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Disentanglement of Rods in Semidilute and Liquid-Crystalline Solutions in Elongational Flow

Theo Odijk

Department of Polymer Technology, Faculty of Chemical Engineering and Materials Science, Delft University of Technology, P.O. Box 5045, 2600 GA Delft, The Netherlands. Received February 12, 1988; Revised Manuscript Received May 4, 1988

ABSTRACT: An analytical theory is presented of the disentanglement of rods in both semidilute and liquid-crystalline solutions within the context of the preaveraged Doi equation. The excluded-volume effect is accounted for in the second virial approximation. It is assumed that the degree of orientational order is high at all times. The diffusion equation and the stress are solved to leading order.

Introduction

A mere glimpse at the experimental literature on the rheology of polymer liquid crystals reveals that many phenomena are not well understood.¹⁻⁵ Nevertheless, the theory advanced by Doi^{6,7} does rationalize several remarkable effects like the sharp decrease in the viscosity when the concentration is increased beyond the isotropic-nematic transition. Moreover, steady-state rheological properties are surprisingly well described by the Doi equations provided two parameters are adjusted to conform to one or two experiments.⁵ The relative success of the reptation theory for liquid crystals has caused a flurry of theoretical activity.⁸⁻¹³

Most previous analyses have concentrated on weak flow. Kuzuu and Doi¹⁴ have analyzed the influence of weak and strong flows on a solution of entangled rods but only for very low volume fractions. Here, we show that it is straightforward to extend their calculations for elongational flow even when the excluded-volume effect is nonnegligible. An asymptotic time-dependent solution to the preaveraged Doi equation^{6,7} is obtained for a high enough degree of orientational order. The latter is a nontrivial function of the elongational rate and the excluded-volume effect. Since the number of rods enveloping a test rod decreases with increasing order there is a distinct possibility of the rods disentangling with strong enough flow. Thus, beyond this critical rate the rotational diffusion should be close to ideal. At very high elongational rates the rods should more or less align along the lines of flow. In that case, the stress is determined mainly by hydrodynamic friction so that Batchelor's limit applies.¹⁵

Several workers¹⁶⁻¹⁸ have attempted to study the isotropic-nematic transition for solutions of rodlike particles in steady elongational flow by adding a term of Kramers' type¹⁹ to the usual free energy. Here, we point out that these analyses contradict the integral equation for the orientational distribution function arising from the Doi equation. In effect, ref 16-18 neglect the effect of entanglement altogether.

Finally, let us recall some of the criticisms that can be leveled at the Doi theory. Arguing that a rigid tube constraint may be too severe, Fixman^{20,21} proposed an alternative model in which the mean-square torque on a test rod is calculated by kinetic arguments. Nevertheless, the rotational diffusion coefficient would still increase with orientational order though less rapidly than in the Doi theory. Next, computer simulations^{20–28} show that entanglement starts developing at much higher concentrations than was originally surmised.^{29,30} The formulation of the hydrodynamic stress has also been criticized.^{13,31–33} Doi and Edwards^{29,30} used the bare rotational friction coefficient, but others^{13,31–33} have opted for a renormalized one. This problem is unresolved. Lastly, the influence of semiflexibility needs to be assessed. There is definitely an influence.³⁴ However, present theories^{35–37} of the rotational diffusion of worms (with identical results) appear to conflict with most data except at very high concentration²⁶ or for a chain trapped in a fixed gel.³⁸ It has been argued that the semiflexibility effect does show up clearly in equilibrium measurements.³⁹ Of these influences only the one pertaining to entanglement^{20–28} will be accounted for here.

