The pair distance distribution function of interacting particles[†]

Supplementary Information

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1 Applicability to Block Copolymer Systems

The relation

$$\gamma_0(r) = -\frac{\varphi}{1 - \varphi}$$ (1)

can be used to link the volume fraction with the real space curves obtained from small angle scattering data. The total correlation function must be $h(r) = -1$ within the r-range $(r - 2R_s) < r < (r + 2R_s)$ for this relation to hold at distance r.

This can be the case for crystalline arrangements, if the next neighbour shell is at a well defined distance with a predictable gap between the particles. Figure 1 shows the regions of the phase diagram of a diblock copolymer, where relation 1 holds.

The maximum volume fractions $\varphi_{\max}$, where eq. 1 holds can be computed from the fact that the distance between the spheres or cylinders must be four times the radius of the particles. Doing so one obtains for hexagonally packed cylinders $\varphi_{\max} = \pi/(8\sqrt{3}) \approx 0.227$. A similar calculation for a body centred cubic (BCC) lattice gives $\varphi_{\max} = \pi\sqrt{3}/64 \approx 0.0850$. Hexagonally closed packed spheres or face centred close packed spheres result in $\varphi_{\max} = \pi/(24\sqrt{2}) \approx 0.0925$.

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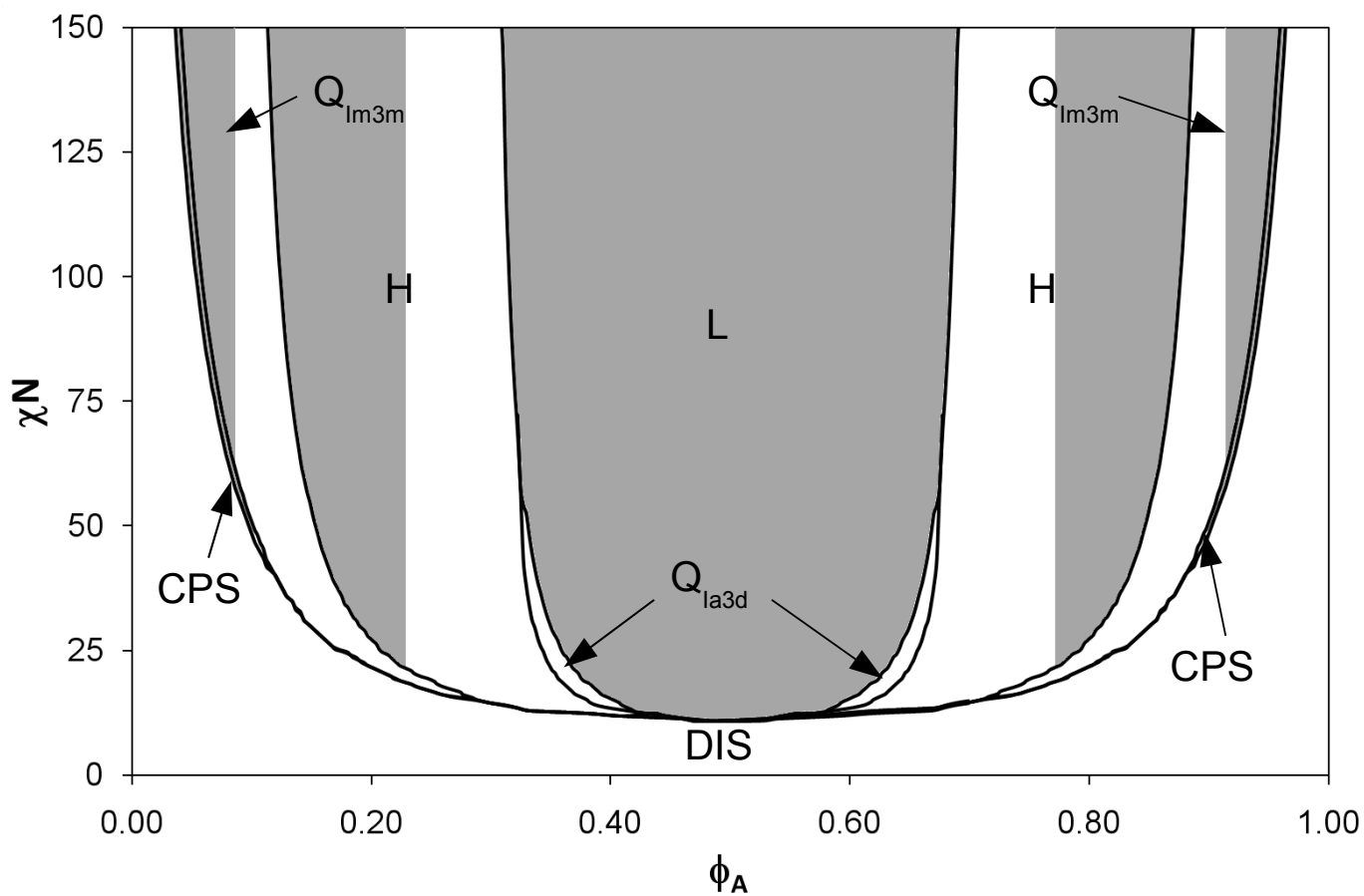
Fig. 1 Phase diagram of diblock copolymers according to Matsen and Bates *Macromolecules* **29**(4), 1091-1098 (1996). The relation of eq. 1

