Electronic Supplementary Material (ESI) for Soft Matter.
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Supplementary Information for Free Energy Cost to Assemble Superlattices of Polymer-Grafted Nanoparticles

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1. WALL POTENTIAL

The confining walls interact with each monomer with a repulsive harmonic potential

$$u_w(r) = \begin{cases} 0, & r < 0 \\ \kappa\epsilon(r/\sigma)^2, & 0 \le r \le \delta \\ \infty, & r > \delta \end{cases} \tag{1}$$

where r is the distance of the monomer from the surface of a wall (x_s in Fig. S1) and δ is the thickness or maximum penetration depth into the wall. Repulsion strength is empirically set as $\kappa = 80$. The overall interaction energy W between N monomers and Z walls is $W = \sum_{i=1}^{N}\sum_{j=1}^{Z} u_w(r_{ij})$.

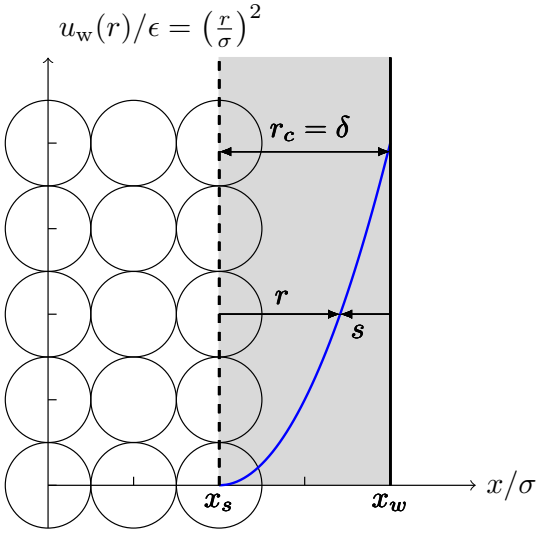

FIG. S1: Wall potential energy and its notation defined in LAMMPS.

The implementation of $u_w(r)$ in LAMMPS [1] follows a different definition

$$E = \begin{cases} \epsilon(s - r_c)^2, & s < r_c \\ 0, & s \ge r_c \end{cases} \tag{2}$$

where ϵ is set to 80 as κ above. The cutoff r_c is the effective thickness δ of the wall and s is the distance from the effective location of the wall (x_w in Fig. S1).

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2. GEOMETRY OF WIGNER-SEITZ POLYHEDRA

TABLE S1: The four types of Wigner-Seitz polyhedra, whose surface area A is expressed in terms of volume V. Number of faces z and the corresponding normal vector $\hat{\mathbf{n}}$ are also listed [2, 3]. Confining walls are placed according to normal vectors $\hat{\mathbf{n}}$'s.

polyhedron	A	z	$\hat{\mathbf{n}}$
truncated octahedron	$\frac{3+6\sqrt{3}}{2\sqrt[3]{2}} V^{2/3} \approx 5.31 V^{2/3}$	6	$(\pm1,0,0),\ (0,\pm1,0),\ (0,0,\pm1)$
		8	$(\pm1,\pm1,\pm1)$
rhombic dodecahedron	$\frac{6}{\sqrt[3]{2}} V^{2/3} \approx 5.35 V^{2/3}$	12	$(\pm1,0,0),(0,\pm1,0),$
			$(\pm1,\pm1,\pm\sqrt{2})$
tetrakaidecahedron	$\left[2+2\sqrt{6}-\left(\frac{2\sqrt{6}}{3}+\frac{1-\sqrt{5}}{2}\right)2^{2/3}\right] V^{2/3}$	4	$(1,0,\pm2),(-1,\pm2,0)$
 Z14	$\approx 5.29 V^{2/3}$	8	$(-1,\pm1,\pm2),(1,\pm2,\pm1)$
		2	$(\pm1,0,0)$
irregular dodecahedron	$\frac{3\sqrt{5}}{2} 2^{2/3} V^{2/3} \approx 5.32 V^{2/3}$	12	$(0,\pm1,\pm2),(\pm1,0,\pm2),$
 Z12			$(\pm1,\pm2,0)$

3. SUMMARY OF FREE ENERGY RESULTS

a is the lattice constant along the nearest neighbor direction. $\bar{\rho} = \frac{N_p N_c}{\left[V - \frac{4\pi}{3}(5\sigma)^3\right]}$ is monomer number density in bulk.

