J|A|C|S

ARTICLES

Surface Forces, Supramolecular Polymers, and Inversion Symmetry

Jasper van der Gucht,* Nicolaas A. M. Besseling, and Martien A. Cohen Stuart

Contribution from the Dutch Polymer Institute/Wageningen University, Laboratory of Physical Chemistry and Colloid Science, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

Received November 14, 2001

Abstract: The effects of supramolecular equilibrium polymers on surface forces are studied by both a phenomenological Landau type analysis and a molecular model based on a Bethe−Guggenheim approximation. We point out that surface forces brought about by equilibrium polymers may be completely different from what can be found with “ordinary” polymers. The new feature is the role of inversion (a)-symmetry or “directionality” of the associating unit molecules (“monomers”). Symmetric B−B monomers (where B denotes a self-complementary binding group) give rise to nondirectional chains and lead to *attractive* forces between similar surfaces. Asymmetric A−D monomers (where A and D denote complementary acceptor and donor groups, respectively) produce directional chains and can cause strong *repulsion*. The range of the attractive force has a maximum at intermediate concentration, while the range of the repulsive force increases over the whole concentration range.

1. Introduction

Surface forces, forces between two solid surfaces immersed in a fluid, play a central role in heterogeneous soft matter.[1] Such forces determine the stability, phase behavior, and dynamics of colloidal systems, and are crucial for a variety of biological processes such as the adhesion and the fusion of biomembranes. There is a more or less established catalog of surface forces comprising the extensively studied DLVO forces (consisting of screened electrostatic and van der Waals interactions), the interactions caused by adsorbing and nonadsorbing polymers,[2−4] and a more loosely defined set of solvent mediated interactions, often referred to as “solvation” (“hydration”) forces. The much debated hydrophobic interaction may be considered as an example of the latter. Finally, there are the forces due to phase transitions occurring in confined space: capillary condensation and evaporation.

Yet, the repertoire of molecular behavior is far from exhausted. Recent research in the domain of supramolecular chemistry has led to numerous new reversible structures held together by weak interactions rather than covalent bonds.[5−12] In this paper we focus on a new kind of surface forces, namely those induced by *supramolecular equilibrium polymers*. These are linear chains, consisting of reversibly linked subunits or “monomers”. They reproduce many of the properties of traditional polymers but also introduce distinctly new features. For example, their molecular weight distribution is not fixed but responds to variable conditions such as the monomer concentration, the temperature, and the presence of external fields, e.g., those arising from shear or from the presence of one or two surfaces. The equilibrium between breaking and formation of bonds results in a polydisperse mixture of chain lengths.[13] The average chain length is determined by the strength of a bond between two monomers (often quantified by the scission free energy), which is obviously related to the association constant. Furthermore, the average length increases proportionally to the square root of the concentration of monomers.[14]

The purpose of this paper is to point out that surface forces induced by supramolecular polymers (which have, so far, received only very little attention[15]) have properties which set them quite apart from the other, more familiar forces. As we will explain in section 2, these special properties are related to the symmetry of the associating molecules. First we give a qualitative argument, based on a phenomenological Landau-

---

* Corresponding author. E-mail: jasper@fenk.wau.nl.

(1) Israelachvili, J. *Intermolecular and Surface Forces*; Academic Press: London, UK, 1991.
(2) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(3) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman and Hall: London, UK, 1993.
(4) Napper, D. H. *Polymeric stabilization of Colloidal Dispersions*; Academic Press: London, UK, 1983.
(5) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.
(6) Ciferri, A. *Supramolecular Polymers*; Marcel Dekker: New York, 2000.
(7) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601−1604.
(8) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097.
(9) Zimmerman, N.; Moore, J. S.; Zimmerman, S. C. *Chem. Ind.* **1998**, 604−610.
(10) Whitesides. G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312−1319.
(11) Boileau, S.; Bouteiller, L.; Lauprêtre, F.; Lortie, F. *New J. Chem.* **2000**, *24*, 845−848.
(12) Velten, U.; Lahn, B.; Rehahn, M. *Macromol. Chem. Phys.* **1997**, *198*, 2789−2816.
(13) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(14) Cates, M. E.; Candau, S. J. *J. Phys. Condens. Matter* **1990**, *2*, 6869−6892.
(15) Schmitt, V.; Lequeux, F.; Marques, C. M. *J. Phys. II* **1993**, *3*, 891−902.