holds within the shaded areas, since there the inter-particle distances are large enough. L is a lamellar phase, H are hexagonally packed

cylinders, Q_{Ia3d} bcontious cubic. Q_{Im3m} are BCC packed spheres, and CPS spheres in close packing.

Please note that the relation 1 also holds for lamellar phases (Vonk in *Small Angle X-ray Scattering*, Eds. O. Glatter and O. Kratky, Academic Press: London, 1982).

2 Examples for various volume fractions

The pair distance distribution functions of homogeneous spheres have been computed for various arrangements and volume fractions (Hard spheres: fig. 2, body centred cubic: fig. 3, face centred cubic: fig. 4, hexagonal closed packing: fig. 5). Similarly the cross section pair distance distribution functions of hexagonally ordered, parallel cylinders have been calculated for different volume fractions (fig. 6).

The samples in crystalline arrangements show at low volume fractions the kink at the distance that corresponds to the diameter of the particles. This kink is a reliable and correct marker for the diameter that can be used for all volume fractions, where it occurs.

The minimum that can be also used to estimate the diameter is always at distances slightly smaller than the actual diameter. The difference is less than 15% for volume fractions up to 0.3 and less than 30% for volume fractions up to 0.6. It can therefore be used as a reasonable estimate for the starting value of a generalised indirect Fourier transformation or for a model approximation.

