Electronic Supplementary Material (ESI) for Nanoscale.
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Supplementary Information: Orientational Phase Behavior of Polymer-Grafted Nanocubes

Brian Hyun-jong Lee and Gaurav Arya*

Department of Mechanical Engineering and Material Science

Duke University, Durham, NC 27708, USA

E-mail: gaurav.arya@duke.edu

Phone: 919-660-5435. Fax: 919-660-8963

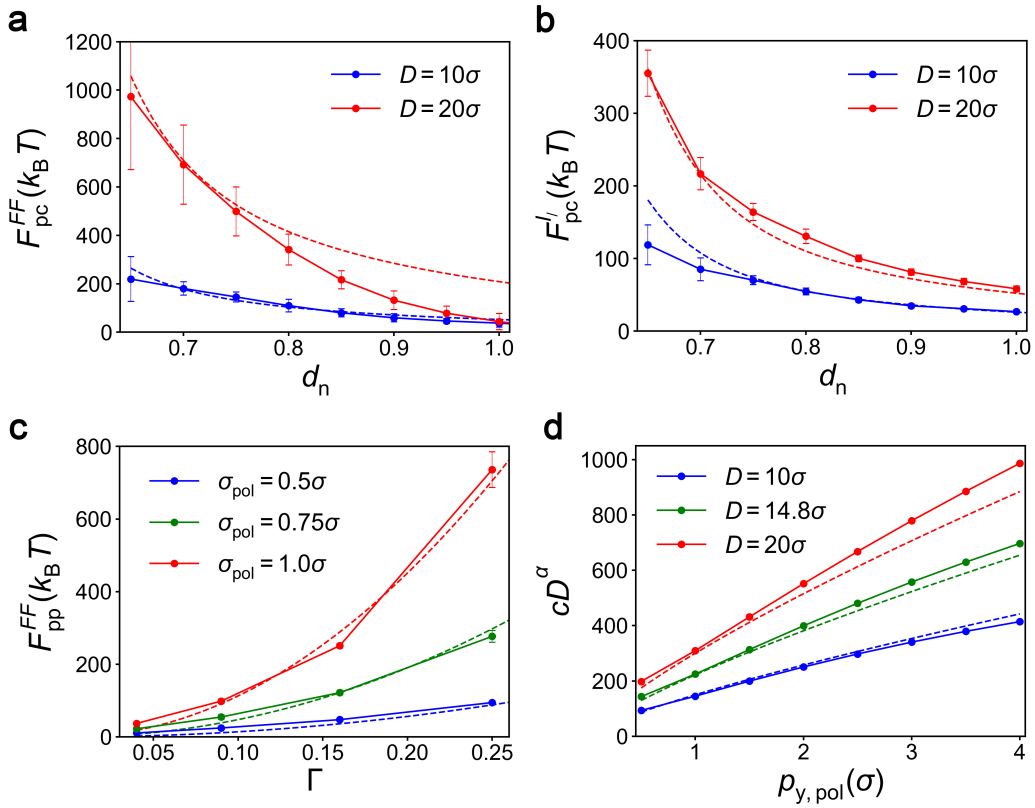

Figure S1: Effect of nanocube size on polymer-surface interaction free energies of the (a) FF phase, (b) $I_/$ phase for nanocubes with $\sigma_{\mathrm{pol}} = 0.5\sigma$, $\varepsilon_{\mathrm{pc}} = 0.05\ k_{\mathrm{B}}T$, and $\Gamma = 0.04/\sigma^2$. (c) Polymer-polymer interaction free energy F_{pp}^{FF} as a function of grafting density Γ for $D = 20\sigma$ nanocubes in the terminal region. (d) cD^{α} for the $I_/$ phase when one nanocube contacts the other at its midpoint as a function of $p_{\mathrm{y,pol}}$, which denotes the location of the most confined grafted segment. $p_{\mathrm{y,pol}}$, which depends on Γ, was used for obtaining the representative configuration of the $I_/$ phase. The coefficients c could be well fitted by the relationship $c = 15p_{\mathrm{y,pol}}^{0.78}$ and $\alpha = 1$.

