Electronic Supplementary Material (ESI) for Soft Matter

Phase behavior of rounded hard-squares

(Supplementary Information)

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1 Simulation details and order parameters

The phase behavior of rounded-corner hard-squares (RCHS) was obtained using Monte Carlo (MC) simulations in the canonical NVT,[1,2] isobaric-isothermal NPT[2–5] and isothermal-isostress $N\sigma_P T$[6] ensembles. In the $N\sigma_P T$ ensemble the shape of the box is allowed to change, which makes it specially attractive for simulations of systems at high-densities in order to stabilize crystalline phases that might not be commensurable with square simulation cells. Compression and expansion runs were used to map out the EoS of RCHS as a function of the roundness of the system ζ, which is defined as $\zeta = \sigma/(L+\sigma)$. The compression runs were started from a low density isotropic state, and the pressure was increased in a sequential manner. Expansion runs were started from perfect crystal structures, which were determined using the method of Filio *et al.*[7] In our simulations, a cycle is defined as N Monte Carlo moves, where N is the total number of particles. For the systems of $N = 400$ and 1600 particles, particle translations, re-orientations, and box volume changes were chosen with probabilities of 47.5%, 47.5%, and 5%, respectively. Equal probabilities were used for isotropic and anisotropic changes of volume when required, i.e., 2.5% each. For the larger system of $N = 4096$ particles, each cycle consists of 4096 particles translation or re-orientations, and approximately four box volume changes. 2.5×10^5 MC cycles were used to equilibrate the system, followed by 1×10^6 production cycles to obtain ensemble averages. In the case of NVT simulations, translation and rotations moves were chosen with equal probability (50% each one). NVT simulations were only used for systems of 5625 particles, hence longer simulations were required in order to equilibrate the system. In this case 1×10^6 cycles were used to stabilize the system, followed by 2×10^6 cycles to obtain ensemble averages. In all cases, the allowed displacements, re-orientations, and volume changes were adjusted to get acceptance probabilities between 30-40% (with the exception of the results presented in Fig. S15, where the re-orientation

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moves were restricted to be less than 5°). In order to characterize the system, several order parameters (that have been defined in the main article) were calculated. We also report the results for the isothermal compressibility $\kappa_T^* = \kappa_T k_B T / A_p$ calculated from fluctuations of the total area of the system.[8]

In the figures shown below, we have used the following acronyms for the different phases: I=isotropic, RHX=hexagonal rotator crystal, RB= rhombic, T=tetratic, and PC=polycrystalline.

2 Results for perfect hard squares using N=196 particles

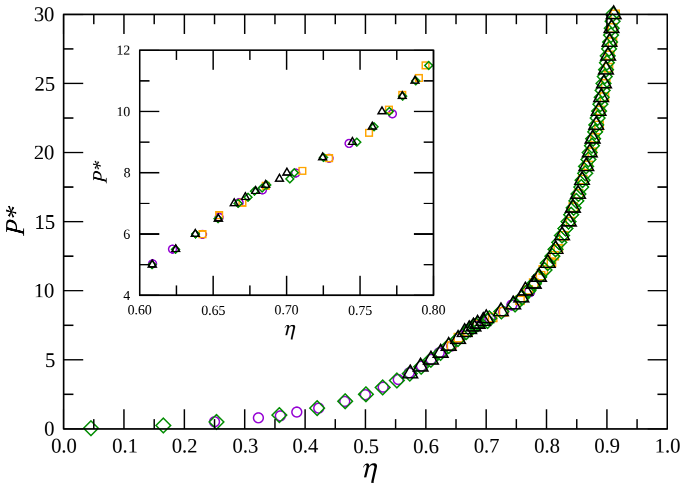

Figure S1: Equation of state for 196 RCHS with $\zeta = 0.01$ obtained by compression ($\Diamond$) and expansion ($\triangle$) runs. The results are compared with the simulations results of the system of 196 perfect hard-squares reported by Wojciechowski and Frenkel[9] obtained by compression ($\circ$) and expansion ($\Box$) runs .

	$N = 196$		
P^*	η (compression)	η (expansion)	η (reference 9)
20.0	0.8715 ± 0.0023	0.8716 ± 0.0018	0.8715
15.0	0.8365 ± 0.0033	0.8370 ± 0.0021	0.8362
12.0	0.8019 ± 0.0030	0.8020 ± 0.0024	0.8010
10.0	0.7699 ± 0.0044	0.7649 ± 0.0048	0.7689
9.0	0.7478 ± 0.0046	0.7448 ± 0.0054	0.7444
8.5	0.7251 ± 0.0066	0.7187 ± 0.0111	0.7294
8.0	0.7052 ± 0.0082	0.7002 ± 0.0063	0.7030
7.8	0.7022 ± 0.0087	0.6951 ± 0.0060	0.6926
7.6	0.6865 ± 0.0047	0.6857 ± 0.0098	0.6857
7.4	0.6781 ± 0.0042	0.6789 ± 0.0077	0.6772
7.0	0.6670 ± 0.0043	0.6643 ± 0.0073	0.6660
6.0	0.6380 ± 0.0030	0.6378 ± 0.0030	0.6379
4.0	0.5734 ± 0.0028	0.5742 ± 0.0018	0.5725
2.5	0.5008 ± 0.0021	—	0.5027

Table S1: Monte Carlo simulation results for 196 RCHS with $\zeta = 0.01$ obtained by compression and expansion runs. The results are compared with the simulations results of the system of 196 perfect hard-squares reported by Wojciechowski and Frenkel.[9]

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3 Results for RCHS with $L^* = 0.25$ ($\zeta = 0.8$)

