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Scattering from small colloidal particles in a semidilute polymer solution

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Abstract. The correlations between the segments of a semidilute polymer solution are found to induce correlations in the positions of small particles added to the solution. Small means a diameter much less than the polymer's correlation length. In the presence of polymer the particles behave as if they attracted each other. It is shown how the polymer's correlation length may be determined from a scattering experiment performed on the spheres.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 83.70.Hq Heterogeneous liquids: suspensions, dispersions, emulsions, pastes, slurries, foams, block copolymers, etc.

1 Introduction

Small colloidal particles in a semidilute polymer solution are shown to interact *via* a long ranged, attractive potential of mean force. This potential of mean force [1] is an effective interaction potential between the particles due to the presence of the polymer. The particles are small with respect to the polymer's correlation length and, as it is this length which determines the range of the attractive potential of mean force, the attractive interactions are long ranged with respect to the direct interaction between the spheres. The effective attractions between the colloidal particles are a result of the correlations between the segments in a semidilute polymer solution [2]. The segments of a polymer molecule in a good solvent follow a self-avoiding walk. Because of this the fraction of the volume of the solution occupied by the polymer segments is highly non-random: if there is a segment at one point then the average density of polymer nearby is much higher than the average density of segments. This implies that the volume *not* occupied by the polymer segments is also highly correlated; if you imagine a picture in which every point is either black or white, then if there is a pattern to the white areas then there must be a pattern to the black areas. But the particles are only free to move in this volume which is free of polymer; they are excluded from the volume occupied by the polymer. So the particles move in a fraction of the solution's volume which has long range correlations and so their positions have long range correlations. In fact the correlations between the spheres resemble those produced by a long ranged attraction. As the correlations in the spheres reflect those in the polymer, scattering experiments [3] on the colloidal particles may be used to probe the structure of a semidilute polymer solution; in particular they provide a way of measuring the correlation length of the polymer.

The colloidal particles could be protein molecules [4,5], surfactant micelles [6,7], or synthetic, polymer or silica, spheres [8,9]. Both protein molecules and micelles typically have diameters of a few nm. The direct interaction between particles is taken to be purely repulsive, there are no attractive interactions. The polymer is considered to be in a good solvent and is therefore swollen due to self-interactions [2]. The polymer's radius of gyration is much larger than the diameter of the particles, ~ 10 nm or more. See references [10–12] for examples of work where the radius of gyration is comparable to or smaller than the diameter of the particles. Recent work of Khalatur *et al.* [13] has dealt with similar mixtures to those considered here using RISM integral equations. It is more numerical and less intuitive than here. The RISM approach is also best suited to higher polymer densities than those considered here, say volume fractions of polymer of 10% and more. Our simple scaling approach breaks down at these densities. All interactions are assumed to be excluded volume interactions, that is two polymer segments may not occupy the same volume and likewise for two particles or a particle and a polymer segment. This is reasonable if the solvent is good for the polymer, and the polymer does not absorb onto the particle.

All three interactions are excluded volume and therefore there are no energy scales, apart from the temperature T. Therefore, the behaviour is a function only of the length scales of the mixture. The length scale of the particles is just their diameter D. A pure semidilute polymer solution

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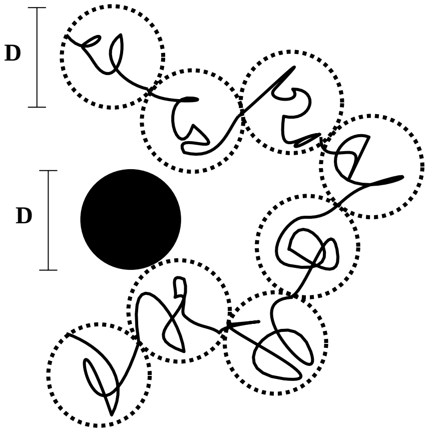

Fig. 1. A schematic picture of a small colloidal sphere, a micelle or a protein molecule, and a nearby part of a polymer chain. The black circle is a spherical particle. The chain is shown as a black curve and the dashed circles represent the rescaled segments of size D.

has only one relevant length scale, the correlation length ξ [2], which is roughly the distance between interactions between segments on different polymer chains. The radius of gyration is not a relevant length scale as it is much larger than ξ and the chain loses its correlations and 'forgets' which polymer it belongs to over a distance of ξ. The mixture then has only two relevant length scales: D and ξ [14–16]. This means that the particle–polymer interaction depends only on their ratio: D/ξ.

