

# Scattering from solutions of star polymers

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**Abstract.** We study the scattering intensity of dilute and semi-dilute solutions of star polymers. The star conformation is described by a model introduced by Daoud and Cotton. In this model, a single star is regarded as a spherical region of a semi-dilute polymer solution with a local, position dependent screening length. For high enough concentrations, the outer sections of the arms overlap and build a semi-dilute solution (a sea of blobs) where the inner parts of the actual stars are embedded. The scattering function is evaluated following a method introduced by Auvray and de Gennes. In the dilute regime there are three regions in the scattering function: the Guinier region (low wave vectors,  $qR \ll 1$ ) from where the radius of the star can be extracted; the intermediate region ( $1 \ll qR \ll f^{2/5}$ ) that carries the signature of the form factor of a star with  $f$  arms:  $I(q) \sim q^{-10/3}$ ; and a high wavevector zone ( $qR \gg f^{2/5}$ ) where the local swollen structure of the polymers gives rise to the usual  $q^{-5/3}$  decay. In the semi-dilute regime the different stars interact strongly, and the scattered intensity acquires two new features: a liquid peak that develops at a reciprocal position corresponding to the star-star distances; and a new large wavevector contribution of the form  $q^{-5/3}$  originating from the sea of blobs.

**PACS.** 87.22.Bt Membrane and subcellular physics and structure – 82.70.Dd Colloids

## 1 Introduction

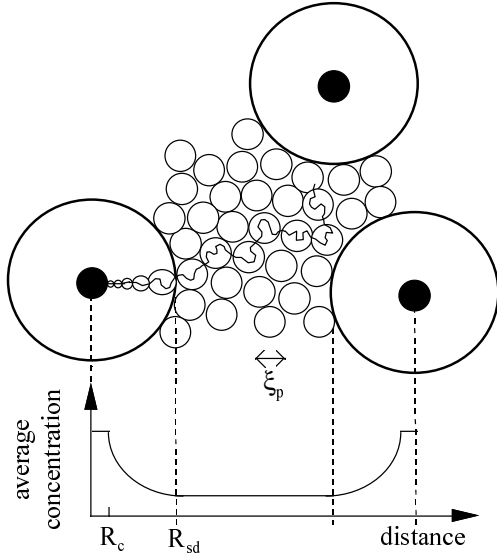
A star polymer is a branched macromolecule with a small central core from where emerge several end-attached linear chains [1]. Not only can star polymers be regarded as prototypes of branched systems, but also can solutions of star polymers be considered as model systems to study polymer colloidal stabilization or the effects of internal segment density on the behaviour of viscoelastic solutions. Experimental work in dilute solutions includes studies of viscoelastic behaviour and chain conformation by rheology [2,3], light scattering [2–6] and Small Angle Neutron Scattering (SANS) [6]. The chain dimensions and structure factors in semidilute solutions or melts has also been studied by SANS [7–9]. Theoretical work on the conformation of star polymers in good solvents was pioneered by Daoud and Cotton [10] and Birshtein and Zhulina [11]. Renormalization group calculations [12–14], Monte-Carlo [15, 16] and molecular dynamics simulations [17, 18] corroborate the Daoud-Cotton (D-C) picture at least in the dilute regime where the simulations have been performed. However, only a limited amount of information is available to describe the scattering intensity  $I(\mathbf{q})$  of star polymers. Analysis of the scattering data in the literature is performed with postulated expressions or limited to the

Guinier regime from where the star radius of gyration can be extracted [19]. In this paper we study the different factors which contribute to the scattering intensity of a star solution at arbitrary concentrations. We follow a method introduced by Auvray and de Gennes [20,21] to evaluate the intensity scattered by an adsorbed polymer layer. This method allows for an explicit computation of the scattered intensity of a star solution in the full wavevector range  $0 < q < (b(b^3/v))^{-1}$ , where  $b$  is the Kuhn length and  $v$  the excluded volume parameter.