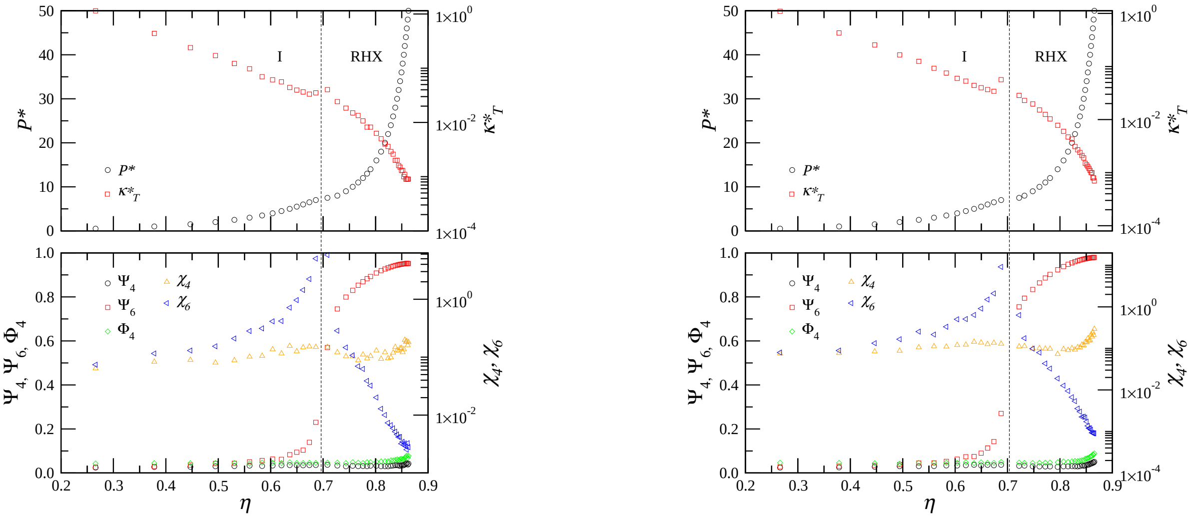


Figure S2: Equation of state for 400 RCHS with $L^* = 0.25$ ($\zeta = 0.8$) obtained by compression (left panel) and expansion (right panel) runs. (Top panel) The pressure, P^*, and the isothermal compressibility, κ_T^*, as a function of the packing fraction η. (Bottom panel) Bond orientational order parameters, Ψ_4 and Ψ_6, orientational order parameter, Φ_4, and susceptibilities of the bond-order parameters, χ_4 and χ_6, as a function of η. Vertical dashed-lines are used to delimit the different phases.

4 Results for RCHS with $L^* = 0.50$ ($\zeta = 0.667$)

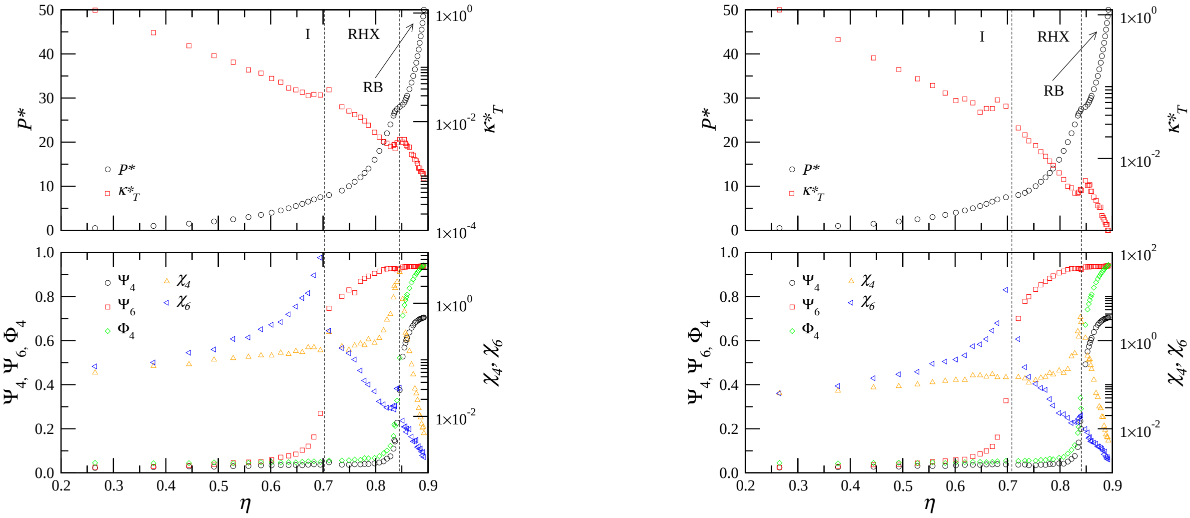


Figure S3: Equation of state for 400 RCHS with $L^* = 0.50$ ($\zeta = 0.667$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

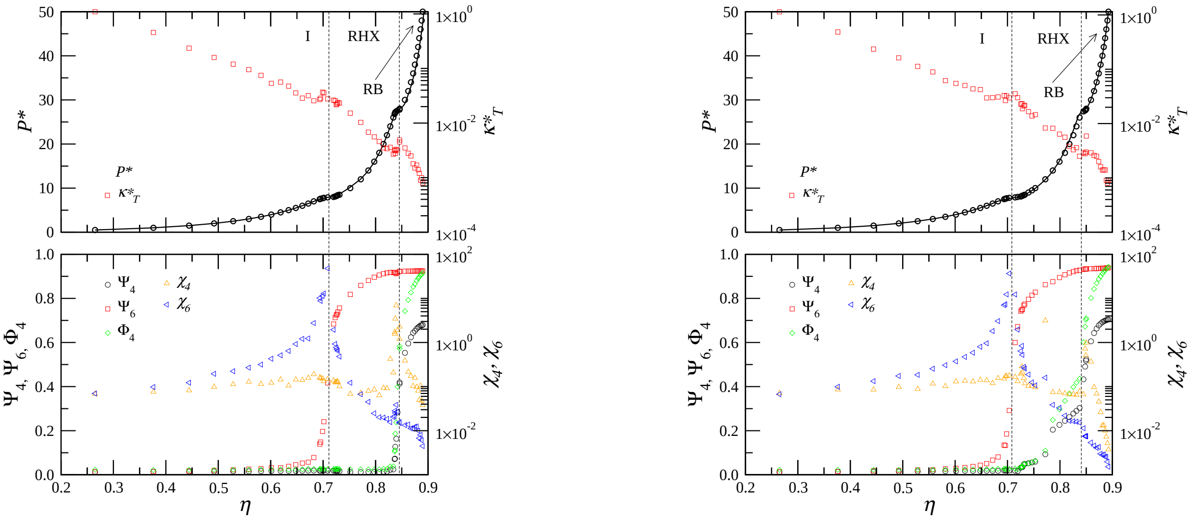
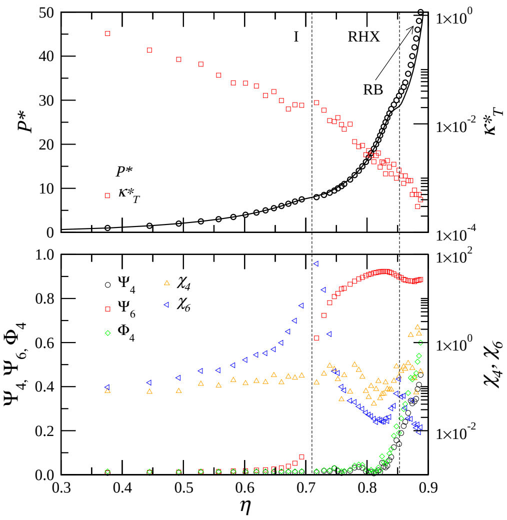