10.1021/ja0125422 CCC: $22.00

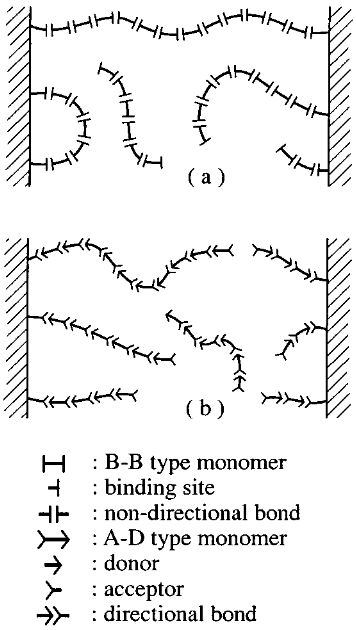

Figure 1. (a) A schematic representation of B−B type associating monomers between two surfaces that have an affinity for the bonding groups. Overlap of the two ordered layers will lead to a further enhancement of the local monomer concentration. Note that loops and bridges may be formed. (b) A−D type associating monomers between two surfaces that have only acceptor sites. Overlap of the two ordered layers will be disruptive.

type analysis, for the difference in behavior of symmetric and asymmetric equilibrium polymers. In section 3 we present numerical results, based on a molecular model, to support our findings.

2. The Role of Inversion Symmetry

To explain the distinct properties of surface forces induced by supramolecular polymers, we should explore not only how the associating molecules interact with surfaces, but also how they interact with each other. It then turns out they come in two classes. Most supramolecular polymers known nowadays are based on associating monomers that have two identical, self-complementary binding functions at either side (see for example ref 7) so that they possess inversion symmetry. One might call these "B−B" monomers; such monomers can form chains provided a B group can form a reversible bond with another B group (see Figure 1a). The second class comprises monomers that do *not* have inversion symmetry because they have two different, *mutually complementary* binding sites. Mutually complementary binding sites are sometimes referred to as a *donor−acceptor* combination (or as a *host−guest* or a *lock−key* combination). A donor and an acceptor can together form a reversible bond, but a donor cannot bind to another donor, and an acceptor cannot bind to another acceptor. Many typical molecular interactions are of some kind of donor−acceptor nature, the best known example being perhaps hydrogen bonding. In biology one can find a large variety of combinations of mutually complementary binding sites, often with a rather complex chemical structure, e.g. the streptavidin−biotin combination. A monomer carrying a donor and an acceptor site may be called an "A−D" monomer (see Figure 1b). A strongly self-assembling A−D type monomer has recently been synthesized.[11]

The distinction between symmetric B−B and asymmetric A−D supramolecular polymers has no consequences for bulk and solution behavior; properties that matter here are length and strength of the chains. However, for the interfacial behavior and for the effect on the surface forces the distinction is quite relevant: there are very interesting *qualitative* differences.

Always when a solid surface is immersed in a fluid, it induces structural changes in the adjoining fluid layer. For a solution of equilibrium polymers the concentration and the orientation distribution of the molecules in the surface region may both be different from that in the bulk of the solution. It is important to realize that, although the interactions between the monomers and between the surface and the monomers are essentially short-ranged, these structural changes extend into the solution, because they "propagate" from the molecular layer immediately adjoining the surface to neighboring molecules, and so on. Hence the thickness of the structured layer exceeds the monomer size, the more so the stronger the bonds (see Figure 1).

The structural difference with the bulk fluid at some distance z from the surface (or the *ordering* with respect to the bulk fluid) may be quantified by one or more *order parameters*. An order parameter can be related to various aspects of the local structure of the fluid. For example, it may be the local excess concentration compared to the bulk of the solution. We will denote this order parameter $\rho(z)$. For apolar spherical molecules such as those of argon, this is the only order parameter that can be defined. For fluids containing asymmetric molecules an order parameter that measures the degree of molecular orientation is important as well. We will denote the latter order parameter $\omega(z)$. An order parameter, being an excess quantity, is necessarily zero far away in the solution, but near the surface it may take either positive or negative values.