## 2 The Daoud-Cotton model for star polymers

The structure of a star polymer with  $f$  arms of polymerization index  $N$  can be described by the Daoud Cotton [10] model. Attachment of the chains to a central core effectively forces the local polymer density to be everywhere inside the star above overlapping concentration. The star can therefore be described as a semi-dilute solution [22, 23], with a local, position dependent screening length  $\xi(r)$ , where  $r$  is the distance from the center. Pictorially, we represent this by associating with each arm a string of blobs of increasing size  $\xi(r)$ . The radial dependence of the blob size  $\xi(r)$  can be obtained by noticing that at a distance  $r$  from the center there are  $f$  blobs of cross

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**Fig. 1.** Schematic representation of a semi-dilute solution of star-shaped polymers. The average concentration profiles between two neighbouring stars is also represented.

section  $\xi(r)^2$  occupying a total area of  $4\pi r^2$ . The blob size thus varies as  $\xi(r) \simeq r f^{-1/2}$  and the corresponding local polymer volume fraction as  $\phi_s(r) \simeq f^{2/3}(b/r)^{4/3}$ . Note that there is a crowded region of size  $R_c \simeq b f^{1/2}$  in the middle of the star where the concentration reaches one. The size of the star can be obtained from monomer conservation  $N f b^3 = 4\pi \int_0^R r^2 dr \phi_s(r)$ . Neglecting the small core region one gets  $R \simeq a N^{3/5} f^{1/5}$ . Figure 1 sketches the structure of the star solution above the overlapping concentration  $\phi^* = f N b^3 / R^3$ . The inner part of each individual star is still described by a position dependent correlation length  $\xi(r)$  and the corresponding concentration profile  $\phi_s(r) \simeq f^{2/3}(b/r)^{4/3}$ . However, the profile doesn't vanish at a distance  $R$  but levels off to a constant value  $\phi_p$  at a distance  $R_{sd}$ , determined from the condition  $\phi_s(R_{sd}) = \phi_p$ . The concentration  $\phi_p$  is the polymer concentration in the region known as the sea of blobs, where the outer sections of the arms overlap. The stars embedded in the sea of blobs occupy a volume fraction  $\Phi_s$  and the sea of blobs the remaining fraction  $1 - \Phi_s$ . Above the overlapping concentration  $\phi^*$ , the values of the polymer concentration in the sea of blobs  $\phi_p$ , of the fraction occupied by the stars  $\Phi_s$  and of the radius of the embedded stars  $R_{sd}$  can be calculated from mass conservation:

$$\Phi_s \simeq \left[ \frac{\phi^*}{\phi} \right]^{5/4}, \quad \phi_p \simeq \phi \quad \text{and} \quad R_{sd} \simeq R \left[ \frac{\phi^*}{\phi} \right]^{3/4}. \quad (1)$$

Notice that an increase of the polymer concentration  $\phi$  leads to an increase of the fraction of space occupied by the sea of blobs and a shrinkage of the inner star dimensions.

### 3 The scattering intensity

The scattering intensity due to the chains in solution is given by [24]

$$I(\mathbf{q}) = \langle a^*(\mathbf{q}) a(\mathbf{q}) \rangle, \quad (2)$$

where  $a(\mathbf{q})$  is the amplitude scattered by the  $\mathcal{N}$  monomers in the system and  $\langle \rangle$  denotes an average taken over all possible configurations. The scattered amplitude is written as

$$a(\mathbf{q}) = \sum_i^{\mathcal{N}} (n_i - n_s) \exp\{j\mathbf{q} \cdot \mathbf{r}_i\} \quad (3)$$

with  $n_i - n_s$  the difference between the scattering lengths of the  $i$ th-monomer and the solvent. We assume hereafter that all monomers have equal scattering lengths,  $n_0$ . Defining  $\phi(\mathbf{r})$  as the monomer volume fraction at position  $\mathbf{r}$ , expression (2) can be written as

$$I(\mathbf{q}) = \frac{c}{\mathcal{N}} \int d^3r \exp\{j\mathbf{q} \cdot \mathbf{r}\} \int d^3r' \langle \rho(\mathbf{r}') \rho(\mathbf{r} + \mathbf{r}') \rangle, \quad (4)$$

with  $\rho(\mathbf{r}) = (n_0 - n_s) \phi(\mathbf{r})$ . The scattering amplitude  $\rho(\mathbf{r})$  of the semidilute solution of polymer stars described above can be represented as

