Interactions between flexible and rodlike macromolecules

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Interactions between flexible and rodlike macromolecules

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Résumé.— Nous étudions les interactions entre des macromolécules flexibles et des batonnets en solution. Si le solvant est un bon solvant pour les chaines flexibles, on peut utiliser une théorie de champ moyen et le coefficient du viriel mutuel est proportionnel au produit des masses moléculaires des deux polymères. Si le solvant est un solvant θ, les deux polymères interagissent comme des sphères dures quand la dimension de l'espace est un peu inférieure à trois. Il existe des corrections logarithmiques en dimension trois. Dans ce cas, le coefficient du viriel mutuel est calculé par la méthode de renormalisation directe de des Cloizeaux.

Abstract.— We study the interactions between flexible and rodlike macromolecules in solution. If the solvent is a good solvent for the flexible chain, a mean-field theory can be used and the mutual virial coefficient is proportional to the product of the masses of the two polymers. If the solvent is a θ solvent, the two polymers interact as hard spheres when the space dimension is slightly smaller than 3. Logarithmic corrections to the hard sphere behavior are found in three dimensions. In this case the mutual virial coefficient is calculated with the use of des Cloizeaux direct renormalization method.

1. Introduction.

In a previous work [1], we have studied the interactions between macromolecules of different chemical species A and B in a dilute solution. The main result is that both in a common good solvent and a common Θ solvent, linear flexible polymer chains interact as hard spheres as soon as the A-B monomer-monomer interaction is repulsive : the second virial coefficient

G_{AB} between A chains and B chains with equal radii R, is proportional to the volume R^d (d is the space dimension), the proportionality constant being universal. This is related to the fact that the free energy of two overlapping chains is larger than the thermal energy kT and thus that limited interpenetration is allowed between different chains. This same problem can be generalized to the case where polymers A and B are not linear chains but are fractal polymers [2]

characterized by their fractal dimensions d_A and d_B respectively [3], i.e. the radius of gyration of polymer i varies with its degree of polymerization as $R_i \approx N_i^{1/d_i}$ ($d_i = 2$ for a Gaussian chain, $d_i = 1$ for a rod like chain and $d_i \approx 1/\nu_F \approx 5/3$ for a linear chain in a good solvent).

In a mean field Flory-like model [4], the two polymers occupying the same volume of radius $R = R_A = R_B$ have $N_A N_B / R^d$ contact points. The free energy of two interpenetrating chains is proportional to this number of contact points

$$F = T v_{AB} \frac{N_A N_B}{R^d} \approx T v_{AB} \ R^{d_A + d_B - d} \qquad (1)$$

where v_{AB} (> 0) is the excluded volume between A and B monomers(^{1}) ; whenever $d > d_A + d_B$, the interpenetration free energy is asymptotically going to zero and a mean field theory may be used to evaluate the mutual virial coefficient G_{AB} ; when $d < d_A + d_B$, the interpenetration free energy is larger than kT and only limited interpenetration is possible : the polymers interact as hard spheres. This is indeed the case for two linear chains in a Θ solvent $d_A = d_B = 2$, $2d_A > d = 3$ or in a good solvent $d_A = d_B \approx 5/3$.

In this paper, we are more specifically interested in the case where the A chains are flexible linear polymers either in a good or a Θ solvent and the B chains are rodlike molecules. The dilution of rodlike molecules in a linear chain matrix might be of some use in the field of non linear optics : the rods could be oriented and provoke the optical anisotropy while the linear chains after a temperature quench below their glass transition would freeze the system in this anisotropic configuration. As in most polymer blends, a solvent is needed to favor the compatibility of the mixture. In this context, it is important to understand in details the interactions between rodlike and flexible macromolecules. Other important practical applications include the production of oriented films and fibers which can be used in resin reinforcement at the molecular level (molecular composites).

If the flexible chain is in a good solvent $d_A + d_B = 1 + 5/3 = 8/3 < 3$ and a mean field theory may be used to calculate the mutual virial coefficient G_{AB}. Equation (1) gives :

(^{1}) We use temperature units where the Boltzman constant k is equal to 1.

$$G_{AB} \approx T v_{AB} \ N_A N_B \qquad (2)$$

Notice that this result is independent of the fractal dimension of the two polymers (as soon as $d_A + d_B < 3$). In particular if A and B are two rods $d_A + d_B = 2$ and equation (2) is the usual Onsager result (up to a numerical constant which we have not determined here).

