

Tunable Primary and Secondary Encapsulation of a Charged Nonspherical Nanoparticle: Insights from Brownian Dynamics Simulations

Houyang Chen*, Eli Ruckenstein*

*Department of Chemical and Biological Engineering, University at Buffalo, The State University
of New York, Buffalo, New York 14260-4200, USA*

* Email: hchen23@buffalo.edu (H. C.).

* Email: feaeliru@buffalo.edu (E.R.).

Section S1. Simulation details.

The simulation system contains a charged nonspherical nanoparticle (NSNP), Janus particles (JPs) and ions (see Figure S1). The charged NSNP and JPs are constructed as a simple cubic cell (SCC) model, with a size of $20 \times 20 (\sigma_0)^2$ single bead layer for the former and a size of $2 \times 2 \times 2 (\sigma_0)^3$ for the latter. If the size of NSNP is taken to represent a modified graphene nanoparticle of approximately $100 \text{ nm} \times 100 \text{ nm}$ ¹, the corresponding size of a JP is $(10 \text{ nm})^3$. The charge of each bead in a NSNP is $+1e$. The upper layer of a JP containing a $-1e$ charge in each bead is denoted as the electrostatic layer (ESI layer), whereas the lower layer of a JP possessing only a van der Waals (VDW) interaction for each bead is denoted as the VDW layer (see Figure S1c). Ions are used to balance the charge in the simulation box. The simulations are performed in a $(60\sigma_0)^3$ simulation box and the number density of JPs is $9.26 \times 10^{-4} (\sigma_0)^{-3}$. We used an implicit solvent model. All simulations were carried out using the Large Atomic/Molecular Massively Parallel Simulator package².

Specifically, we conducted Brownian dynamics (BD) simulations^{3,4,2,5}, in which the motion of each bead is subject to the Langevin equation

$$m_i \ddot{\mathbf{r}}_i(t) = -\nabla \sum_j [E_{ij}(\mathbf{r}_{ij}) + E_c] - m_i \zeta \dot{\mathbf{r}}_i(t) + \mathbf{F}_i^r(t) \quad (\text{S1})$$

where \mathbf{r}_i and m_i are position vector and mass of bead i , respectively. The friction coefficient

$\zeta = 1.0 \tau^{-1}$ ($\tau = (m_0 \sigma_0^2 / \varepsilon_0)^{1/2}$) and $m_i = m_0$. The random force $\mathbf{F}_i^r(t)$ applied to each bead is

$\langle \mathbf{F}_i^r(t) \cdot \mathbf{F}_j^r(t') \rangle = 6k_B T m \zeta \delta_{ij} \delta(t - t')$ (k_B is the Boltzmann constant, T is the temperature, and

δ is the Dirac delta function). The units of length σ_0 , energy ε_0 and mass m_0 are employed.

The interactions between beads in particles and/or ions follow the Lennard-Jones (LJ) potential

$$E_{ij} = \begin{cases} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] & r_{ij} \leq r_{c,ij} \\ 0 & r_{ij} > r_{c,ij} \end{cases} . \quad (\text{S2})$$

where ε_{ij} is the interaction strength between beads i and j , and $r_{c,ij}$ and r_{ij} are the cutoff distance and the distance between the centers of two beads, respectively. The LJ potential parameters are presented in Table S1. The electrostatic interactions between point charge pair are described by

$$E_c = k_B T l_B \frac{q_i q_j}{r_{ij}}, \text{ where } q_i \text{ and } q_j \text{ are the charges in beads } i \text{ and } j, \text{ respectively, and Bjerrum}$$

length $l_B = e^2 / (\epsilon k_B T)$ with the dielectric constant ϵ and elementary charge e .