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_s} \delta(\mathbf{r} - \mathbf{r}_i) \otimes [\rho_s(\mathbf{r}) \Pi(\mathbf{r})] + \rho_p(\mathbf{r}) \left[ 1 - \sum_{i=1}^{N_s} \delta(\mathbf{r} - \mathbf{r}_i) \otimes \Pi(\mathbf{r}) \right], \quad (5)$$

where  $N_s = \mathcal{N}/(Nf)$  is the number of micelles in the volume  $\mathcal{V}$ , the symbol  $\otimes$  denotes the convolution integral  $f(\mathbf{r}) \otimes g(\mathbf{r}) \equiv \int d^3r' f(\mathbf{r} - \mathbf{r}') g(\mathbf{r}')$  and  $\Pi(\mathbf{r})$  the step function  $\Pi(\mathbf{r}) = 1$  for  $r \leq R_{sd}$ ;  $\Pi(\mathbf{r}) = 0$  for  $r > R_{sd}$ . The first term on the r.h.s. of equation (5) effectively locates  $N_s$  spherical inner parts of stars at positions  $\mathbf{r}_i$ . The second term accounts for the monomers in the sea of blobs. The scattering amplitudes of the inner parts of the star  $\rho_s(\mathbf{r})$  and of the sea of blobs  $\rho_p(\mathbf{r})$  can be expressed as the sum of an average contribution and of a fluctuating part

$$\begin{aligned} \rho_s(\mathbf{r}) &= (n_0 - n_s) \phi_s(\mathbf{r}) + (n_0 - n_s) \delta \phi_s(\mathbf{r}), \\ \rho_p(\mathbf{r}) &= (n_0 - n_s) \phi_p(\mathbf{r}) + (n_0 - n_s) \delta \phi_p(\mathbf{r}). \end{aligned} \quad (6)$$

By inserting expressions (5, 6) into equation (4) we evaluate the total scattering intensity under the following approximations: i) density fluctuations in different stars are uncorrelated; ii) density fluctuations in the sea of blobs are uncorrelated to density fluctuations in the inner part of the stars. This is a reasonable assumption except perhaps for the correlations between the outer blob layer of the stars and the neighbouring blob layer in the sea of blobs; iii) we also ignore fluctuations in the shape of the inner parts, that is taken as a sphere of radius  $R_{sd}$ . In the appendix we show that under this assumptions the total scattering intensity can be written as a sum of three terms

$$I(\mathbf{q}) = (n_0 - n_s)^2 [I_{pp}(\mathbf{q}) + I_{ss}(\mathbf{q}) + I_S(\mathbf{q})]. \quad (7)$$

The first term  $I_{pp}$  accounts for density fluctuations in the sea of blobs

$$I_{pp}(\mathbf{q}) = (1 - \Phi_s) \langle \delta\phi_p^2(\mathbf{q}) \rangle, \quad (8)$$

the second term  $I_{ss}$  accounts for density fluctuations in the inner part of the stars

$$I_{ss}(\mathbf{q}) = \Phi_s \langle \delta\phi_s^2(\mathbf{q}) \rangle, \quad (9)$$

and the third term  $I_S$  expresses correlations between the different stars:

$$I_S(\mathbf{q}) = \Phi_s S(\mathbf{q}) \Delta\phi(\mathbf{q})^2. \quad (10)$$

This last expression contains the stars structure factor  $S(\mathbf{q}) = 1/N_s \sum_{m,n=1}^{N_s} \exp\{j\mathbf{q}(\mathbf{r}_m - \mathbf{r}_n)\}$  that expresses correlations between the positions of the stars in the solution. It is weighted by the form factor of the average polymer concentration in inner parts of the stars  $\Delta\phi(\mathbf{q})^2 = (\phi_p(\mathbf{q}) - \phi_s(\mathbf{q}))^2$ . We do not attempt here a calculation of the structure factor  $S(\mathbf{q})$ , our results provide instead a systematic approach for extracting  $S(\mathbf{q})$  from the experimental data.