3 Influence of polydispersity

Figure 7 shows a hard sphere system at a volume fraction of 0.1 with various polydispersities. The size distribution is simulated to be a Schultz distribution. The curves shown here are the results of an indirect Fourier transformation of the simulated scattering curves, where the interaction effects have been taken into account be means of the effective hard sphere structure factor model (Weyerich, Brunner-Popela, and Glatter, *J. Appl. Cryst.* (1999). **32**, 197-209).
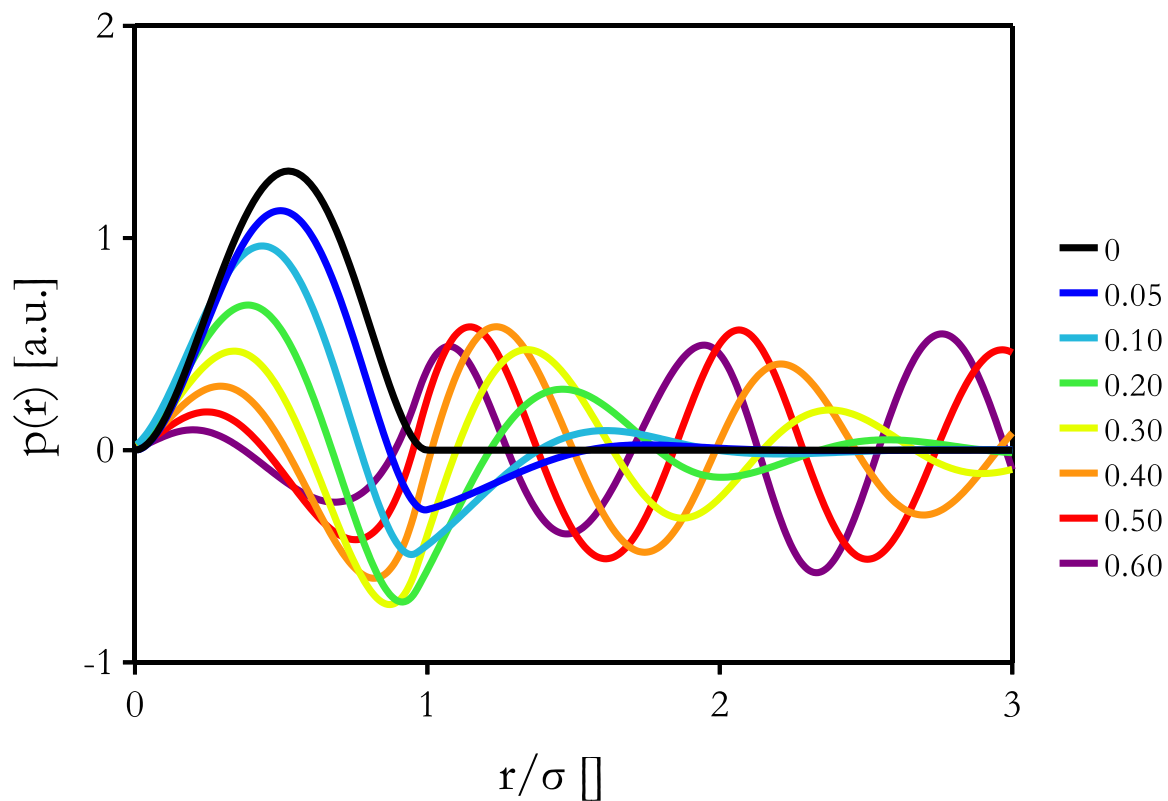
Fig. 2 Pair distance distribution functions of homogeneous hard spheres at various volume fractions from 0 to 0.6. The volume fractions are
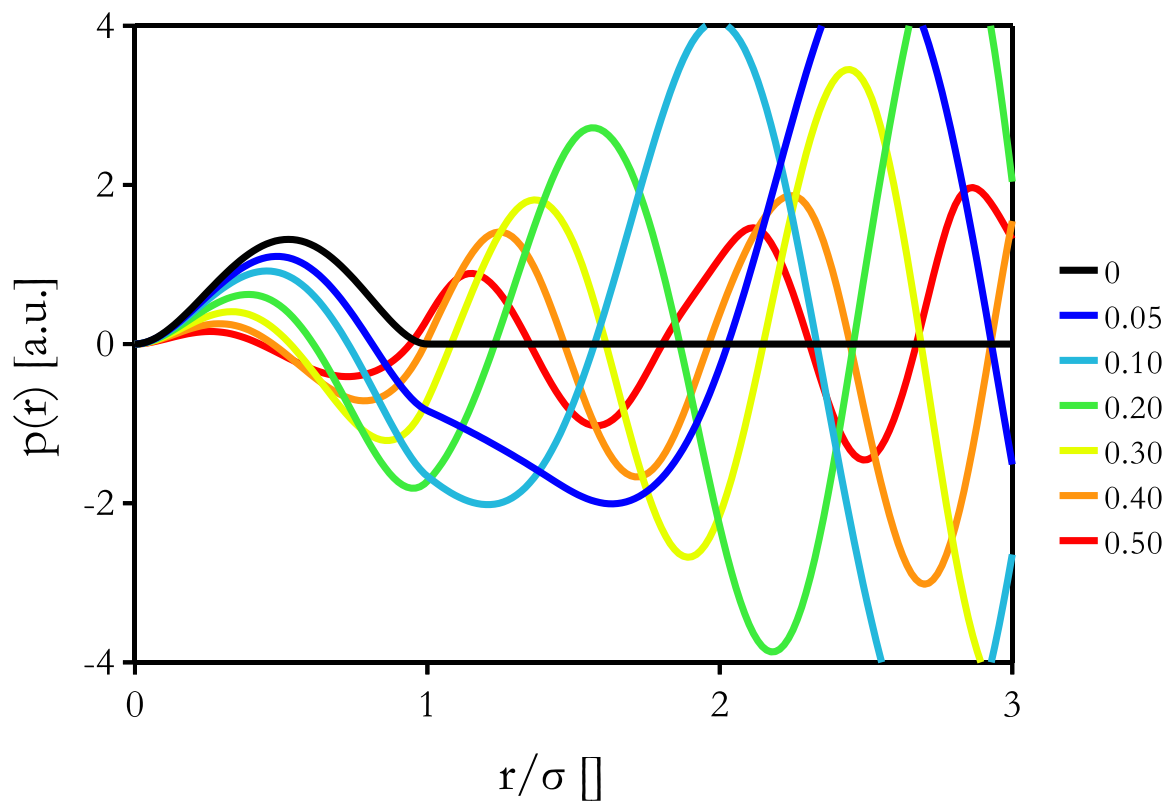
listed at the right hand side.