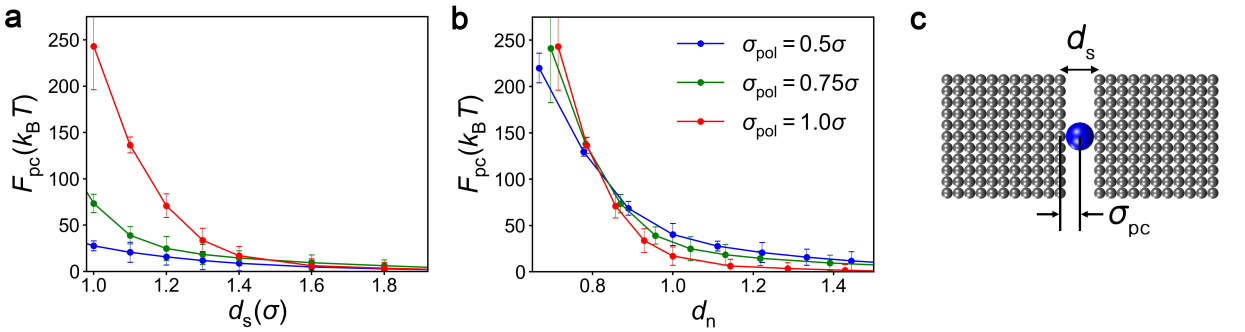

Figure S2: Distance normalization of polymer-cube interactions. Free energy F_{pc} for $D = 10\sigma$ nanocubes with $\Gamma = 0.04/\sigma^2$ and $\varepsilon_{\mathrm{pc}} = 0.05\ k_{\mathrm{B}}T$ is plotted with respect to (a) separation distance d_{s} and (b) normalized separation distance $d_{\mathrm{n}} \equiv d_{\mathrm{s}}/2\sigma_{\mathrm{pc}}$ for three different values of σ_{pol}. All three free energies curves roughly collapse onto a single curve when plotted with respect to d_{n}. (c) Schematic showing the basis for this distance normalization: the distance between the two nanocube faces at which the polymer bead (blue) bridges the two surface without getting squeezed is given by $2\sigma_{\mathrm{pc}} = \sigma_{\mathrm{pol}} + \sigma_{\mathrm{cc}}$, where σ_{cc} is the size of the atoms (gray) making up the nanocubes.

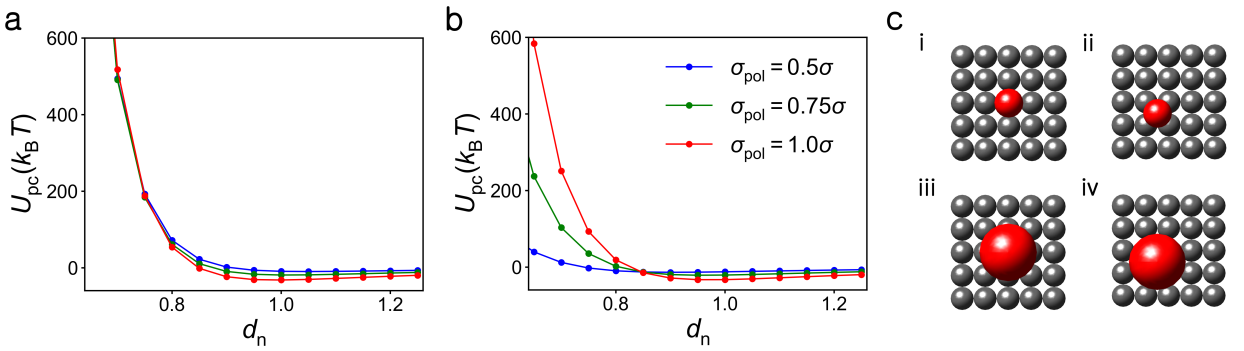

Figure S3: Effect of atomic surface roughness of nanocubes on the polymer-nanocube potential energies $U_{\rm pc}$. (a) Potential energy $U_{\rm pc}$ of a single polymer bead hovering directly above one of the lattice atoms on the surface of the nanocube. This energy, when plotted as a function of normalized distance $d_{\rm n}$ of the bead from the surface, is largely independent of the size of the polymer bead $\sigma_{\rm cc}$. (b) $U_{\rm pc}$ of a polymer bead located above the center of the cavity formed between four atoms of a square unit cell on the surface. Significant reduction in $U_{\rm pc}$ is observed when the polymer bead size becomes smaller than the size of this cavity. (c) Schematics showing a small polymer bead of $\sigma_{\rm pol} = 0.5\sigma$ (*i* and *ii*) and a large bead of $\sigma_{\rm pol} = 1.0\sigma$ (*iii* and *iv*) sitting atop (*i* and *iii*) a surface atom or and atop the cavity formed between nanocube lattice atoms (*i* and *iv*).

