Effective Excluded Volume of Stiff Macromolecules

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ABSTRACT: The parameter of local asymmetry, i.e., the ratio of the persistence length to the diameter of the chain, is suggested to characterize a polymer chain. Analysis of data on the segment lengths and the chain diameters for various macromolecules is carried out. Dependence of the effective excluded volume on the chain local asymmetry and solvent quality is obtained as well as the expected dependence of the theta point on the stiffness of chains with strong bends. The second virial coefficient of flexible and stiff chains in good and pure solvents is discussed briefly.

As is already known[1-3] the flexibility of the polymer chain may be characterized by its persistence length $a = \langle h^2\rangle_0/2L$ or by the length of the Kuhn segment $A = 2a$ (L is the contour length of the chain and $\langle h^2\rangle_0$ is the mean unperturbed end-to-end distance). Chains are usually called "flexible" if the characteristics of the rigid chain segment (such as dimensions, optical anisotropy, dipole moment) are only 5–10 times higher than those for the chain unit. But if the characteristics mentioned are 15–100 times higher than those for the unit then chains are treated as semirigid or rigid. At the theta point, when the excluded volume effects are eliminated, statistical properties of polymer chains are determined only by the flexibility parameter and the reduced contour length L/a.

On the other hand many important properties of polymer chains are influenced not only by interactions along the chain but also in the transverse direction. Examples of such properties are the degree of folding and polymer packing in amorphous and crystalline states, value and origin of the volume effects in macromolecules in solution, formation of the intramolecular compact structures, etc. These characteristics depend not only on the persistence length a but also on the diameter d of the rigid segment or, more correctly, on the ratio $p = a/d$ which characterizes the shape of the persistence segment of a chain. We shall call p the parameter of the local asymmetry of a chain.

It is clear that the change of stiffness in real chains cannot be described with the linear change in scale L/a only. The similarity transformation is valid only in the case when transverse dimensions vary simultaneously with linear ones. To put it in another way, the chains are similar if their L/a and d/a are the same.

In all theories the volume interactions affect the properties of a polymer chain by means of the parameter

$$z \sim v_s(L/2a)^{1/2}/(2a)^3 \sim v_s \cdot n^{1/2}/(\langle h^2\rangle_0/n)^{3/2} \qquad (1)$$

where v_s is effective excluded volume of the segment of length $2a$ (Kuhn segment), and $n = L/2a$ is the number of these segments. It is to be pointed out that z must be invariant on dividing the chain into interacting segments. To make this possible, the value of the excluded volume of the chain segment must increase as the square of the number of its components, i.e., as the length squared of the segment. Hence, if the monomer unit is chosen as the interacting segment then

$$z \sim v_m \cdot N^{1/2}/(\langle h^2\rangle_0/N)^{3/2} \qquad (2)$$

where N is the degree of polymerization and v_m is the effective excluded volume of a monomer unit determined as

$$v_m = v_s/(2a/l)^2 \qquad (3)$$

where $l = L/N$ is the monomer unit length. It may readily be shown that if eq 3 is given, then eq 1 and 2 are just the same.

To determine the parameter v_s or v_m and to find its dependence on the geometric characteristics of the chain (i.e., on its diameter and stiffness) and on the interaction with solvent, the real structure of the chain must be analyzed. This analysis is available in what follows.

Local Asymmetry of Macromolecules

In Table I the persistence lengths of various macromolecules obtained from the chain dimensions at theta conditions or from the extrapolated data are given. The chain diameters obtained as distances between the neighbor chains in crystals from the x-ray data[5] or by hydrodynamic methods are also listed. Experimental values a and d yield the parameter of local asymmetry p. The majority of polymers can be roughly divided into three classes as given in Table I. Flexible polymers with a up to 10 Å, $d \approx 5$–10 Å, and, consequently, small local asymmetry $p \approx 1$ form the first class. The diameter of such chains is approximately equal to their rigid segment length. The second class is formed by the stiff and relatively thin polymer chains with the persistence length about several tens or hundreds ångströms; such chains have considerable local asymmetry $p \approx 10$–20.

Large transverse dimensions are the main feature of the third class of polymers conventionally referred to as "pseudorigid". This class is formed by the comblike polymers with long side groups and graft copolymers. When there are no side groups the chain backbone is flexible but this flexibility cannot be realized in thick chains; the persistence length, i.e., the interval where a chain bends, cannot be less than the chain diameter. Therefore for bulky polymers $a \approx d$ must be assumed and, consequently, $p \approx 1$. Hence, pseudorigid macromolecules are characterized by a large value of a, the local asymmetry being small. To emphasize the point, the pseudorigid macromolecules are analogues for the flexible chains examined as if with a "magnifying glass"; the scale factor a varies but the ratio d/a remains the same.