Fig. 3 Pair distance distribution functions of homogeneous spheres in body centred cubic arrangement at various volume fractions from 0 to

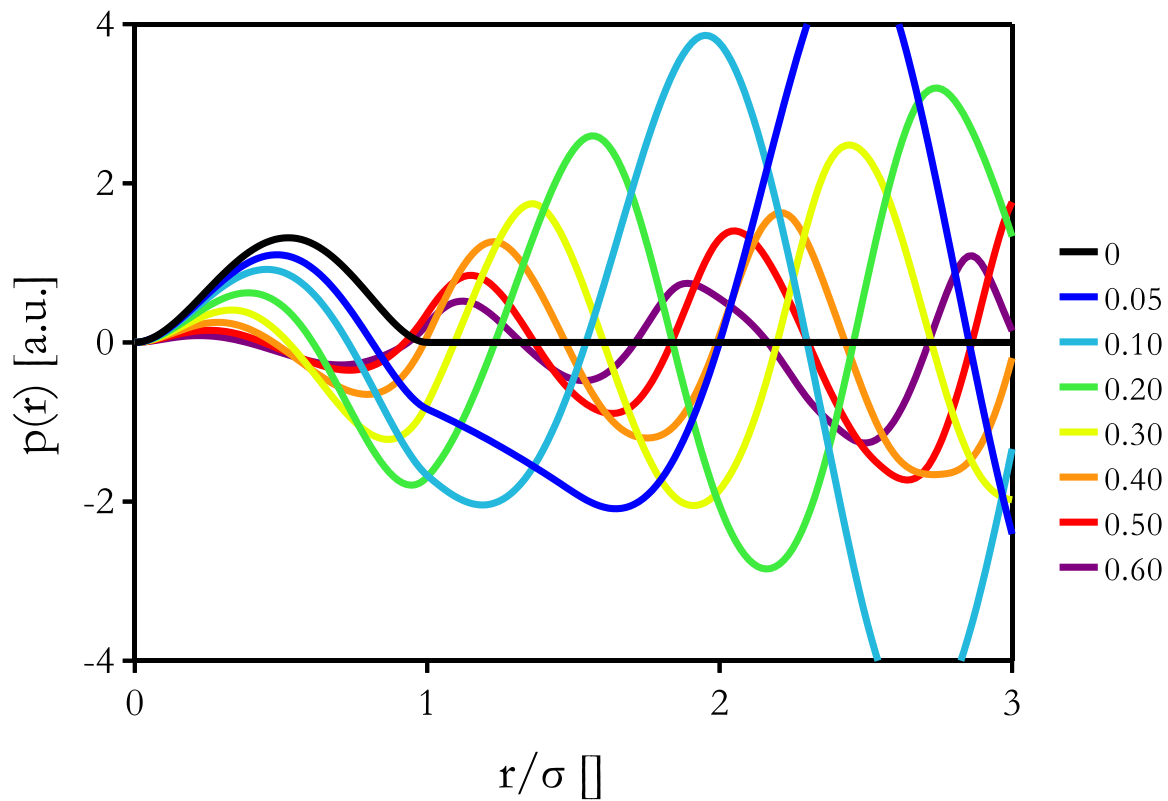0.5. The volume fractions are listed at the right hand side.

