Interaction force between incompatible star-polymers in dilute solution

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Abstract. We consider a low-density assembly of spherical colloids, such that each is clothed by \( L \) endgrafted chemically incompatible polymer chains either of types \( A \) or \( B \). These are assumed to be dissolved in a good common solvent. We assume that colloids are of small size to be considered as star-polymers. Two adjacent star-polymers \( A \) and \( B \) interact through a force \( F \) originating from both excluded-volume effects and chemical mismatch between unlike monomers. Using a method developed by Witten and Pincus (Macromolecules 19, 2509 (1986)) in the context of star-polymers of the same chemical nature, we determine exactly the force \( F \) as a function of the center-to-center distance \( h \). We find that this force is the sum of two contributions \( F_\text{c} \) and \( F_\text{m} \). The former, that results from the excluded volume, decays as \( F_\text{c} \sim A_L h^{-1} \), with the \( L \)-dependent universal amplitude \( A_L \sim L^{3/2} \). While the second, which comes from the chemical mismatch, decays more slowly as \( F_\text{m} \sim \chi B_L h^{-1 - \tau} \), where \( \tau \) is a critical exponent whose value is found to be \( \tau \approx 0.40 \), and \( \chi \) is the standard Flory interaction parameter. We find that the corresponding \( L \)-dependent universal amplitude is \( B_L \sim L^{(3+\tau)/2} \). Theses forces are comparable near the cores of two adjacent star-polymers, i.e. for \( h \sim h_c \sim a^{1/\tau} \sqrt{L} \) (a is the monomer size). Finally, for two star-polymers of the same chemical nature \( (A \) or \( B) \), the force \( F \) that simply results from excluded-volume effects coincides exactly with \( F_\text{c} \), and then the known result is recovered.

PACS. 82.70.Dd Colloids – 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 64.75.+g Solubility, segregation, and mixing; phase separation

1 Introduction

Colloids are particles of mesoscopic size, which are subject of extensive studies due to their abundant industrial applications. Most colloidal systems are made of grains, which often flocculate because of the existence of long-range van der Waals forces. To avoid this flocculation, one may introduce adequately soluble polar head polymer chains. This is the grafting phenomenon. As a consequence, two adjacent grains with end-grafted chains repel each other due to the excluded-volume forces between monomers, which assist in stabilizing the colloids. Grafted polymers onto solid surfaces or fluid interface are of considerable interest, and have many physicochemical applications [1], such as adhesion [2], wetting [3], chromatography [4] and colloidal stabilization [5–7].

Consider a set of colloidal particles clothed by \( L \) end-grafted polymer chains (or branches) in a dilute solution. We assume that they are of small diameter, so that they can be regarded as star-polymers. Such an assumption allows us to take advantage of the results already established within the star-polymers field. A star-polymers is a typical branched macromolecule, which possesses a central core from which many end-attached linear chains emerge. The physics of star-polymers is the subject of a great deal of attention from theoretical [8–20] and experimental [21] point of view. Theoretical works pioneered by Daoud and Cotton (DC) [9]. Their model is based on a blob picture, according to which, in a dilute solution, each chain or branch can be viewed as a sequence of growing spherical blobs.

Fourteen years ago, Witten and Pincus (WP) [22] were interested in the computation of the interaction force between small spherical colloids with \( L \) end-grafted flexible chains, which is due to the excluded-volume effects. They assimilated these clothed particles to star-polymers and used the blob picture of DC. They found that the force decays with separation \( h \) according to the power law \( A_L h^{-1} \), with the \( L \)-dependent universal amplitude \( A_L \sim L^{3/2} \). Our purpose is precisely an extension of this result to determine the interaction force between two chemically incompatible star-polymers \( A \) and \( B \), which are a finite distance \( h \) apart. More precisely, the question is: how does the chemical mismatch affect the interaction force?
We start by considering a low-density assembly of colloidal particles, such that each is clothed either by end-grafted $A$ or $B$ chains. We assume that the particles are dissolved in a common good solvent. For the sake of simplicity, we assume that the particles are small enough to be considered as star-polymers ($A$ or $B$). Two adjacent star-polymers $A$ and $B$ interact via a force $F$, which results from both the excluded volume and the chemical mismatch between unlike monomers. We are interested in the determination of this force as a function of the center-to-center distance $h$. Since excluded-volume and segregation interactions are of short range, the effect should be appreciable only for separations, $h$, below the star-polymer size $2R \sim 2aL^{1/3}N^{3/5}$, $i.e.$ $h < 2R$, where $N$ is the polymerization degree of chains and $a$ is the monomer size.