Figure S4: Equation of state for 1600 RCHS with $L^* = 0.50$ ($\zeta = 0.667$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.



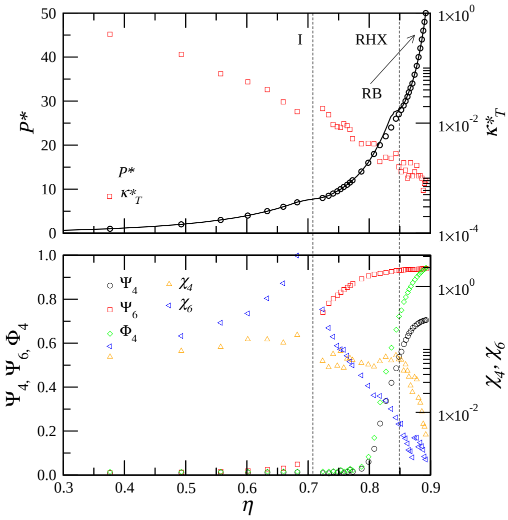


Figure S5: Equation of state for 4096 RCHS with $L^* = 0.50$ ($\zeta = 0.667$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

5 Results for RCHS with $L^* = 0.75$ ($\zeta = 0.571$)

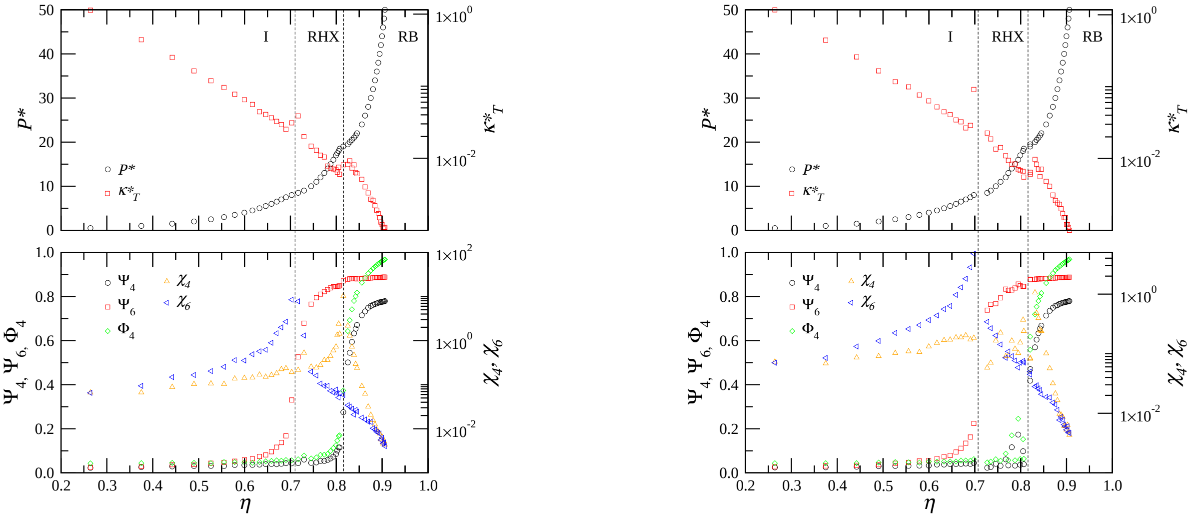


Figure S6: Equation of state for 400 RCHS with $L^* = 0.75$ ($\zeta = 0.571$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

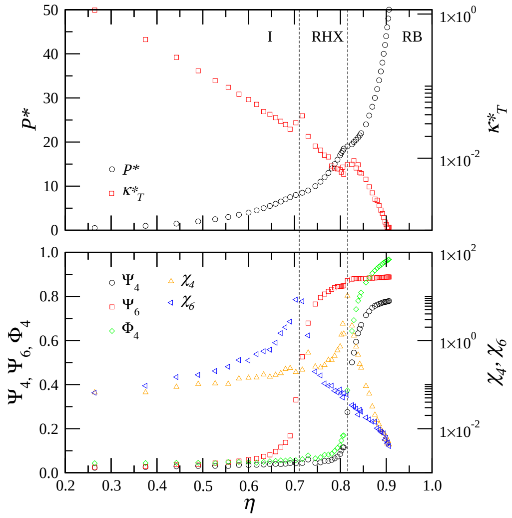


Figure S7: Equation of state for 1600 RCHS with $L^* = 0.75$ ($\zeta = 0.571$) obtained by compression runs. Legend as in Fig. S2.