If the flexible chain is a pure Gaussian chain or a chain in a Θ solvent, $d_A + d_B = 3$, we are in a marginal case : for two polymers of equal radius R, we expect a virial coefficient G_{AB} proportional to the volume R^3 but with logarithmic corrections. Below 3 dimensions we expect a hard sphere behavior.

In the following we calculate, using des Cloizeaux direct renormalization method [6-7], the logarithmic corrections to the mutual virial coefficient G_{AB} in a Θ solvent in 3 dimensions. We also study the universal hard sphere behavior of G_{AB} in 3-ε dimensions ; this could be used for chains and rods trapped at an interface (in a Langmuir monolayer) or for comparison with computer simulations in 2 dimensions. Finally, we discuss qualitatively the demixing phase separation between flexible and rodlike macromolecules.

2. Virial coefficient between a Gaussian chain A and a rodlike chain B.

We first assume that the flexible chain A is a pure Gaussian chain with no interactions between the monomers. Following des Cloizeaux [6], we introduce the Gaussian surface S : the end to end distance $R^2 = N_A a^2$ (a is the monomer size) is equal to :

$$R^2 = dS \qquad (3)$$

In a continuous model, the flexible chain is represented by a continuous curve $\mathbf{r}(s)$ where s is a Gaussian area ranging from 0 to S. The propagator of the chain is

$$p(\mathbf{r}, s) = \frac{1}{(2\pi s)^{d/2}} \exp -\frac{r^2}{2s} \qquad (4)$$

The rod has a length L (proportional to the number of monomers N_B). The flexible chain being isotropic, the rod orientation is of no importance, we fix it along the z axis. The rod is represented by a continuous segment $\mathbf{r}'(\ell) = e_z \ell$ where ℓ is a length ranging from 0 to L and e_z the unit vector along the z axis.

The repulsive interactions between chains and rods are described in terms of a pseudopotential.

$$V_{AB} = Tb_{AB} \int_0^s \mathrm{d}s \int_0^L \mathrm{d}\ell \, \delta\left[\mathbf{r}(s) - \mathbf{r}'(\ell)\right] \quad (5)$$

b_{AB} is proportional to the standard excluded volume parameter between monomers v_{AB}. Dimensional analysis on equation (5) gives $b_{AB} \approx (\text{length})^{d-3}$. We recover here the result announced earlier that $d = 3$ is an upper critical dimension : upon renormalization of the unit length, b_{AB} increases with the unit length if $d < 3$ and the interaction potential V_{AB} is not relevent, it decreases if $d > 3$ and may be treated as a perturbation.

In order to have a well defined asymptotic limit, we fix the ratio of the radii of the two polymers $\sigma = R/L = (dS)^{1/2}/L$ and we let both L and S go to infinity. The radius ratio σ is a

B   A   B   A
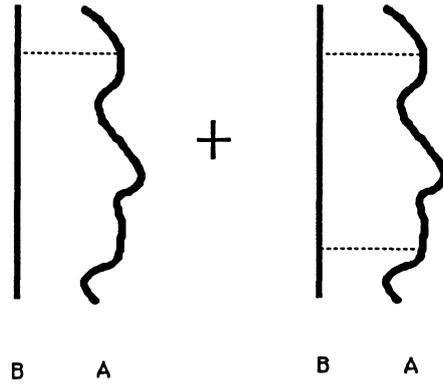
Diagrammatic expansion of the second virial coefficient between chains and rods G_{AB}.

parameter which could be measured experimentally for instance in an elastic light scattering experiment.

The diagramatic expansion of the mutual virial coefficient G_{AB} is shown in the figure. It leads to :

$$G_{AB} = b_{AB}SL - 2b_{AB}^2 \int_0^S \mathrm{d}s_1 \int_0^{S-s_1} \mathrm{d}s_2 \int_0^L \mathrm{d}\ell_1 \int_0^{\ell_1} \mathrm{d}\ell_2 \, p(\ell_2 e_z, s_2) \quad (6)$$

The first term is the mean field result of equation (2) with slightly different notations ; the second term is the first order perturbation. The integrals over the Gaussian areas of the flexible chains have short distances divergences, they must be calculated as Cauchy principal parts.