Fig. 4 Pair distance distribution functions of homogeneous spheres in face centred cubic arrangement at various volume fractions from 0 to 0.6. The volume fractions are listed at the right hand side.
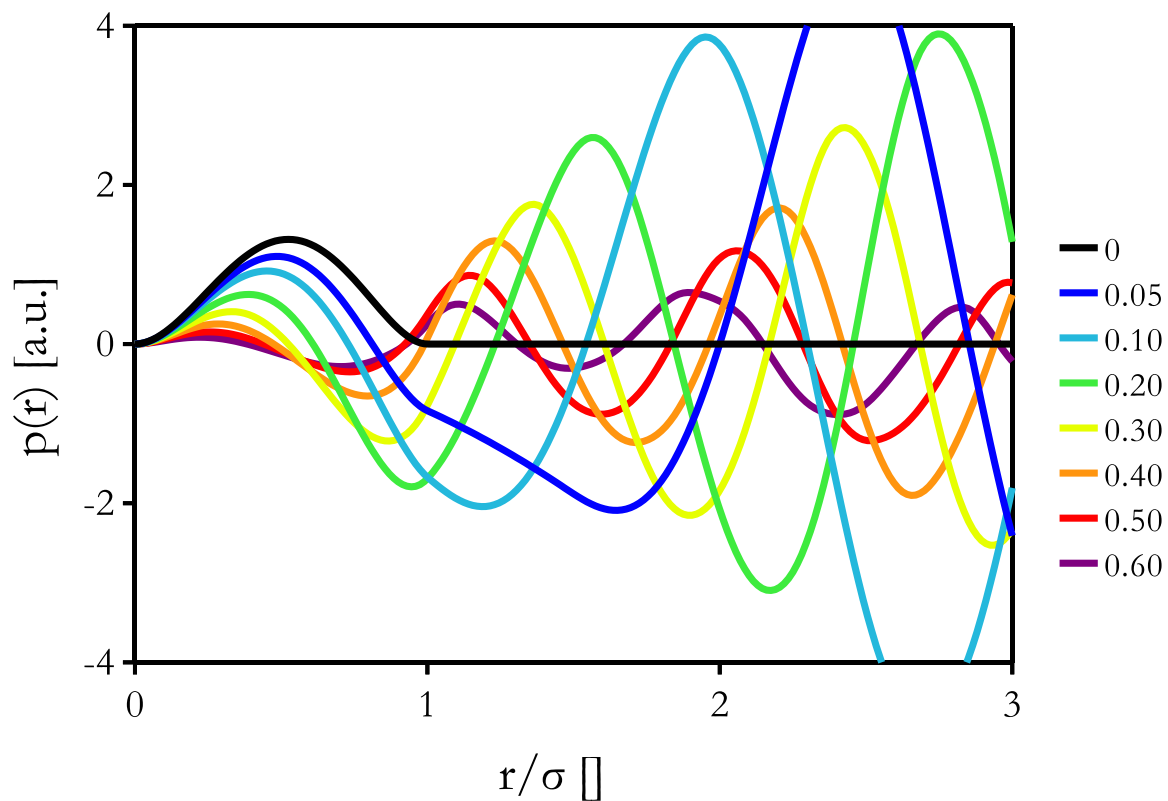
Fig. 5 Pair distance distribution functions of homogeneous spheres in hexagonal closed packing arrangement at various volume fractions from 0 to 0.6. The volume fractions are listed at the right hand side.
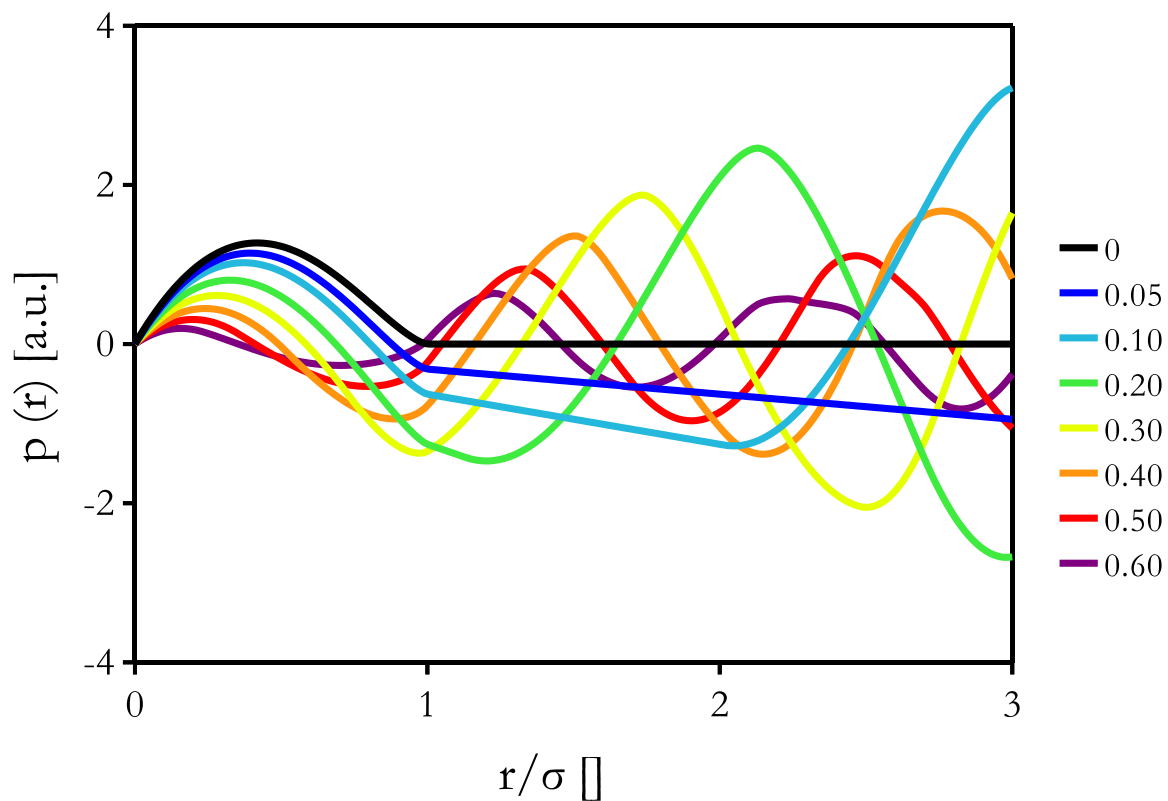
Fig. 6 Cross section pair distance distribution functions of homogeneous parallel cylinders in hexagonal arrangement at various volume fractions from 0 to 0.6. The volume fractions are listed at the right hand side.