It should be emphasized that the analogy between a polymer with long side chains and the usual flexible chains is correct only in the case when the side chains attached to the backbone are sufficiently close to each other. Otherwise the effect of heterogeneity will be observed because of the different chemical nature of the side chains and backbone. And last but not least, the microstructure of the diameter of a macromolecule with long side chains is determined mainly by the properties of the side chains themselves, in particular their local asymmetry.

Excluded Volume in Flexible Chains

As follows from Table I the sequence of tightly connected beads (or cubes) which can freely rotate about the junction point (see Figure 1a) may be used as a model for both flexible and pseudorigid chains. The inherent volume of the rigid segment in these chains is $V_s \approx a^3 \approx d^3$ and the effective excluded volume of the segment in the hard sphere approximation, i.e., in good solvent, is $v_s \approx V_s \approx d^3$ (the excluded

Table I
Classes of Polymers of Different Local Asymmetry

Class of polymers	Polymer	Persistence length a, Å	Diameter d, Å	Local $p = a/d$
Flexible	Polystyrene[3]	9	10	~1
	Polyethylene[3]	6	4	~1
Stiff	Cellulose trinitrate[6]	100	8	~10
	Ladder poly(diphenylsiloxane)[7]	70	7	~10
	Poly(butyl isocyanate)[8]	500	8	~60
Pseudorigid	Graft polymers (poly(methyl methacrylate)[11])	~40	~40	~1
	Polymers with long side groups (poly-n-acrylates[9,10])			

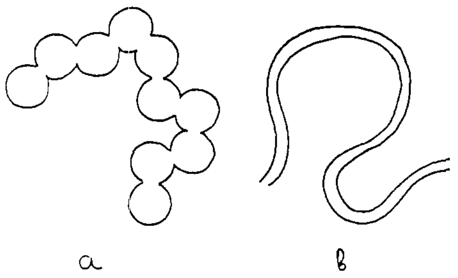

Figure 1. Model for the flexible (or pseudorigid) polymer chain; each bead corresponds to the chain segment (a). Model for the stiff polymer chain; sliglhtly bent cylinder describes the chain segment (b).

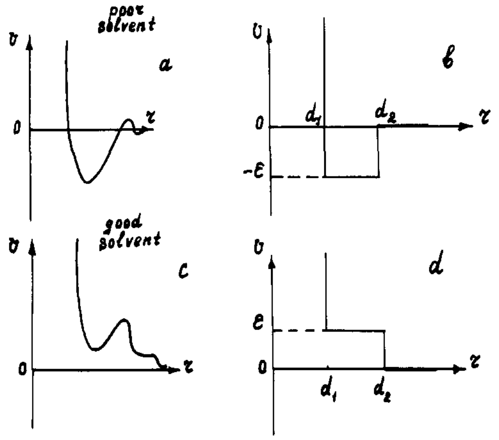

Figure 2. The effective interaction potential for the polymer chain units in poor (a, b) and good (c, d) solvents; a, c and b, d are for real and model potentials, respectively.

volume of the interacting pair of spheres or cubes is eight times the inherent volume and, as above, the numerical coefficients are omitted). Therefore

$$z \sim (d/a)^3(L/2a)^{1/2} \approx (L/2a)^{1/2} \tag{4}$$

and, consequently, depends only on the number of Kuhn segments in a macromolecule. The simultaneous growth of the diameter and length of a chain does not change the value of z in accordance with the geometric similarity principle relating flexible and pseudorigid chains. On the other hand, if the diameter of the chain of given contour length L increases by a factor of d_2/d_1, the stiffness increases by the same factor; hence, the number of segments is smaller and the volume effect parameter decreases by a factor of $(d_2/d_1)^{1/2}$.

Excluded Volume in Stiff Macromolecules

The sequence of thin long cylinders (or prolate ellipsoids) joined to each other (Figure 1b) is taken as a model of the stiff macromolecule with considerable local asymmetry. Effective excluded volume of a cylinder of height A and diameter d is as follows[12]

$$v_c = V_c[A/d + (\pi + 3)/2 + \pi d/4A] \tag{5}$$

where $V_c = \pi A d^2/4$ is the volume of a cylinder. In eq 5 the first term in the brackets arises from the fact that the cross-intersection of cylinders is forbidden whereas the two other terms are connected with elimination of any longitudinal intersection.