The results presented above can also be used for dilute solutions of polymer stars. Formally, one sets the sea of blobs contribution equal to zero and takes the limit  $S(\mathbf{q}) \rightarrow 1$ . The volume fraction occupied by the stars is in this limit  $\Phi_s = \phi/\phi^*$ .

We now calculate explicitly the polymer contributions to the three different terms (8–10). The contribution from polymer-polymer correlations in the sea of blobs can be written as the fourier transform of  $g(r)$ , the pair correlation function for density fluctuations. This is a function which decays algebraically as  $r^{-4/3}$  and vanishes rapidly for distances larger than the correlation length  $\xi_p = \xi(\phi_p)$ :  $g(r) \sim \exp\{-r/(\sqrt{27/20}\xi_p)\}/r^{3/4}$ . The numerical value  $\sqrt{20/27}$  is chosen such that the correlation length can be directly measured from the lorentzian decay of the structure factor at low wave vector  $\langle \delta\phi_p^2(\mathbf{q}) \rangle \sim (1 + (q\xi_p)^2)^{-1}$ . Performing the fourier transform of the correlation function leads to

$$\langle \delta\phi_p^2(X) \rangle = Cte \left[ \frac{\xi_p}{b} \right]^{1/3} \frac{\sqrt{5} \sin \left\{ \frac{2}{3} \arctan \sqrt{27/20} X \right\}}{\sqrt{3} (X^3 + 27/20 X^5)^{1/3}} \quad (11)$$

with the dimensionless wavevector  $X = q\xi_p$ . For small wavevectors ( $X \ll 1$ ) one has by construction  $\langle \delta\phi_p^2(X) \rangle \simeq Cte(\xi_p/b)^{1/3}(1 + X^2)^{-1}$  while for large wavevectors ( $X \gg 1$ ) one gets  $\langle \delta\phi_p^2(X) \rangle \simeq Cte\sqrt{5/4} (20/27)^{1/3}(\xi_p/b)^{-4/3}q^{-5/3}$ .

The contribution from the density fluctuations inside the stars can be regarded as the scattering from a semidilute solution with a position dependent correlation length:

$$\begin{aligned} \langle \delta\phi_s^2(X) \rangle &= Cte \left[ \frac{\xi_p}{b} \right]^{1/3} \sqrt{\frac{5}{3}} \\ &\times \int_{\alpha}^1 y^{7/3} dy \frac{\sin \left\{ \frac{2}{3} \arctan \sqrt{27/20} X y \right\}}{((Xy)^3 + 27/20(Xy)^5)^{1/3}} \end{aligned} \quad (12)$$

with  $\alpha = R_c/R_{sd}$ , the ratio between the compact core radius  $R_c$  and the inner star radius  $R_{sd}$ . The form of this contribution is similar to the contribution from the sea of blobs. For instance, in the large wavevector limit ( $X \gg 1$ ) one has  $\langle \delta\phi_s^2(X) \rangle = 9/5 \langle \delta\phi_p^2(X) \rangle$ .

The form factor  $\Delta\phi(\mathbf{q})^2$  in equation (10) is calculated from

$$\Delta\phi(\mathbf{q})^2 = \frac{12\pi}{R_{sd}^3} \left[ \int_0^{R_{sd}} r^2 dr \frac{\sin qr}{qr} (\phi(r) - \phi_p) \right]^2 \quad (13)$$

with  $\phi(r) = 1$  for  $r < R_c$ ;  $\phi(r) = f^{2/3}(b/r)^{4/3}$  for  $R_c < r < R_{sd}$  and  $\phi_p$  a constant over all the integration range. Performing the integral leads to