2 Theory

The polymer molecules consist of flexible linear chains of segments of size a. These segments are much smaller than the spherical particles, $D \gg a$ and so the volumes which the segments exclude to the spheres overlap. Each segment excludes a sphere from a volume $\sim (D+a)^3$ centred on itself but as the segments are part of a chain there are always two segments a away from any segments, another two $\sim 2a$ away, *etc.* This problem of the excluded volumes overlapping can be reduced if the polymer segment length is rescaled from a to D. This is illustrated in Figure 1, which shows a sphere and a part of a polymer chain. As semidilute polymer solutions are scale invariant [2] at length scales much less than the correlation length ξ we are free to perform this rescaling. Now that the polymer segment length is D the excluded volumes of adjacent segments overlap much less strongly, although they still overlap. Each rescaled segment consists of many segments, for $D \gg a$, and so acts like a polymer coil of the same size as the particles. The particles cannot penetrate coils of their own size [17] and so the segments exclude particles from a volume $\sim D^3$. The ratio of the number of segments of size D to those of size a is $\sim (a/D)^{5/3}$ if the polymer is in a good solvent.

From now on we only consider the scaled polymer segments of size D, see Figure 1. Treating the polymer as a sequence of rescaled segments of size D makes it clear that the only relevant length scales are D and the polymer's correlation length. So, the polymer density $c_{\rm P}$ is the density of these polymer segments. These segments exclude each other from a volume $\sim D^3$ just as dilute polymer coils exclude each other from a volume of order of their radius of gyration cubed. We have approximated the interaction between a segment and a sphere by a hard-sphere interaction of diameter D; the same interaction as between the spheres. This is an approximation of course; the segments do not interact with a completely hard potential, they are only very approximately spherical and they are connected into chains.

2.1 Scaling theory for semidilute polymers

First, we briefly summarize the scaling theory for polymer solutions in good solvents, it is described in detail by de Gennes [2]. Our spheres will be added to a semidilute solution of polymer molecules in a good solvent. As noted above we have rescaled the polymer segment length from a to D. The size of an single isolated polymer coil of n_D segments is measured by its radius of gyration $R_{\rm G}$ which is given by $R_{\rm G} \sim D n_D^{3/5}$, in a good solvent [2]. The correlations (fluctuations) in an isolated polymer coil extend across the entire coil; the correlation length ξ is thus $\sim R_{\rm G}$. When polymer coils overlap, interactions between different chains reduce the correlation length ξ. The overlap volume fraction c^* is $c_{\rm P}^* = D^{-3} n_D^{-4/5}$. This volume fraction is the boundary between the dilute and semidilute regimes; below c^* the interactions between chains can be treated as a perturbation but above $c_{\rm P}^*$ the interaction between a pair of chains is $\gg k_{\rm B}T$. In the dilute regime $\xi = R_{\rm G}$, and in the semidilute regime. $\xi = D^{-5/4} c_{\rm P}^{-3/4}$.

We require the pair distribution function for the polymer segments $g_{\rm P}(r)$, where r is the magnitude of the separation of the two segments [18]. It is

$$g_{\rm P}(r) \sim \begin{cases} 0 & r \lesssim D \\ \left(\dfrac{\xi}{r}\right)^{4/3} & D \lesssim r \lesssim \xi \\ 1 + \dfrac{\xi \exp(-r/\xi)}{r} & \xi \lesssim r. \end{cases} \qquad (1)$$

Note that we define our pair distribution function differently from reference [2]. The first line of equation (1) just reflects the mutual impenetrability of polymer segments, the second is the density of a self-avoiding random walk, and the third line reflects the screening of correlations at distances greater than ξ. Note that for $r \ll \xi$ the dominant contribution to $g_{\rm P}$ is the contribution from a single chain.