Longitudinal intersections are not realized for a long macromolecule, therefore these latter terms can be omitted. Thus, the effective excluded volume of the Kuhn segment in a stiff macromolecule is

$$v_s \approx \frac{\text{length}}{\text{diameter}}\,(\text{inherent volume}) \tag{6}$$

or $v_s \approx pad^2 \approx a^2d$ and, consequently,

$$z \sim (L/2a)^{1/2}p^{-1} \tag{7}$$

Equations 6 and 7 are also valid in the case of flexible chains when the local asymmetry is about 1, since, as has been pointed out, the effective excluded volume of the segment chosen as a unit of interaction varies as its length squared. In fact, a polymer chain of any stiffness may be treated as a more or less bent cylinder. Each element of the cylinder makes contacts with others essentially in two-dimensional space, one dimension being always occupied by the chain itself. Stiff chains are effectively thinner than flexible ones and therefore the mutual influence of their units which are far apart in sequence is less. Hence, the dimensions of stiff chains must be comparatively slightly influenced by the solvent quality (in good solvents). At the same time in the bulk state where high segment density can be brought about only if long thin segments are ordered the regularity and orderliness are greater than for flexible chains. In particular, it is macromolecules with great local asymmetry which form liquid crystals (in solvents at sufficient concentration).[13,14]

In contrast, flexible and pseudorigid polymers, whatever the length of the side chain, do not form liquid-crystallike packing. (This does not concern the packing of side chains as has been pointed out.)

If there is intramolecular transverse attraction, then a similar situation occurs. In this case the intramolecular condensation of stiff chains leads to crystallike structures in contrast to the flexible chain globularization.[15]

Effect of Solvent on the Effective Excluded Volume

Let the mean-force potential of the interaction of atoms and chain segments in solution be of the form given in Figures 2a and 2c.[16] As approximated by the square well potential shown in Figures 2b and 2d it provides an effective excluded volume of a sphere as follows

$$v_{\text{sph}} = V_1 + (1 - \exp\{-\epsilon/kT\}) \cdot V_2 \tag{8}$$

when the definition of the excluded volume

$$v_0 = \int (1 - \exp\{-V(z)/kT\})\, \mathrm{d}z \tag{9}$$

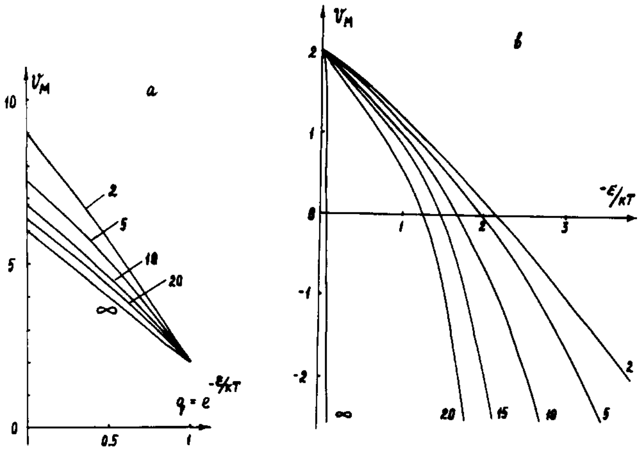

Figure 3. Dependence of the effective excluded volume of the chain unit in the repulsion (a) and attraction (b) energy regions. Figures indicate values A/d.

is used. Here V_1 and V_2 are the impenetrable volume and the volume of interaction, respectively, ϵ is the interaction energy. Equation 8 describes, at any rate qualitatively, the solvent and temperature variations of the effective excluded volume for the segment in a flexible chain, the value ϵ being the free-energy difference for the polymer–polymer and polymer–solvent contacts corresponding to the parameter χ in the thermodynamic theory of Flory.[17]

From eq 8 the theta point conditions for flexible chains can be derived as

$$\epsilon_\Theta/kT = \ln(1 + V_1/V_2) \qquad (10)$$

For the stiff chain where a segment is a long thin cylinder (see Figure 1b) we considered and calculated the effective excluded volume of interacting cylinders of length A spaced on the simple cubic lattice. As before, the interpenetration along the axes of cylinders is left out of the account.

Let the diameter of the cylinder (segment) d be equal to the lattice spacing; the number of interacting elements (cubes) is then $k = A/d$. The diameter of the interacting layer (attractive or repulsive) is also assumed to be d ($d_2 = 2d_1$ in Figure 2). A statistical weight $q = \exp\{-\epsilon/kT\}$ corresponds to each pair of elements in contact, i.e., in adjacent lattice sites. Intergration over the whole space in eq 9 reduces to summing over two kinds of configurations: for the intersecting ones, the repulsive energy is infinite, and their total excluded volume is $2dA^2$; for the contacting ones the statistical weight is q^i where i is the number of elements in contact.