6 Results for RCHS with $L^* = 1.00$ ($\zeta = 0.5$)

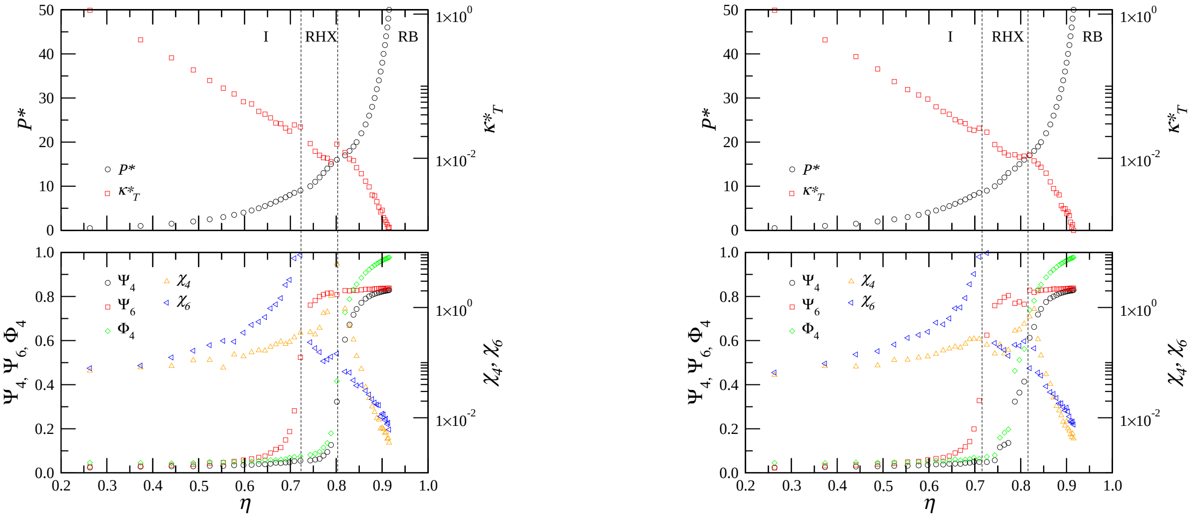


Figure S8: Equation of state for 400 RCHS with $L^* = 1.00$ ($\zeta = 0.5$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

7 Results for RCHS with $L^* = 1.25$ ($\zeta = 0.444$)

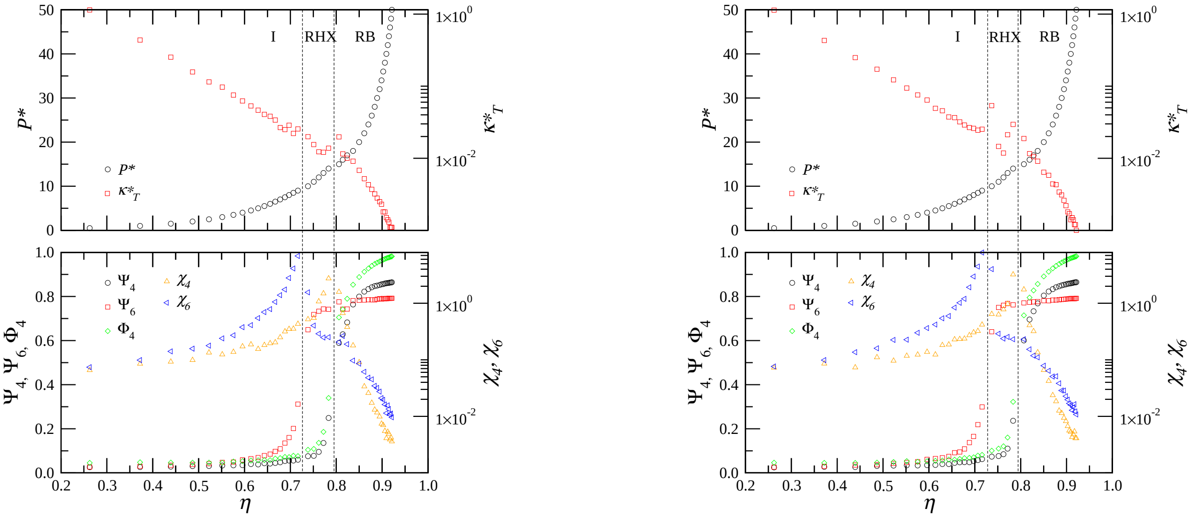


Figure S9: Equation of state for 400 RCHS with $L^* = 1.25$ ($\zeta = 0.444$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

8 Results for RCHS with $L^* = 1.50$ ($\zeta = 0.400$)

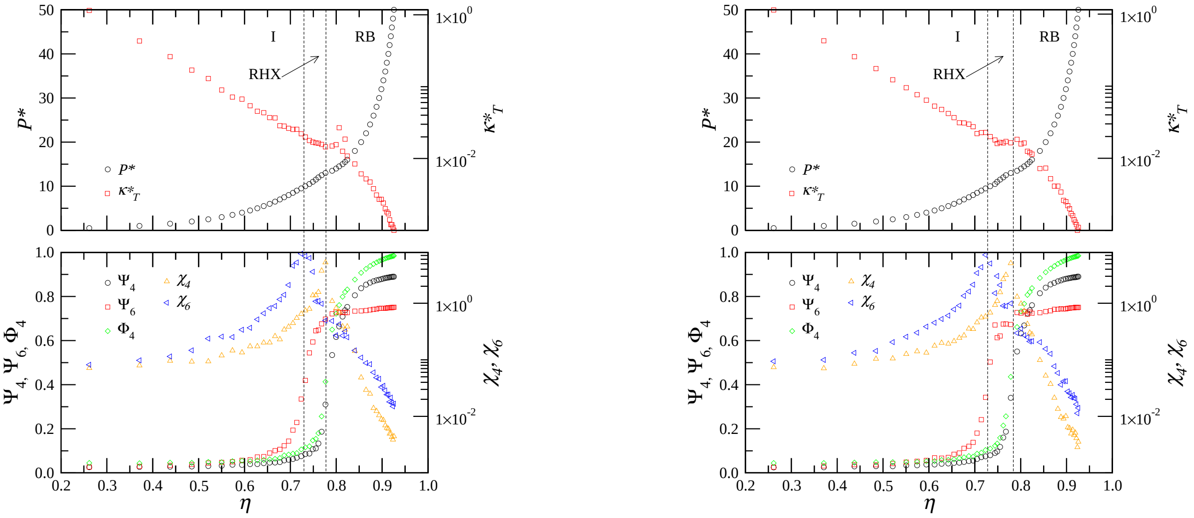


Figure S10: Equation of state for 400 RCHS with $L^* = 1.50$ ($\zeta = 0.400$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