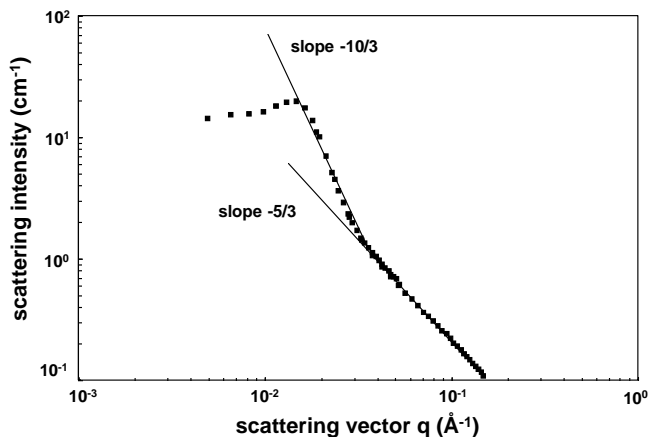
$$\begin{aligned} \Delta\phi(Z)^2 &= \frac{4\pi R_{sd}^3}{3} \left[ \frac{b}{\xi_p} \right]^{8/3} \left[ \alpha^{5/3} g(\alpha Z) - g(Z) \right. \\ &\quad \left. + \frac{3}{Z^{5/3}} \int_{\alpha Z}^Z dy \frac{\sin y}{y^{1/3}} \right]^2 \end{aligned} \quad (14)$$

where we defined a dimensionless wavevector  $Z = qR_{sd}$ . The asymptotic behaviour of the form factor for large wavevectors ( $Z \gg 1$ ) is  $\Delta\phi(Z)^2 \sim R_{sd}^{-1/3} \xi_p^{-8/3} q^{-10/3}$ .

Comparison of the three factors described above show that the scattered intensity is dominated at high  $q$  vectors by the  $q^{-5/3}$  behaviour that is due, in dilute star solutions, to concentration fluctuations inside the star and, in semidilute star solutions, to concentration fluctuations in both the inner part of the stars and in the sea of blobs. At low wave vectors we predict for dilute solutions a Guinier regime followed by a  $q^{-10/3}$  slope in a log-log representation, due to the form factor of the stars. For semidilute solutions, correlations between different stars are important, and the form factor multiplies the structure factor which measures those correlations. In practice this must lead to the appearance of one or more correlation pics in the Guinier zone or above. The crossover between the  $q^{-5/3}$  and the  $q^{-10/3}$  regimes is expected to occur at wave vectors  $qR_{sd} \sim f^{2/5}$  in semidilute solutions and at  $qR \sim f^{2/5}$  in dilute solutions.

## 4 Comparison with experiments

The general form of the scattering intensity of a polymer star solution, as outlined above, is in good agreement with results from both experiments and simulations. In this section we quantitatively confront our predictions to experimental data from reference [8]. The stars considered in reference [8] are synthesized by the so-called core-first method. In this method, a core of divinylbenzene (DVB) is synthesized and from the surface of the core, anionic polymerization of polystyrene takes place. This method has the advantage of providing high functionality objects, but with the inconvenient of a high polydispersity of the functionality (polydispersity of core masses). Also, since the linear chains are grown from, sometimes, massive DVB

