Relating monomer to centre-of-mass distribution functions in polymer solutions

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Abstract. – A relationship between the measurable monomer-monomer structure factor, and the centre-of-mass (CM) structure factor of dilute or semi-dilute polymer solutions is derived from Ornstein-Zernike relations within the "polymer reference interaction site model" (PRISM) formalism, by considering the CM of each polymer as an auxiliary site and neglecting direct correlations between the latter and the CM and monomers of neighbouring polymers. The predictions agree well with Monte Carlo data for self-avoiding walk polymers, and are considerably more accurate than the predictions of simple factorization approximations.

There have recently been a number of attempts to represent polymer coils in solution as systems of soft, penetrable particles of fixed [1,2] or variable [3] shape, and size proportional to the radius of gyration R_{g}, which interact via effective pair forces obtained by averaging over individual monomer degrees of freedom. A similar approach has proved very successful in the description of star polymer solutions [4]. The advantage of this reductionist strategy is that the effective pair forces act only between single interaction sites within each polymer, rather than between the large number of individual monomers or Kuhn segments belonging to the interpenetrating coils. A natural (but by no means unique) choice of the single interaction site is the centre-of-mass (CM) of the polymers. This coarse-graining leads to an enormous reduction (by a factor equal to the number ν of monomers or segments in each polymer) in the number of interacting degrees of freedom, thus allowing, *inter alia*, efficient simulation of large-scale phenomena involving many polymers.

The price to pay is that the effective interactions are state-dependent, *i.e.* the pair potentials resulting from the coarse-graining procedure depend in general on polymer concentration, temperature, and the degree of polymerization, although the latter dependence is negligible for sufficiently large ν such that the scaling regime is reached in practice. In ref. [1] the state-dependent effective pair potential between the CM of non-intersecting self-avoiding walk (SAW) polymers in dilute and semi-dilute solutions was derived from a very accurate Statistical Mechanics inversion procedure of the CM pair distribution function $g_{cc}(r)$. The latter had to be determined for each polymer concentration from fully microscopic Monte Carlo (MC)

simulations of samples involving hundreds of SAW polymers. This "exact" procedure is obviously very computer intensive, and in a certain sense defeats the original purpose, which is to replace a detailed, monomer level description of polymer coils by a projected representation involving only their CMs.

To overcome this methodological bottleneck, one is naturally led to the use of approximate theories of intermolecular correlations between polymers. One obvious candidate is the "polymer reference interaction site model" (PRISM), which provides a successful theory of such correlations, particularly so in the melt, where polymers are known to behave as Gaussian coils [5]. However, PRISM provides only monomer-monomer pair distribution functions $g_{mm}(r)$, and an accurate procedure is needed to extract the CM-CM pair distribution function $g_{cc}(r)$ from a knowledge of $g_{mm}(r)$. In this letter the PRISM formalism is extended to derive such a relationship, which also involves the form factors (or internal structure factors) of individual polymers. The relation is tested against MC simulation data, and turns out to be vastly superior to previous proposals [2, 6].

Consider a monodisperse solution of N linear polymers with ν monomers or segments each, in a volume V; the polymer number density is $\rho = N/V$. Let $\boldsymbol{R}^i$ ($1 \leq i \leq N$) be the CM position vector of the i-th polymer, and $\boldsymbol{r}^i_\alpha = \boldsymbol{R}^i + \boldsymbol{u}^i_\alpha$ ($1 \leq \alpha \leq \nu$) the positions of the ν monomers in that chain. The Fourier components of the monomer and CM density operators are

$$\rho_{\boldsymbol{q}} = \sum_{i=1}^{N} \sum_{\alpha=1}^{\nu} e^{i\boldsymbol{q}\boldsymbol{r}^i_\alpha}, \tag{1a}$$

$$\rho_{\boldsymbol{q}}^{\text{CM}} = \sum_{i=1}^{N} e^{i\boldsymbol{q}\boldsymbol{R}^i}. \tag{1b}$$

