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막대형 고분자의 희석용액의 유변학
- 새로운 약식 계산방법의 응용 -

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Rheology of Rodlike Macromolecules in Dilute Solution
- Application of a New Closure Approximation -

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요 약

막대형 고분자 희석용액의 분자론적 운동을 새롭게 개발된 약식 계산방법에 의하여 다루었다. 체계적으로 개발된 새로운 방법은 한쪽 방향성이 있는 경우나 전혀 방향성이 없는 경우에서 적절한 값을 갖도록 유도되었다. 이것을 한쪽 방향으로의 연신 흐름에 적용한 결과 알려진 해석해와 잘 일치하였으며, 난순 선단 흐름에 적용한 결과 흐름의 세기가 약할 때는 좋은 결과를 나타내었으나 흐름의 세기가 강할 때는 상당한 차이를 보여주었다.

Abstract—Molecular dynamics of rod-like macromolecules in dilute solution is considered by using a new systematic closure approximation. It gives the proper limits for both random alignment and strong uniaxial alignment. The new closure approximation is applied to a uniaxial extensional flow, and the result is in an excellent agreement with the known exact solution. It is also applied to simple shear flow and shows proper behavior for weak flow strength, but not satisfactory results for strong flow field.

Keywords: Dilute polymer solution/ Rigid polymer/ Molecular rheology/ Closure approximation/ Orientational tensor.

INTRODUCTION

Molecular dynamics of rodlike macromolecules in dilute solutions has been considered by a lot of authors including Bird *et al.* [1] and Doi *et al.* [2] who published excellent books separately. The significance of such system lies in the fact that it can serve as a theoretical basis not only for rigid polymers such as biopolymers but also for the short fiber composites [3], concentrated polymer solutions of rigid polymers, and even polymeric liquid crystal systems [4,5] with some minor modifications. In general, there are two ways to handle the dynamics of rigid rod molecule immersed in a viscous medium. One of them is to

... distribution function of such ... precisely. It is a complicated task, and it is often impossible to obtain such functions in detail or even if possible, it requires significant numerical efforts. The other way to solve this problem can be accomplished by obtaining the well-defined orientation tensors describing the average orientation of such rods. In this way it is often possible to obtain the exact solution and saves computing time and can serve as a starting point for the further numerical works. In doing so, we often encounter the fourth order orientation tensor, which is necessary to be approximated with combinations of lower order orientation tensors to make the system soluble. It is called the "closure approximation". There are several restrictions imposed for the proper closure approximation, which will be explained later. As shown in Table 1, several approximations have been developed, but they are always valid for a restricted region. For example, the random alignment closure (R) and the linear closure (L) are valid near the random alignment, and decoupling closure (D) is good for only strong alignment. Linear combinations of these two (LND) was tried to give not satisfactory results [3]. Hinch and Leal [4] tried two kinds of linear combinations of the weak and strong flow limits for the $<u_iu_j\,u_ku_l>e_{kl}$, which gave us somewhat improved results but it is very complicated to use. Here a newly designed closure approximation (NEW) is constructed through a systematic way to give a good result for the extensional flow throughout the region of flow field strength.

In sec.2, the general theory describing the dynamics of rigid rod molecules with arbitrary aspect ratio (r_e) in the viscous medium is reconsidered briefly. In sec.3, a new closure approximation is constructed and applied for the extensional flow and shear flow separately in sec.4 to demonstrate the validity of such a closure approximation. This approximation can be readily applied to the dynamics of concentrated solutions and the dynamics of polymer liquid crystals [5,6]. This latter topic is the subject of the next paper.

THEORY

Let u_i be a unit directional vector parallel to the rod and $\psi\,(u_i;\,t)$ be its distribution function.

Table 1. Range of Validity of Several Closure Approximations

	No Flow	Weak Flow Shear Flow	Strong Flow Elongational Flow
Alignment	Random		Strong
Orientation Parameter (S)	0		1
Closure Approximation	R,L	LND NEW	D

$$R:\ <u_iu_ju_ku_l>_R = \frac{1}{15}(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})$$

$$L:\ <u_iu_ju_ku_l>_L = -\frac{1}{35}(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})$$