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9 Results for RCHS with $L^* = 1.75$

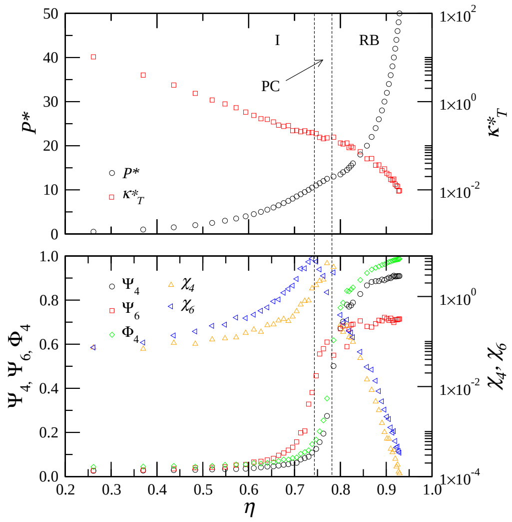

Figure S11: Equation of state for 400 RCHS with $L^* = 1.75$ ($\zeta = 0.364$) obtained by compression runs. Legend as in Fig. S2.

10 Results for RCHS with $L^* = 2.00$

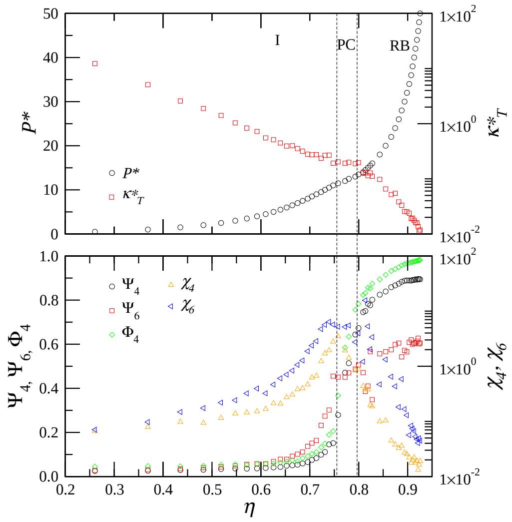

Figure S12: Equation of state for 400 RCHS with $L^* = 2.00$ ($\zeta = 0.333$) obtained by compression runs. Legend as in Fig. S2.

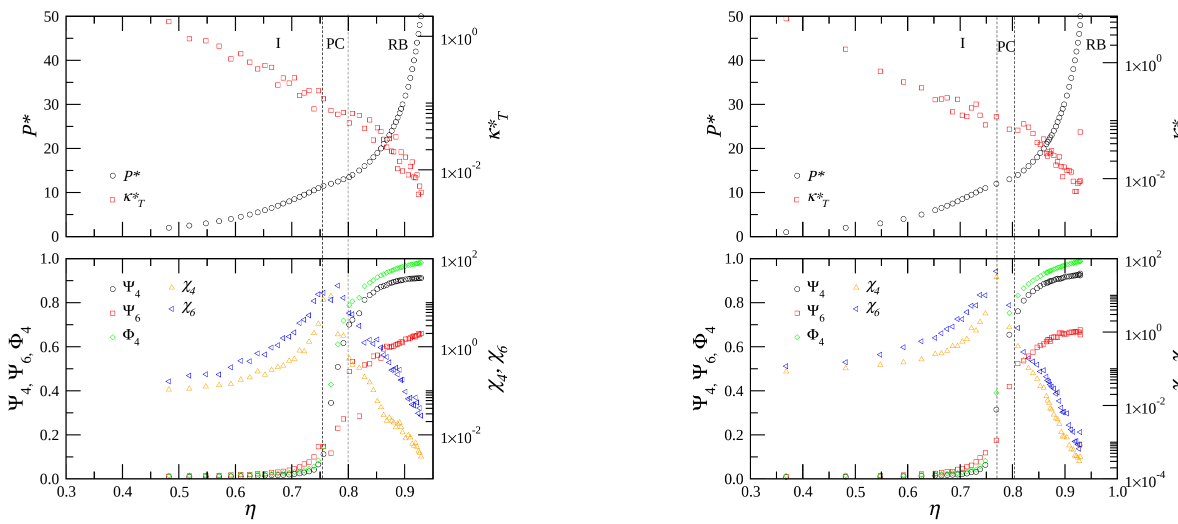

Figure S13: Equation of state for 4096 RCHS with $L^* = 2.00$ ($\zeta = 0.333$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

11 Results for RCHS with $L^* = 2.25$ ($\zeta = 0.308$)

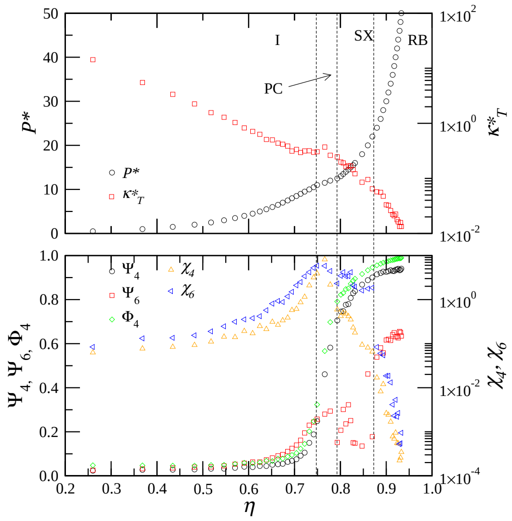

Figure S14: Equation of state for 400 RCHS with $L^* = 2.25$ ($\zeta = 0.308$) obtained by compression runs. Legend as in Fig. S2.