2.2 Scaling theory for spheres in a semidilute polymer solution

In order to examine the pair correlations and hence the scattering from spheres in a semidilute solution we require the pair distribution function of the spheres, $g_{\mathrm{S}}(r)$. For $r < D$ this is 0 due to the hard-sphere interaction but for $r > D$, g_{S} is not equal to 1 due to the fact that the cavities in the polymer solution are correlated; see [19]. The cavities are the points in the polymer solution where there is no polymer within a distance D, and so where it is possible to insert a sphere [19]. In the limit of very low sphere density c_{S} we need only consider the two spheres which form the pair; there are no other spheres present in this limit and so the correlations between the spheres are entirely due to correlations in the cavities:

$$\lim_{c_{\mathrm{S}}\to 0} g_{\mathrm{S}}(r) = \begin{cases} 0 & r < D \\ y_{\mathrm{P}}(r) & r > D. \end{cases} \tag{2}$$

where $y_{\mathrm{P}}(r)$ is the cavity–cavity correlation function [18], equal to the probability of inserting a pair of spheres a distance r apart divided by the square of the probability of inserting one sphere. The probability of inserting a single sphere will be denoted by α. Below we start by estimating α and then go on to consider the probability of being able to insert a pair of spheres which yields an estimate of y_{P}.

The concentration of segments is c_{P} and each segment excludes spheres from a volume of $\sim D^3$. If we ignore the fact the segments are connected then as the polymer density is low, we can also neglect the overlaps of excluded volumes of nonadjacent segments and we arrive at the conclusion that the fraction of the volume denied to the spheres is $c_{\mathrm{P}}D^3$ [14,15]. Using $\xi = D^{-5/4}c_{\mathrm{P}}^{-3/4}$ this fraction can also be written as $(D/\xi)^{4/3}$, and the fraction of the volume available to the spheres, α, is

$$\alpha \sim 1 - \left(\frac{D}{\xi}\right)^{4/3}. \tag{3}$$

Equation (3) has a probabilistic interpretation which will be used below. It is the probability that there is no polymer segment within D of a randomly chosen point in the solution.

In order to calculate the pair distribution function between spheres, g_{S}, we relate it, using equation (2), to the distribution function between pairs of cavities y_{P}, *i.e.*, pairs of points with no polymer segments within a distance D of either of them. Then we express y_{P} in terms of α and g_{P}, both of which are known, equations (3, 1). In order to relate y_{P} to g_{P} we use the fact that for a pair of points, labeled 1 and 2, there are 4 possibilities: 1 and 2 both have polymer segments within a distance D; 1 does but 2 does not; 2 does but 1 does not; and neither does. Therefore, the probability of the fourth possibility occurring, which is $\alpha^2 y_{\mathrm{P}}$, is equal to 1 minus the sum of the probabilities of the other possibilities. The probability of both points being within D of a polymer segment is the square of the probability of one point having a nearby segment, $(D/\xi)^{8/3}$, times $g_{\mathrm{P}}(r)$, where r is the magnitude of the separation $\mathbf{r}$ between points 1 and 2. In deriving this result we have integrated over spheres of diameter D around both points; therefore, it is only valid for $r > 2D$ but we will use it for $r > D$. This is a very minor approximation, y_{P} still has the correct behaviour near $r = D$. The probability of point 1 being near a segment and point 2 not being near a segment, is the probability of point 1 being near a segment, $(D/\xi)^{4/3}$, times the probability of there being no polymer segment near a point $\mathbf{r}$ away from a segment $1 - (D/\xi)^{4/3}g_{\mathrm{P}}(r)$. This second probability is just 1 minus the probability of there being a segment at a separation $\mathbf{r}$ from another segment. So,

