Solvophobic and Solvophilic Effects on the Potential of Mean Force between Two Nanoparticles in Binary Mixtures

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Received October 14, 2001; Revised Manuscript Received November 11, 2001

ABSTRACT

We apply the integral equation theory to study the solvent-induced potential of mean force between two passivated nanoparticles in binary mixtures. We consider a particular model mixture involving two solvent components, where the nanoparticle is weakly solvophilic with respect to one component and solvophobic with respect to the other one. We show that the increase in the mole fraction of the second component results in a more attractive interaction potential between two nanoparticles due to the enhancement of the solvophobic attraction between them, and that these changes in the interaction potential are comparable to the thermal energy. Our results indicate the possibility of using cosolvents in order to tune the degree of solvation and the interaction strength between nanoparticles in solution.

The study of matter on a nanometer length scale is becoming increasingly important due to the development of novel technologies leading to significant reduction in the size of electronic and optical devices. Of great importance to future technology is the ability to assemble metallic and semiconducting nanoparticles into well-defined configurations in space. The spatial arrangements of these nanoparticles can be employed to build increasingly complex structures, thereby extending the variety of chemical materials that can be used for different purposes.

Colloidal nanoparticles spontaneously form ordered 2D and 3D arrays provided that the size distribution of the nanoparticles is sufficiently narrow and that proper conditions are fulfilled. By now, self-assembly of nanoparticles is a well-established phenomenon and has been demonstrated experimentally for a wide variety of materials, including metallic nanocrystals such as gold[1−4] and silver,[5−7] magnetic nanoparticles such as cobalt[8,9] and Fe_3O_4,[10] and semiconductor nanocrystals including CdSe,[11−13] CdS,[14] and InP.[15]

One of the key quantities governing the structure of self-assembled systems is the *solvent mediated* interparticle interaction potential. In our recent work, we have employed the integral equation theory to compute the solvent mediated potential of mean force (PMF) between two nanoparticles in solution.[16] Our microscopic model for a nanoparticle included both the nanocrystal core and its passivation layer. By adjusting the coupling strength between the solvent and the passivation shell we were able to tune the solvent-induced

PMF to desired values. Specifically, in the case of strong solvent-passivation coupling (solvophilic nanoparticle), it is energetically favorable for the nanoparticles to keep their respective solvation shells, and the overlap of these shells at close separations results in a strongly repulsive solvent-mediated PMF (this is known as desolvation effect). On the other hand, in the case of weak solvent-passivation coupling, the two nanoparticles exhibit a strong "solvophobic attraction", which is due to the energetically favorable dewetting process. To achieve the delicate balance of repulsive and attractive forces required for self-assembly, it was found necessary to employ values of the solvent-passivation coupling strength that were intermediate between solvophobic and solvophilic cases.

On the experimental side, the solvent-passivation coupling strength can be tuned by changing the chemical composition of the passivation layer (e.g., by fluorinating the hydrocarbon tails of the molecules comprising the layer, which would enhance their polarity, thereby increasing the range and strength of their interactions with the solvent).[17] Another possible way of fine-tuning the solvent-passivation coupling is by adding to the solution a small amount of cosolvent, which differs strongly in its interactions from the dominant solvent. In fact, there exists substantial experimental evidence that the addition of cosolvents can have a profound effect on the nanoparticle self-assembly process in solution.[4,13] In view of that, it would be useful to develop a microscopic

theoretical treatment of this phenomenon. This is the goal of the present study.

We start by generalizing our previous treatment of the interactions between nanoparticles in a neat (one-component) solvent[16] to the case of multicomponent solutions. To this end, we consider an $(n + 1)$-component system, with two dilute nanoparticles labeled as component 0, and various solvent components labeled by index i running from 1 to n. The solvent-mediated PMF between two nanoparticles is given by the following exact relations:[18]

$$W(R) = \int_R^\infty F(R')\, \mathrm{d}R' \tag{1}$$

where $F(R)$ is the projection of the force along the line connecting the two solutes and the force is given by

$$\vec{F}(R) = -\sum_{i=1}^n \int \mathrm{d}\vec{r}\, \nabla u_{0i}^A(r)\rho_i(\vec{r}; R) \tag{2}$$

In the above, $\rho_i(\vec{r}; R)$ is the conditional probability of finding the particle of the ith solvent component at $\vec{r}$ given that one nanoparticle (labeled A) is at the origin, and the other nanoparticle (labeled B) is located at $\vec{R}$. The direct interaction potential between the nanoparticle and the ith solvent is given by u_{0i}^j, where $j = A, B$.