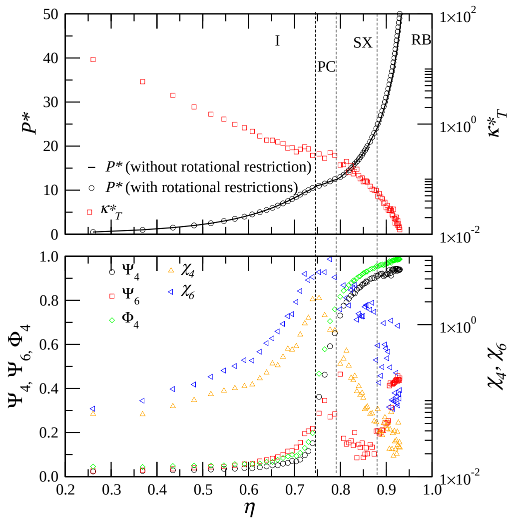

Figure S15: Equation of state for 400 RCHS with $L^* = 2.25$ ($\zeta = 0.308$) obtained by compression runs. During the simulations, only re-orientations of less than 5° were allowed. The EoS for the system without restrictions during the rotational moves (S14) is shown (continuous curve) for comparison. Legend as in Fig. S2.

12 Results for RCHS with $L^* = 2.50$ ($\zeta = 0.286$)

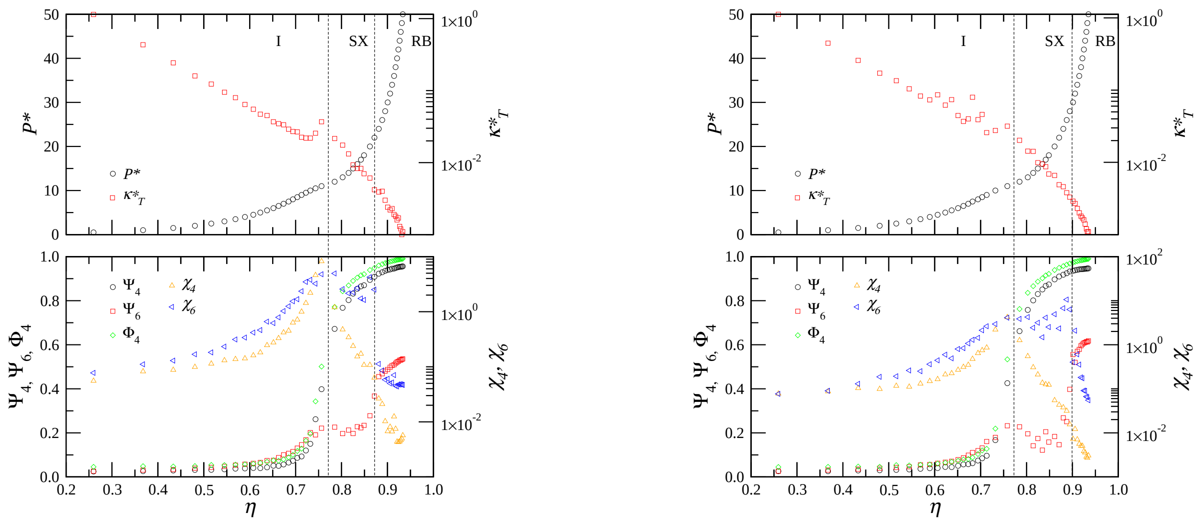

Figure S16: Equation of state for 400 RCHS with $L^* = 2.50$ ($\zeta = 0.286$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

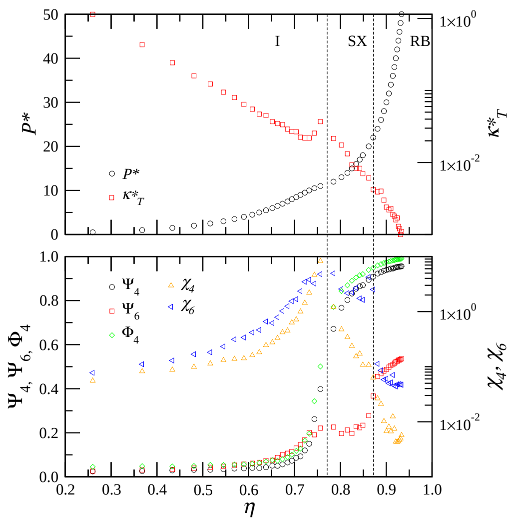

Figure S17: Equation of state for 1600 RCHS with $L^* = 2.50$ ($\zeta = 0.286$) obtained by compression runs. Legend as in Fig. S2.