After a direct calculation in real space, we obtain :

$$G_{AB} = b_{AB}SL \left\{ 1 - \pi^{1-d/2} 2^{-\frac{1+d}{2}} b_{AB} S^{\frac{3-d}{2}} \left[\frac{1}{\left(2 - \frac{d}{2}\right)\left(\frac{3-d}{2}\right)} + f(\sigma) \right] \right\} \quad (7)$$

where $f(\sigma)$ is a regular function of the radius ratio σ for space dimensions d close to 3.

$$f(\sigma) = -\frac{1}{\left(3 - \frac{d}{2}\right)\left(\frac{5-d}{2}\right)} - \int_0^1 \mathrm{erfc}\left(\frac{d}{2u\sigma^2}\right)^{1/2} \left\{ \frac{1}{2 - \frac{d}{2}} u^{\frac{1-d}{2}} - \frac{1}{3 - \frac{d}{2}} u^{\frac{3-d}{2}} \right\} \mathrm{d}u \quad (7')$$

erfc(x) being the complement error function [8]

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{+\infty} e^{-t^2} \mathrm{d}t$$

We now use des Cloizeaux direct renormalization method to obtain the value of the virial coefficient G_{AB} in the asymptotic limit where S goes to infinity. We first consider a space dimension $d = 3 - \varepsilon$ close to 3.

The Fixman expansion parameter is defined

as $z = b_{AB}S^{(3-d)/2}(2\pi)^{(1-d)/2}$. We also define a dimensionless virial coefficient g_{AB}.

$$g_{AB} = \frac{G_{AB}}{L\left(\frac{R^2}{d}\right)^{\frac{d-1}{2}}} (2\pi)^{\frac{1-d}{2}}$$

Up to second order in z and leading order in ε the perturbation calculation (7) gives :

$$g_{AB} = z \left(1 - \frac{2z}{\varepsilon}\right) \qquad (8)$$

Below three dimensions, we expect no interprenetration between chains and rods and g_{AB} must go to a universal fixed point value when S or z goes to infinity. This fixed point is determined by calculating $w(g_{AB}) = z \, d/dz \, g_{AB}$

$$w(g_{AB}) = g_{AB} - \frac{2}{\varepsilon}g_{AB}^2 \qquad (9)$$

At the fixed point g^*, $w(g^*) = 0$ or

$$g^* = \frac{\varepsilon}{2} \qquad (10)$$

For long but not infinite chains we also obtain the correction to the scaling behavior

$$g_{AB} = g^* - \frac{cst}{S^\Delta} \qquad (11)$$

where the crossover exponent Δ given by the derivative of w at the fixed point g^* is equal to $\varepsilon/2$ up to first order in ε.

Below three dimensions, up to first order in ε the mutual virial coefficient is thus

$$G_{AB} = \left(\frac{2\pi R^2}{d}\right)^{\frac{d-1}{2}} L \frac{\varepsilon}{2} \left(1 - \frac{cst}{S^\Delta}\right) \qquad (11')$$

In the more realistic case where the space dimension is exactly $d = 3$, with the same definitions of the reduced virial coefficient g_{AB} and the Fixman expansion parameter z.

$$g_{AB} = z(1 - z \, \mathrm{Log}N_A) \qquad (12)$$

This requires the introduction of a short distance cutoff in the Gaussian areas $s_0 \sim a^2$ such that $S = N_A S_0$. The behavior of g_{AB} in the asymptotic limit is given by

$$w(g_{AB}) = \frac{dg_{AB}}{d \, \mathrm{Log}N_A} = -g_{AB}^2 \qquad (13)$$

As expected the fixed point is at $g_{AB} = 0$; in the vicinity of this fixed point

$$g_{AB} = \frac{1}{\mathrm{Log} \, N_A} \qquad (14)$$

The mutual virial coefficient is :

$$G_{AB} = \frac{2\pi}{3} \frac{LR^2}{\mathrm{Log}N_A} = \frac{2\pi LS}{\mathrm{Log}N_A} \qquad (15)$$

This gives the logarithmic corrections to the mean field result of equation (2). Up to this first order, the mutual virial coefficient is independent of the local monomer interaction b_{AB}. The value of the mutual virial coefficient g_{AB} does not explicitly depend on the radius ratio σ ; this is due to our particular choice of a volume to define the reduced virial coefficient g_{AB}. Calculations at higher order may explicitly depend on σ as can be seen from equation (7). The asymptotic limit is then meaningful if $1/\mathrm{Log}N_A < \sigma < \mathrm{Log}N_A$.