Our findings are the following. Using that method developed by WP [22], we find that the force $F$ is the sum of two contributions $F_c$ and $F_e$. The former results from the excluded-volume effects and decays as $F_c \sim A_L h^{-1}$, with the $L$-dependent universal amplitude $A_L \sim L^{3/2}$. The second, which originates from the chemical segregation between $A$ and $B$ monomers, decays more slowly according to $F_e \sim \chi B_L h^{-1-\tau}$, with the $L$-dependent universal amplitude $B_L \sim L^{(3+\tau)/2}$. Here, $\chi$ is the standard Flory interaction parameter, and $\tau$ is a critical exponent whose value is found to be $\tau \approx 0.40$. As we will show below, the exponent $\tau$ can be related to the cubic anisotropy exponent, as pointed out by Joanny, Leibler and Ball in their theoretical work [23]. We find that the forces $F_c$ and $F_e$ become comparable near the cores of two adjacent star-polymers, $i.e.$ for $h \sim h_c \sim a\chi^{1/\tau}\sqrt{L}$.

Finally, for two star-polymers of the same chemical nature ($A$ or $B$), the force $F$ simply originates from the excluded volume, and thus, coincides exactly with $F_c$. The WP result is then recovered.

The remainder of the presentation proceeds as follows. Section 2 gives a succinct recall of the useful ingredients for the present study. Determination of the expected force expression and related discussions are the aim of Section 3. We draw our conclusions in Section 4.

## 2 Basic relationships

The aim of this section is to recall the necessary ingredients for the determination of the interaction force between two star-polymers $A$ and $B$ of different chemical nature. We will first write the complete asymptotic expression of the osmotic pressure for a semi-dilute solution of two kinds of homopolymers $A$ and $B$, taking into account the chemical mismatch. From the expression for osmotic pressure we are then able to compute the expected forces. Details concerned with the influence of the chemical mismatch can be found in reference [23]. Second, we will briefly recall the essential details of the conformational study of an isolated star-polymer. More precisely, we will recall how to get the expressions of the local monomer concentration and the star-polymer radius, which can be found in reference [9].

### 2.1 Chemical mismatch corrections to the osmotic pressure

Consider, first, a dilute solution made of two incompatible homopolymers $A$ and $B$, dissolved in a common good solvent. We denote by $M$ the molecular weight assumed to be the same for $A$ and $B$ chains. Let $c = c_A + c_B$ be the total monomer concentration. We recall that, in a dilute solution, $A$ and $B$ chains behave like separated swollen coils of gyration radius $R_G \sim M^\nu$ ($\nu = 3/5$), which avoid each other completely, and so cannot phase separate.

For a weak solution, that is below the threshold $c^* \sim M^{-4/5}$ [24,25], the osmotic pressure can be expanded in powers of the concentration (virial expansion). The second virial coefficients, which measure the effective interaction between two $A$ chains, two $B$ chains and an $A$ and a $B$ chain, have the dimension of a volume. They become infinite in the high molecular weight limit ($M \to \infty$). From a practical point of view, one usually introduces the dimensionless virial coefficients or interpenetration functions [26], denoted by $\psi_i$’s ($i = AA, BB, AB$). In fact, these functions depend on the molecular weight and are bounded from below. According to the renormalization theory [23,26-30], in the infinite long-chains limit ($M \to \infty$), the functions $\psi_i$’s rapidly go to a universal value $\psi^* \equiv 0.24$, independently on the chemical nature of both polymers and solvent. This result means that an $A$ chain cannot distinguish between an $A$ and a $B$ chain. Hence, the chemical mismatch is irrelevant for physics. Actually, the chemical difference between unlike chains is important and can affect drastically some physical quantities, such as osmotic pressure which allows us to compute the interaction force between a pair of incompatible star-polymers (see below). For higher but finite molecular weight, one has

$$\psi_i \to \psi^* + \text{const. } M^{-\Delta_1}, \quad (i = AA, BB), \quad (1)$$

$$\psi_{AB} \to \psi^* + \text{const. } M^{-\Delta_2}, \quad (2)$$

where, $\Delta_1$ and $\Delta_2$ are two crossover exponents. The former ($\Delta_1$), which is relative to homopolymers problem, was computed by des Cloizeaux [25] to second order in $\varepsilon = 4 - d$ ($d$ being the space dimensionality), using the direct renormalization method [25]. The second exponent $\Delta_2$ that characterizes the chemical mismatch between species $A$ and $B$, was calculated by Joanny and coworkers [23] to the same order using the same method. In their theoretical work [31], Schäfer, Lehr and Kappeler calculated the exponent $\Delta_2$ to third order in $\varepsilon$, using the $n \to 0$ limit of the associated field theory. Combining the $\varepsilon$-expansion with the Padé-Borel resummation method, the best three-dimensional values for these crossover exponents are obtained, $i.e.$ $\Delta_1 \cong 0.47$ [25] and $\Delta_2 \cong 0.23$ [31]. The inequality $\Delta_1 > \Delta_2$ implies that the interaction $\psi_{AB}$ reaches its asymptotic value $\psi^*$ much more slowly than $\psi_{AA}$ and $\psi_{BB}$.

Now, assume that one is in a semi-dilute solution, that is, above the threshold $c^* \sim M^{-4/5}$. We recall that, in a