To compute the solvent density profile $\rho_i(\vec{r}; R)$, we employ the anisotropic hypernetted chain (HNC) integral equation theory,[19] whose accuracy was tested for a one-component solvent:[16,20]

$$\rho_i(\vec{r}; R) = \chi_i\rho_b \exp[-\beta(u_{0i}^A(r) + u_{0i}^B(|\vec{r} - \vec{R}|)) +$$
$$\sum_{j=1}^n \int \mathrm{d}\vec{r}'\, c_{ij}(|\vec{r} - \vec{r}'|)(\rho_j(\vec{r}'; R) - \chi_j\rho_b)] \tag{3}$$

where $\beta = 1/k_BT$, ρ_b is the bulk number density, χ_i is the mole fraction of the ith solvent component, and $c_{ij}(r)$ is the direct pair correlation function for solvent particles of type i and j. The latter is obtained by solving the multicomponent Ornstein−Zernike (OZ) equation:[21]

$$h_{ij}(r) = c_{ij}(r) + \rho_b \sum_{k=1}^n \int \mathrm{d}\vec{r}'\, c_{ik}(|\vec{r} - \vec{r}'|)h_{kj}(r') \tag{4}$$

coupled with the HNC closure

$$h_{ij}(r) = \exp[-\beta u_{ij}(r) + h_{ij}(r) - c_{ij}(r)] \tag{5}$$

where $h_{ij}(r)$ is the total pair correlation function and $u_{ij}(r)$ is the direct interaction potential for solvent particles of type i and j.

It is worth pointing out that the word "anisotropic" in the present context refers to the fact that the solvent density profile induced by the nanoparticles is not spherically symmetric. This needs to be distinguished from the inho-
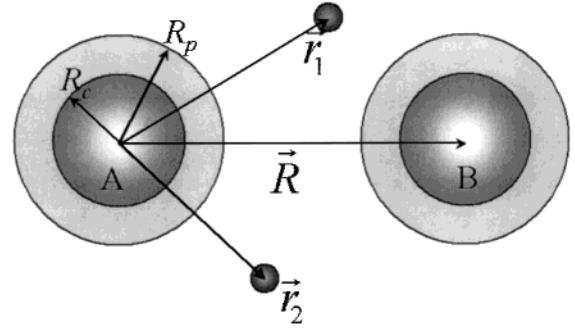

Figure 1. A sketch of the model used to describe the passivated nanoparticles. R_c and R_p are the radii of the core and passivation layer, respectively, and $\vec{R}$ is the position vector of nanoparticle B given that nanoparticle A is at the origin. The position vector of representative solvent molecules of type 1 and 2 are given by $\vec{r}_1$ and $\vec{r}_2$, respectively.

mogeneous integral equation method of Kjellander and co-workers,[22] where the word "anisotropic" refers to the solvent pair correlation functions. In our approach, only isotropic correlation functions are used, and the method belongs to the class of singlet integral equations; it is also known as "dumbbell singlet HNC" or "three-point extension of HNC".[19] With the above, the solvent-mediated PMF between two nanoparticles can be computed once the interaction potentials for the solvent and nanoparticles are specified.

We employ the same microscopic model for the nanoparticles as in our previous work.[16] In this model, a nanoparticle consists of a central core of radius R_c surrounded by a spherical shell of thickness $(R_p - R_c)$, which represents the passivation layer (see Figure 1). The nanoparticle core and passivation shell are uniformly composed of Lennard-Jones (LJ) particles with parameters ϵ_c and σ_c (with number density ρ_c), and ϵ_p and σ_p (with number density ρ_p), respectively.

We assume that the solvent particles interact with each other via a shifted LJ potential:

$$u_{ij}(r) = \begin{cases} u_{ij}^{LJ}(r) - u_{ij}^{LJ}(R_{ij}^{cut}), & r \le R_{ij}^{cut} \\ 0 & r > R_{ij}^{cut} \end{cases} \tag{6}$$

with

$$u_{ij}^{LJ}(r) = 4\epsilon_s^{ij}\left[\left(\frac{\sigma_s^{ij}}{r}\right)^{12} - \left(\frac{\sigma_s^{ij}}{r}\right)^6\right] \tag{7}$$

In the above, ϵ_s^{ii} and σ_s^{ii} are the well depth and the diameter for the ith solvent component: the corresponding parameters for the $i-j$ pair are obtained from the standard combining rules ($\epsilon_s^{ij} = \sqrt{\epsilon_s^{ii}\epsilon_s^{jj}}$ and $\sigma_s^{ij} = 1/2(\sigma_s^{ii} + \sigma_s^{jj})$), and R_{ij}^{cut} is the cutoff parameter for the $i-j$ pair.