Entanglement Condition

We consider a semidilute or concentrated solution of slender rods of length L and number density ν . The solution is either isotropic or uniaxially ordered; the single-rod orientational distribution function $f(\mathbf{u},t)$ depends on time and the unit vector **u** pointing along the axis of a test rod and defined with respect to some preferred axis. Doi and Edwards^{7,30} have calculated the average number N(r) of rods intersecting a tube of radius r whose axis is aligned along a test rod. On averaging N(r) over all orientations of the probe we obtain

 $\langle N(r) \rangle \approx \nu r L^2 \rho$

where

$$= \frac{4}{\pi} \langle \sin \gamma \rangle$$

= $\frac{4}{\pi} \int \int d\mathbf{u} d\mathbf{u}' \sin \gamma f(\mathbf{u},t) f(\mathbf{u}',t)$ (2)

and γ is the angle between the test rod and another one with orientations **u** and **u'**, respectively. The parameter ρ equals unity when the distribution is isotropic. Note that $\langle N(r) \rangle$ is essentially the number density scaled by an excluded-volume proportional to $L^2 r \langle \sin \gamma \rangle$.

The purpose of deriving eq 1 is to determine the preaveraged radius a of the tube in which the test rod is dynamically constrained. Originally, the average number of rods needed was supposed to be of order unity^{29,30} so that $\langle N(a) \rangle \approx \nu a L^2 \rho \approx 1$. The onset of entanglement ν^* was supposed to be at $a \approx L$ so that $\nu^* \approx L^{-3}$ when $\rho = 1$. However, for isotropic solutions many authors²⁰⁻²⁸ have shown that the onset occurs at much higher densities, viz., $\nu^* = EL^{-3}$, where E is a number between about 30 and 70. This implies that $\langle N(a) \rangle \approx E$ is more realistic. We now postulate that the same relation is valid even when the solution is uniaxially ordered. In other words E rods are needed to make an effective tube constraint irrespective of whether the orientational order is due to flow or the excluded-volume effect.

If we use $a \approx E/\nu L^2 \rho$ instead of $a \approx (\nu L^2 \rho)^{-1}$, the preaveraged rotational diffusion coefficient valid in the entangled state is given by^{7,29,30}

$$\bar{D}_{\rm r} \approx (E/L^3 \nu \rho)^2 D_{\rm ro} \tag{3}$$

When the rods are not entangled, their diffusion coefficient

is equal to the infinite dilution value $D_{\rm ro}$. Here, the prefactor in eq 3 defines entanglement

$$h = L^3 \nu \rho > E \tag{4}$$

Diffusion Equation

Having defined our entanglement condition, we study the mean-field dynamics of the rods by using the preaveraged diffusion equation introduced by Doi⁶

$$\frac{\partial f}{\partial t} = \bar{D}_{\mathbf{r}} \nabla_{\mathbf{u}} \cdot (\nabla_{\mathbf{u}} f + f \nabla_{\mathbf{u}} V) - \nabla_{\mathbf{u}} \cdot (\dot{\mathbf{u}} f)$$
(5)

with

$$V(\mathbf{u}) = (8c/\pi) \int d\mathbf{u}' \sin \gamma(\mathbf{u},\mathbf{u}') f(\mathbf{u}')$$
(6)

$$c = (\pi/4)L^2 D\nu \tag{7}$$

$$\dot{\mathbf{u}} = \boldsymbol{\kappa} \cdot \mathbf{u} - (\mathbf{u} \cdot \boldsymbol{\kappa} \cdot \mathbf{u}) \mathbf{u} \tag{8}$$

The nematic potential V (scaled by $k_{\rm B}T$ with T the temperature and $k_{\rm B}$ Boltzmann's constant) is exerted on the test rod by the surrounding macromolecules. It is consistent with the second virial approximation as developed by Onsager⁴⁰ for a liquid crystal of slender rods. The dimensionless parameter c is the number density scaled by the isotropic excluded volume $(\pi/4)L^2D$, where D is the rod diameter $(L \gg D)$. Deviations from equilibrium are caused by macroscopic flow given in terms of κ , the transpose of the velocity gradient tensor. Equation 8 describes the rate of change of the orientation of a test particle.