It proves also convenient to define the Fourier components of the intramolecular monomer density of the i-th polymer:

$$\rho_{\boldsymbol{q}}^i = \sum_{\alpha=1}^{\nu} e^{i\boldsymbol{q}\boldsymbol{u}^i_\alpha}, \tag{1c}$$

in terms of which one may express the following form factors, which characterize the internal structure of each individual polymer coil, in the presence of all surrounding polymers:

$$\omega_{mm}(q) = \frac{1}{\nu} \langle \rho_{\boldsymbol{q}}^i \rho_{-\boldsymbol{q}}^i \rangle, \tag{2a}$$

$$\omega_{cm}(q) = \langle \rho_{\boldsymbol{q}}^i \rangle. \tag{2b}$$

The brackets denote canonical averages weighted by the Boltzmann factor involving the total interaction energy between all monomers on all polymers, and accounting for the connectivity constraints. The resulting form factors are independent of the index i, because all polymers are equivalent, and depend only on the modulus $q = |\boldsymbol{q}|$ of the wave vector due to rotational invariance (the polymer solutions are isotropic).

The total monomer structure factor, as measured, e.g., by coherent neutron or light scattering experiments, is defined by

$$S_{mm}(q) = \frac{1}{N\nu^2} \langle \rho_{\boldsymbol{q}} \rho_{-\boldsymbol{q}} \rangle = \frac{1}{N\nu^2} \left\langle \sum_i \sum_j \sum_\alpha \sum_\beta e^{i\boldsymbol{q}(\boldsymbol{r}^i_\alpha - \boldsymbol{r}^j_\beta)} \right\rangle, \tag{3}$$

and naturally splits into intramolecular ($i = j$) and intermolecular ($i \neq j$) contributions:

$$S_{mm}(q) = S_{mm}^{\text{intra}}(q) + S_{mm}^{\text{inter}}(q) = \frac{\omega_{mm}(q)}{\nu} + S_{mm}^{\text{inter}}(q). \tag{4}$$

The intermolecular contribution may be rewritten as

$$S_{mm}^{\text{inter}}(q) = \frac{1}{N\nu^2} \sum_i \sum_{j \neq i} \left\langle e^{i\boldsymbol{q}(\boldsymbol{R}^i - \boldsymbol{R}^j)} \rho_{\boldsymbol{q}}^i \rho_{-\boldsymbol{q}}^j \right\rangle. \tag{5}$$

A common decoupling approximation is to assume that the intramolecular conformations of any two polymers are independent of each other and of the mutual positions of their CM, so that the statistical average in (5) factorizes according to

$$S_{mm}^{\text{inter}}(q) \simeq \frac{1}{N\nu^2} \sum_i \sum_{j \neq i} \left\langle e^{i\boldsymbol{q}(\boldsymbol{R}^i - \boldsymbol{R}^j)} \right\rangle \langle \rho_{\boldsymbol{q}}^i \rangle \langle \rho_{-\boldsymbol{q}}^j \rangle = \frac{\omega_{cm}(q)^2}{\nu^2} [S_{cc}(q) - 1], \tag{6}$$

where $S_{cc}(q)$ is the CM structure factor:

$$S_{cc}(q) = \frac{1}{N} \left\langle \rho_{\boldsymbol{q}}^{\text{CM}} \rho_{-\boldsymbol{q}}^{\text{CM}} \right\rangle = 1 + \rho h_{cc}(q), \tag{7}$$

and $h_{cc}(q)$ is the Fourier transform of the CM-CM pair correlation function $h_{cc}(r) = g_{cc}(r) - 1$. Substituting eqs. (6) and (7) into eq. (4), one arrives at

$$S_{mm}(q) = \frac{\omega_{mm}(q)}{\nu} + \rho h_{mm}(q) = \frac{\omega_{mm}(q)}{\nu} + \rho \frac{\omega_{cm}(q)^2}{\nu^2} h_{cc}(q), \tag{8}$$

which leads to the desired approximate relation between the Fourier transforms of the monomer-monomer and CM-CM correlation functions:

$$h_{cc}(q) = \frac{\nu^2}{\omega_{cm}(q)^2} h_{mm}(q). \tag{9}$$

Equation (9) is the approximation proposed by Koyama [6] and is formally identical to the so-called "free-rotation" approximation for rigid molecules; it requires a knowledge of the form factor $\omega_{cm}(q)$ defined by eq. (2b).