TABLE S2: FENE bond only. $N_p = 20$, $V_0 = 13727.6$, $R_0 = 14.85$.

		BCC				FCC				A15		
$V/V0$	$\bar{\rho}$	a	F_V	F_S	F	a	F_V	F_S	F	F_V	F_S	F
0.546	0.573	21.36	2836.1	-911.2	1924.9	21.97	2844.7	-914.7	1930.0	2840.0	-918.0	1922.1
0.583	0.535	21.82	2334.7	-807.9	1526.8	22.45	2342.1	-811.0	1531.1	2339.4	-812.1	1527.3
0.626	0.495	22.35	1876.9	-704.6	1172.4	23.00	1883.8	-706.7	1177.1	1882.6	-708.1	1174.4
0.670	0.461	22.86	1529.8	-618.1	911.7	23.52	1536.3	-619.8	916.5	1535.6	-621.0	914.6
0.728	0.422	23.51	1183.9	-522.7	661.2	24.18	1190.7	-523.5	667.2	1190.9	-525.0	665.9
0.787	0.389	24.12	931.5	-444.1	487.4	24.81	936.9	-444.3	492.5	938.1	-445.9	492.2

TABLE S3: FENE bond and bond angle. $N_p = 20$, $V_0 = 13290.8$, $R_0 = 14.69$.

		BCC				FCC			
$V/V0$	$\bar{\rho}$	a	F_V	F_S	F	a	F_V	F_S	F
0.5643	0.573	21.36	2956.5	-961.4	1995.1	21.97	2965.1	-966.1	1999.1
0.602	0.535	21.82	2411.3	-846.5	1564.8	22.45	2420.0	-849.4	1570.6
0.647	0.495	22.35	1914.6	-730.7	1183.9	23.00	1923.1	-733.3	1189.8
0.692	0.461	22.86	1543.0	-635.2	907.8	23.52	1550.4	-636.2	914.2
0.737	0.431	23.35	1257.4	-554.2	703.2	24.02	1264.4	-554.8	709.5
0.798	0.397	23.97	969.9	-463.8	506.1	24.66	976.6	-463.9	512.7

TABLE S4: FENE bond only. $N_p = 40$, $V_0 = 40556.9$, $R_0 = 21.32$.

		BCC				FCC			
$V/V0$	$\bar{\rho}$	a	F_V	F_S	F	a	F_V	F_S	F
0.395	0.517	27.49	4725.3	-1244.5	3480.8	28.28	4732.9	-1254.1	3478.8
0.444	0.458	28.60	3493.6	-1034.7	2458.9	29.42	3502.0	-1042.1	2459.8
0.518	0.391	30.10	2358.6	-812.2	1546.4	30.97	2365.4	-816.9	1548.5
0.616	0.327	31.90	1505.0	-611.3	893.7	32.82	1510.0	-614.1	895.9
0.715	0.281	33.52	1014.5	-472.5	542.0	34.49	1019.0	-473.8	545.3
0.838	0.239	35.35	652.2	-348.3	304.0	36.36	656.0	-348.9	307.1

TABLE S5: FENE bond and bond angle. $N_p = 40$, $V_0 = 39874.5$, $R_0 = 21.19$.

		BCC				FCC			
$V/V0$	$\bar{\rho}$	a	F_V	F_S	F	a	F_V	F_S	F
0.401	0.517	27.49	5093.0	-1331.4	3761.6	28.28	5099.9	-1338.9	3761.0
0.451	0.458	28.60	3717.2	-1094.6	2622.6	29.42	3724.8	-1101.2	2623.5
0.502	0.411	29.62	2807.4	-918.4	1889.0	30.47	2815.1	-924.0	1891.1
0.577	0.356	31.03	1932.0	-725.3	1206.7	31.92	1938.8	-729.4	1209.5
0.677	0.302	32.73	1248.1	-546.6	701.4	33.67	1254.1	-548.4	705.8
0.803	0.254	34.64	771.5	-394.2	377.4	35.64	776.6	-394.8	381.8

TABLE S6: FENE bond only. $N_p = 60$, $V_0 = 78836.1$, $R_0 = 26.60$.