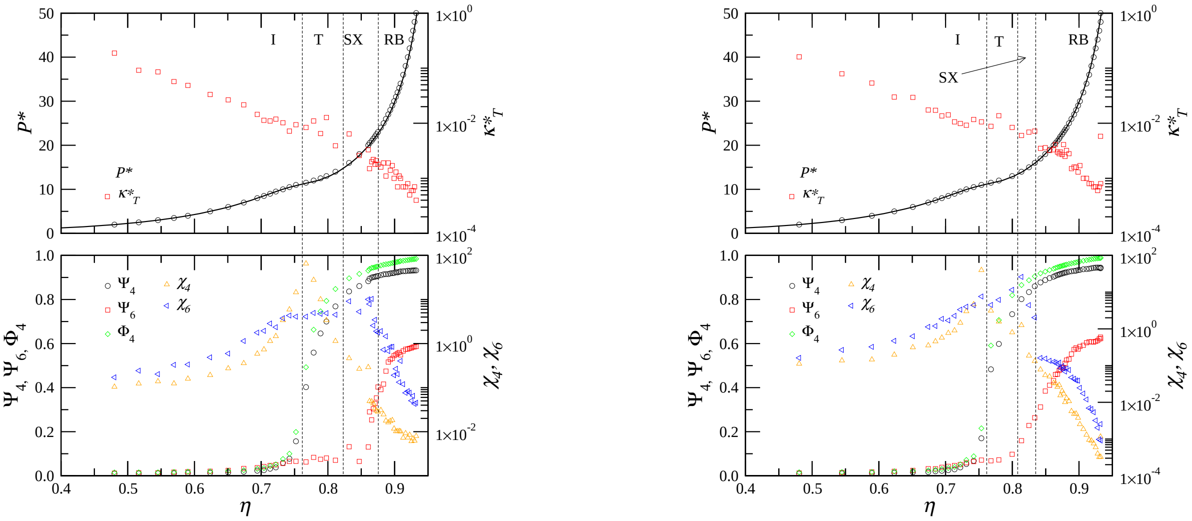

Figure S18: Equation of state for 4096 RCHS with $L^* = 2.50$ ($\zeta = 0.286$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

13 Results for RCHS with $L^* = 3.00$ ($\zeta = 0.25$)

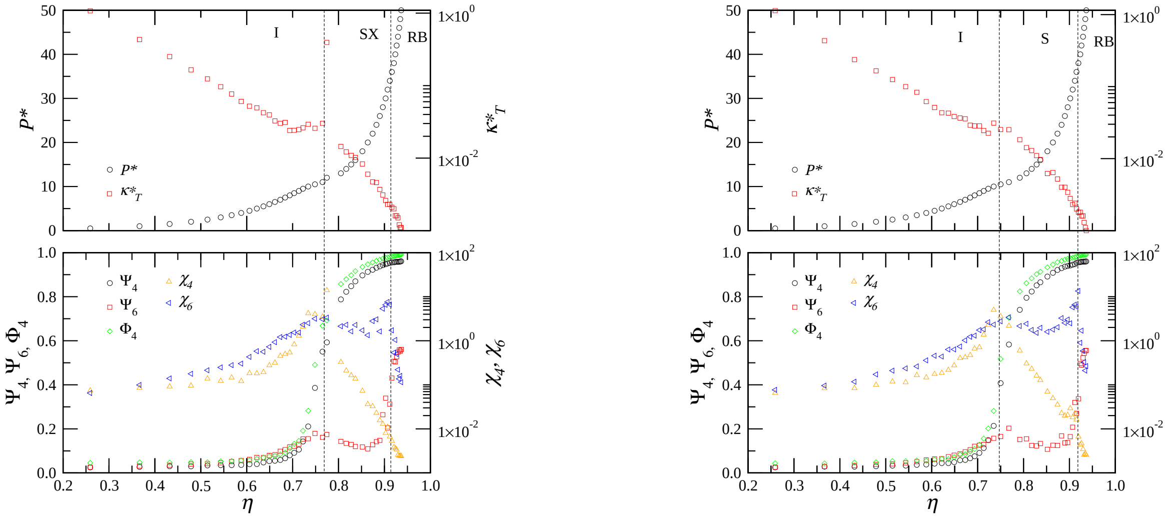

Figure S19: Equation of state for 400 RCHS with $L^* = 3.0$ ($\zeta = 0.25$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

14 Results for RCHS with $L^* = 5.00$

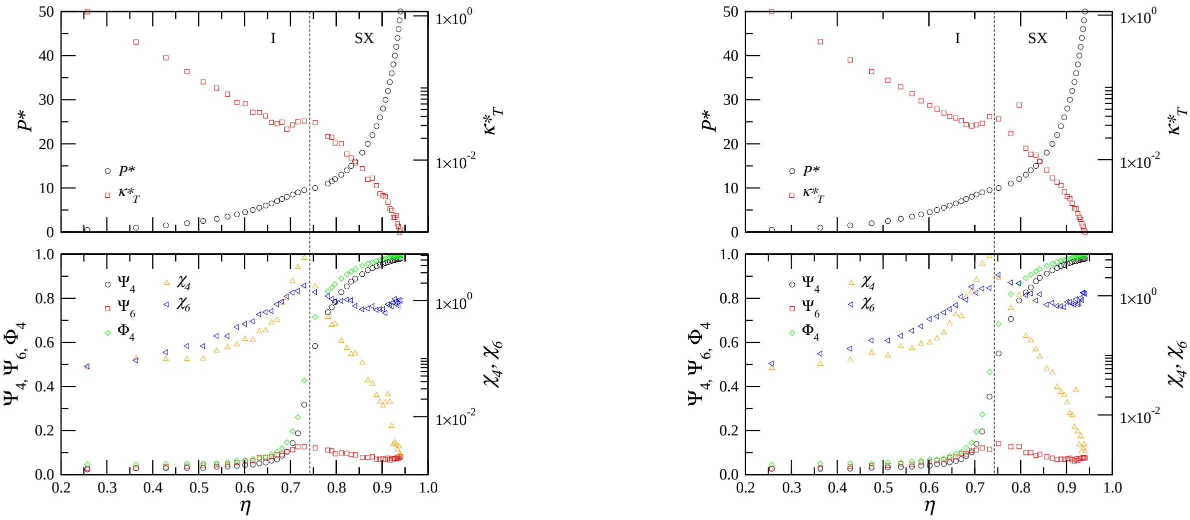

Figure S20: Equation of state for 400 RCHS with $L^* = 5.0$ ($\zeta = 0.167$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