Here, we confine ourselves to elongational flow so that κ is expressed as a function of the elongational rate $\epsilon(t)$ by

$$\kappa = \kappa(t) = \begin{bmatrix} -1/2 & 0 & 0\\ 0 & -1/2 & 0\\ 0 & 0 & 1 \end{bmatrix} \dot{\epsilon}(t)$$
(9)

Furthermore, we assume the director is always aligned along the z direction. Accordingly, eq 5 is simplified considerably upon switching to polar coordinates (θ, φ) with $w = \cos \theta$ and noting that f = f(w)

$$\frac{\partial f}{\partial t} = \bar{D}_{\rm r} \frac{\partial}{\partial w} \left[(1 - w^2) \left(\frac{\partial f}{\partial w} + f \frac{\partial V}{\partial w} - \bar{\beta} w f \right) \right] \quad (10)$$

where

$$\bar{\beta} = \frac{3\dot{\epsilon}(t)}{2\bar{D}_{\rm r}} \tag{11}$$

Kuzuu and Doi¹⁴ have analyzed eq 10 for V = 0, assuming the rods are always entangled. Here we take both the excluded-volume potential and disentanglement into consideration.

Entangled Steady State

If the imposed flow has a constant elongational rate $\dot{\epsilon}(t)$ = $\dot{\epsilon}$, the solution will eventually attain a steady state. Equation 10 reduces to

$$\log f(w) = \text{constant} - V(w) + \frac{1}{2}\bar{\beta}w^2 \qquad (12)$$

This integral equation does not agree with ref 16–18 because, here, $\bar{\beta}$ depends on the degree of entanglement of the rods (when $h \gtrsim E$). In ref 16–18, $\bar{\beta}$ is simply set equal to β

$$\beta = \frac{3\dot{\epsilon}}{2D_{\rm ro}} \tag{13}$$

Then, eq 11 can be functionally integrated, yielding a free energy consisting of the usual term (as discussed in ref 40, for instance) and a term similar to the one introduced by Kramers.¹⁹ In our case, trying to obtain the free energy is complicated by the fact that $\bar{\beta}$ is already a functional of the distribution function f.

Equation 12 may have more than one solution. But it is anticipated that there will only be one that is stable if the degree of orientational order is high, as will be supposed here. We now focus on the leading behavior of this f. We assume θ is small and set $w = 1 - \frac{1}{2}\theta^2 + \dots$ Let us for the moment put $\bar{\beta}$ equal to zero in order to recall the form of f for the unperturbed nematic state.

At first sight the nematic potential V in eq 12 looks unwieldy because of the awkward sin γ kernel in eq 6. But it is feasible to derive the expansion of V for small angles. First, we expand the kernel in terms of Legendre polynomials of even order

$$\sin \gamma = \sum_{n=0}^{\infty} d_{2n} P_{2n}(\cos \gamma)$$

Next, we note that upon using the addition theorem⁴¹ we have

$$\frac{1}{2\pi} \int_0^{2\pi} \mathrm{d}\varphi' \sin \gamma = \sum_{n=0}^\infty d_{2n} P_{2n}(\cos \theta) P_{2n}(\cos \theta')$$

and so

$$V(\theta) = \frac{8c}{\pi} \sum_{n=0}^{\infty} d_{2n} P_{2n}(\cos \theta) \langle P_{2n}(\cos \theta') \rangle$$
(14)

Hence, the potential is a straightforward expansion in θ^2 . However, the coefficients are very tedious to calculate. A simpler route is to observe that eq 12 (with $\overline{\beta} = 0$) and eq 14 prove the leading term of the asymptotic expansion for f is Gaussian

$$f \sim \frac{\alpha_0}{4\pi} \exp\left(-\frac{1}{2}\alpha_0 \theta^2\right) \qquad 0 \le \theta < \frac{1}{2}\pi \qquad (15)$$
$$f(\theta) = f(\pi - \theta) \qquad \alpha_0 \gg 1$$

