McEwan et al.\(^1\) measure the structure factor, \(S(q)\), for polymer grafted nanospheres (\(N\) is the degree of polymerization of the graft and \(P\) is the degree of polymerization of the matrix chains.) and state: “In general, both \(S(q)\) and \(g(r)\) characterize the particle micro-structure as they relate the local particle density to the probability of finding nearest and subsequent particle neighbors.”

a) Define \(S(q)\) and \(g(r)\). How do they describe micro-structure?

b) Explain Equation 1: \(I(q) = f_c V_p (Δρ)^2 P(q) S(q)\). How can you experimentally find the form factor, \(P(q)\) and the structure factor \(S(q)\)?

c) \(S(q) = 1 + 4πρ_p \int_0^\infty (g(r) - 1)r^2 \sin(qr) \frac{dr}{qr} \)  \(\text{(2)}\)

Figure 4 shows the behavior of \(S(q)\) as a function of concentration of grafted spheres. Explain this behavior.

d) Figure 5 shows the behavior of \(g(r)\), the correlation function, for short and long chain grafts (\(N\)). For low graft density, \(σ = 0.008\), in figure 1 explain this behavior of \(g(r)\).

e) McEwan et al. use the Ornstein–Zernike function,

\[ \gamma(r) = h(r) - c(r) = \rho_p \int h(r') c(|r - r'|) dr' \]  \(\text{(5)}\)

\(\gamma(r)\) to calculate \(g(r)\). They state, “Successful application of the theory rests upon the analysis of correlation functions that relate the interactions, \(U(r)\), between two particles in the presence of the \(N - 2\) remaining particles through the Ornstein–Zernike (OZ) relation which decomposes the total correlation function, \(h(r) = g(r) - 1\), into direct and indirect contributions, \(c(r)\) and \(\gamma(r)\), respectively. Explain what \(\gamma(r)\), and \(c(r)\) correspond to.

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**Fig. 1** Theoretical wetting phase diagram of dimensionless graft density \(σ\) versus swelling ratio \(P/N\) for homopolymer melt in contact with a chemically identical grafted brush.

**Fig. 2** (a) A schematic of polymer-grafted particles of center-to-center separation distance \(r\), surface-to-surface separation \(h\), brush height \(L\) and core radius \(a_c\). (b) The potential energy per lattice site of two grafted particles modeled through SCF calculations between flat plates. Schematics are not to scale.
Fig. 4  Comparison of experimental and theoretical structure factors $S(q)$ for radius $R \approx 100$ nm silica nanoparticles grafted with 25 kg mol$^{-1}$ PDMS in 13 kg mol$^{-1}$ PDMS with varying core volume fractions $\phi_c = 0.09 - 0.47$. Thin solid lines are predictions of $S(q)$ from Percus–Yevick closure from eqn (13) for particles with a size distribution of $109 \pm 13$ nm obtained from analysis of USAXS intensities.

Fig. 5  Comparison of the magnitude of peak in radial distribution function $g(r)$ at a silica core volume fraction of $\phi_c = 0.27$ to the storage modulus, $G'$, taken at an angular frequency of $\omega = 1$ rad s$^{-1}$; (a) experimentally extracted $g(r)$ of $R = 100$ nm silica nanoparticles grafted with 25 kg mol$^{-1}$ PDMS in 2 kg mol$^{-1}$ PDMS (black) and 13 kg mol$^{-1}$ PDMS (gray); and (b) storage modulus, $G'$, versus $\phi_c$, with concentration corresponding to (a) encircled. Higher magnitude of peak in $g(r)$ in 2 kg mol$^{-1}$ PDMS corresponds to increased particle ordering due to brush stretching, leading to enhancement in $G'$ in the lower molecular weight melt.


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a) $S(q)$ is the structure factor and reflects the organization of matter. The peak in $S(q)$ occurs at $q^* = 2\pi/d$ for the spacing of the material.  
$g(r)$ is the binary correlation function. The probability of finding matter at a distance “$r$” from matter integrated over all of the positions where matter exists. It reflects the average probability of finding matter separated at a distance “$r$”.

b) $I_0(q)/\phi_0$ at low concentrations is $P(q)$. $(I(q)/\phi)/(I_0(q)/\phi_0) = S(q)$.

c) As the concentration increases the organization of matter becomes sharper and the peak becomes narrower and larger. A second order peak appears at high concentration indicating long range order of the material as it begins to crystallize. Each order of reflection occurs at $nq^*$ where $n$ is an integer.

d) The chains are in the “complete wetting” regime of Figure 1 for the 2,000 g/mole chains. When the molecular weight of the grafts, $N$, increases to 13,000 g/mole the chains de-wet and the organization of the spheres decreases. The transition is driven by the conformational change of the grafted chains. Normally one would expect that ordering should increase with $N$ as is shown in Figure 2. However, with $N \gg P$ the grafted chains are not as compatible with the matrix chains and they are not swollen to the extent that they are fully extended as in Figure 2.

e) The direct correlation function $c(r)$ corresponds to the correlation function for nearest neighbor binary interactions. The indirect correlation function, $\gamma(r)$, corresponds to the impact of non-binary interactions on binary interactions. For three particles, 1, 2, 3, interactions between 1 and 2 can be influenced by interactions between 2 and 3. $\gamma(r)$ describes this influence. $c(r)$ describes the low concentration behavior where there are only 1-2 interactions.