$$+\frac{1}{7}(<u_iu_j>\delta_{kl}+<u_ku_l>\delta_{ij}+<u_iu_k>\delta_{jl}$$

$$+<u_ju_l>\delta_{ik}+<u_iu_l>\delta_{jk}+<u_ju_k>\delta_{il})$$

$$D:\ <u_iu_ju_ku_l>_D = <u_iu_j><u_ku_l>$$

$$LND:\ <u_iu_ju_ku_l>_{LND} = (1-f)<u_iu_ju_ku_l>_L$$

$$+f<u_iu_ju_ku_l>_D$$

$$H\text{-}L:\ <u_iu_ju_ku_l>_{H-L} = -\frac{1}{5}<u_iu_j><u_ku_l>+$$

$$\frac{3}{5}(<u_iu_k><u_ju_l>+<u_ju_k><u_iu_l>)$$

$$-\frac{2}{5}\delta_{ij}<u_pu_l><u_pu_k>+\frac{2}{5}\delta_{ij}<u_ku_l>$$

$$NEW:\ <u_iu_ju_ku_l>_{NEW} = f<u_iu_j><u_ku_l>$$

$$+(\frac{f}{3}-\frac{1}{5})(\delta_{ij}<u_ku_l>+\delta_{kl}<u_iu_j>)$$

$$+(\frac{f}{3}-\frac{1}{5})(-\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})$$

$$+(\frac{2}{5}-\frac{1}{2}f)(<u_iu_k>\delta_{jl}+<u_ju_l>\delta_{ik}+<u_iu_l>\delta_{jk}$$

$$+<u_ju_k>\delta_{il})$$

$$u_iu_i = 1 \qquad (2\text{-}1)$$

Here we use the Cartesian summation convention [6] where repeated subscripts imply summation. In very dilute solution, the rotational motion of the rods is independent of the translational motion, so that it can be described by the Smoluchowski equation for rotational diffusion [5]:

$$\frac{\partial \psi}{\partial t} = D \frac{\partial}{\partial u_i} \left(\frac{\partial \psi}{\partial u_i} \right) - \frac{\partial}{\partial u_i} (\dot{u}_i \psi) \qquad (2\text{-}2)$$

Here D is the rotational diffusion constant given by

$$D = 3kT \frac{\ln(r_e)}{\pi \mu_s L^3} \qquad (2\text{-}3)$$

Here kT is the Boltzmann temperature, L and r_e are the length and the aspect ratio of the rod. μ_s is the shear viscosity of the solvent. $\dot{u}_i$ is the local rate of change of the unit directional vector due to the macroscopic velocity field, which can be given by

$$\dot{u}_i = \omega_{ij} u_j + \lambda e_{ij} u_j - \lambda e_{kl} u_k u_l u_i \qquad (2\text{-}4)$$

here λ is a form factor related to the aspect ratio r_e as followings.

$$\lambda = \frac{(r_e^2 - 1)}{(r_e^2 + 1)} \qquad (2\text{-}5)$$

The macroscopic velocity field can be described with the vorticity tensor ω_{ij} and the rate of strain tensor e_{ij}, which are defined with the position vector x_i and the velocity vector v_i

$$\omega_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i} \right). \qquad (2\text{-}6a)$$

$$e_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \qquad (2\text{-}6b)$$

Here we define the orientation tensor which is closely related not only to the stress tensor but also refractive index tensor.

$$S_{ij} = \langle u_i u_j \rangle - \frac{1}{3} \delta_{ij} \qquad (2\text{-}7)$$

where $\langle B \rangle = \int d^2u\, \psi B$. (2-8)

Then it is easy to construct an equation for S_{ij} by multiplying equation eq (2-2) by $u_i u_j - \frac{1}{3}\delta_{ij}$, and then integrating over u_i domain.

$$\frac{\partial S_{ij}}{\partial t} = -6DS_{ij} + \omega_{ik}\langle u_k u_j \rangle + \omega_{jk}\langle u_k u_i \rangle + \lambda e_{ik} \langle u_k u_j \rangle + \lambda e_{jk}\langle u_k u_i \rangle - 2\lambda e_{kl}\langle u_k u_l u_i u_j \rangle \qquad (2\text{-}9)$$

NEWLY DEVELOPED CLOSURE APPROXIMATION

As shown in eq(2-9), it is necessary to approximate e_{kl} $\langle u_k u_l u_i u_j \rangle$ as a combination of lower order orientation tensors. Due to the symmetry of i and j,k and l, $\langle u_i u_j u_k u_l \rangle$ can be approximated as follows