It may easily be shown that the excluded volume for such a model is

$$\begin{aligned} v_s &= 2dA^2 + 4d^3 \sum_{i=1}^{k} \sum_{j=1}^{k} (1-q) \\ &\quad + 4d^3\Big[2\sum_{i=1}^{k}(1-q^i) - (1-q^k)\Big] = 2dA^2 + 4dA^2(1-q) \\ &\quad + 8Ad^2 - 4d^3(1+q)(1-q^k)/(1-q) \qquad (11) \end{aligned}$$

The first two terms describe the interaction of segments which are perpendicular to each other and the remaining terms give that of parallel sliding ones. If there is no interacting layer ($q = 1$), eq 11 reduces to eq 6 for impenetrable cylinders. In the case of infinite repulsion of layers ($q \to 0$) the value of v_s is tripled in accordance with eq 11 and converges to $6dA^2$.[21]

Consider the dependence of the excluded volume of a unit on the contact energy. In the repulsive energy region at $q \leqslant 1$, v_m, just as the effective excluded volume v_s in flexible chains, shows linear dependence on q (Figure 3a). The theta-point conditions ($v_m = 0$) in the attractive energy region correspond to different values of attractive energy ϵ_Θ/kT depending on the length of rigid segment A (Figure 3b). It is to be emphasized that computer calculations for the chains of various stiffness[18] yield the similar dependence of ϵ_Θ/kT on the segment stiffness as well as the simple model of the interacting cylinders. Thus, being effectively thinner, the stiff molecules are less disturbed by the volume interactions in good solvents and therefore the attractive forces required to provide the theta conditions are smaller than those in flexible chains. In the case of nonsolvents, i.e., solvents worse than theta solvents, the dependence of the excluded volume on the interaction energy becomes sharper with increasing stiffness (Figure 3). Sharp change of the geometric and thermodynamic characteristics of stiff chains when intramolecular globularization or crystallization occurs is due to this cause (see ref 19).

It should be noted that the result obtained is correct only for chains with strong bends yielding the hairpinlike conformation. If there are no conformations of this kind then the chain segment interactions are provided mainly by the crosslike single contacts. It is easily shown that

$$v_s = 2dA^2 + 4dA^2(1-q) \qquad (12)$$

and the effective excluded volume is then given by eq 8.

Second Virial Coefficient of Flexible and Stiff Chains

Treating the effective excluded volume v_s we dealt only with the intramolecular interactions in the polymer chain. But all the foregoing concerns also the intermolecular interactions. The second virial coefficient is, indeed, as follows[20]

$$A_2 \approx [\eta] \cdot F(\alpha^2 - 1)/M \approx V \cdot F(\alpha^2 - 1)/M^2 \qquad (13)$$

where M is molecular weight, $[\eta]$ is intrinsic viscosity, $V \approx \langle h^2\rangle^{3/2} \approx (La)^{3/2}$ is the volume of chain, and F is a continuous function of the expansion factor α.

The value of A_2 for the stiff polymers in good solvents is obviously higher than that for flexible ones with just the same M and L since their volume increases as $a^{3/2}$. As distinguished from flexible chains the variations of temperature or solvent (the latter being good) only marginally change A_2 of the stiff chains. In the repulsion region the volume interactions are, indeed, small in the stiff chains; owing to this their dimensions and, consequently, A_2 are practically constant.

On the other hand dimensions and thermodynamic characteristics of stiff chains change more abruptly than those of flexible chains, the range of temperature and solvents used being in the neighborhood of the theta conditions.[19] Hence, the value of A_2 for stiff chains in this region sharply decreases with the solvent deterioration, the sharpness of decrease growing with the chain stiffening.

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(21) For the cylinder of doubled diameter the effective excluded volume is $4dA^2$ in accordance with eq 5. As can be seen, the distinction is connected with the shape of a segment in the lattice model if there is a repulsive layer. The segment cross section has the form of a four-petal rosette.

