference state. Knowledge of the modifier chain length, concentration and particle size dependence of  $\mu$  can be used to predict self-assembly and dispersability (phase behavior) in these systems. The traditional Widom [6] method for calculating  $\mu$  using computer simulations works well for small molecules and moderate densities, but severe difficulty arises for polymers and other molecular aggregates such as colloids, due to the high probability of steric overlaps. As a result the Widom method samples almost exclusively the high-energy overlap contributions to the chemical potential. EEMC is a powerful approach

that overcomes these sampling limitations in free energy calculations. [7-14] Additional ensemble variables are introduced to define a reversible and efficient path between two desired states of free energy measurement. These states are sampled according to probabilities determined from the partition function. We have adapted this method to polymer-nanocolloid mixtures by inserting nanoparticles into the system incrementally in a series of smaller diameter increments. [15]

In this paper we have applied the EEMC method for calculating nanoparticle chemical potentials in the presence of two broad classes of polymeric modifiers: nonadsorbing and freely adsorbing. We use the hard sphere (HS) potential to model nonadsorbing modifiers and the Lennard-Jones (LJ) 6-12 potential to model freely adsorbing modifiers. In each of these cases we calculate infinite dilution nanoparticle chemical potential as a function of both modifier chain length ( $n$ ) and particle diameter ( $\sigma_c$ ) and discuss the physical interpretation of these dependencies. Finally, we present empirically-derived scaling relationships which describe nanoparticle chemical potential as a power law function of  $n$  and  $\sigma_c$ .

## THEORY

To adapt the EEMC approach to nanoparticle-polymer mixtures, the particle diameter (the “expansion variable”) is allowed to vary between zero (fully removed) and full size via increments and decrements. These increments or decrements are accepted according to a Metropolis type acceptance criterion. A predefined number of intermediate diameters of the particle are allowed by prescribing them as the different “states” of the EE. Incremental chemical potentials, calculated at each diameter describe the free energy of increasing diameter from  $d_i$  to  $d_{i+1}$ . The full chemical potential is recovered by summing the incremental values from zero to the desired particle size. The statistical mechanical details of this method have been presented in a recent publication. [15]

## SIMULATION DETAILS

The simulations were performed in a cubic box with periodic boundary conditions. In all cases our system consisted of a single colloidal particle dispersed in a dilute polymer solution. Polymer chains are fully flexible and consist of tangent segments with a constant bond length of  $\sigma_p$  (bead spring model). The polymer segment density  $\rho_p$  is maintained constant for all the simulations at  $\rho_p = 0.05$ , which corresponds to a packing fraction of  $\Phi = 0.026$ . The chain length of the polymer was varied from  $n = 2$  to a maximum of  $n = 60$ . The effect of colloid size on the chemical potential was also studied by varying  $\sigma_c$  from  $1\sigma_p$  to  $15\sigma_p$ . In all of the simulations, the box length  $L$  (typically  $40\sigma_p$ ) was greater than  $n/2$  and  $\sigma_c$ , to prevent artificial intrachain or intraparticle interactions.

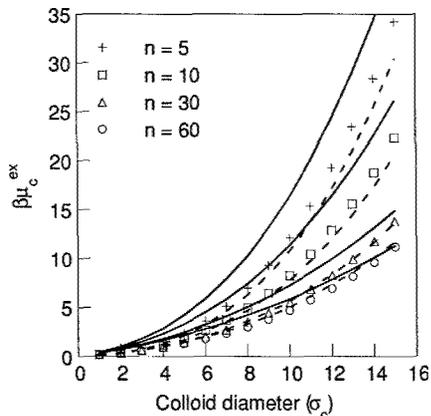
## RESULTS

### Nonadsorbing modifiers (HS potential)

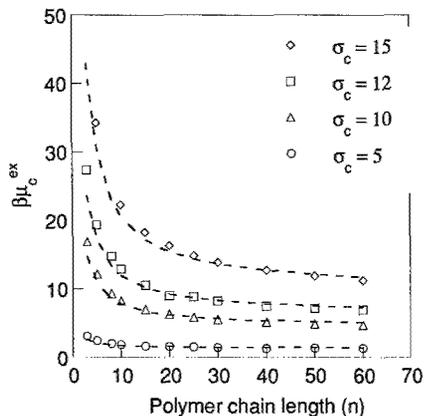
The HS potential, used here to model nanoparticles in the presence of nonadsorbing modifiers in a good solvent, gives purely the entropic or configurational contribution to the chemical potential. The HS model system provides a stringent test of EEMC chemical potential

