Published in final edited form as:

AIP Conf Proc. 2016 ; 1736(1): . doi:10.1063/1.4949655.

Hydrodynamic Radius Fluctuations in Model DNA–Grafted Nanoparticles*

Fernando Vargas–Lara^{1,2,a)}, Francis W. Starr², and Jack F. Douglas¹

¹Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899, USA

²Department of Physics and Department of Molecular Biology and Biochemistry, Wesleyan University, Middletown, CT, 06459, USA

Abstract

We utilize molecular dynamics simulations (MD) and the path–integration program ZENO to quantify hydrodynamic radius (R_h) fluctuations of spherical symmetric gold nanoparticles (NPs) decorated with single–stranded DNA chains (ssDNA). These results are relevant to understanding fluctuation–induced interactions among these NPs and macromolecules such as proteins. In particular, we explore the effect of varying the ssDNA–grafted NPs structural parameters, such as the chain length (L), chain persistence length (l_p), NP core size (R), and the number of chains (N) attached to the nanoparticle core. We determine R_h fluctuations by calculating its standard deviation (σ_{R_h}) of an ensemble of ssDNA–grafted NPs configurations generated by MD. For the parameter space explored in this manuscript, σ_{R_h} shows a peak value as a function of N , the amplitude of which depends on L , l_p and R , while the broadness depends on R .

INTRODUCTION

Dispersed nanoparticles (NPs) in solution and in polymer matrices are normally “dressed” by grafted polymer layers or by layers of adsorbed polymers, an effect that greatly influences their solubility and their interaction with each other and other “crowding” macromolecules in their environment. This issue is especially important for protein adsorption onto nanoparticles in aqueous solution [1] and for understanding inter–nanoparticle interactions [2, 3, 4]. Characterization of the diffuse interfacial layers of these NPs is a notoriously difficult problem, and the inherent NP shape complexity of many NPs further complicates NP characterization. In the present work, we show how the program ZENO [5] can be used to gain insight into the chain conformation fluctuations of model ssDNA–grafted gold NPs studied previously both computationally [6, 7] and experimentally [8, 9]. First, we generate ensembles of this kind of NPs by molecular dynamics simulations

*Official contribution of the U.S. National Institute of Standards and Technology - Not subject to copyright in the United States.

^{a)}Corresponding author: fernando.vargaslara@nist.gov.

DISCLAIMER

This article identifies certain commercial materials, equipment, or instruments to specify experimental procedures. Such identification implies neither recommendation or endorsement by the National Institute of Standards and Technology nor that the materials or equipment identified were necessarily the best available for the purpose.

(MD) and we calculate the distribution of the hydrodynamic radii (R_h) for these NPs where the NP radius (R), number of strands attached to the NP core (N), ssDNA chain length (L), and the ssDNA chain persistence length (l_p) are varied to determine the distribution of R_h and its standard deviation (σ_{R_h}) as a function of relevant molecular parameters.

NUMERICAL RESULTS AND CONCLUSIONS

We briefly describe the coarse-grained model for spherical symmetric gold nanoparticles (NPs) decorated with single-stranded DNA chains (ssDNA) utilized in our calculations. In this molecular model, we represent each ssDNA chain as a set of “beads” (blue spheres on Figure 1) connected by “springs” [10]. One end of each chain is tethered to a spherical symmetric particle (orange sphere on Figure 1a) representing a gold core NP in the experimental system). In more detail, we use a Weeks–Chandler–Andersen potential (U_{WCA}) to simulate the excluded volume interaction among all the beads and between each bead and the NP core,

$$U_{WCA}(r) = U_{LJ}(r - r_s) - U_{LJ}(r_c) - (r - r_c) \left. \frac{dU_{LJ}(r - r_c)}{dr} \right|_{r=r_c}. \quad (1)$$