An alternative approximation is based on the rigid particle assumption used by Pagonabarraga and Cates [2], according to which intramolecular conformations and CM positions are independent, and intramolecular conformations of different polymers are correlated as if they belonged to the same polymer ("rigid particle" assumption), *i.e.*:

$$\begin{aligned} S_{mm}(q) &\simeq \frac{1}{N\nu^2} \sum_i \sum_j \left\langle e^{i\boldsymbol{q}(\boldsymbol{R}^i - \boldsymbol{R}^j)} \right\rangle \langle \rho_{\boldsymbol{q}}^i \rho_{-\boldsymbol{q}}^j \rangle \\ &= S_{cc}(q) \frac{1}{\nu^2} \langle \rho_{\boldsymbol{q}}^i \rho_{-\boldsymbol{q}}^i \rangle \\ &= \frac{\omega_{mm}(q)}{\nu} S_{cc}(q), \end{aligned} \tag{10}$$

leading to

$$h_{cc}(q) = \frac{\nu}{\omega_{mm}(q)} h_{mm}(q). \tag{11}$$

The relations (9) and (11) are clearly based on uncontrolled factorization approximations; they will be tested below against "exact" simulation data, and compared to the relation which we now set out to establish within the framework of the PRISM theory [5]. PRISM is based on the assumption that all correlation functions between monomers are independent of their positions along the chain, *i.e.* end effects are neglected, which is true in the scaling limit $\nu \to \infty$. This unique correlation function $h_{mm}(q)$ is related to a unique monomer-monomer direct correlation function $c_{mm}(q)$ by the PRISM Orstein-Zernike (OZ) relation:

$$h_{mm}(q) = \omega_{mm}(q)c_{mm}(q)\big[\omega_{mm}(q) + \rho\nu h_{mm}(q)\big]. \tag{12}$$

The key idea now is to consider the CM of each polymer as an additional non-interacting site, which is linked to the monomer position vectors by the defining "connectivity" constraint

$$\boldsymbol{R}^i = \frac{1}{\nu} \sum_{\alpha=1}^{\nu} \boldsymbol{r}_\alpha^i. \tag{13}$$

This trick of introducing auxiliary sites to compute special correlation functions dates back to the early days of the "reference interaction site model" (RISM) theory (from which PRISM is an extension) [7] and has been first proposed by Chandler [8]. Since the CM auxiliary site does not interact with any of the ν segments, it must clearly be treated separately; thus, each polymer now has two species of sites, namely the CM and the ν equivalent interaction sites associated with the physical segments.

The single OZ relation (12) is now replaced by a 2×2 matrix of OZ relations. The latter are further simplified by the plausible assumption that the direct correlation functions between the CM of one polymer, and the CM as well as the interaction sites of the other polymers are identically zero, *i.e.*

$$c_{cc}(q) \equiv 0, \tag{14a}$$

$$c_{mc}(q) = c_{cm}(q) \equiv 0. \tag{14b}$$

The four coupled OZ relations are then given by (12), which is not modified by the presence of the auxiliary, non-interacting site [9], together with

$$h_{cm}(q) = \omega_{cm}(q)c_{mm}(q)\big[\omega_{mm}(q) + \rho\nu h_{mm}(q)\big], \tag{15a}$$

$$h_{mc}(q) = \omega_{mm}(q)c_{mm}(q)\big[\omega_{mc}(q) + \rho\nu h_{mc}(q)\big], \tag{15b}$$

$$h_{cc}(q) = \omega_{cm}(q)c_{mm}(q)\big[\omega_{cm}(q) + \rho\nu h_{cm}(q)\big]. \tag{15c}$$

These equations immediately lead to the desired relation:

$$h_{cc}(q) = \frac{\omega_{cm}(q)^2}{\omega_{mm}(q)^2} h_{mm}(q), \tag{16}$$

which is independent of any specific closure relation, except for the assumptions (14).