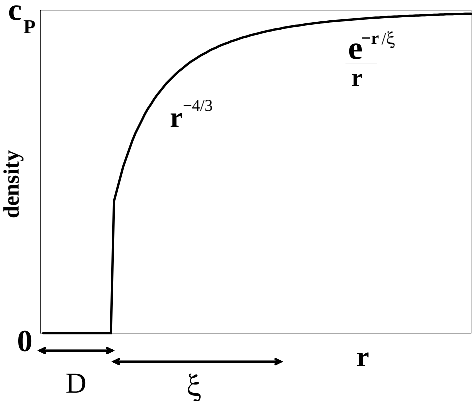

Fig. 2. The polymer density around a sphere/cavity in the polymer solution. If there is a sphere at the origin then there can be no polymer segment there and so the polymer density is reduced in the surrounding volume. The x-axis of the graph is r the distance from the sphere and the y-axis is the polymer density. The segment density in contact with the sphere is less than c_{P} but non-zero; it relaxes to the bulk value c_{P} at a rate $\sim r^{-4/3}$ for $r < \xi$ and exponentially when $r > \xi$.

$$\left(1 - (D/\xi)^{4/3}\right)^2 y_{\mathrm{P}}(r) \sim 1 - (D/\xi)^{8/3}g_{\mathrm{P}}(r) - 2(D/\xi)^{4/3} \times \left(1 - (D/\xi)^{4/3}g_{\mathrm{P}}(r)\right) \quad r > D, \tag{4}$$

and

$$y_{\mathrm{P}}(r) \sim 1 + \frac{(D/\xi)^{8/3}}{\left(1 - (D/\xi)^{4/3}\right)^2}\left(g_{\mathrm{P}}(r) - 1\right) \qquad r > D. \tag{5}$$

Note that $\alpha^2 y_{\mathrm{P}}(D) \sim \alpha$ which is at it should be, the probability of inserting two particles next to each other is almost the same as the probability of being able to insert one particle. The probability of inserting a sphere close to where a sphere has already been successfully inserted is higher than at a randomly chosen point in the polymer solution. This is because the density of segments near a point which is free of polymer is lower than in the bulk. The fractional reduction in density near a sphere/cavity is given by the term in parentheses on the right of equation (4) [20]. It is illustrated in Figure 2. The methodology of the derivation of equation (5) is quite general, it may also be used to derive y_{P} for ideal chains and for other dimensionalities.

The positions of the spheres in the polymer solution are correlated over a range ξ; they are distributed as if there is an attractive part to their interaction. The effective attraction is expressed as an effective potential between two spheres, called the potential of mean force $w(r)$ [1]. This is defined by

$$w(r) = -T \ln g_{\mathrm{S}}(r) \tag{6}$$

which is, using equation (5),

$$w(r) \sim \begin{cases} \infty & r < D \\ -T \ln \left[1 + \dfrac{(D/\xi)^{8/3}}{\left(1-(D/\xi)^{4/3}\right)^2} (g_{\mathrm{P}}(r) - 1) \right] & r > D. \end{cases} \tag{7}$$

As $D/\xi \ll 1$, we may linearize the logarithm

$$w(r) \sim -T \frac{(D/\xi)^{8/3}}{\left(1 - (D/\xi)^{4/3}\right)^2} (g_{\mathrm{P}}(r) - 1) \qquad r > D. \tag{8}$$

Then from equations (1, 8) we see that the depth of the well in the potential of mean force is $T(D/\xi)^{4/3} \ll T$. The potential is weak but long ranged, and as the range is increased the depth of the well decreases.