If two surfaces approach each other, the ordered layers ensuing from either surface interfere. Such interference results in an interaction between the two surfaces, the strength of which varies with the distance between the surfaces. It can be shown[16−18] that the force between the two surfaces is *attractive* if overlap of the ordered layers results in an *enhancement* of the ordering between the two surfaces, i.e., if there is a constructive interference of the ordering ensuing from each of the two surfaces. This is the case if the sign of the order parameter near both surfaces is the same. On the other hand, if the ordering is *reduced* by an overlap of the two ordered layers (i.e. if there is a destructive interference), the force between the two surfaces is *repulsive*.[17−19] This is the case if the sign of the order parameter is opposite near the two surfaces.

These rules for the interaction between two surfaces emerge from a phenomenological Landau-type analysis, similar to what was put forth in the context of hydration forces.[16−19] From such an analysis it follows that for not too small distances z to the surface, the order parameter decays exponentially. The decay length (or coherence length) ξ is a measure of the thickness of the ordered zone. The interaction between the surfaces, too, decays exponentially with increasing distance between the surfaces, with the same decay length ξ as the order parameter.

Where does this lead us when we consider directional and nondirectional equilibrium polymers? First, if the affinity of

---

(16) Eriksson, J. C.; Ljunggren, S.; Claesson, P. M. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 163−176.
(17) Besseling, N. A. M. *Langmuir* **1997**, *13*, 2113-2122.
(18) Besseling, N. A. M. In *Water in Biomaterials Surface Science*; Morra, M., Ed.; John Wiley and Sons Ltd.: New York, 2001; pp 91−125.
(19) Marcelja, A.; Radic, N. *Chem. Phys. Lett.* **1976**, *42*, 129−130.

monomers for the surface is low, the monomer concentration close to the surface is lower than in the bulk (this is called depletion). The relevant order parameter $\rho(z)$, associated with the excess monomer concentration, is thus negative at both surfaces. The order parameter argument tells us that this must lead to attraction between the surfaces, whatever the nature of the monomers.

If the monomers can bind to the surface with their binding groups, things become more complicated. One consequence is that now the monomer concentration near the surfaces is higher than in the bulk (adsorption). For nondirectional, symmetric polymers, this is all that can happen. The order parameter $\rho(z)$ is thus positive near both surfaces. Consequently, the interaction between the two surfaces is always *attractive*. We note that such is also the case for "ordinary" polymers with a quenched molecular weight distribution that tend to stick to a surface (provided equilibrium between the interface and the bulk prevails).[3]

When directional A−D monomers attach to the surface by either donor or acceptor groups, there are *two* effects. Not only is the concentration of the monomers near the surface affected, but also their *orientation distribution*. Associated with this is an order parameter $\omega(z)$. Consider two identical surfaces approaching each other. Depending on the preference for either A or D groups, the order parameter at a given surface takes a positive or a negative sign. At the other surface, which has similar binding properties, the net orientation is inverted, and hence the order parameter has the opposite sign. Interference of the ordered layers will yield a repulsive surface force contribution. Figure 1b illustrates this in a pictorial way.

3. Numerical Results from a Molecular Model

Without further information the Landau analysis can only predict the sign of an interaction; it does not provide values for ρ, ω, and the associated decay lengths ξ_ρ and ξ_ω, and thus cannot tell us anything about the range or strength of the forces. To make progress, we need a molecular model. For this, we use a statistical mechanical approach, which was developed by one of us to describe the properties of water.[20] The method was successful in reproducing the bulk behavior of water,[20] in dealing with hydration forces,[17] and in calculating the lengths of equilibrium polymers in solution and near nonbinding surfaces.[21] In this theory the orientation-dependent intermolecular interactions are accounted for in a Bethe−Guggenheim approximation. Self-assembling monomers of both B−B and A−D type can be handled in a straightforward manner. From given properties such as BB or AD binding energies, monomeric flexibility, and bulk concentration, properties such as the concentration profile, the chain-length distribution, and the free energy of interaction between two surfaces can be calculated.