calculation since the configurational contribution is the most difficult part of the calculation. In addition it has been shown that self-assembly can be driven by entropic depletion forces in the presence of nonadsorbing polymer. [16, 17] Figure 1 shows the infinite dilution chemical potential,  $\beta\mu_c^{ex}$  versus the colloid diameter  $\sigma_c$  for polymer chain lengths of  $5 < n < 60$ . In general  $\beta\mu_c^{ex}$  increases as a cubic polynomial in  $\sigma_c$  for all chain lengths, reflecting the increase in the probability of overlaps and excluded volume. Figure 1 compares the simulation results with the predictions of the PRISM-based colloid-polymer model of Fuchs and Schweizer (FS model). [18, 19] The FS model compares very well with the simulations except that at chain lengths above 30 the FS model slightly overpredicts the chemical potential, and at chain lengths less than 30, the predictions are slightly lower than the simulated results. Minor quantitative deviations are due to the assumed Gaussian intramolecular polymer structure factor in the model. Results from a field-theoretic (FT) model are also shown for comparison.[20]

Figure 2 shows the effect of the polymer chain length on the infinite dilution chemical potential,  $\beta\mu_c^{ex}$ , for different colloid diameters  $\sigma_c$ . The chemical potential decreases with chain length for all particle sizes. For a constant polymer segment density, longer chain length (i.e., lesser number of chains) results in less excluded volume for the particle due to chain connectivity constraints on the location of polymer segments. This explains the decrease of chemical potential with chain length. From Figure 2 we observe that for all particle sizes, there is a sharp decrease in colloid chemical potential from  $n = 2$  to  $n = 20$ . In this regime inserting the colloid particle requires the free energy of creating additional volume by doing work against the polymer fluid osmotic pressure. However for larger chain lengths only an internal section of the polymer chain needs to be rearranged as the colloid particle sees only a part of the chain. Hence we see that for  $n > 20$  the change in chemical potential is comparatively small. This is an interesting result since it tells us that firstly, even in the absence of attraction, a large reduction in



**Figure 1.** Infinite dilution HS colloid chemical potential vs. colloid diameter in a dilute HS polymer solution at different polymer chain lengths ( $n$ ). Dotted line: FS model. Solid line: FT model.



**Figure 2** Infinite dilution HS colloid chemical potential vs. polymer chain length in a dilute HS polymer solution for different colloid diameters. The dotted lines are predictions from the FS model.

the colloid chemical potential can be brought about by adding short chain polymers (modifiers) and secondly, increasing polymer chain length beyond a particular value yields little additional reduction in chemical potential. In addition, the chemical potential reduction effect from adding polymer chains increases as particle size increases.

### **Freely adsorbing modifiers (LJ 6-12 potential)**

The LJ 6-12 potential, used to model freely adsorbing homopolymer modifiers incorporates attraction and chain adsorption effects. The LJ model captures the essential physical features of many organic molecules and remains sufficiently general to be of broad, predictive value. All the simulations were performed at a reduced temperature of  $T^* = 3.0$  ( $T^* = T k_B / \epsilon$ ) and LJ energy parameters  $\epsilon_{cc} = \epsilon_{pp} = \epsilon_{cp} = 1$ , where  $\epsilon_{cc}$ ,  $\epsilon_{pp}$  and  $\epsilon_{cp}$  are the colloid, polymer and colloid-polymer LJ interaction parameters respectively. Figure 3 shows a plot of infinite dilution chemical potential,  $\beta\mu_c^{ex}$  versus the colloid diameter  $\sigma_c$  for polymer chain lengths of  $5 < n < 30$ . For all chain lengths,  $\beta\mu_c^{ex}$  decreases with  $\sigma_c$  and shows a cubic dependence on  $\sigma_c$ . The chemical potential decreases with  $\sigma_c$  because the LJ attractive energy increases linearly with  $\sigma_c$  and this results in stronger attractive (negative) interactions between the particle and the polymeric modifiers and thereby, a lower chemical potential. These results demonstrate that in the case of strongly adsorbing modifiers, attractive energetics dominate the repulsive and excluded volume interactions that are predominant in nonadsorbing modifier systems.

The effect of chain length of adsorbing modifiers on particle chemical potential is shown in Figure 4. As in the case of nonadsorbing modifiers, here too we observe that for all particle diameters,  $\beta\mu_c^{ex}$  decreases with increasing chain length. However, more than the decrease in excluded volume due to chain connectivity constraints, it is chain adsorption on the particle surface that leads to lowering of particle chemical potential in this case. As we increase the chain length, the entropy loss associated with chain adsorption decreases and hence more chain segments get adsorbed onto the particle surface. This results in the particle getting a larger number of attractive negative interactions and thus, a lower chemical potential.