$$\begin{aligned} \langle u_i u_j u_k u_l \rangle = {} & \lambda_1 \langle u_i u_j \rangle \langle u_k u_l \rangle + \lambda_2 (\langle u_i u_k \rangle \langle u_j u_l \rangle + \langle u_i u_l \rangle \langle u_j u_k \rangle) + \lambda_3 \delta_{ij} \\ & \langle u_p u_k \rangle \langle u_p u_l \rangle + \lambda_4 \delta_{kl} \langle u_i u_p \rangle \langle u_j u_p \rangle + \lambda_5 \delta_{kl} \langle u_i u_j \rangle + \lambda_6 (\delta_{ik} \\ & \langle u_j u_l \rangle + \delta_{il} \langle u_j u_k \rangle + \delta_{jk} \langle u_j u_k \rangle + \delta_{jk} \langle u_i u_l \rangle + \delta_{jl} \langle u_i u_k \rangle) + \lambda_7 \delta_{ij} \\ & \langle u_k u_l \rangle + \lambda_8 \delta_{ij} \delta_{kl} + \lambda_9 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \end{aligned} \qquad (3\text{-}1a)$$

It now remains to determine the constant λ 's. They must satisfy the normalization condition,

$$\langle u_i u_i u_k u_l \rangle = \langle u_k u_l \rangle \qquad (3\text{-}2)$$

Then it can be easily seen

$$\lambda_1 + 4\lambda_6 + 3\lambda_7 = 1 \qquad (3\text{-}3a)$$

$$2\lambda_2 + 3\lambda_3 = 0 \qquad (3\text{-}3b)$$

$$\lambda_4 = 0 \qquad (3\text{-}3c)$$

$$\lambda_5 + 3\lambda_8 + 2\lambda_9 = 0 \qquad (3\text{-}3d)$$

The next condition is that the approximation should approach the proper limit for the extreme cases. For random alignment, both the second moment and fourth moment should be isotropic.

Therefore,

$$\frac{1}{15} = \frac{\lambda_1}{9} + \frac{\lambda_3}{9} + \frac{1}{9}\lambda_4 + \frac{1}{3}\lambda_5 + \frac{1}{3}\lambda_7 + \lambda_8 \qquad (3\text{-}4a)$$

$$\frac{1}{15} = \frac{1}{9}\lambda_2 + \frac{2}{3}\lambda_6 + \lambda_9 \qquad (3\text{-}4b)$$

More conditions are needed to determine the coefficients. For the extremely strong alignment, if we can assume the unit directional vector u_i should be aligned with a fixed directional vector n_i then we have

$$\lambda_1 + 2\lambda_2 = 1 \qquad (3\text{-}5a)$$

$$\lambda_3 + \lambda_7 = 0 \qquad (3\text{-}5b)$$

$$\lambda_4 + \lambda_5 = 0 \qquad (3\text{-}5c)$$

$$\lambda_6 = \lambda_8 = \lambda_9 = 0 \tag{3-5d}$$

Equations (3-3), (3-4) and (3-5) can be solved to give us a unique set of coefficients.

$$\lambda_1 = -\frac{1}{5},\ \lambda_2 = \frac{3}{5},\ \lambda_3 = -\frac{2}{5},\ \lambda_7 = \frac{2}{5}$$

all other $\lambda = 0$ (3-6)

It is nothing but Hinch-Leal approximation [7].

As another choice for the strong alignment, we can assume that $<u_iu_ju_ku_l>A_{kl}$ approaches to the exact limit. Here A_{kl} is a symmetric, 2nd order tensor. There is no restriction imposed on the tracelessness of A_{ij}, so that it is possible to approximate the terms related to the external electric or magnetic field. The underlying physical implication is that such an external field is not too strong to lock u_i to a fixed direction n_i, but strong enough to give the nearly uniaxial distribution around n_i parallel to the external vector field H_i. So that the $<u_iu_ju_ku_l>H_kH_l$ goes to a proper limit.

Then we have

$$\lambda_1 + 2\lambda_2 + \lambda_4 + \lambda_5 + 4\lambda_6 + 2\lambda_9 = 1 \tag{3-7a}$$

$$\lambda_3 + \lambda_7 + \lambda_8 = 0 \tag{3-7b}$$

Additionally, the normalization condition of $<u_iu_ju_ku_k> = <u_iu_j>$ is used.

$$\lambda_1 + 4\lambda_6 + 3\lambda_5 = 1 \tag{3-8a}$$

$$2\lambda_2 + 3\lambda_4 = 0 \tag{3-8b}$$

$$\lambda_3 = 0 \tag{3-8c}$$

$$\lambda_7 + 3\lambda_8 + 2\lambda_9 = 0 \tag{3-8d}$$

Then we have a set of one parameter solution

$$\lambda_1 = f \tag{3-9a}$$

$$\lambda_2 = \lambda_3 = \lambda_4 = 0 \tag{3-9b}$$

$$\lambda_5 = \lambda_7 = \lambda_9 = -\lambda_8 = \frac{1}{3}f - \frac{1}{5} \tag{3-9c}$$

$$\lambda_6 = \frac{2}{5} - \frac{1}{2}f \tag{3-9d}$$

The unknown parameter f can be arbitrarily chosen. It will be explained later.