In Figure 2, we present results for the interaction free energy as a function of distance. In Figure 2a, the calculations refer to B−B type polymers between two surfaces that have a favorable interaction with the functional groups (the situation of Figure 1a). The free energy is negative in this case, i.e., the surfaces attract each other. For not too small distances between the surfaces, the interaction strength decays exponentially with increasing distance. The force has the same decay length ξ_ρ as the density profile. Figure 3 shows the decay length ξ_ρ (which is a measure for the range of the force) as a function of the monomer volume fraction ϕ in the bulk. Two regimes can be distinguished. In the dilute regime, in which the chains are present as individual coils separated from each other, the decay length ξ_ρ is proportional to the average radius of gyration. For equilibrium polymers the radius of gyration *increases* with increasing concentration and with decreasing temperature.[14] In a mean-field approximation,[14,21] the average length $\langle N\rangle$ is proportional to the square root of the concentration, so that $\xi_\rho \sim \langle N\rangle^{1/2} \sim \phi^{1/4}$. In a more concentrated solution, in which the coils overlap (the so-called semidilute regime), ξ_ρ is determined by the typical mesh size of the polymer network, which *decreases* with increasing concentration.[2,3] Between the dilute and the semidilute concentration regime ξ_ρ has a maximum (see ref 21 for more details).

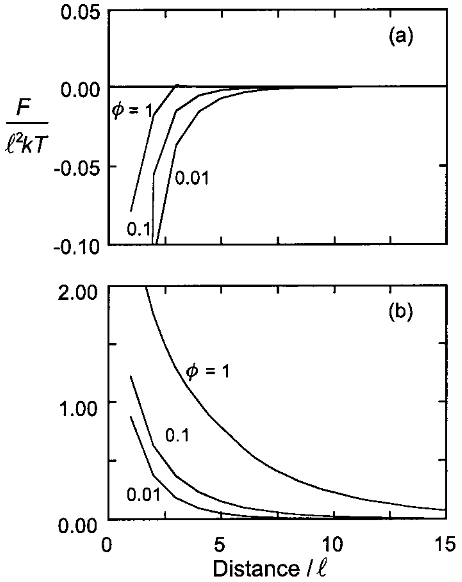

Figure 2. (a) The free energy of interaction per unit area between two surfaces immersed in a solution of B−B type associating monomers as a function of separation distance (expressed in units of monomer length l) for various monomer volume fractions ϕ. The surfaces are fully occupied with binding sites of type B. The scission free energy of the bonds between the functional groups is $10kT$. (b) The same as part A for a solution of A−D type monomers. The surfaces have only acceptor sites. The scission free energy is again $10kT$, such that the molecular weight distribution in the bulk of the solution is the same as for the B−B type monomers. Note that the scales on the vertical axes are different in both figures.

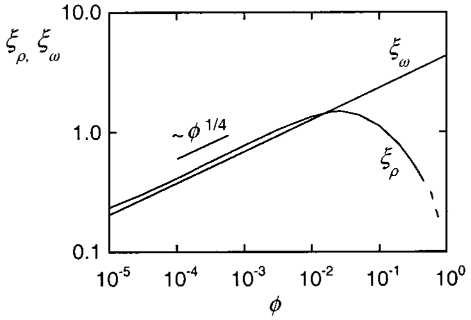

Figure 3. The decay length ξ of the interaction free energy versus distance curves of Figure 2 as a function of the bulk volume fraction of monomers for both B−B and A−D type monomers.

In Figure 2b we give results for A−D polymers between two surfaces that carry only acceptor sites (the situation depicted in

---

(20) Besseling, N. A. M.; Scheutjens, J. M. H. M. *J. Phys. Chem.* **1994**, *98*, 11597−11622.

(21) Van der Gucht, J.; Besseling, N. A. M. *Phys. Rev. E*. Submitted for publication.