The parameter α_0 is calculated by minimizing the free energy^{39,40}

$$\alpha_0 = \frac{4c^2}{\pi} \tag{16}$$

The validity of eq 15 has also been established numerically.⁴² Thus, eq 14 may be rewritten in view of eq 12 and 16

$$V(\theta) = V(0) + \pi^{-1/2} \alpha_0^{1/2} c \theta^2 + \dots$$
(17)

Note that the excluded-volume interaction tries to align a test rod along the director (the z direction).

For highly oriented systems it is immediately clear that the solution to eq 12 must also have the Gaussian form

$$f \sim \frac{\alpha}{4\pi} \exp\left(-\frac{1}{2}\alpha\theta^2\right) \qquad 0 \le \theta < \frac{1}{2}\pi \qquad (18)$$
$$f(\theta) = f(\pi - \theta) \qquad \alpha \gg 1$$

In this case $V(\theta)$ is given by eq 17 with α_0 replaced by α . The use of eq 18 is restricted by the requirement

$$(L/D)^2 \gg \alpha \gg 1 \tag{19}$$

The first inequality expresses the fact that the rods must be sufficiently slender if the second virial approximation is to hold;³⁹ the second expresses the dominance of the leading order solution. Equations 2 and 18 give

$$\rho = 4(\pi \alpha)^{-1/2}$$
 (20)

and eq 11 becomes

$$\bar{\beta} = \beta h^2 E^{-2} = 16\pi^{-1} \alpha^{-1} (\nu L^3 E^{-1})^2 \beta$$
(21)

Equations 12, 17, and 21 finally yield the relation between α and β (for h > E)

$$8(\nu L^3/E)^2\beta = \frac{1}{2}\pi\alpha^2 - \pi^{1/2}c\alpha^{3/2}$$
(22)

This expression reduces to eq 16 as β goes to zero and to eq 19 of Kuzuu and Doi¹⁴ when c is set equal to zero and E to unity. Equation 22 shows that the orientational effect of flow becomes comparable to the excluded-volume effect when

$$eta^+pprox E^2arphi^2$$

where the volume fraction $\varphi = cD/L$.

Disentanglement

Equations 4 and 20 show that the rods become disentangled when the degree of orientational order is high enough

$$\alpha^{1/2} > 16\pi^{-3/2} (L/D) c E^{-1}$$
(23)

Note that our calculations are of qualitative use only when $c \gg E$. The first inequality of eq 19 will not be obeyed if one wants eq 23 to be satisfied. Equations 22 and 23 allow α to be eliminated so that we have an explicit condition for the scaled elongational rate to force disentanglement

$$\beta > \beta^* = 256\pi^{-3} \left(\frac{L}{D}\right) (c/E)^2 \left(\frac{L}{D} - \frac{1}{8}\pi E\right)$$
 (24)

Short enough rods $(L/D < {}^1/_8 \pi E)$ are disentangled at all elongational rates, but for slow rates of flow the incipient state must be liquid crystalline in view of the second inequality of eq 19.

For $\beta > \beta^*$ we can write an expression for α in terms of $\overline{\beta} = \beta$ in an analogous fashion

$$\alpha^{1/2} = \pi^{-1/2}c + (\pi^{-1}c^2 + \beta)^{1/2}$$
(25)

This reduces to two well-known limits as either c or β tend to zero.

