

Interaction of Colloidal Particles Bearing Grafted Polymer Chains onto their Surfaces

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Introduction

Colloidal particles bearing polymer chains grafted by one end onto their surfaces are known as spherical polymer brushes. When the density of grafted chains is high enough, the constrained geometrical environment limits the available space the polymers can occupy forcing the chains to stretch out, normal to the surface. These colloidal systems are found to be particularly relevant in many aspects of polymer science and technology [1,2]. Just to mention: the stabilization of colloidal systems such as paints, glues, food emulsions, and pharmaceuticals; as potential drug carriers [3,4], forming stationary phases in chromatography and, more recently, they are found to be useful in the synthesis of nanocrystals in the so called quantum dot assembly process. Thus, a clear understanding of the polymer induced forces between brushes is essential to precisely determine the effect of polymer additives in chemical and biological systems.

As a first approximation, the interaction potential between two planar brushes was deduced in the context of a self-consistent theory by Milner-Witten-Cates [5,6] and Zhulina-Priamitsyn-Borisov [7,8]. Lately, Semenov [9] showed that extending directly the interaction potential for two planar brushes to the spherical case led to a negative monomer density close to the surface that is not physically acceptable. There have been several attempts to study the interaction of such spherical brushes, however, the validity of the results is restricted to specific limiting cases. The limit in which chains extend far beyond the core size reproduces the observed behaviour of star polymer systems [10], whereas if the core radius is much larger than the chain length, it is possible to use the interaction potential between planar surfaces with the Derjaguin approximation [11]. Our purpose is to study the interaction of such colloidal particles in two different situations:

- i)* The interaction between two spherical brushes in the regime where the chain extent is of the same order of the core size, where no theory has demonstrated its usefulness in describing properly their behaviour.
- ii)* The behaviour of a spherical brush confined inside a spherical cavity of variable size. This problem is directly related to the study of dense colloidal solutions and, in general, to the problem of constrained spherical brushes regarding the properties of encapsulated dendrimers, liposomes, vesicles and micropores containing nanoparticles with grafted chains.

Interaction between two spherical brushes

We present for the first time the results of extensive three-dimensional off-lattice Monte-Carlo (MC) simulations of two interacting spherical brushes [12] (Figure 1). We have calculated the force for different values of the chain length N and number of grafted chains f . We have found that the force profile can be divided into

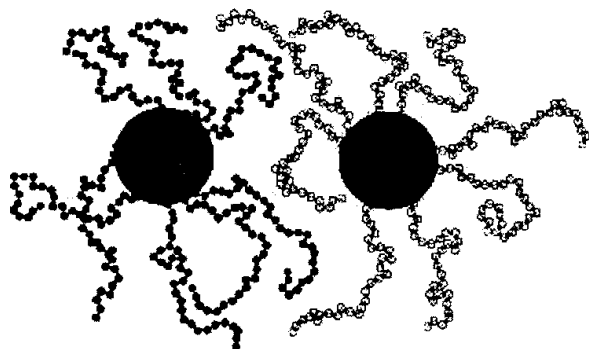


Figure 1 – Schematic representation of two spherical brushes separated a distance R . Each brush consists of f polymers of length N grafted to a spherical surface of radius r_c .

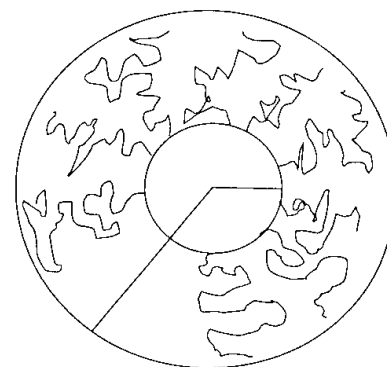


Figure 2 – Schematic representation of a spherical brush, with an impenetrable core of radius r_c inside an spherical cavity of radius R .

two regimes as indicated in Figure 3. When the brushes are located within a relative close distance, the measured force is well described by the Witten-Pincus (WP) theory, whereas as the separation between the brushes increases, the force is reproduced by extending the theory of Flory for dilute polymer solutions.

WP found that the change in the free energy bringing two of such brushes from the infinity to a very close distance is equal to the free energy of a single and isolated brush bearing a double number of chains grafted onto its surface. WP found the interaction potential between brushes to depend logarithmically on their separation, $V_{WP} = A \cdot \ln(r_c / (R - 2r_c))$, being R the distance between the centers of the colloidal particles, and r_c the core radius. Therefore this result is expected to work when the colloids are within a close distance. The force is simply given by $F_{WP}(R) = A / (R - 2r_c)$, and the constant A was predicted to follow a power-law dependence with the number of grafted chains f , namely $A \sim f^{3/2}$.