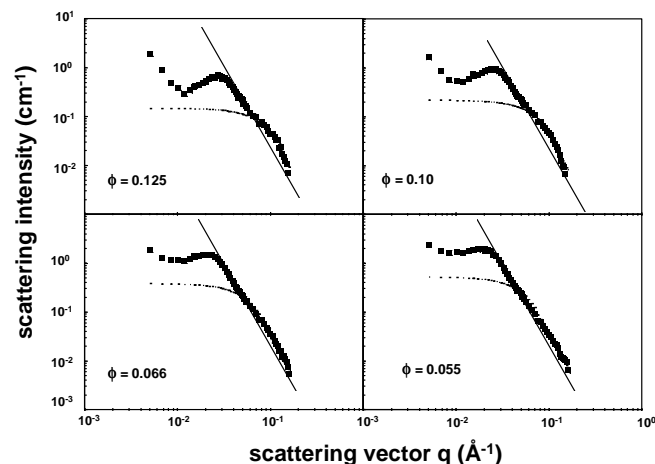


**Fig. 2.** Scattering intensity as a function of the scattering vector in a log-log scale for a solution of star polymers. The concentration is  $50 \text{ mg/cm}^3$  and the average functionality (overestimated) is 130. The star branch mass targeted in synthesis was  $M_n = 2 \times 10^4$ . Straight lines of slopes  $-5/3$  and  $-10/3$  are also represented in the figure.

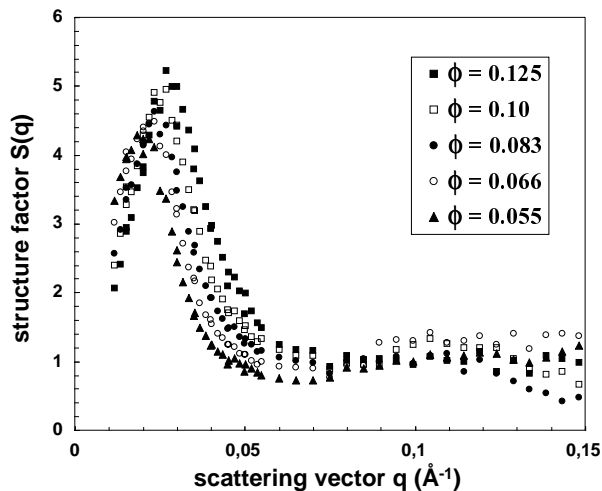
nodules, steric repulsion between monomers in the early stage of the polymerization are probably responsible for branches which are longer than the value targeted during synthesis. In the present case, the branch mass was targeted to be  $M_n \sim 2 \times 10^4$ . The values used here for  $R_{sd}$  are:  $35.4 \text{ \AA}$ ;  $41.5 \text{ \AA}$ ;  $50.2 \text{ \AA}$ ,  $53.7 \text{ \AA}$ ;  $57.1 \text{ \AA}$ , for polymer volume fractions of, respectively,  $0.125$ ;  $0.1$ ;  $0.083$ ;  $0.066$ ;  $0.055$ .

We plot in Figure 2 a typical scattering curve from a semidilute star solution. The intermediate and large  $q$  ranges clearly exhibit slopes  $-10/3$  and  $-5/3$  as predicted. In order to extract the structure factor of the stars solution we first subtract the large wavevector contributions. The unknown constant of equations (11, 12) can be obtained from data on semidilute solutions of linear polymers. Indeed, the scattering at small angles of linear polymers in a semi-dilute regime is given by an Orstein-Zernicke equation containing the same multiplicative constant of equations (11, 12). In our case we extracted the numerical value of the constant from data on polystyrene in deuterated toluene [25]. We fixed the ratio  $\alpha$  at the value  $0.1$ . The curves obtained after subtraction are presented in Figure 3. For the more diluted sample,  $\phi = 0.055$ , the slope of data in a log-log representation approaches the theoretical slope of  $-10/3$ . Deviations from this slope for the more concentrated samples might have several origins. Second or higher order pics in the structure factor would fall in this range, therefore introducing oscillant deviations from a pure linear slope in the log-log plot. Also, the quality of the stars may be here of importance, particularly the size, shape and functionality of the star cores. A few large cores with a small number of attached arms would also contribute significantly to the scattered intensity in the intermediate range.

As a final step we divide data from Figure 3 by the calculated form factor of equation (14). The structure factors obtained by this method are plotted in Figure 4 for five



**Fig. 3.** Scattering intensity as a function of the scattering vector in a log-log scale for solutions of very polydisperse star polymers at different concentrations when  $q^{-5/3}$  terms have been subtracted. The slope  $-10/3$  is also shown for every data set.