Figure 1b). As anticipated from the Landau argument, the orientation effect now comes into play. Moreover, it appears to be dominant, because a strong repulsion is found. The interaction decays again exponentially, but now with a decay length ξ_ω that increases with concentration as $\xi_\omega \sim \phi^{1/4}$ over the whole concentration range (see Figure 3). Hence, the range of the repulsive force is largest in a melt of A−D monomers (for $\phi = 1$). This is in contrast to the decay length ξ_ρ of the above-mentioned attraction, which has a maximum at intermediate concentration. The order parameter associated with the repulsive forces is clearly related to the orientation of the monomers. Monomer orientations with the donor pointing toward the surface (which contains an excess of acceptors) enrich the surface region. The concentration is also enhanced, but apparently this is the lesser effect. It is interesting to note that the surface forces induced by equilibrium polymers are very similar to hydration forces in aqueous systems. These also can be either attractive or repulsive[17] depending on the extent to which the surfaces orient the molecules.

One can easily envisage variations in molecular properties that would modify the surface behavior of equilibrium polymers. For example, the directional structure of surface layers of A−D type equilibrium polymers and the ensuing repulsive surface forces will be partially spoiled by the addition of a few percent of A−A or D−D type monomers. An even more interesting playground turns out to be a combination of concentration effects (giving an attractive force contribution) and orientation effects (giving a repulsive force contribution). As a result of the different decay lengths associated with these two contributions (see Figure 3), this may lead to nonmonotonic force−distance dependencies. Such a situation can occur for example if a solution of A−D type monomers is confined between two surfaces that have a strong affinity for the donor groups, and a smaller affinity for the acceptor groups. An example is shown in Figure 4.

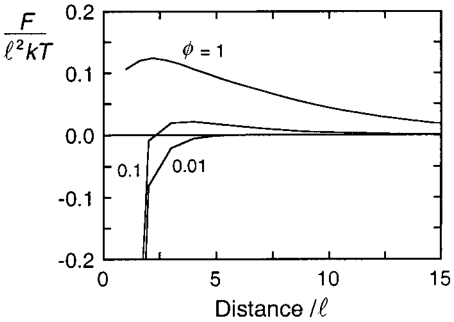

Figure 4. Nonmonotonic surface forces: free energy of interaction versus distance between two surfaces immersed in a solution of A−D monomers. The surfaces have a favorable interaction of $-10kT$ with the donor groups and $-8kT$ with the acceptor groups. The scission free energy of the bonds between the functional groups is $10kT$.

4. Concluding Remarks

Using both a phenomenological Landau-type analysis and a molecular model, we have shown that surface forces induced by supramolecular equilibrium polymers have properties that are completely different from what can be found with “ordinary” polymers. While symmetric B−B type monomers always give rise to attractive surface forces, asymmetric A−D type monomers can cause strong repulsion. The range of the attractive force has a maximum at intermediate concentration, while the range of the repulsive force increases over the whole concentration range. Furthermore, nonmonotonic force−distance curves can be obtained with A−D type monomers. It can be concluded that supramolecular equilibrium polymers induce new and tunable patterns of surface attraction and repulsion that yield, in turn, new rheological properties and phase behavior in colloidal systems.

To validate our theoretical predictions experimentally, self-associating monomers of both B−B and A−D type are needed. Most self-associating monomers available nowadays are of the B−B type (based on multiple-hydrogen bonds[5−10] or on metal−ligand interactions[8,12]). On the other hand, there are very few strongly associating A−D type monomers.[11] Further research in this direction is in progress.[22] Furthermore, surfaces are needed that have a preference for either donor or acceptor groups. In the case of hydrogen-bonded supramolecular chains, many surfaces have such a preference because they have an excess of either hydrogen bond acceptor or donor groups. Alternatively, one could modify surfaces by chemically attaching donor or acceptor groups onto it. The group of Meijer is currently working on this.[22]

Similar mechanisms as described in this paper might also play a role in certain biological systems. For example, the polymerization of globular actin into filaments is an equilibrium process under certain conditions.[23] Since actin filaments are directional chains, they should give rise to repulsive surface forces when growing from a surface.

Acknowledgment. The research of N. A. M. Besseling has been made possible by a fellowship of the Royal Dutch Academy of Arts and Sciences.

JA0125422

---

(22) Sijbesma, R. P.; Meijer, E. W. Personal communication.
(23) Oosawa, F.; Asakura, S. *Thermodynamics of the Polymerization of Proteins*; Academic Press: London, UK, 1975.