Normal Stresses in Dilute Polymer Solutions. The Effects of Preaveraging the Hydrodynamic Interaction Tensor

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ABSTRACT: The two normal stress differences, σ_1 and σ_2, are calculated for a dilute solution of random coil polymers without preaveraging the Oseen tensor used to describe the intramolecular hydrodynamic interaction. ($\sigma_1 = \sigma_{xx} - \sigma_{zz}$ and $\sigma_2 = \sigma_{zz} - \sigma_{yy}$ where σ_{xx}, etc., are elements of the stress tensor and the unperturbed solvent velocity filed is $V_x{}^0 = Kz$, $V_y{}^0 = V_z{}^0 = 0$.) The perturbation theory developed by Fixman is carried out to second order and the results show that σ_1 decreases by 15% from the nondraining result of the Rouse–Zimm theory. Previous calculations of σ_2 in dilute solutions of random coil macromolecules yield $\sigma_2 = 0$. In this calculation, due to avoidance of preaveraging the Oseen tensor, σ_2 is non-zero and has the value $\sigma_2 = -0.01\sigma_1$.

In order to completely characterize the rheological properties of a non-Newtonian fluid, three quantities must be determined: the viscosity and the two normal stress differences. A great deal of theoretical work has been done on the viscosity of dilute polymer solutions, but relatively little work has been done on normal stresses. Although normal stress differences are more difficult to measure, they are more sensitive to details of molecular structure than are viscosities. Normal stresses play an important role in stability and secondary flow phenomena and have recently been considered as being responsible for the observation of drag reduction in dilute polymer solutions.[1]

Tanner and Stehrenberger[1] and Curtiss, Bird, and Hassager[2] have recently reviewed previous calculations of normal stresses in dilute polymer solutions from a molecular approach. We simply note here that all calculations on random coil or stiff chain models of polymer statistics have either neglected hydrodynamic interaction completely or have preaveraged the Oseen tensor that describes the hydrodynamic interaction. Consequently, while these calculations result in non-zero values for the first normal stress difference, σ_1, the second normal stress difference, σ_2, is zero (see below for definitions of σ_1 and σ_2). One exception to this is the calculation of Segawa and Ishida,[19] based on the boson formulation of Fixman.[20,21] This formulation, while applicable to nonideal conditions, uses a hydrodynamic interaction tensor averaged over some steady state. Thus fluctuations in the hydrodynamic interaction are neglected. They obtained a nonvanishing result for σ_2/κ^2, where κ is the shear rate, for finite κ, but no numerical results were presented. For the rigid rod macromolecule, Kotaka[3] has calculated non-zero values for both σ_1 and σ_2 by not preaveraging the Oseen tensor.

The purpose of this paper is to calculate the normal stress differences in a dilute solution of random coil macromolecules without preaveraging the hydrodynamic interaction tensor. Our approach is to employ the perturbation theory developed by Fixman[4] and applied to intrinsic viscosity calculations by Fixman and Pyun.[5,6] This method is based on the general theory of irreversible processes in solutions of macromolecules developed by Kirkwood.[7,8]

Method of Calculation

We begin by briefly recapitulating the perturbation theory developed by Fixman[4] and Fixman and Pyun.[5,6] The reader is referred to the original articles for the detailed presentation of the theory. Unless otherwise specified, the notation of ref 5 and 6 will be adhered to in what follows. The model considers a dilute solution of linear, flexible polymer chains, each consisting of N equal segments. The equation of motion of each segment is determined by balancing the thermal, Brownian motion force, the intersegmental forces, and the force arising from hydrodynamic resistance of segment motion relative to solvent, including hydrodynamic interaction between segments on one molecule. The segments are assumed to interact through a spring, or Hooke's law, potential, S, which at equilibrium determines a Gaussian, random coil distribution function. In addition, the hydrodynamic interaction between segments is described by the Oseen interaction tensor in the nonpreaveraged form (see below). The equation of motion of each segment along with the equation of continuity determines the diffusion equation for the distribution function, ψ, for the polymer segments in coordinate space.

Let ψ be written as

$$\psi = \psi_0\rho \qquad (1)$$

where ψ_0 is the equilibrium distribution function. The equation for ρ is written as

$$\frac{\partial\rho}{\partial t} + L\rho = 0 \qquad (2)$$

The operator L can be split into the sum of a self-adjoint operator, A, with a scalar product defined with ψ_0 as a weighting function and an external perturbation operator B. These operators are defined by the equations

$$A\rho = -kT\nabla^{\mathrm{T}}(D\nabla\rho) + (\nabla^{\mathrm{T}}S)D(\nabla\rho) \qquad (3)$$

$$B\rho = \nabla^{\mathrm{T}}(V^0\rho) - (1/kT)(\nabla^{\mathrm{T}}S)V^0\rho \qquad (4)$$

Here ∇ is an $N \times 1$ matrix whose ith element is the column matrix operator

$$\nabla_i = (\partial/\partial x_i,\ \partial/\partial y_i,\ \partial/\partial z_i) \qquad (5)$$