On the other hand, we can extend the Flory theory for dilute polymer solutions [13] to model the interaction when the particles are separated a distance far enough. Flory assumed that for very dilute polymer solutions, each polymer can be seen as a collection of monomers forming a rather spherical object characterized by a Gaussian-like monomer density profile. Bringing together two of such polymers might eventually result in an overlapping of the domains. Hence, in the presence of a good solvent, a repulsive force appears between them. The derived expression for the force takes the form $F_F(R) = C \cdot R \cdot \exp(-D \cdot R^2)$, where C and D are constants described by $C \sim M^2 / \langle r^2 \rangle^{5/2}$ and $D \sim 1 / \langle r^2 \rangle$. Being M the mass or the total number of segments inside the globular polymer, and $\langle r^2 \rangle$ the averaged end-to-end square distance. We can apply this result to the case of two interacting spherical brushes provided that they are sufficiently apart not to feel the presence of the inner core of the brush. Under these circumstances, we can take $M = N \cdot f$ in the above expression, and $\langle r^2 \rangle$ can be defined as the averaged square distance of the monomer chain-ends forming the brush to the core.

The best fit to the numerical data determine the values of the adjustable constants A , C and D that appear in the WP and Flory theories respectively. The best fit to the A behaviour gives a slope of 1.50 ± 0.02 in agreement with the expected power-law dependence $A \sim f^{3/2}$. The behaviour of D as a function of $1 / \langle r^2 \rangle$ gives a

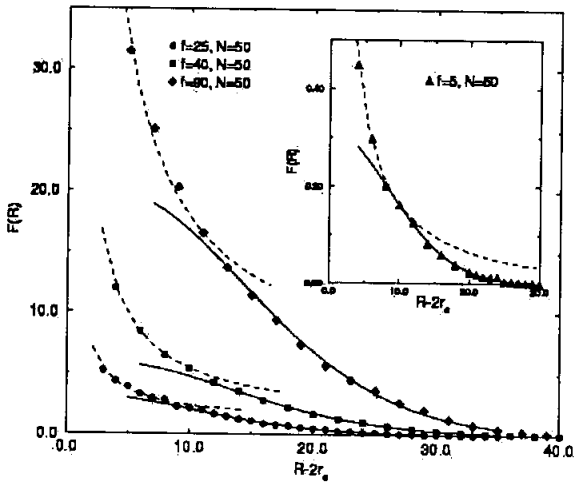


Figure 3 - Forces between two interacting spherical brushes. At small relative distance, MC data reproduces the WP theory (dashed curves), whereas at larger distances the force profile follows the Flory theory (solid lines).

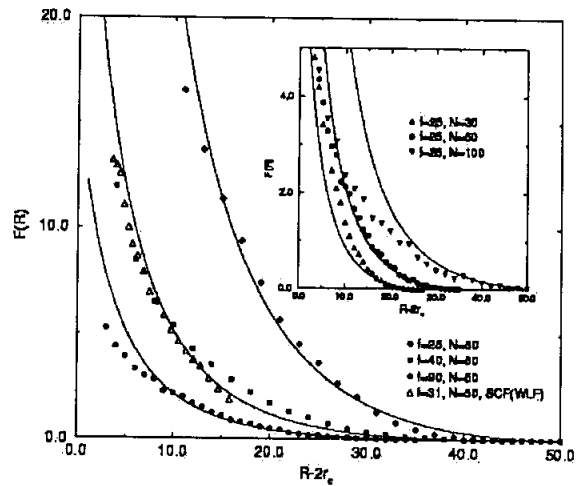


Figure 4 - Comparison between Monte-Carlo force profiles and the theoretical predictions of the DL theory (solid lines). The open triangles in this figure correspond to the force derived by the WLF-SCF[16] lattice model for $f=31$ and $N=50$.

slope of 1.06 ± 0.05 in agreement with the expected linear relationship. Similarly, the behaviour of C is proved to follow the theoretical prediction in most of the simulated systems. Only deviations from this behaviour are found in systems with large f and small N values, precisely where the assumption of a Gaussian monomer density profile fails. In the first case, large f values force the chains to be strongly stretched, whereas small chain lengths are out of the asymptotic limit where the Gaussian distribution for a globular polymer is found.