Here, U_{LJ} is the Lennard–Jones potential, r represents the distance between two beads or one bead and the NP core, r_s is the distance that the origin of the potential has been shifted, and r_c is a cutoff distance. We chose $r_c = r_s + 2^{1/6}\sigma$ (the defining choice for the WCA potential), where σ is the LJ length parameter, to generate particles having a radius $R_{particle} = r_s + \frac{\sigma}{2}$. For the blue beads we consider $r_s = 0$ and we set $\sigma = 0.65$ nm [8], for the NP core we vary $r_s = 0.675$ nm or $r_s = 4.675$ nm to generate NPs having core radius $R = 1.0$ nm or $R = 5.0$ nm, respectively. The beads along the chain and the first bead of each chain are connected by using a FENE potential,

$$U_{FENE}(r) = -\frac{kR_0^2}{2} \ln \left[1 - \left(\frac{r - r_s}{R_0} \right)^2 \right]. \quad (2)$$

For this potential, we select $k = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$. Additionally, we use a three-body angular potential ($U_{lin}(\theta)$) to control the ssDNA chain stiffness,

$$U_{lin}(\theta) = k_{lin}(1 + \cos\theta). \quad (3)$$

We consider $k_{lin} = (1 \text{ or } 50) \epsilon$ (ϵ is the LJ energy parameter) to generate chains having persistence lengths $l_p = (2.0 \pm 0.1 \text{ nm})$ (a representative value for ssDNA chains in solution in the salt concentration range normally considered [11]) and $l_p = 33.0 \pm 0.07$ nm (a value much bigger than the values experimentally reported for ssDNA in solution), respectively. Here, l_p is defined as the characteristic length where the bond orientation correlation

function $\langle \vec{u}(s) \cdot \vec{u}(s') \rangle$ reaches the value of $\exp(-1)$. Here, $\vec{u}(s)$ is a unit vector tangent to the chain that is located at the position s . We consider ssDNA chains having chain lengths $L = (5, 10, 18, \text{ or } 40)$ Thymine bases (T).

We consider a canonical ensemble (NVT) with fixed reduced temperature $T^* = 1.0 \text{ } e/k_B$ for all our simulations (k_B is the Boltzmann constant) and it is controlled by using the Nosé–Hoover method [12, 13]. We perform MD simulations for periods of time 10^7 time steps and we compute the hydrodynamic radius (R_h) for 10^3 different thermal equilibrated configurations (see Figure 1(b)) using the path–integration program ZENO [5], employing 10^5 random paths to achieve low uncertainty. We compute the standard deviation for the hydrodynamic radius (σ_{R_h}) for the 10^3 calculations and the error bars represent one standard deviation of σ_{R_h} by performing block averaging for every 200 values of R_h . We carry out MD simulations using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [16] and we render the left panel of Figure 1 using the Visual Molecular Dynamics (VMD) program [14].

Figures 2 and 3 show how σ_{R_h} of the probability density function for R_h , calculated as in Figure 1(b), changes with the number of grafted ssDNA chains having variable L , R , and l_p . We first see from Figure 2 that the R_h fluctuations for a $R = 5.0 \text{ nm}$ NP and $l_p = 2.0 \text{ nm}$ rises rapidly at first with N peaking around $N = 12$, which corresponds to a grafting density of $\approx 0.038 \text{ chains/nm}^2$, and σ_{R_h} then falls slowly towards zero with increasing N . The inset in Figure 2 shows that the peak height increases roughly linearly with increasing L . We also find from Figure 3 that the peak height from σ_{R_h} is higher for a larger NP core and for more flexible chains. Additionally, Figure 3(a) shows that the number of strands at which the position σ_{R_h} reaches its peak depends on R , an effect that evidently derives from the higher interfacial area of the larger NP. Similar trends are observed for the radius of gyration of these ssDNA–grafted NPs (not shown). We then see that it is possible to “tune” the NP shape and mobility fluctuations of the NPs by varying the NP core size, polymer chain length and chain grafting density to control the mutual interaction of these NPs with other molecules and surfaces in their environment.

Recent work has established that the presence of a fluctuating layer of grafted chains on NPs can lead to self–assembly of the NPs into large–scale string and sheet clusters [3]. This many–body effect is under active investigation [4], but it appears that the fluctuating segment density or “segmental polarizability” gives rise to directional interactions by a spontaneous symmetry breaking process similar to directional interactions arising from dielectric fluctuations in colloidal particles [15]. The characterization of segmental density fluctuations is then expected to be important in modeling and controlling many–body attractive interactions between particles that lead them to cluster and self–assemble into large scale structures in solutions and polymer matrices.