Time Dependence

For high degrees of order eq 10 can be solved explicitly at the inception of steady flow

$$\begin{aligned} \dot{\epsilon}(t) &= 0 & t < 0 \\ &= \dot{\epsilon} & t > 0 \end{aligned} \tag{26}$$

It is straightforward to prove that the leading order solution is Gaussian again.

$$f \sim \frac{\alpha(t)}{4\pi} \exp\left(-\frac{1}{2}\alpha(t)\theta^2\right) \qquad 0 \le \theta < \frac{1}{2}\pi \quad (\alpha(t) \gg 1)$$
(27)

When the macromolecular solution is entangled (h(t) > E), eq 10, 17, and 21 yield

$$\frac{\partial \alpha}{\partial t} = g(\alpha,\beta) = \frac{\pi}{8} D_{\rm ro} (E/\nu L^3)^2 (16\pi^{-1}\beta\alpha(\nu L^3/E)^2 - \alpha^3 + 2\pi^{-1/2}c\alpha^{5/2})$$
(28)

If we start with a liquid-crystalline state, i.e., g = 0 and $\alpha_0^{1/2} = 2\pi_0^{-1/2}c$ for t < 0, it is easy to show that at some time t > 0 $g(\alpha,\beta)$ has a maximum at $\alpha = \alpha_m$ given by

$$\beta = \frac{\pi}{16} (E/\nu L^3)^2 (3\alpha_{\rm m}^2 - 5\pi^{-1/2} c \alpha_{\rm m}^{-3/2})$$
(29)

(provided the solution is still entangled at α_m). However, the function g is never negative so that $\alpha(t)$ increases with

time. The nonmonotone behavior of the time derivative of $\alpha(t)$ can also be proved for initially isotropic states provided the elongational rate is high enough. Equation 29 with c = 0 still holds, but $\alpha(t)$ must be much larger than unity if eq 27 is to remain a satisfactory approximation.

It is of interest to compare the behavior of $\alpha(t)$ with that of the order parameter $S(t) = \langle 3/2 \cos^2 \theta - 1/2 \rangle$. The time derivative is given by

$$\frac{\partial S}{\partial t} \sim 3\alpha^{-2}g(\alpha,\beta) \tag{30}$$

It is easy to prove that both S and $\partial S/\partial t$ show a monotone time dependence: the first increasing and the second decreasing.

The disentangled state is now characterized by the time-dependent form of eq 3. Thus, $\alpha(t)$ increases according to eq 28 until $\alpha(t)$ becomes so large that

$$4\pi^{-1/2}L^3\nu\alpha^{-1/2}(t) < E \tag{31}$$

In that case eq 10 also has an asymptotic solution, with eq 27 as the first term and $\alpha(t)$ given by

$$\frac{\partial \alpha}{\partial t} = 2\alpha D_{\rm ro}(\beta - \alpha + 2 \pi^{-1/2} c \alpha^{1/2}) \tag{32}$$

This derivative has a maximum for

$$\alpha_{\rm m}^{1/2} = \frac{3}{4} \pi^{-1/2} c + \frac{1}{4} (9\pi^{-1}c^2 + 8\beta)^{1/2}$$
(33)

Again, both S and $\partial S/\partial t$ have a monotone time dependence.

Elongational Stress

The stress tensor is approximated by the usual expression⁷

$$\sigma = 3\nu k_{\rm B} T \langle \mathbf{u}\mathbf{u} - \frac{1}{3}\mathbf{I} \rangle + \nu k_{\rm B} T \langle (\nabla_{\mathbf{u}} \mathbf{V})\mathbf{u} \rangle + \frac{1}{2}\nu \zeta \kappa \langle \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} \rangle$$
(34)

with I the unit tensor. The first term arises from the decrease in entropy, the second arises from the self-consistent nematic field, and the third is the hydrodynamic stress proportional to the (effective) rotational friction coefficient of a rod. We neglect hydrodynamic interactions between the rods.