The values (11') and (15) of the mutual virial coefficient are valid strictly speaking for Gaussian chains without any interactions. In a real Θ solvent both two-body and three-body interactions between different monomers of the flexible chain must be taken into account. These A-A interactions must be considered while calculating the various partition functions. However, when we calculate the mutual virial coefficient G_{AB} which is a ratio of partition functions, the contribution of all A-A interactions factorizes out if we limit the expansion to second order in the interaction parameters. The diagramatic expansion of G_{AB} in a Θ solvent is the same as for Gaussian chains as shown in the figure. Furthermore if we limit the expansions to lowest order, we may approximate the radius of the flexible chain by its Gaussian value (In a sense [9], this is the definition of the Θ compensation temperature). At lowest order in ε, we may thus use at the Θ point the results obtained for a Gaussian chain in equations (15) and (11') (In Eq. (11') the actual radius of chains A[10] (R) and not the Gaussian radius $R_0 = (dS)^{1/2}$ should however be used).

3. Discussion.

We have calculated the virial coefficient G_{AB} between flexible and rodlike macromolecules in a solvent which is either a good solvent or a θ solvent for the flexible chain when the monomer-monomer interaction is repulsive. In both cases, G_{AB} is proportional to the product of the molecular masses of the two molecules, the proportionality constant being the monomer-monomer interaction in a good solvent and the inverse of the logarithm of the molecular mass in a θ solvent.

In a more concentrated solution as in usual polymer blends, these repulsions can provoke a segregation between the two types of molecules. If the solution is still dilute and remains isotropic when this demixing phase transition occurs, the free energy of the mixture per unit volume may be written as :

$$\frac{F}{T} = C_A \ \mathrm{Log} C_A + C_B \ \mathrm{Log} C_B + \frac{1}{2} \sum_{i,j} G_{ij} C_i C_j \qquad (17)$$

where C_A and C_B are the number densities of flexible and rodlike chains respectively and $G_{ij} \ (i, j = A, B)$ are the virial coefficient between i and j chains. The first two terms represent the free energy of an ideal solution of A and B chains and we have made a virial expansion of the interaction energy : the virial coefficient between flexible chains G_{AA} vanishes in a θ solvent and is proportional to their volume R^3 in a good solvent ; the virial coefficient between rods G_{BB} has been studied by Onsager and varies as the square of the rod length L^2 ; the mutual virial coefficient G_{AB} is given by equation (2) in a good solvent and equation (11') in a θ solvent.

A detailed study of the free energy [11,12] would lead to the determination of a phase diagram of the solution. This is beyond the scope of this work and we will limit our discussion to the stability of the homogeneous phase. This is done by studying the concavity of the free energy (16). We obtain the so-called spinodal line

$$\left(\frac{1}{C_A} + G_{AA} \right) \left(\frac{1}{C_B} + G_{BB} \right) = G_{AB}^2 \qquad (17')$$

A necessary condition for the spinodal to exist is that the determinant $G_{AA} G_{BB} - G_{AB}^2$

be negative. This is indeed true both in a good and a θ solvent $\left(G_{AB}^2 \gg G_{AA} G_{BB} \right)$ and we thus expect phase separation between chains and rods.

This conclusion however is based on equation (16) for the free energy which assumes both that the solution is dilute and isotropic. At higher concentrations, this free energy must be modified in two ways :

i) the virial expansion for the flexible chains is valid only if the concentration C_A is smaller than the overlap concentration. In the semidilute regime, concentration correlations between A chains must be taken into account ;

ii) the solution remains isotropic only if the rod concentration C_B is smaller than the Onsager concentration. Above the Onsager concentration, the rods order in a nematic phase.

A more complete theory should take these two effects into account. Qualitatively, we still expect a segregation between chain and rods but we also expect a nematic-isotropic phase transition of the rods. We hope to study in details the complete phase diagram of the solution and the interplay between these two transitions in a future work. This phase diagram has already been studied within the framework of a lattice model by Flory [13].

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