After initial configurations were generated, simulations with 3×10^5 BD steps at high T^* ($T^* = k_B T / \varepsilon_0 = 5$) were carried out to avoid local minima. Later, annealing simulations in which the temperature was decreased from $T^*=5$ to the target temperature were performed. Then, we performed simulations at target temperatures with 10^7 BD steps and a time step 0.005τ . For each case, we performed multiple (≥ 3) simulations, using different initial configurations and different cooling rates. To examine the processes of the secondary encapsulation at a selected case, the initial configuration is chosen from the equilibrium configuration in the corresponding primary encapsulation. Then, the reciprocal temperature or the Bjerrum length was changed gradually as the simulation time increases.

Table S1. Lennard-Jones Potential parameters in the simulations

Interaction pairs	Energy (ε_0)	Size (σ_0)	Cutoff distance(σ_0)
B_N-B_N (bead-bead in the NSNP)	$\varepsilon_{\text{BNBN}}=1.0$	$\sigma_{\text{BNBN}}=\sigma_0$	$2^{1/6} \sigma_{\text{BNBN}}$
B_N-B_E (bead in the NSNP-bead in the ESI layer of JPs)	$\varepsilon_{\text{BNBE}}=1.0$	$\sigma_{\text{BNBE}}=\sigma_0$	$2^{1/6} \sigma_{\text{BNBE}}$
B_N-B_V (bead in the NSNP-bead in the VDW layer of JPs)	$\varepsilon_{\text{BNBV}}=1.0$	$\sigma_{\text{BNBV}}=\sigma_0$	$2.5 \sigma_{\text{BNBV}}$
B_N-I (bead in the NSNP-ion)	$\varepsilon_{\text{BNI}}=1.0$	$\sigma_{\text{BNI}}=\sigma_0$	$2^{1/6} \sigma_{\text{BNI}}$
B_E-B_E (bead-bead in the ESI layer of JPs)	$\varepsilon_{\text{BEBE}}=1.0$	$\sigma_{\text{BEBE}}=\sigma_0$	$2^{1/6} \sigma_{\text{BEBE}}$
B_E-B_V (bead in the ESI layer of JPs – bead in the VDW layer of JPs)	$\varepsilon_{\text{BEBV}}=1.0$	$\sigma_{\text{BEBV}}=\sigma_0$	$2^{1/6} \sigma_{\text{BEBV}}$
B_E-I (bead in the ESI layer of JPs – ion)	$\varepsilon_{\text{BEI}}=1.0$	$\sigma_{\text{BEI}}=\sigma_0$	$2^{1/6} \sigma_{\text{BEI}}$
B_V-B_V (bead-bead in the VDW layer of JPs)	$\varepsilon_{\text{BVBV}}=1.0$	$\sigma_{\text{BVBV}}=\sigma_0$	$2.5 \sigma_{\text{BVBV}}$
B_V-I (bead in the VDW layer of JPs - ion)	$\varepsilon_{\text{BVI}}=1.0$	$\sigma_{\text{BVI}}=\sigma_0$	$2^{1/6} \sigma_{\text{BVI}}$
I-I (ion-ion)	$\varepsilon_{\text{II}}=1.0$	$\sigma_{\text{II}}=\sigma_0$	$2^{1/6} \sigma_{\text{II}}$

Figure S1. The model in the work. (a) a positively charged nonspherical nanoparticle (NSNP); (b) and (c) a Janus particle (JP) viewed from different angles; and (d) an ion. Blue: beads from the NSNP; red: negatively charged beads of the JPs; white: non-charged beads of the JPs; orange: ions.