It is straightforward to calculate the stress when the solution is relatively highly ordered ($\alpha(t) \gg 1$). In view of eq 9 and 27, eq 34 reduces to

$$\sigma_{33} - \sigma_{11} = 3\nu k_{\rm B} T (1 - 3\alpha^{-1}(t)) - 6\pi^{-1/2} \nu k_{\rm B} T c \alpha^{-1/2}(t) (1 - A\alpha^{-1}(t)) + \frac{1}{2}\nu \zeta \epsilon (1 - 6\alpha^{-1}(t))$$
(35)

An explicit solution of the stress can be obtained by inserting $\alpha(t)$, the solution to eq 28 when h(t) > E and the solution to eq 32 when h(t) < E. Note that we are forced to include a factor $(1 - A\alpha^1)$ in the term stemming from the nematic potential (proportional to c). The constant A would equal $5^{13}/_{16}$ if the Onsager trial function were to be employed. The stress must be zero when flow is absent. The first term in eq 35 agrees with the expansion calculated by Kuzuu and Doi.¹⁴

There are several proposals for the form of the friction coefficient. One extreme is to assume that hydrodynamic dissipation is involved only when a test rod reorients in the pure solvent and none occurs as it slides along the "wall" of the constraining tube⁷

$$\zeta = \zeta_0 = \frac{k_{\rm B}T}{D_{\rm ro}} \approx \frac{1}{4}\pi\eta_{\rm s}L^3 \tag{36}$$

where η_s = viscosity of the solvent. The opposite extreme³¹ is to postulate that the rod rotates through an effective

medium having a viscosity $\eta_{\rm eff} = \eta_{\rm s} D_{\rm ro} / D_{\rm r}$

$$\zeta = \zeta_{\rm eff} = \frac{k_{\rm B}T}{\bar{D}_{\rm r}} \tag{37}$$

Others^{15,43} have tried to account for hydrodynamic interactions by using an effective ζ_H depending on the hydrodynamic screening length ζ_H

$$\zeta = \zeta_H \approx \frac{\pi \eta_s L^3}{3 \log \left(\xi_{H/D}\right)} \tag{38}$$

In particular, Batchelor's limit¹⁵ is obtained as follows. If the elongational rate is very high, the rods eventually align parallel to the direction of elongation, which implies $\beta \approx$ $\alpha \gg L/D$. Hence, the first inequality of eq 19 breaks down so that the rods can no longer be viewed as very slender. Although the entanglement equations 2, 4, and 23 cease to be valid and higher virial terms now come into play, a moment's reflection shows that the rods are not entangled if the volume fraction φ is much smaller than unity. Even with additional interactions, the terms analogous to the first two in eq 36 will be negligible for very high $\dot{\epsilon}$. Thus we obtain¹⁵

$$\sigma_{33} - \sigma_{11} = \frac{1}{2}\nu\zeta_H \dot{\epsilon}$$
(39)

where $\xi_H \approx D \varphi^{-1/2}$ is of the order of the average distance between the rods.

It is easy to assess the impact of the hydrodynamic stress for the liquid-crystalline phase in the limit of weak steady flow. If we denote the ratio of the hydrodynamic to the elastic stress by H, we find that the elongational viscosity in the entangled state, h > E, is given by

$$\bar{\eta}_{0} = \frac{\sigma_{33} - \sigma_{11}}{\epsilon} \bigg|_{\epsilon=0} \sim \frac{72\eta_{s}}{\pi c E^{2}} \bigg(\frac{L}{D}\bigg)^{3} [1 + O(c^{-2}) + H(1 + O(c^{-2}))]$$
(40)

where

$$H = \frac{\pi}{144} (D/L)^2 E^2 c^2 \tag{41}$$

if eq 36 applies and where

$$H = \frac{4}{9}\pi^{-1}c^2 \tag{42}$$

if eq 37 is correct. Equation 40 agrees with ref 8 and 9 if we neglect the hydrodynamic stress.