**Fig. 4.** Structure factors of solutions of polydisperse stars at different concentrations obtained from the procedure described in the text.

different polymer concentrations. The functions obtained display the usual features of liquid structure factors, in particular the position of the peak increases with concentration as  $\phi^{1/3}$  [8]. It is also important to stress that the procedure of subtraction is extremely sensitive to both the chemical quality of the stars and the correspondent quality of the scattered data. We expect that structure factors of better quality can be extracted from data of a carefully defined chemical nature. Such structure factors could then be confronted to existing theories of liquid structuration.

## 5 Conclusions

In this paper we have studied the scattering intensity of a star-polymer solution, both in the dilute and semidilute regimes. The structure of the solution and the

conformation of the stars has been described by the Daoud-Cotton [10] model, and the intensity calculated following a method introduced by Auvray and de Gennes [20, 21]. Our results show that the scattering intensity can be described as the sum of three terms. The first term is the product of the structure factor of the solution by the form factor of the star. We did not evaluate the structure factor for a star solution, but our results provide a procedure that allows its extraction from experimental data. The form factor is the fourier transform of the average concentration profile of the star. This term gives rise to a characteristic  $q^{-10/3}$  wavevector dependence in the intermediate  $q$  range ( $1 \ll qR_{sd} \ll f^{2/5}$ ). The second and third terms are independent of the structure factor and measure concentration fluctuations in the inner parts of the stars and in the sea of blobs. They have both a  $q^{-5/3}$  dependence, and dominate the scattering spectra at high wavevectors  $qR_{sd} \gg f^{2/5}$ . Our data is consistent with available experimental data on star solutions.

We would like to thank J.F. Joanny for many fruitful discussions.

## Appendix A: The de Gennes-Auvray method

In this appendix we expand expression (4) by inserting therein the representations (6, 5) for the concentration and performing the averages under the assumptions stated in Section 3. More precisely we calculate

$$\int d^3\mathbf{r} \exp\{j\mathbf{q}\cdot\mathbf{r}\} \int d^3\mathbf{r}' \langle \rho(\mathbf{r}') \rho(\mathbf{r} + \mathbf{r}') \rangle = A + B + C + D \quad (\text{A.1})$$

with

$$\begin{aligned} A &= \int d^3\mathbf{r} \exp\{j\mathbf{q}\cdot\mathbf{r}\} \int d^3\mathbf{r}' \int d^3\mathbf{r}'' \int d^3\mathbf{r}''' \\ &\times \sum_{n=1}^{N_s} \sum_{m=1}^{N_s} \delta(\mathbf{r}' - \mathbf{r}_n - \mathbf{r}'') \delta(\mathbf{r}' + \mathbf{r} - \mathbf{r}_m - \mathbf{r}''') \\ &\times \Pi(\mathbf{r}'') \Pi(\mathbf{r}''') \langle \rho_s(\mathbf{r}'') \rho_s(\mathbf{r}''') \rangle, \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned} B &= \int d^3\mathbf{r} \exp\{j\mathbf{q}\cdot\mathbf{r}\} \int d^3\mathbf{r}' \int d^3\mathbf{r}'' \\ &\times \sum_{n=1}^{N_s} \delta(\mathbf{r}' - \mathbf{r}_n - \mathbf{r}'') \Pi(\mathbf{r}'') \\ &\times \left[ 1 - \int d^3\mathbf{r}''' \sum_{m=1}^{N_s} \delta(\mathbf{r}' + \mathbf{r} - \mathbf{r}_m - \mathbf{r}''') \Pi(\mathbf{r}''') \right] \\ &\times \langle \rho_s(\mathbf{r}'') \rho_p(\mathbf{r} + \mathbf{r}') \rangle, \end{aligned} \quad (\text{A.3})$$