The interactions between the ith solvent particle and the individual particles comprising the core and the passivation layer of the nanoparticle are modeled via (nonshifted) LJ potentials. We use the standard combining rules for the cross terms $\epsilon_{sc}^i = \sqrt{\epsilon_s^{ii}\epsilon_c}$ and $\sigma_{sc}^i = 1/2(\sigma_s^{ii} + \sigma_c)$, and for $\sigma_{sp}^i = 1/2(\sigma_s^{ii} + \sigma_p)$, while ϵ_{sp}^i (the coupling strength between the solvent and the passivation shell) is taken to be an independent parameter, which makes it possible to tune the interac-

tion strength between the solvent and the nanoparticle. The analytic forms for solvent−nanoparticle ($u_{0i}(R)$) and nanoparticle−nanoparticle ($u_{00}(r)$) direct interaction potentials are obtained by integrating the individual LJ interactions over the volume of the corresponding spheres.[16,23]

In our previous work on the PMF between nanoparticles in a one-component solvent,[16] the direct interactions between the solvent particles were modeled via the repulsive soft-sphere potential, which can be obtained from eq 6 as $u_{11}(r)$ (for a neat solvent $i = j = 1$) with the cutoff parameter taken to be $R_{11}^{cut}/\sigma_s^{11} = 2^{1/6}$. To achieve a delicate balance between repulsive and attractive nanoparticle−nanoparticle forces within the above model, it was found necessary to make the nanoparticle *weakly* solvophilic (specifically, we set the solvent-passivation coupling parameter to be $\epsilon_{sp}/\epsilon_s^{11} = 0.045$). When ϵ_{sp} is increased, the solvent-mediated PMF between the two nanoparticles becomes more and more repulsive (due to the desolvation effect), while decreasing the value of ϵ_{sp} results in the strong solvophobic attraction between the nanoparticles.

As already mentioned, the strength of the interaction between nanoparticles can be tuned not only by varying the solvent-passivation coupling parameter, but also by adding to the solution a small amount of cosolvent, whose interactions differ substantially from the dominant solvent. Consider, for example, a situation, where the dominant solvent (labeled as component 1) is modeled as a soft-sphere fluid, while the cosolvent (labeled as component 2) is modeled as a LJ fluid (with nonshifted LJ interaction potential given by eq 7). In this case, the interactions between particles of type 1 are purely repulsive, while the interactions between particles of type 2 have a strong attractive component. If the solvent-passivation coupling parameter is taken to be relatively small for *both* components, then the solvent particles of type 1 will be attracted to the nanoparticle more strongly than to each other, while the solvent particles of type 2 will be attracted to to each other more strongly than to the nanoparticle. In other words, the nanoparticle will be weakly solvophilic with respect to component 1 and solvophobic with respect to component 2. In view of the above, one can expect that the increase of the mole fraction of component 2 would result in a more attractive solvent-mediated (and total) PMF between two nanoparticles in solution due to the enhanced solvophobic attraction. This indeed will be seen below.

To study the effect of the cosolvent on the nanoparticle interactions, we consider a simple model involving two dilute nanoparticles in a mixture of two solvent components. All the potential parameters for the two components are taken to be identical (i.e., $\sigma_s^{11} = \sigma_s^{22} \equiv \sigma_s$ and $\epsilon_s^{11} = \epsilon_s^{22} \equiv \epsilon_s$) *except* for the cutoff parameters, which are taken to be $R_{11}^{cut}/\sigma_s^{11} = 2^{1/6}$ and $R_{22}^{cut}/\sigma_s^{11} = R_{12}^{cut}/\sigma_s^{11} = \infty$. The solvent-passivation coupling strength is assumed to be the same for both components: $\epsilon_{sp}^1 = \epsilon_{sp}^2 \equiv \epsilon_{sp} = 0.045\epsilon_s$. The values of the remaining direct interaction potential parameters are taken to be as follows:[16] $\rho_c^* = \rho_p^* = 1$, $\epsilon_c^* = 2$, $\epsilon_p^* = 0.2$, $\epsilon_{sp}^* =$
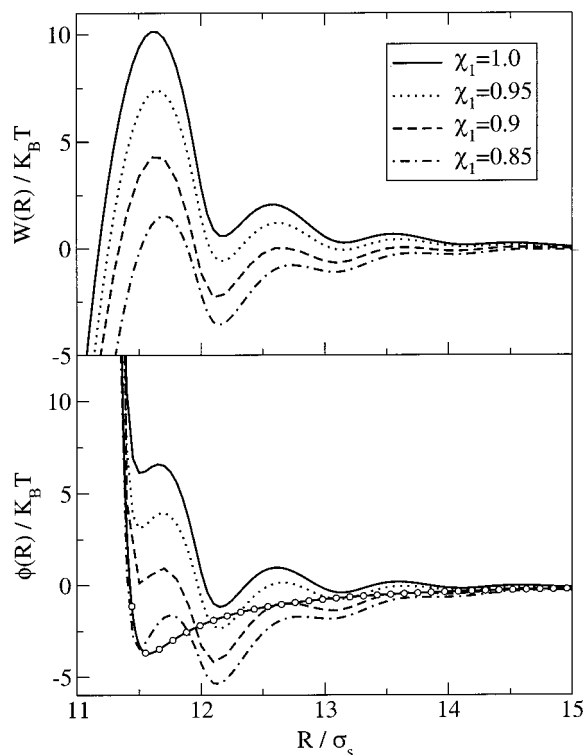