Now that the distribution function between spheres has been obtained we can calculate the structure factor $S(q)$, where q is the wavevector. $S(q)$ could be measured in a scattering experiment performed on the mixture; note that it is not the total structure factor for the mixture, just the partial structure factor of the spheres. If we define the total correlation function for the spheres $h_{\mathrm{S}}(r) = g_{\mathrm{S}}(r) - 1$ [18], then

$$S(q) = 1 + c_{\mathrm{S}} h_{\mathrm{S}}(q). \tag{9}$$

The Fourier transform of the total correlation function, $h_{\mathrm{S}}(q)$, is

$$h_{\mathrm{S}}(q) = \int h_{\mathrm{S}}(r) \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}} \mathrm{d}\mathbf{r}, \tag{10}$$

where h_{P} is the polymer segment–segment total correlation function. Using equations (2, 5), equation (10) becomes

$$h_{\mathrm{S}}(q) = -\int_0^D \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}} \mathrm{d}\mathbf{r} + \frac{(D/\xi)^{8/3}}{\left(1 - (D/\xi)^{4/3}\right)^2} \int_D^\infty h_{\mathrm{P}}(r) \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}} \mathrm{d}\mathbf{r}, \tag{11}$$

where $h_{\mathrm{P}}(r) = g_{\mathrm{P}}(r) - 1$. The first integral of equation (11) is just the lowest order, in density, approximation to the Fourier transform of the total correlation function between hard spheres [18]. The second term of equation (11) is not the Fourier transform of $h_{\mathrm{P}}(r)$ because the region of integration is restricted to $r > D$. However, this region only contributes a fraction $(D/\xi)^{5/3}$ to the integrand, for $q \ll D^{-1}$, and so we approximate the integral of the second term of equation (11) by $h_{\mathrm{P}}(q)$. Then, equation (11) becomes

$$h_{\mathrm{S}}(q) \sim -4\pi D^3 \left(\frac{j_1(qD)}{qD} \right) + \frac{(D/\xi)^{8/3}}{\left(1 - (D/\xi)^{4/3}\right)^2} h_{\mathrm{P}}(q), \tag{12}$$

where j_1 is the first spherical Bessel function, $j_1(z) = \sin(z)/z^2 - \cos(z)/z$. We have related $h_{\mathrm{S}}(q)$ and hence $S(q)$ to the polymer segment–segment correlation function h_{P} and so h_{P}, and therefore ξ, can be measured using only scattering from the spheres.

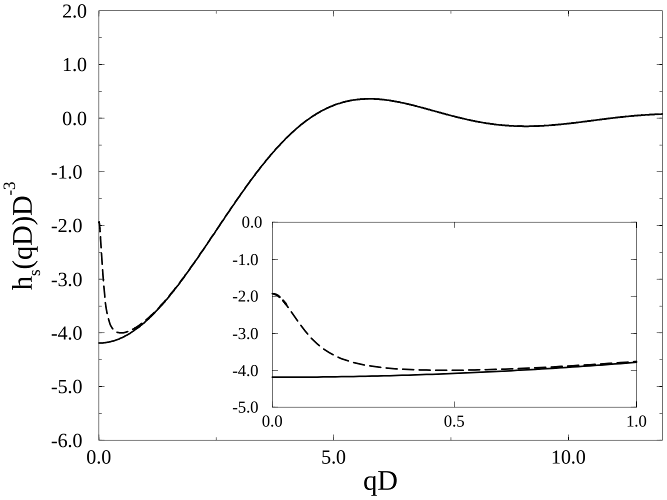

Fig. 3. The total correlation function for low-density hard spheres. The solid curve is for pure hard spheres and the dashed curve is for spheres in a semidilute polymer solution with $\xi/D = 10$. The inset shows the small q part at a larger scale.