15 Results for RCHS with $L^* = 10.00$ ($\zeta = 0.09$)

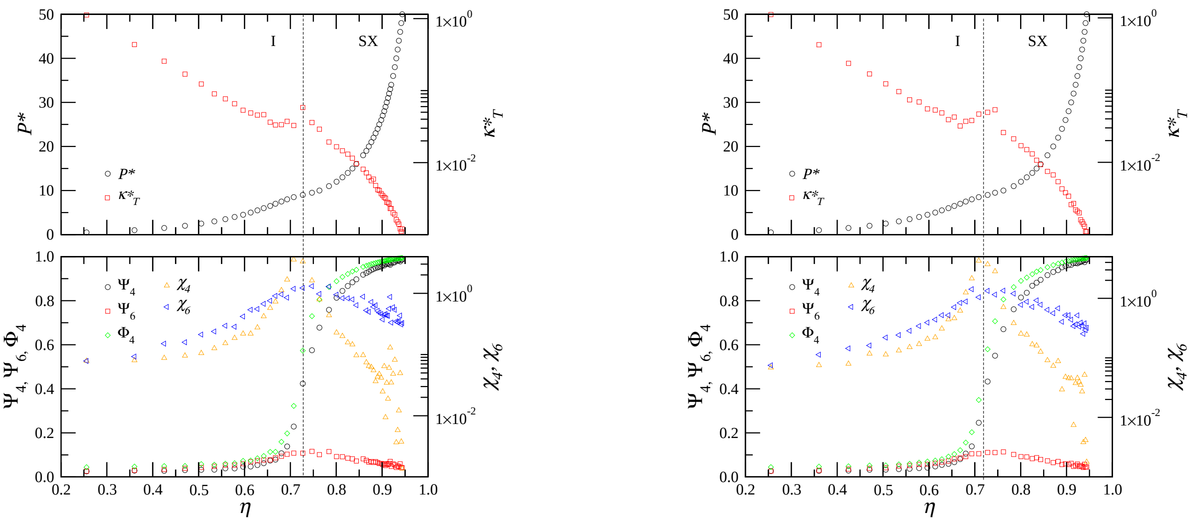

Figure S21: Equation of state for 400 RCHS with $L^* = 10.0$ ($\zeta = 0.09$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

16 Results for RCHS with $L^{*} = 100.00$ ($\zeta = 0.01$)

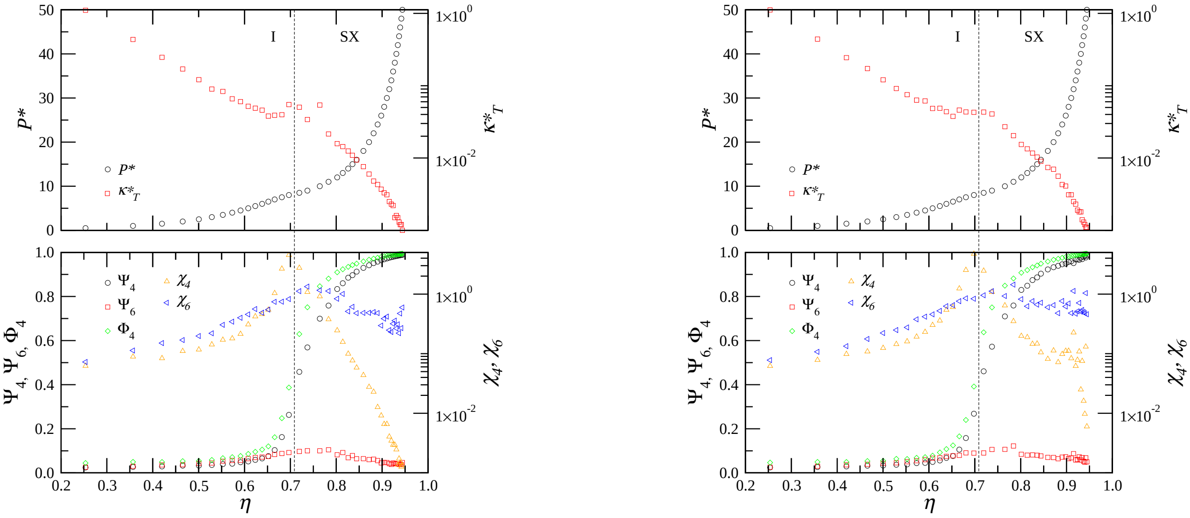

Figure S22: Equation of state for 400 RCHS with $L^{*} = 100.0$ ($\zeta = 0.01$) obtained by compression (left panel) and expansion (right panel) runs. Legend as in Fig. S2.

17 Lattice angles for the densest rhombic phase

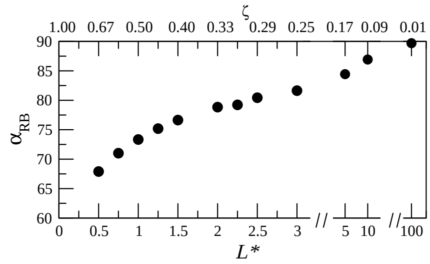

Figure S23: Lattice angle of the densest rhombic phase as a function of L^* (ζ), obtained from the simulations of RCHS using the method of Filio *et al.*[7] employing four particles.

References

[1] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, *J. Chem. Phys.*, 1953, **21**, 1087.

[2] D. Frenkel and B. Smit, *Understanding Molecular Simulation*, Academic Press, London, 2nd edn., 2002.

[3] W. W. Wood, *J. Chem. Phys.*, 1968, **48**, 415.

[4] W. W. Wood, *J. Chem. Phys.*, 1970, **52**, 729.

[5] D. P. Landau and K. Binder, *A Guide to Monte Carlo Simulations in Statistical Physics*, Cambridge University Press, Cambridge, UK, 2nd edn., 2005.

[6] M. Parrinello and A. Rahman, *J. Appl. Phys.*, 1981, **52**, 7182.

[7] L. Filion, M. Marechal, B. van Oorschot, D. Pelt, F. Smallenburg and M. Dijkstra, *Phys. Rev. Lett.*, 2009, **103**, 188302.

[8] M. Lagache, P. Ungerer, A. Boutin and A. H. Fuchs, *Phys. Chem. Chem. Phys.*, 2001, **3**, 4333.

[9] K. W. Wojciechowski and D. Frenkel, *Comp. Met. Sci. Technol.*, 2004, **10**, 235.