DYNAMICS OF MACROMOLECULES IN CONVERGENT-CHANNEL FLOWS

Z. P. Shul'man, É. A. Zal'tsgendler, and B. M. Khusid

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The deformation of flexible and rigid macromolecules is analyzed under conditions of convergent-channel flows.

Certain pieces of equipment employed in chemical technology as well as in biotechnology make use of a dispersion medium to compress the stream of a macromolecular solution. For this case it is necessary to evaluate the effect of the shape of the convergent nozzle, the rate of flow, and the characteristics of the macromolecules on the deformation which takes place during the flow in the convergent channel and after passage through the channel (Fig. 1). The simplest of macromolecules have been used for these calculations, i.e., in the shape of flexible dumbbells and rigid axisymmetric ellipsoids. The deformation of the macromolecular flow near the axis of the convergent channel is close to elongational (the radius of the stream of the solution is considerably smaller than the radius of the convergent channel).

Flexible Macromolecules. The behavior of flexible macromolecules in various hydrodynamic situations has been analyzed in a number of papers, among which we will cite [1-6]. Flexible macromolecules are modeled by dumbbells with identical "spheres" and a nonlinear elastic link between them. If we neglect the inertial forces, then, as a consequence of the low macromolecular mass, it is possible to have

\[ \mathbf{F}_1 + \mathbf{F}_f + \mathbf{F}_B + \mathbf{F}_{\text{th}} = 0. \]  

(1)

The elastic force \( \mathbf{F}_1 = -3Nk\xi (r'/R)\mathbf{r}'/R^2 \). For the nonlinear function \( \xi (r'/R) \) we take the Warner approximation \( \xi (r'/R) = [1 - (r'/R)^2]^{-1} \). With such an approximation the elastic force sharply increases in proportion to the straightening of the circuit and tends toward infinity as \( r' \to R \), which is in accord with physical sense (for any conformation of the circuit, the length of the "head-to-tail" vector of the macromolecule cannot be greater than the length of the totally straightened circuit). The force of hydrodynamic friction which arises as a consequence of the relative motion of the solution and the spheres of the "dumbbell" is given by \( \mathbf{F}_f = \xi (r'/R)(\mathbf{v} - \mathbf{r}') \). The parameter of external friction, a function of the conformation of the circuit, is taken [5, 6] to be equal to \( \xi = \xi_0 Q(r'/R) = \xi_0 \sqrt{Nr'/R} \);
the velocity \( v_i = G_{ij} x_j \). The statistical Brownian force exerted on the "spheres" of the dumbbell is given by \( F_B = -kN \ln \psi \). The force of internal friction \( F_{iv} \) in the macromolecule is proportional to the rate of deformation, i.e., \( F_{iv} = -q/N(\bar{F}' - \bar{F}) \). The quantity \( \Omega \) can be determined from the fact that the resulting moment of the internal friction forces is equal to zero, i.e., \( \sum_{i=1}^{2} \bar{R}_i \times \bar{F}_{iv} = 0 \), which yields \( F_{iv} = -q/N(\bar{F}'-\bar{F}) \).

In deriving the equations for the moments \( <x_i x_j> \) we have to determine the form of the probability-density function \( \psi(t, \bar{F}') \). The equation of conservation (the Liouville equation) for this is

\[
\frac{\partial \psi}{\partial t} + \nabla (\vec{r} \psi) = 0.
\] (2)

With the chosen type of functional relationship for the forces included in Eq. (1), the sought quantity \( \bar{F}' \) is equal to

\[
\bar{F}' = -\frac{kN}{\bar{F}'} \left[ \bar{F}' \ln \psi - \frac{q/N}{\bar{F}' + \frac{e}{\bar{F}'} N} \left( \bar{F}' \ln \psi \right) e_r \right] - \frac{3Nk\bar{F}'}{\left( \frac{e}{N} + \frac{q/N}{\bar{F}'} \right) [1 - (r'/R)^2]} \frac{r'}{R} + \bar{G} \frac{\bar{F}'}{\bar{F}'} - \frac{q/N}{\bar{F}' + \frac{e}{\bar{F}'} N} \left( \bar{F}' \ln \psi \right) e_r.
\] (3)

Let us derive the equation for the second-order moments \( <x_i x_j> \). The averaging is accomplished with utilization of the distribution function. Utilization of (2) and (3) after algebraic transformations leads to the following equations for the moments:

\[
d \frac{d}{dt} <x_i x_j> = 2k \theta \left( \frac{\delta_{ij}}{\bar{F}'} - \frac{1}{\bar{F}'} \frac{d}{dr} \left[ \frac{1}{\bar{F}'} \frac{d}{dr} \left[ \frac{1}{\bar{F}'} \right] \right] x_i x_j \right) - \frac{6Nk \theta}{R^2} <x_i x_j> - \frac{2Nk \theta}{R^2} \frac{x_{x \bar{F}'} \delta_{ij}}{r'^2} + \frac{G_{x \bar{F}'} (x_i x_n) \delta_{ij} + (x_i x_n) \delta_{ij}}{r'^2},
\] (4)

\( i, j = 1, 2, 3. \)

The resulting equation includes the function \( \xi = \xi(r'/R) \), whose value is dependent on the conformation of the flow circuit. Two averaging methods are possible: substitute the explicit expressions for \( \xi = \xi(r'/R) \) into Eq. (4) and then do the averaging, or assume that \( \xi = \xi(\bar{F}'/R) \). For the numerical solution selected for this paper, we have chosen the second method, although we should point out that the first version presents no fundamental difficulties. For purposes of closing Eqs. (4)-(5), the fourth-order moments are expressed in terms of second-order moments. In addition, in analogy with the selected method of averaging for the terms containing \( \xi(r'/R) \), for the Warner function we assume that \( 1 - (r'/R)^2 = 1 - (r'^2/R)^2 \). The system of equations (4) is expanded to include the initial conditions at which \( t = 0; \)

\[
<x^2> = <y^2> = <z^2> = R^2/[3(N + 1)], \quad <xy> = <xz> = <yz> = 0
\] (5)

(in its original state the macromolecular solution was at rest). Analysis of problem (4)-(5) shows that under conditions of elongational flow, when only the nondiagonal components in the tensor \( G_{ij} \) are different from zero, with macromolecular deformation the diagonal components of the tensor \( a_{ij} = <x_i x_j> \) remain equal to zero.