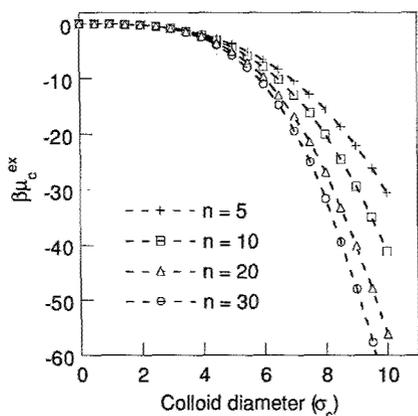
### **Scaling relationships**

The chemical-physics of nanocolloid-polymer mixtures can be described by simplified scaling relationships which capture the dependence of thermodynamic properties on physical molecular parameters. These relationships reflect the physics that is observed in the simulations and could be used to compare, interpolate or extrapolate experimental data. With this motivation we performed power law regression of the chemical potential data for the two classes of modifiers using  $\sigma_c$  and  $n$  as the functional molecular parameters and arrived at the following relationships:

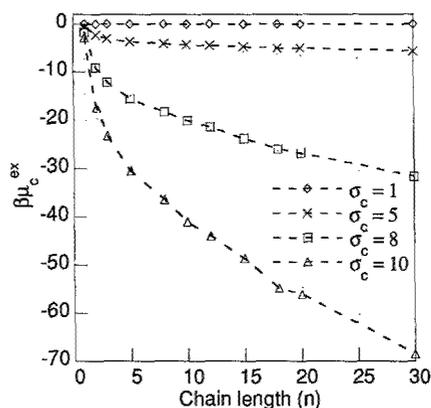
$$\text{Nonadsorbing modifiers} \quad \beta\mu_c^{ex} = 0.13\sigma_c^{2.34} n^{-0.48}$$

$$\text{Freely adsorbing modifiers} \quad \beta\mu_c^{ex} = -0.012\sigma_c^{3.07} n^{0.44}$$

For nonadsorbing modifiers modeled with the HS potential it has been shown that the chemical potential shows a cubic polynomial dependence on  $\sigma_c / R_g$  where  $R_g$  is the radius of gyration of the polymer. [15, 18, 19] Hence the empirical power law scaling exponents shown above have little physical significance and are a mathematical consequence of reducing a cubic



**Figure 3** Infinite dilution LJ colloid chemical potential vs. colloid diameter in a dilute LJ polymer solution at different polymer chain lengths. The line is a guide to the eye.



**Figure 4** Infinite dilution LJ colloid chemical potential vs. polymer chain length in a dilute LJ polymer solution for different colloid diameters. The line is a guide to the eye.

polynomial to a power law function of the independent molecular parameters. However, for the freely adsorbing modifiers, we believe that a physical import can be attributed to the exponents in the scaling relationship. The cubic dependence on  $\sigma_c$  is essentially a product of a linear term ( $\sigma_c$ ) and a square term ( $\sigma_c^2$ ). The linear dependence represents *unit particle-polymer interaction energy* since the LJ attractive energy varies linearly with the particle diameter. The square term is a surface area effect which is indicative of the number of chains that adsorb on the particle i.e., the *number of particle-polymer interactions*. The chain length exponent arises out chain adsorption and represents the thickness of the adsorbed layer. For chains that are anchored on a surface in a theta solvent, the mean field theory predicts that the thickness of the adsorbed layer scales with  $n^{0.5}$ . [21] In the case of freely adsorbing modifiers, the chains would tend to swell a little more compared to tethered chains and hence one would expect that the exponent would be slightly lower than 0.5. In addition, since the adsorbed chains are closely packed near the particle surface, the attractive and repulsive interactions between the chain segments would be relatively balanced, thereby simulating close to theta solvent conditions.

## CONCLUSIONS

The EEMC method was adapted and applied to calculate the infinite dilution nanoparticle chemical potential in the presence of organic surface modifiers as a function of particle diameter and modifier chain length. Two broad classes of organic modifiers were explored: nonadsorbing modifiers and freely-adsorbing modifiers. For both cases it was shown that the addition of short chain organic modifiers ( $n < 20$ ) brings about a substantial reduction in the chemical potential, compared to pure monomer solvent at the same volume fraction. The dependence of particle chemical potential on polymer chain length and particle diameter was found to be represented well by empirical power law scaling relationships of the form  $\beta\mu_c^{ex} \propto \sigma_c^a n^b$  for both types of

modifiers. For nonadsorbing modifiers the  $\sigma_c$  and  $n$  dependencies arise purely out of excluded volume and entropic contributions. However for adsorbing modifiers, the LJ attraction energy, surface area and chain adsorption are responsible for the dependence of  $\beta\mu_c^{ex}$  on  $\sigma_c$  and  $n$ . These scaling relationships, though empirical, could be used to guide experiments and efforts towards theoretical development of chemically specific equations of state for these complex nanoparticle-polymer mixtures.

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