Acknowledgments

This work was supported by NIST awards 70NANB13H202 and 70NANB15H282.

References

1. Welsch N, Lu Y, Dzubiella J, Ballauff M. *Polymer*. 2013; 54:2835–2849.
2. Chevigny C, Dalmas F, Cola ED, Gimes D, Bertin D, Bou F, Jestin J. *Macromolecules*. 2011; 44:122–133.
3. Akcora P, Liu H, Kumar SK, Moll J, Li Y, Benicewicz BC, Schadler LS, Acehan D, Panagiotopoulos AZ, Pryamitsyn V, Ganesan V, Ilavsky J, Thiagarajan P, Colby RH, Douglas JF. *Nature Materials*. 2009; 8:354–359. [PubMed: 19305399]
4. Silvera Batista CA, Larson RG, Kotov NA. 2015; 350:1242477–10.
5. Mansfield M, Douglas J. *Physical Review E*. 2008; 78:046712–11.
6. Starr FW, Sciortino F. *Journal of Physics Condensed Matter*. 2006; 18:L347–353. [PubMed: 21690795]
7. Padovan-Merhar O, Lara FV, Starr FW. *The Journal of Chemical Physics*. 2011; 134:244701–7. [PubMed: 21721651]
8. Chi C, Vargas-Lara F, Tkachenko AV, Starr FW, Gang O. *ACS Nano*. 2012; 6:6793–6802. [PubMed: 22793369]
9. Ko SH, Vargas-Lara F, Patrone PN, Stavis SM, Starr FW, Douglas JF, Liddle JA. *Soft Matter*. 2014; 10:7370–7378. [PubMed: 25080973]
10. Kremer K, Grest GS. *The Journal of Chemical Physics*. 1990; 92:5057–5086.
11. Sim AYL, Lipfert J, Herschlag D, Doniach S. *Physical Review E*. 2012; 86:021901–6.
12. Nosé S. *The Journal of Chemical Physics*. 1984; 81:511–519.
13. Hoover WG. *Physical Review A*. 1985; 31:1695–1697.
14. Humphrey W, Dalke A, Schulten K. *Journal of Molecular Graphics*. 1996; 14:33–38. [PubMed: 8744570]
15. Barros K, Luijten E. *Physical Review Letters*. 2014; 113:017801–5.
16. Plimpton S. *Journal of Computational Physics*. 1995; 117:1–19.

FIGURE 1.

We show an snapshot for a representative configuration of a simulated ssDNA-grafted NP. Here, the gold NP core is 5.0 nm in radius (orange sphere) and there are 60 ssDNA chains (connected blue spheres) grafted onto the NP core. Each ssDNA chain is formed by 18 T bases with a persistence length $l_p = 2.0$ nm. b) The hydrodynamic radius R_h calculations are based on 10^3 configurations of the type shown in the panel a). The probability density function from the ensemble of configurations is shown to the left. The R_h of these NPs shows fluctuations associated with shape variations of the grafted chains.

FIGURE 2.

The standard deviation of the hydrodynamic radius σ_{R_h} as a function of the number of ssDNA chains attached to the NP core N . Here, we fix the radius of the core $R = 5.0$ nm and the chain persistence length $l_p = 2.0$ nm and we vary the ssDNA chain length $L = (5, 10, 18, 40)$ T bases. We find σ_{R_h} shows a peak value whose magnitude increases roughly linearly with L . The inset shows the peak value of σ_{R_h} as a function of L . Dashed lines are a guide to the eyes.

FIGURE 3.

The standard deviation of the hydrodynamic radius σ_{R_h} as a function of the number of ssDNA chains attached to the NP core N . In the left panel, we fix the ssDNA chain length $L = 10$ T and the ssDNA chain persistence length $l_p = 2.0$ nm and we vary the core radius $R = 1.0$ nm (black circles) or $R = 5.0$ nm (red squares). The inset shows the average R_h for the same NPs. In the right panel, we fix the core radius $R = 5.0$ nm and ssDNA chain length $L = 10$ T bases, and we vary the ssDNA chain persistence length $l_p = 2.0$ nm (green circles) or $l_p = 33.0$ nm (orange squares). The dashed lines guide the eyes.