Fig. 7 Cross section pair distance distribution functions of homogeneous parallel cylinders in hexagonal arrangement at various volume

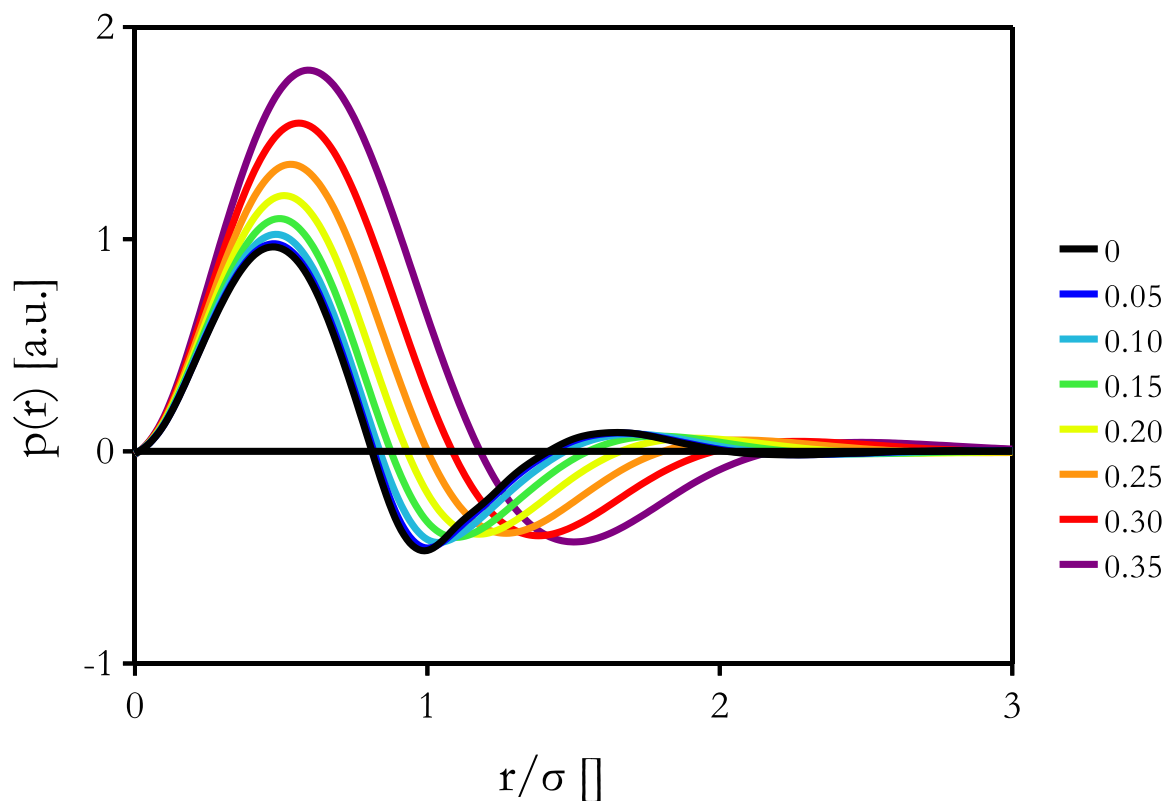fractions from 0 to 0.6. The volume fractions are listed at the right hand side.

The simulations show that the minimum at large distances is present, even for polydisperse systems.

The shift of its position can be explained by the presence of larger particles that dominate the scattering.

Therefore, the position of the minimum does not directly correspond to the diameter of the most common

size of spheres within the sample, but with the diameter of the spheres that contribute most to the scattering

pattern. If $D(a)$ is the size distribution that tells, how many spheres of radius a are within the simulated

sample, then the maximum of $a^6 \cdot D(a)$ agrees within 5% with the position of the minimum.