Concluding Remarks

Evidence for the disentanglement of stiff polymers by strong elongational flow is implied in Figure 16 of ref 44. Peiffer et al. measured the steady-state retardation or birefringence of semidilute solutions of xanthan as a function of the elongational rate. When the birefringence is normalized to 100% concentration, the measurements for two solutions (1350 and 2000 ppm) coincide beyond some rate $\dot{\epsilon}_c$. Hence, the steady-state equations governing the reorientation of the macromolecules must also be identical for these two semidilute solutions (for $\dot{\epsilon} > \dot{\epsilon}_c$). But the more highly concentrated solution (2000 ppm) reorients faster when $\dot{\epsilon} < \dot{\epsilon}_c$. These phenomena are consistent with the idea of disentanglement proposed here. Unfortunately, quantitative comparison is precluded because the sample used by Peiffer et al. was very polydisperse.

Further evidence for the increase of rotational diffusion with elongational rate is presented by Odell et al.²³ They measured \bar{D}_r for a semidilute solution of a very stiff heterocyclic polymer. For small $\dot{\epsilon}$, D_r exhibited a linear dependence on $\dot{\epsilon}$ but leveled off at higher values. The data for higher ϵ are in good agreement with the $\epsilon^{1/2}$ dependence predicted by eq 3, 20, and 22 for c = 0 (and derived previously by Kuzuu and Doi¹⁴).

It is useful to have a look at the order of magnitude of the rate needed to cause disentanglement. Let us choose E to be equal to the lower numerical bound.³⁰ Then, the equilibrium liquid crystal state would always be entangled (see eq 16 and 23). If the aspect ratio L/D is 20 and the volume fraction $\varphi = Dc/L$ is 0.3, we would need an elon-gational rate $\dot{\epsilon}$ of about $36D_{ro}$ in order to achieve disen-tanglement (see eq 24). This solution would be a liquid crystal at equilibrium. For semidilute solutions flow can force the rods to disentangle even when they are quite long. If L/D is large, say about 100, β^* in eq 24 can be simplified as $\beta^* \approx 8 \ (\varphi/E)^2 (L/D)$. An initially semidilute solution $(\varphi = 0.003; h > E)$ would become disentangled at a rate $\dot{\epsilon}$ of only $5D_{\rm ro}$.

Finally, it is pertinent to point out that eq 40 and eq 41 predict that the elongational viscosity $\bar{\eta}_0$ for a liquid crystal has a minimum at a volume fraction $\varphi = 12\pi^{-1/2}E^{-1}$. By contrast, if the rods are assumed to rotate through an effective medium (eq 37 and 40), $\bar{\eta}_0$ would show a monotone increase with concentration because $c \gtrsim 4.2$ in the nematic state. Accordingly, measurements of the elongational viscosity could be a useful means of discriminating between the two extremes proposed for ζ .

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Polymer Localization by Random Fixed Impurities: Gaussian Chains

Jack F. Douglas

National Bureau of Standards, Polymers Division, Gaithersburg, Maryland 20899. Received February 24, 1988; Revised Manuscript Received May 26, 1988

ABSTRACT: Simple dimensional analysis is employed to discuss the relevance of impurity interactions on the molecular dimensions of flexible polymers in the limits of high- and low-impurity densities. Scaling arguments account for the universal behavior of static properties observed by Baumgärtner and Muthukumar in their recent Monte Carlo simulations. An approximate model of the random impurity interaction is introduced by considering the random impurities as being analogous to an "effective surface" with which the polymer interacts. Qualitatively the same conclusions are obtained as in the scaling arguments except that the effective surface analogy provides closed form scaling functions describing the variation of the molecular dimensions as a function of the dimensionless disorder interaction. The transition to a collapsed state is found to be characterized by a critical impurity density which is a function of the chain length.

1. Introduction

Recently, Baumgärtner and Muthukumar¹ (MB) investigated the configurational properties of a polymer in an array of randomly distributed fixed obstacles ("impurities") and found a crossover from random coil to "collapsed" chain configurations with an increasing impurity concentration. For the idealized random walk model that they consider, the limiting collapsed chain dimensions are found to be independent of chain length and dependent in a universal way on the impurity concentration.