Equation (16) provides the desired link between the monomer-monomer correlation function, which may be calculated from PRISM theory, and the CM-CM correlation function which is the basic input into the coarse-graining scheme, since the state-dependent effective pair potential between the centres of mass follows directly from standard inversion procedures [1]. To extract $h_{cc}(q)$ from $h_{mm}(q)$ also requires a knowledge of the form factors $\omega_{mm}(q)$ and $\omega_{cm}(q)$. These are known explicitly for Gaussian chains [10], and PRISM theory generally
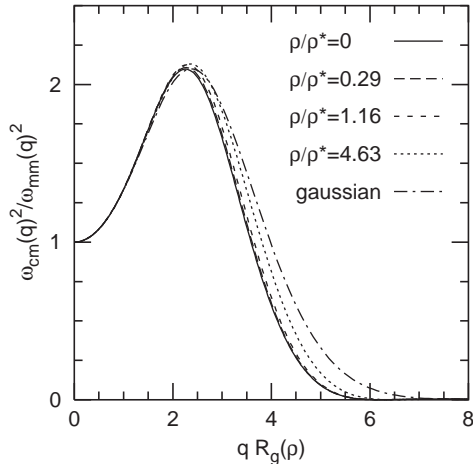
Fig. 1 – Density dependence of the ratio $\omega_{cm}(q)^2/\omega_{mm}(q)^2$ as a function of the wave number scaled by the density-dependent radius of gyration $R_{\mathrm{g}}(\rho)$, as obtained by MC simulations of $\nu = 500$ SAW polymers on a simple cubic lattice. For comparison, the corresponding function for Gaussian chains is also shown.

uses the Gaussian chain form factor in the OZ relation (12), which is strictly valid only in the melt. In polymer solutions, we expect the form factors to depend on polymer concentration. To investigate this dependence, we have carried out MC simulations of $\nu = 500$ SAW polymers on a simple cubic lattice for reduced densities $\rho/\rho^* = 0$, 0.29, 1.16, and 4.63, where the overlapping density ρ^* is defined through the relation $4\pi\rho^* R_{\mathrm{g}}^3(\rho = 0)/3 = 1$. Results for the ratio $\omega_{cm}(q)^2/\omega_{mm}(q)^2$, relevant for the mapping (16) of $h_{mm}(q)$ onto $h_{cc}(q)$, are shown in fig. 1. They are compared with the corresponding ratio for Gaussian chains, which is found to qualitatively reproduce the shape of the curves obtained by computer simulation. When the wave number q is scaled with the radius of gyration $R_{\mathrm{g}}(\rho)$ appropriate for each density, which decreases from 16.8 to 14.8 lattice spacings as the density increases, the low-density results $(\rho/\rho^* \lesssim 1)$ are seen to fall practically on a single master curve. The results at $\rho/\rho^* = 4.63$, which is well into the semi-dilute regime, deviate from this master curve, towards the result for a Gaussian chain, as one might expect.

Having determined the "exact" form factors, we are now in a position to test the relations between $h_{mm}(q)$ and $h_{cc}(q)$, as predicted by the factorization approximations (9) and (11), and by the PRISM-based equation (16). For the test to be meaningful, we have used as input the "exact" (rather than PRISM-generated) $h_{mm}(q)$. Figure 2 shows the MC results for $S_{cc}(q)$, together with the results obtained by combining eq. (7) with each of the three approximations (9), (11) and (16), using the "exact" form factors, at $\rho/\rho^* = 1.16$. In the case of approximation (16), results based on the Gaussian chain form factors are also shown. The agreement between the "exact" structure factor and the predictions from eq. (16) is seen to be excellent at small q; some deviations are seen at intermediate wave numbers $qR_{\mathrm{g}} \simeq 4$, where the "exact" $S_{cc}(q)$ has a small maximum. Similar agreement is found at the other densities, as shown in fig. 3 for $\rho/\rho^* = 4.63$. The decoupling approximations (9) and (11) are seen to fail. Interestingly, approximation (16) combined with the analytic Gaussian form factors also yields good agreement.