Figure 2. A plot of the potential of mean force between two passivated nanoparticles in a binary mixture computed from the anisotropic HNC theory. The upper panel shows the solvent mediated potential of mean force. The lower panel shows the total potential of mean force and the bare interaction potential between two nanoparticles (circles connected by a solid line).

0.045, $\sigma_c^* = \sigma_p^* = 1$, $R_c^* = 3.5$, and $R_p^* = 5.5$ (from now on we employ dimensionless units defined in terms of the σ_s and ϵ_s).

With the above values of the model potential parameters, we compute the solvent-mediated PMF between two nanoparticles from eq 1, as well as the total PMF given by $\phi(r) = W(r) + u_{00}(r)$. The model calculations are performed at the following thermodynamic conditions of the solvent: $\rho^* = \rho\sigma_s^3 = 0.7$ and $T^* = k_BT/\epsilon_s = 1.2$. We consider the following four values of the mole fraction of the cosolvent: $\chi_2 = 0, 0.05, 0.1$, and 0.15 (the first case corresponds to the neat solvent 1). Our results for the solvent-mediated PMF are shown in the upper panel of Figure 2, while the total PMF and the bare nanoparticle−nanoparticle interaction potential are displayed in the lower panel of Figure 2. As expected, one sees that the increase in χ_2 results in a more attractive PMF. However, the overall effect is dramatic and the changes observed in the PMF in going from one value of χ_2 to the next one (i.e., a change of 5% in the mole fraction) are on the order of a few k_BT. This observation is of importance, since the nanoparticle self-assembly process requires the presence of potential wells and barriers comparable to thermal energy.

Our results can be used to provide a microscopic explanation to recent experimental results regarding the effects of binary solvent mixtures on the self-assembly process of nanoparticles.[4,13] In the case of metallic gold nanocrystals, adding a polar solvent results in the formation of multilayer

domains.[4] In the context of the present theory, the polar solvent induces stronger solvophobic attractions between the nanoparticles, resulting in the formation of a thicker assembled layer due to the stronger nanoparticle−nanoparticle interactions.

To summarize, in the present work we have generalized our previous microscopic treatment of the interactions between nanoparticles in a neat solvent to the case of multicomponent mixtures. The solvent-mediated PMF between two dilute nanoparticles was obtained from the anisotropic HNC integral equation theory suitably generalized for mixtures. We considered a particular model mixture involving two solvent components, where the nanoparticle is weakly solvophilic with respect to the dominant solvent and solvophobic with respect to the cosolvent. We showed that a small increase in the mole fraction of the cosolvent results in a dramatic change in the PMF between two nanoparticles due to the enhancement of the solvophobic attraction between them. These changes in the PMF in going from one value of χ_2 to the next one (i.e., a change of 5% in the mole fraction of the second solvent) are on the order of a few $k_B T$.

The results obtained in this work indicate that: (a) it is possible to vary the interaction strength between nanoparticles in solution by an amount comparable to thermal energy by adding a cosolvent with respect to which the nanoparticles are solvophobic, and therefore to provide an important parameter that can be used to control the structures obtained in the self-assembly process; and (b) it is possible to use solvent mixtures in order to vary the degree of solvation of the nanoparticles, thus extending the variety of solvents that can be used to control the self-assembly process. Preliminary studies along these lines have already been carried out experimentally for metallic[4] as well as semiconductor[13] nanocrystals.

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NL015645R