A close quantum mechanical analogue of this problem, the scattering of an electron in an array of randomly distributed impurity centers, has been studied extensively over the last 30 years, and this formalism can be transcribed with little variation to the polymer problem.²⁻¹² The polymer collapse transition due to impurities in a quantum mechanical context corresponds to a change from a free-electron (conducting) state to a localized (nonconducting) state with increasing impurity concentration. Calculations by Edwards^{8,10} using the path integral formulation of the one-electron Green's function averaged over random impurities indicate that this transition occurs because the randomly distributed impurities generate a net attractive interaction, giving rise to the localization transition for sufficient disorder. MB give the same interpretation to the polymer collapse due to a net effective attractive interaction generated by impurities.¹ Edwards and others have also noted the close mathematical analogy between electron localization and polymer collapse due to binary self-attractive excluded volume interactions.^{8,10,13}

2. The Model

Following the standard model²⁻¹² for impurity interacting electrons, MB introduce the impurity-averaged end-to-end vector distribution function for the polymer as

$$\langle G(\mathbf{R}, \mathbf{0}; N) \rangle = \int d\mathbf{R}_{\alpha} P(\mathbf{R}_{\alpha}) \int_{\mathbf{R}(0)=\mathbf{0}}^{\mathbf{R}(N)=\mathbf{R}} D[\mathbf{R}(\tau)] \exp(-H/K_{\mathrm{B}}T) \quad (2.1a)$$
$$H/K_{\mathrm{B}}T = H_{0} + H_{\mathrm{I}} \qquad (2.1b)$$

$$H_0 = (d/2l) \int_0^N d\tau |d\mathbf{R}(\tau)/d\tau|^2$$
$$H_I = (\beta_p^0/l) \sum_{\alpha=1}^{N_I} \int_0^N d\tau \,\delta[\mathbf{R}(\tau) - \mathbf{R}_{\alpha}] \qquad (2.1c)$$

where $N_{\rm I}$ is the number of impurities in the system at positions \mathbf{R}_{α} and β^{0}_{p} is a coupling constant for the point impurity-polymer interaction. $P(\mathbf{R}_{\alpha})$ describes the distribution of impurities which is taken to be random in the simulation of MB. Other choices of $P(\mathbf{R}_{\alpha})$ are of course possible, and β_{p}^{0} can be more generally taken as a random variable as well. The variable N is the chain length, d is the dimension, l is the Kuhn length, and τ is the contour distance measured along the chain. In the analogue quantum mechanical problem, N is replaced by imaginary time, the dimension d by electron mass, and the Kuhn length l by Plank's constant \hbar . See ref 2, 3, and 10 for a detailed discussion of the impurity-averaging formalism and the quantum mechanical analogue of (2.1) corresponding to the average propagator for an electron moving in a background of fixed random scatterers.

Below we introduce dimensionless units for the position vectors of the impurities and polymer chain, \mathbf{R}_{α} and $\mathbf{R}(\tau)$, respectively, and the chain length N = nl as

$$\mathbf{R}(x)(d/\langle \mathbf{R}^2 \rangle_0)^{1/2} = \mathbf{r}(x)$$
$$\mathbf{R}_{\alpha}(d/\langle \mathbf{R}^2 \rangle_0)^{1/2} = \mathbf{r}_{\alpha} \qquad x = \tau/N \quad (2.2)$$

The Hamiltonian $H/K_{\rm B}T$ in these units is equal to

$$H_{0} = (1/2) \int_{0}^{1} dx |d\mathbf{r}(x)/dx|^{2}$$
$$H_{I} = \beta_{p}^{0} (d/2\pi l^{2})^{d/2} n^{1-d/2} \sum_{\alpha=1}^{N_{I}} \int_{0}^{1} dx (2\pi)^{d/2} \delta[\mathbf{r}(x) - \mathbf{r}_{\alpha}]$$
(2.3)