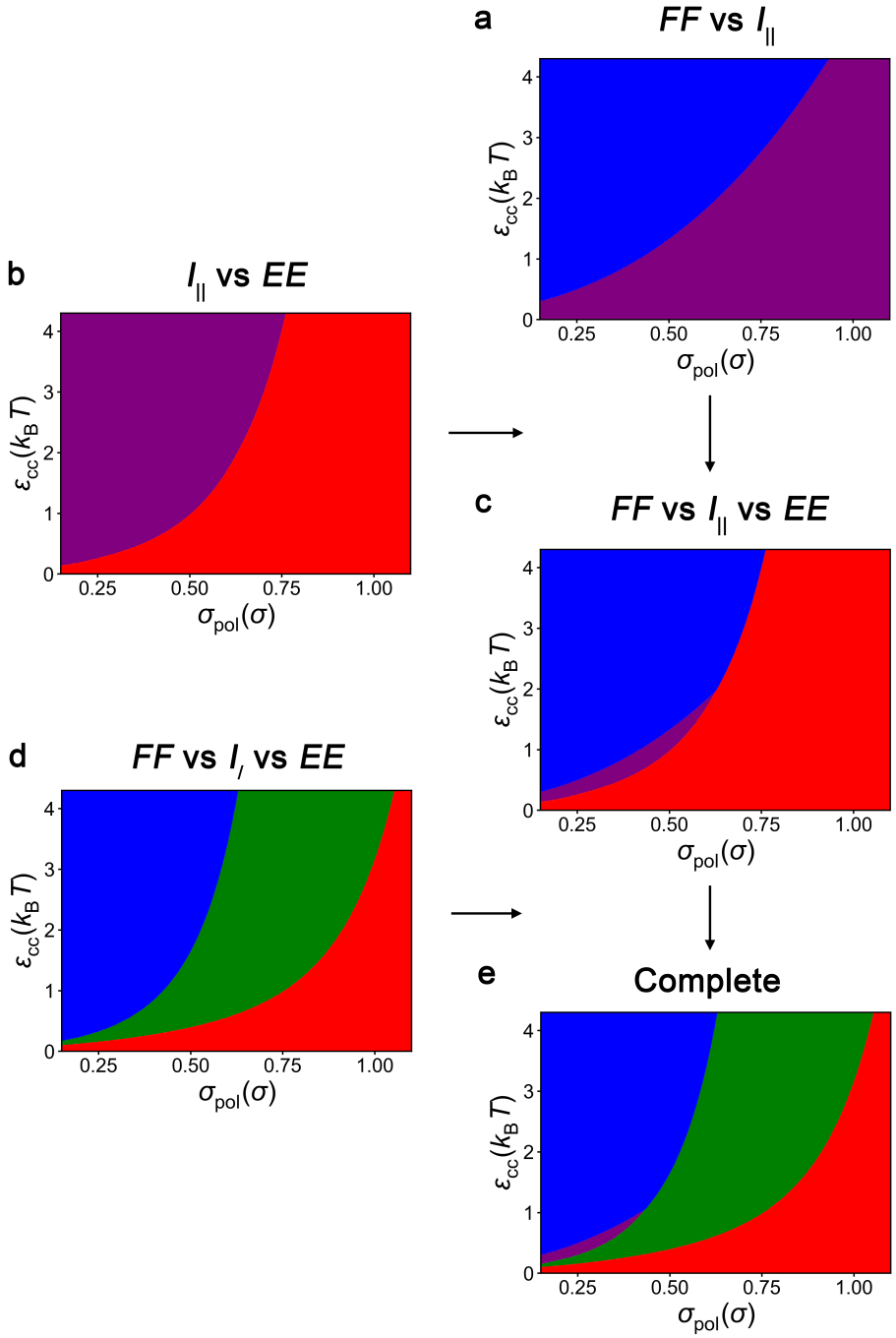

Figure S4: Intermediate phase diagram of nanocubes with $D = 10\sigma$ and $\Gamma = 0.16/\sigma^2$ considering only *subsets* of possible phases: (a) *FF*-$I_{||}$, (b) $I_{||}$-*EE*, (c) *FF*-$I_{||}$-*EE*, and (d) *FF*-$I_{/}$-*EE*. (e) Complete phase diagram considering all four phases.

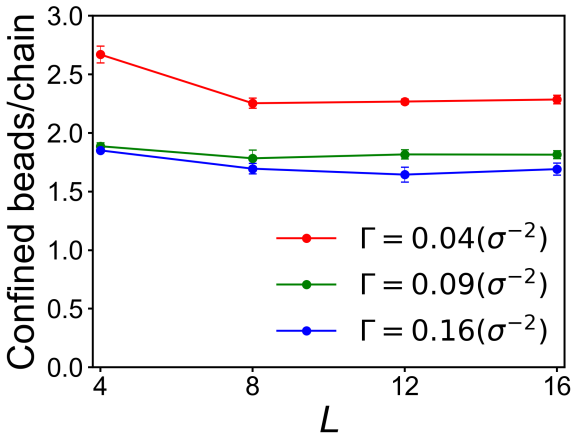

Figure S5: Number of confined beads per polymer chain in the *FF* configuration for $D = 10\sigma$ nanocubes. Results demonstrate that for the nanocube sizes investigated increasing the chain length does not lead to increased number of confined polymer beads.