Our results have been also compared to the phenomenological theory of Doroszowski-Lambourne (DL) [14]. This theory predicts a repulsive force between two brushes originated in the increase of the osmotic pressure: $F_{DL}(R) = \Delta\Pi \cdot (R_o - R/2) \cdot (R_o + R/2)$ where R_o is the characteristic radial size of an unperturbed brush measured from the center of the core. From our numerical studies R_o is found to follow the same scaling relationship with the chain length N and number of grafted chains f as in the star-polymer systems $R_o \sim N^{3/5} f^{1/5}$. The change in the osmotic pressure, $\Delta\Pi$, is a rather complicated expression given in terms of a truncated expansion of the volume fraction occupied by the monomers in the compressed state. Figure 4 shows that the overall behaviour predicted by our MC simulations is qualitatively well reproduced, except at short distances, with the phenomenological DL theory for high density of grafted chains. In all the cases studied, systematic deviations from the DL theory are observed at small separating distances between the two brushes. Whereas the DL theory assumes the interacting polymer chains to recoil and keep inside the domain of its own brush, at small distances this requirement cannot be fulfilled together with the excluded volume criteria, thus chains are forced to interpenetrate. We should emphasize that the DL model is an osmotic model that neglects the change in the free energy associated to the available chain configurations. The DL theory assumes the osmotic term to be much larger than the configurational one as it happens in planar surfaces. The qualitative agreement with our Monte Carlo simulations confirms this result for spherical and

high grafting densities.

Our MC results have been also compared with previous numerical studies based on the self-consistent field lattice formalism of Lind and Gast [15], and Wijmans-Leermakers-Fleer (WLF) [16] (see Figure 4). The differences observed between them are due basically to the fact that the SCF formalism does not account for monomer correlations resulting in an overestimated repulsive force at short distances.

Spherical brushes compressed inside a spherical cavity

We present extensive three-dimensional Monte-Carlo (MC) and self-consistent mean field (SCF) calculations of a single brush constrained inside a spherical cavity (see Figure 2). SCF calculations proceed by evaluating the recurrence law for the probability density function of a single chain [17]. A comparison between radial densities obtained from SCF and MC calculations is shown in Figure 5. SCF data shows a rather good agreement with the MC results. Small systematic deviations are observed due to the fact that SCF do not account for monomer correlations. As a consequence, SCF calculations give a higher monomer concentration at large distances and a smaller monomer density close to the core when compared with the MC data. In the case of constrained brushes (Figure 6) a comparison between SCF and MC compression forces reveals that in the case of free or softly compressed brushes, SCF is in a rather good agreement with the MC results. However, important differences are found at intermediate and high compression values. The mismatches between SCF and MC results are due to a twofold effect. For high compressions, the SCF assumption of a linear dependence of the mean-field potential with the density breaks out, in fact, SCF simulations allow the systems to be compressed to volumes less than the own monomer volume without feeling an infinite repulsive force. In the intermediate regime, stronger forces obtained with SCF method are originated in the absence of monomer correlations allowing higher

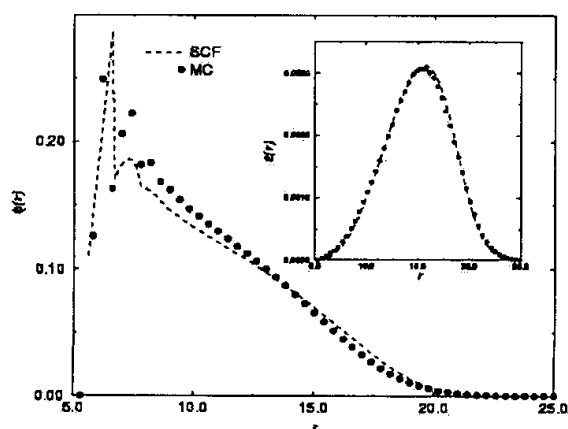


Figure 5 - Monomer Radial density profile $\phi(r)$ obtained using MC and SCF methods for an uncompressed brush ($N=30, f=25$). Inset: chain-end radial density profile $\varepsilon(r)$.

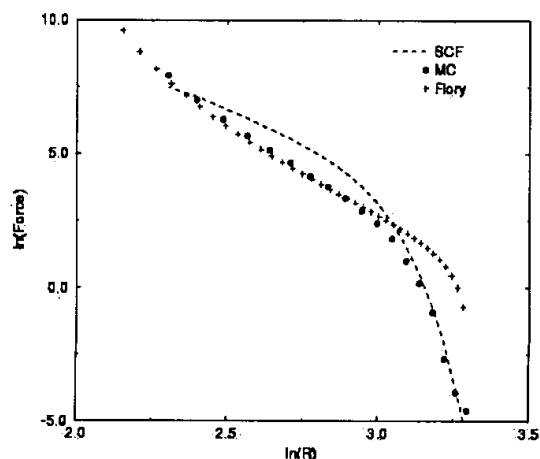


Fig.6 - Log-log plot of compression force profile vs the cavity size radius R , ($N=50, f=25$). Filled circles corresponds to MC results, dashed line corresponds to results obtained with SCF calculations. Crosses show the prediction derived from Flory theory adapted to this case.

average densities in the system than in the MC case. Therefore, stronger repulsions among monomers must be found and higher forces must be required to compress the brush.