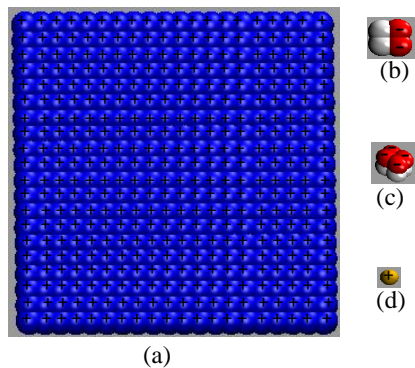
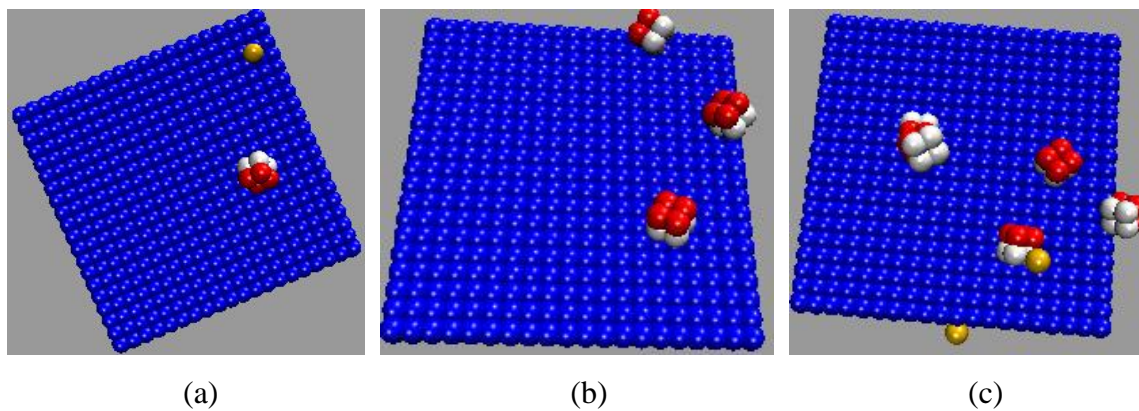
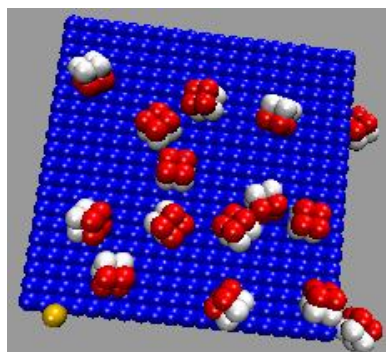
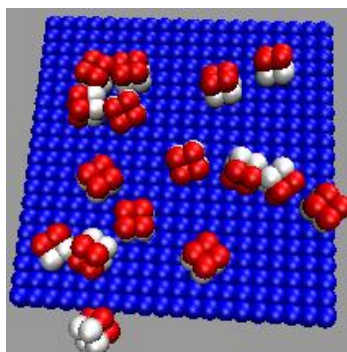


Figure S2. Dynamics of primary encapsulation of a charged nonspherical nanoparticle when the Bjerrum length $l_B = 0.1 \sigma_0$ and the reciprocal temperature increases. (a): $(1/T^*)=0.198$; (b): $(1/T^*)=0.229$; (c): $(1/T^*)=0.315$; (d): $(1/T^*)=0.368$; (e): $(1/T^*)=0.565$; (f): $(1/T^*)=1.0$; (g) $(1/T^*)=1.0$ after 10^7 BD steps.

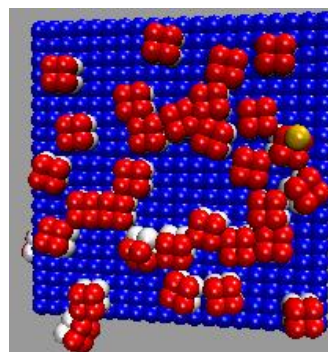




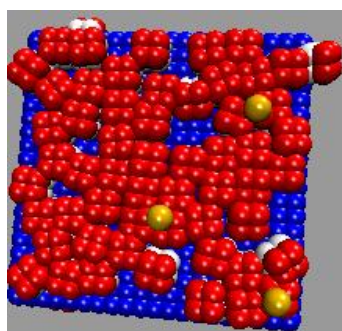
(d)



(e)



(f)



(g)

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