For $h_{\mathrm{P}}(q)$ we use the Ornstein-Zernike form, valid for small q, $q \ll \xi^{-1}$,

$$h_{\mathrm{P}}(q) \sim \frac{\xi^3}{(q\xi)^2 + 1}, \tag{13}$$

which is the Fourier transform of the third line of equation (1). Although this gives the correct behaviour at small q, at $q \gg \xi$, h_{P} varies as $q^{-5/3}$ not the q^{-2} given by equation (13): 5/3 is the exponent for a self-avoiding walk and at length scales smaller than ξ the segment–segment interactions are not screened and the chains are self-avoiding [2]. We take equation (13) as unless the difference between ξ and D is very large, say $\mathcal{O}(100)$ which requires a very large polymer, then the behaviour at small enough values of q to distinguish between 5/3 and 2 will be obscured by first term in equation (12) and so not observable in measurements of $S(q)$. Then,

$$h_{\mathrm{S}}(q) \sim -4\pi D^3 \left(\frac{j_1(qD)}{qD} \right) + \frac{D^{8/3} \xi^{1/3}}{(1 - (D/\xi)^{4/3})^2} \left(\frac{1}{(q\xi)^2 + 1} \right). \tag{14}$$

In Figure 3 we have plotted $h_{\mathrm{S}}(q)$ both with and without a semidilute polymer solution. The $h_{\mathrm{S}}(q)$ is just what we would expect for particles interacting *via* a short ranged repulsion — the hard sphere interaction — and a long ranged attraction — the attractive potential of mean force due to the polymer. Figure 3 may be compared with the Figure 5 of Khalatur *et al.* [13] who observe the same effect. Note that at large values of q the polymer has no effect, h_S is dominated at large q by the hard-sphere interactions. While at low q h_S is less negative when polymer is present. We can compare this with a van der Waals fluid in which the attractive interaction is infinitely long ranged; in that case $h_S(q) = h_{HS}(q)$, for h_{HS} the hard-sphere total correlation function, except for $q = 0$ where $h_S > h_{HS}$ by an amount proportional to the extent of the attraction [18]. Due to the long range of the attraction, ξ, as compared to the repulsion, D, the spheres behave very much like a van der Waals fluid. Indeed, they are an even better approximation to a van der Waals fluid than are simple fluids such as the noble gases. The ratio of the range of the attractive interaction to that of the repulsive interaction is smaller for noble gases than for the spheres in the polymer solution. However, this is only true at low densities of spheres. When the density of spheres becomes comparable to the density of polymer (rescaled) polymer segments the correlations between polymer segments will be affected by the spheres and ξ reduced. The distribution of spheres in the mixture is much more uniform than that of the polymer, although as we have shown there are significant correlations in the positions of the sphere. So, we estimate that even if the density of spheres is comparable to that of the polymer segments the spheres will not greatly affect the correlations. The situation where the density of spheres is high is quite subtle and so far beyond this work.

The interactions studied here between spheres in a polymer solution are similar to those between spheres in a near-critical binary mixture [21]. There too the spheres behave as if they attracted each other, due to correlations (inhomogeneities) in the solvent in which they are suspended. Both these interactions are analogous to the quantum-mechanical Casimir interaction [21].

3 Conclusion

The pair distribution function of small hard spheres in a semidilute polymer has been obtained, equation (14), and it has been shown how to determine the polymer's correlation length from the structure factor of the spheres. The correlations in the distribution function are long ranged, *i.e.*, the ratio of the range of the polymer induced effective attraction, ξ, to the range of the repulsion, D, is much larger than the ratio of the attractive to the repulsive forces in simple fluids such as the noble gases. Note that this effective attraction is in a mixture where all interactions are purely repulsive excluded volume interactions. As the range of the attraction is just ξ, it is a function of the polymer concentration and can be varied at will within the semidilute regime. Also the depth of the attractive well between two spheres varies with ξ; as the range increases the well depth decreases. Finally, we note that as only the ratio in size between the particle and the polymer's correlation length is important, the behaviour described above would also occur if the polymer is not a flexible polymer but a semiflexible biopolymer such as DNA or wormlike micelles [22,23] and the particles are much larger particles with diameters of a few hundred nm.

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