We must remark that the SCF method has a minor computer cost, that can be of three to four orders of magnitude lower than MC simulations. Thus, SCF formalism seems to be useful in such a cases where brushes are free or softly compressed, obtaining a notorious improvement in computer times.

Alternatively, we provide another way of computing the pressure inside the cavity by extending Flory theory for ideal polymer solutions [13].

The idea is that for small cavities or high dense systems, grafted chain systems behave as a melt of free chains. In both cases, a high number of contacts with the inner core will exist. Thus, the osmotic pressure can be written as $\Pi = -1/V_1 (\ln(1-v_2) + (1 - 1/N) \cdot v_2 + \chi_1 \cdot v_2^2)$. Where V_1 that originally stood for the volume of the solvent is replaced here by the remaining free space in the cavity once we have substracted the volume occupied by the polymers $V_1 = (\tau - aNf)$. In this case τ is the volume of the cavity, and a is the volume of a single monomer. v_2 stands for the monomer volume fraction. In the present study we set $\chi_1=0$ that reproduces the condition of a dry-brush. This means that all contributions to the free energy come from the available polymer configurations. The force to compress the cavity will be proportional to the area of the cavity wall multiplied by change in the osmotic pressure, thus $F(R) \sim 4\pi R^2 \cdot \Delta\Pi(R)$. This result has the advantage to be computationally non-expensive. We have taken as a reference state for the Flory predictions a cavity with radius equal to the radius at which $\ln(\text{Force}) \rightarrow -\infty$ for MC and SCF results.

The predictions obtained from Flory extension (Figure 6) are in good agreement with the MC simulations for high and medium compressions. For very dilute systems, that is, large cavities, the difference between grafted and free polymers turns out to be evident, and Flory formalism leads to an overestimation of the pressure.

Finally, we have analyzed the behaviour of cavity pressure with the volume fraction of the monomers in the system v_2 . For intermediate and large compression values we find a power-law behaviour of the form $P \sim v_2^\alpha$. For the MC simulations, the best fit to the numerical data gives an exponent $\alpha = 2.73 \pm 0.04$ whereas for the SCF results we obtain an exponent $\alpha = 2.15 \pm 0.05$ (Figure 7). The SCF value of the exponent α is very close to $9/4$ obtained by des Cloiseaux in the semi-dilute regime [17]. For large concentrations, this theory predicts that all thermodynamic properties must reach to values that are independent of the degree of polymerization, as we have observed for both MC and SCF methods. We must be aware that the des Cloiseaux law is deduced from scaling arguments and it neglects non-linear

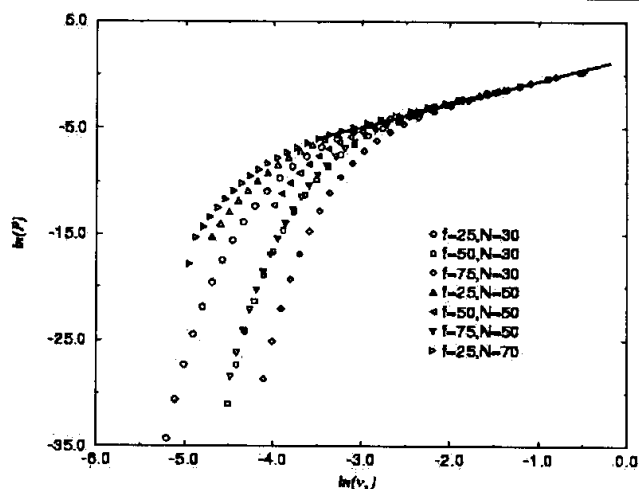


Figure 7- Log-log plot of the system pressure vs the monomer volume fraction v_2 , obtained from the results using SCF method. A solid line of slope 2.15 is included to guide the eye.

dependences on the monomer concentration. This fact might explain the close agreement between SCF and the des Cloiseaux law, whereas the correlation effects present in our MC simulations are responsible of a larger value of the exponent α .

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