		BCC				FCC			
$V/V0$	$\bar{\rho}$	a	F_V	F_S	F	a	F_V	F_S	F
0.304	0.511	31.47	7216.6	-1618.3	5598.3	32.38	7226.4	-1630.7	5595.6
0.342	0.453	32.73	5446.0	-1362.0	4084.1	33.67	5455.0	-1373.4	4081.6
0.393	0.394	34.28	3931.9	-1116.2	2815.7	35.26	3941.0	-1124.4	2816.6
0.444	0.348	35.69	2960.6	-936.8	2023.7	36.72	2968.4	-943.6	2024.8
0.507	0.304	37.32	2163.2	-770.3	1392.9	38.39	2168.0	-776.2	1391.8
0.571	0.270	38.81	1632.9	-645.4	987.5	39.92	1638.5	-648.9	989.7
0.634	0.243	40.20	1263.4	-547.5	715.9	41.35	1267.8	-549.3	718.5
0.710	0.216	41.74	951.3	-453.8	497.4	42.94	955.4	-455.2	500.1

TABLE S7: FENE bond and bond angle. $N_p = 60$, $V_0 = 78047.2$, $R_0 = 26.51$.

		BCC				FCC			
$V/V0$	$\bar{\rho}$	a	F_V	F_S	F	a	F_V	F_S	F
0.308	0.511	31.47	7875.1	-1740.8	6134.4	32.38	7883.6	-1753.8	6129.8
0.346	0.453	32.73	5873.0	-1449.9	4423.1	33.67	5883.6	-1461.1	4422.5
0.384	0.407	33.90	4531.5	-1233.4	3298.0	34.88	4542.1	-1243.7	3298.4
0.436	0.358	35.35	3340.4	-1020.8	2319.6	36.36	3349.1	-1027.3	2321.9
0.487	0.320	36.68	2547.3	-860.9	1686.4	37.74	2554.5	-867.0	1687.5
0.551	0.283	38.23	1880.7	-710.9	1169.9	39.32	1885.8	-714.9	1170.9
0.615	0.253	39.65	1428.7	-596.2	832.5	40.79	1433.9	-598.6	835.3
0.679	0.229	40.99	1109.9	-504.8	605.1	42.16	1114.2	-507.3	606.9

4. DISTRIBUTION OF GRAFTED POLYMERS FOR $N_p = 40$ AT $V = 34000$

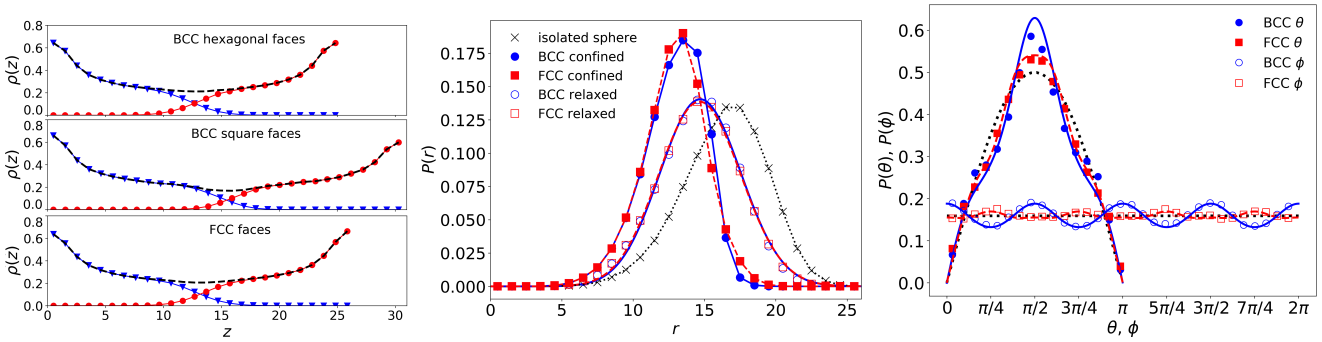

FIG. S2: Density profile $\rho(z)$, distribution $P(r)$, $P(\theta)$, $P(\phi)$ for BCC and FCC structure at $V = 34000$. Symbol conventions are the same as the $V = 18000$ figure in main text. Number of monomers per chain $N_p = 40$.