The success of eq. (16) in obtaining the CM correlations from the monomer correlations suggests that the inverse route could also be profitable. This may be expected to be
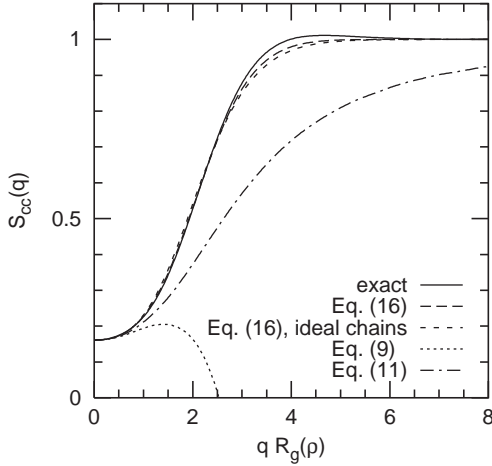
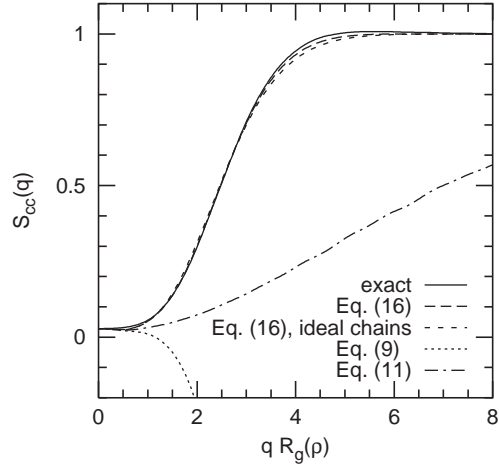Fig. 2   Fig. 3

Fig. 2 – CM structure factor $S_{cc}(q)$ for $\nu = 500$ SAW polymers on a simple cubic lattice at a reduced density $\rho/\rho^* = 1.16$. The "exact" structure factor is compared with the various approximations proposed in the text using the "exact" monomer correlation function $h_{mm}(q)$ and form factors $\omega_{cm}(q)$ and $\omega_{mm}(q)$. For comparison, in the case of approximation (16), results based on the Gaussian chain form factors are also shown.

Fig. 3 – Same as fig. 2, at a reduced density $\rho/\rho^* = 4.63$.

more difficult because one appears to move from less information (CM) to more information (monomers). In fact, attempts to invert eq. (16) result in problems of a rather general kind because $\omega_{cm}(q)$, which can be zero, is now in the denominator, leading to spurious singularities. $\omega_{cm}(q)$ for Gaussian coils does not cross zero, so that it may be used more profitably to obtain $S_{mm}(q)$ from $S_{cc}(q)$, but the results are still not as good as what is seen in figs. 2 and 3. We found empirically that the inverse of eq. (16) still works well for $qR_{\mathrm{g}} \leq 2$, but for larger q deviations occur. While the other two approximations do not show the spurious singularity, they do show other spurious effects.

To conclude, we have proposed a new relation between the monomer-monomer and CM-CM correlation functions of polymers based on an extension of PRISM theory. It has been tested for polymers in good solvent and it is found to be quantitatively accurate except for discrepancies at intermediate wave numbers where $h_{cc}(q)$ changes sign and exhibits a small maximum, while $h_{mm}(q)$ is a monotonically increasing function of q. These discrepancies must be traced back to assumptions (14), which are the only approximations involved here (apart from the neglect of end effects in PRISM, that is known to have minor consequences). The factorization approximations (9) and (11), on the other hand, appear to perform less well. It should be added that approximation (11) was derived for use in the melt, a regime which has not been tested in this paper, and where the connection between CM and monomer correlations may be different.

The present analysis stresses the need for developing a reliable theory for the state-dependent form factors $\omega_{mm}(q)$ and $\omega_{cm}(q)$, in particular in the dilute and semi-dilute solution regimes that have been investigated here. In this respect, it is worth stressing that $\omega_{cm}(q)$ has hitherto attracted very little attention [11], probably because it is not of direct experimental relevance. Our MC results point to a near universality of the ratio $\omega_{cm}(q)/\omega_{mm}(q)$ as

a function of qR_g in the dilute regime. Accurate form factors in the dilute and semi-dilute regime would also provide a crucial input into PRISM calculations of $h_{mm}(q)$. Work along these lines is in progress.

Various extensions of this work are currently under investigation. Firstly, using the two-component PRISM OZ relation [12], it is easy to extend the present formalism to colloid-polymer mixtures and simple inhomogeneous situations (polymers near a wall for instance), that have recently attracted much attention. Secondly, the relation (16) does not rely on any assumption on the monomer interactions, so it would be interesting to test its relevance for other classes of polymers such as linear polymers in θ or poor solvents, branched polymers, polyelectrolytes, etc. This could be very helpful in interpreting experiments, which typically only have access to monomer-monomer correlations.

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