$$\begin{aligned} C &= \int d^3\mathbf{r} \exp\{j\mathbf{q}\cdot\mathbf{r}\} \int d^3\mathbf{r}' \\ &\times \left[ 1 - \int d^3\mathbf{r}''' \sum_{n=1}^{N_s} \delta(\mathbf{r}' - \mathbf{r}_n - \mathbf{r}''') \Pi(\mathbf{r}''') \right] \\ &\times \sum_{m=1}^{N_s} \int d^3\mathbf{r}'' \delta(\mathbf{r}' + \mathbf{r} - \mathbf{r}_m - \mathbf{r}'') \\ &\times \Pi(\mathbf{r}'') \langle \rho_p(\mathbf{r}') \rho_s(\mathbf{r}'') \rangle, \end{aligned} \quad (\text{A.4})$$

$$\begin{aligned} D &= \int d^3\mathbf{r} \exp\{j\mathbf{q}\cdot\mathbf{r}\} \int d^3\mathbf{r}' \\ &\times \left[ 1 - \int d^3\mathbf{r}'' \sum_{n=1}^{N_s} \delta(\mathbf{r}' - \mathbf{r}_n - \mathbf{r}'') \Pi(\mathbf{r}'') \right] \\ &\times \left[ 1 - \int d^3\mathbf{r}''' \sum_{m=1}^{N_s} \delta(\mathbf{r}' + \mathbf{r} - \mathbf{r}_m - \mathbf{r}''') \Pi(\mathbf{r}''') \right] \\ &\times \langle \rho_p(\mathbf{r}') \rho_p(\mathbf{r}' + \mathbf{r}) \rangle. \end{aligned} \quad (\text{A.5})$$

By further decomposing each of the concentration variables into their average and fluctuating values one gets

$$\begin{aligned} A/(n_0 - n_s)^2 &= \sum_{n,m=1}^{N_s} \langle \exp\{j\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n)\} \rangle \phi_s(\mathbf{q}) \phi_s(-\mathbf{q}) \\ &+ N_s \int d^3\mathbf{r} \exp\{j\mathbf{q}\cdot\mathbf{r}\} \int d^3\mathbf{r}' \Pi(\mathbf{r}') \\ &\times \langle \delta\phi_s(\mathbf{r}') \delta\phi_s(\mathbf{r} + \mathbf{r}') \rangle \end{aligned} \quad (\text{A.6})$$

where  $\phi_s(\mathbf{q}) = \int d^3\mathbf{r} \Pi(\mathbf{r}) \exp\{j\mathbf{q}\cdot\mathbf{r}\} \phi_s(\mathbf{r})$ ;

$$\begin{aligned} (B + C)/(n_0 - n_s)^2 &= - \sum_{n,m=1}^{N_s} \langle \exp\{j\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n)\} \rangle \\ &\times \phi_p \left[ \phi_s(\mathbf{q}) \int d^3\mathbf{r} \Pi(\mathbf{r}) \exp\{-j\mathbf{q}\cdot\mathbf{r}\} \right. \\ &\left. + \phi_s(-\mathbf{q}) \int d^3\mathbf{r} \Pi(\mathbf{r}) \exp\{j\mathbf{q}\cdot\mathbf{r}\} \right] \end{aligned} \quad (\text{A.7})$$

$$\begin{aligned} D/(n_0 - n_s)^2 &= \left[ \nu - N_s \int d^3\mathbf{r} \Pi(\mathbf{r}) \right] \\ &\times \int d^3\mathbf{r} \exp\{j\mathbf{q}\cdot\mathbf{r}\} \langle \delta\phi_p(0) \delta\phi_p(\mathbf{r}) \rangle \\ &+ \sum_{n,m=1}^{N_s} \langle \exp\{j\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n)\} \rangle \phi_p^2 \\ &\times \int d^3\mathbf{r}'' \exp\{j\mathbf{q}\cdot\mathbf{r}''\} \Pi(\mathbf{r}'') \\ &\times \int d^3\mathbf{r}''' \exp\{-j\mathbf{q}\cdot\mathbf{r}'''\} \Pi(\mathbf{r}''') \end{aligned} \quad (\text{A.8})$$

All contributions to pure forward scattering (terms proportional to  $\delta(\mathbf{q})$ ) have been discarded. Grouping the different terms leads to equation (7).

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