5. DISTRIBUTION OF GRAFTED POLYMERS FOR $N_p = 60$ AT $V = 24000$ AND $V = 56000$

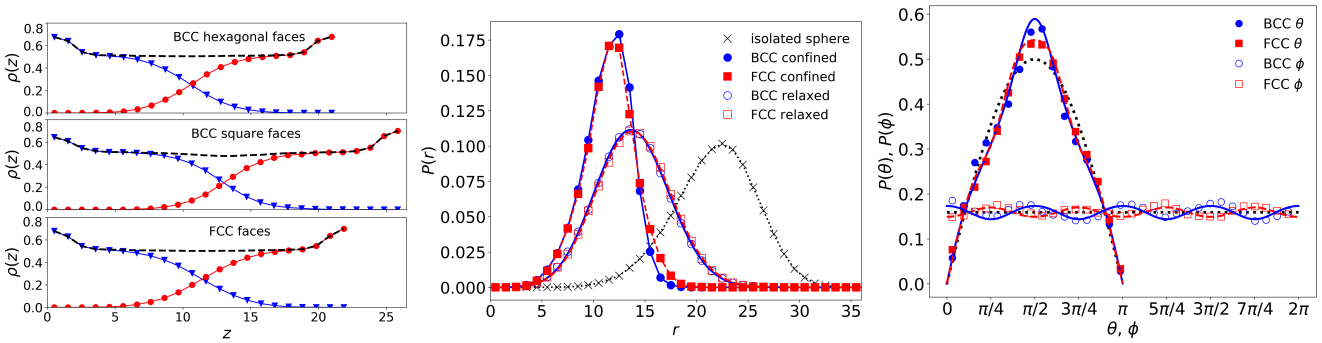

FIG. S3: Density profile $\rho(z)$, distribution $P(r)$, $P(\theta)$, $P(\phi)$ for BCC and FCC structure at $V = 24000$ and $N_p = 60$.

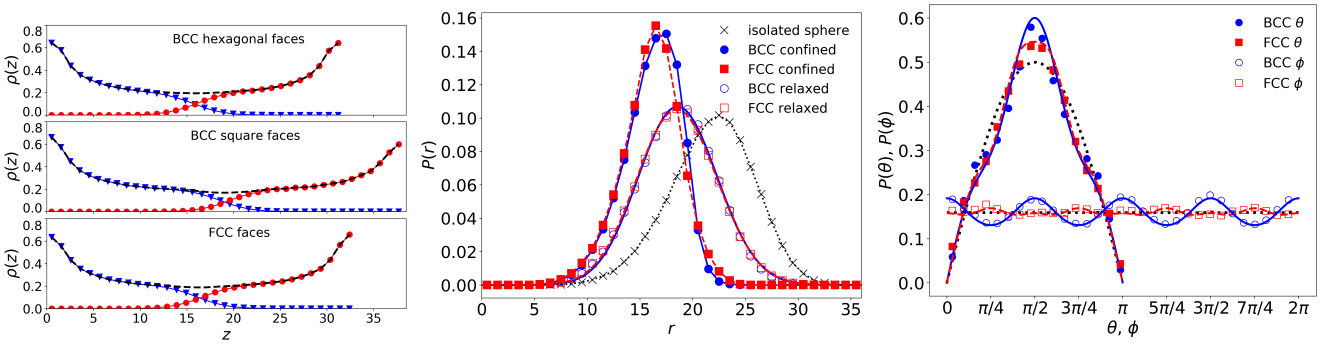

FIG. S4: Density profile $\rho(z)$, distribution $P(r)$, $P(\theta)$, $P(\phi)$ for BCC and FCC structure at $V = 56000$ and $N_p = 60$.

The corresponding entropy S of the distribution $P(\mathbf{r})$ for $N_p = 60$ systems is summarized in Table S8.

TABLE S8: Entropy S of the distribution $P(\mathbf{r})$ and its radial and angular contributions at $V = 24000$ and $V = 56000$. Grafted polymers are of $N_p = 60$ and flexible with FENE bonds.

V	24000		56000	
	BCC	FCC	BCC	FCC
S_r	7.860	7.892	8.541	8.547
S_θ	1.836	1.837	1.829	1.837
S_ϕ	0.688	0.690	0.685	0.689
S	10.373	10.415	11.050	11.069

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