In summary, the newly designed closure approximation is given as follows.

$$<u_iu_ju_ku_l> = f<u_iu_j><u_ku_l> + \left(\frac{f}{3} - \frac{1}{5}\right)(-\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \left(\frac{f}{3} - \frac{1}{5}\right)(<u_iu_j>\delta_{kl} + <u_ku_l>\delta_{ij}) + \left(\frac{2}{5} - \frac{1}{2}f\right)(<u_iu_k>\delta_{jl} + <u_ju_l>\delta_{ik} + <u_ku_l>\delta_{jk} + <u_lu_k>\delta_{il}) \tag{3-1b}$$

Now the eq(2-9) can be converted into eq (3-10)

$$\frac{\partial S_{ij}}{\partial t} = -6DS_{ij} + \omega_{ik}S_{kj} + \omega_{jk}S_{ki} + \frac{2}{5}\lambda e_{ij} + \lambda\left(2f - \frac{3}{5}\right)(e_{ik}S_{kj} + e_{jk}S_{ki}) - 2\lambda f S_{kl}e_{kl}S_{ij} - 2\lambda\left(\frac{2}{3}f - \frac{1}{5}\right)S_{kl}e_{kl}\delta_{ij} \tag{3-10}$$

Once the orientational tensor S_{ij} is obtained, the stress tensor due to the polymer chain can be given as the sum of the elastic stress and viscous stress (See eq(8-123) in the book of Doi and Edwards [2]). Here the case of thin rod with $\lambda = 1$ is considered.

$$T_{ij} = 3ckTS_{ij} + \frac{ckT}{2D}e_{kl}<u_iu_ju_ku_l> \tag{3-11a}$$

Then, we have

$$T_{ij} = \frac{3}{2}ckTS_{ij} + \frac{ckT}{4D}\left(\omega_{ik}S_{kj} + \omega_{jk}S_{ki} + \frac{2}{3}e_{ij} + e_{ik}S_{kj} + e_{jk}S_{ki}\right) \tag{3-11b}$$

APPLICATION TO STEADY FLOW FIELDS

Extensional flow

The uniaxial extensional flow case is examined in detail to test the new closure approximation. The flow field is governed by the following two tensors.

$$\omega_{ij} = 0 \tag{4-1a}$$

$$e_{ij} = \frac{3}{2}\dot{\epsilon}\left(\delta_{i1}\delta_{j1} - \frac{1}{3}\delta_{ij}\right) \tag{4-1b}$$

Here $\dot{\epsilon}$ is the rate of strain imposed.

In this case, it is natural to assume the S_{ij} has the same axial symmetry.

$$S_{ij} = S\left(\delta_{i1}\delta_{j1} - \frac{1}{3}\delta_{ij}\right) \tag{4-2}$$

Then eq(3-10) reduces to

$$10f\xi S^2 + (5 + 3\xi - 10f\xi)S - 3f\xi = 0 \tag{4-3}$$

where $\xi = \dot{\epsilon}/6D$. Then the analytic solution for S is

$$S = \frac{10f-3}{20f} - \frac{1}{4f\xi} + \sqrt{\frac{(10f+3)^2}{400f^2} + \frac{(3-10f)}{40f^2\xi} + \frac{1}{16f^2\xi^2}} \quad (4\text{-}4a)$$

To see the validity of this approximation, let us compare it with the exact result and the approximate result of Doi and Edwards [2] which is obtained by using the decoupling closure approximation. The approximate result from H-L closure is also compared.

$$S_{EXACT} = \frac{\int_0^1 dt\,(\frac{3}{2}t^2 - \frac{1}{2})\exp(\frac{9}{2}\xi t^2)}{\int_0^1 dt\,\exp(\frac{9}{2}\xi t^2)} \quad (4\text{-}4b)$$

$$S_{DOI} = \frac{1}{4} - \frac{1}{4\xi} + \sqrt{\frac{9}{16} - \frac{1}{8\xi} + \frac{1}{16\xi^2}} \quad (4\text{-}4c)$$

$$S_{H-L} = \frac{1}{8} - \frac{5}{8\xi} + \sqrt{\frac{49}{64} - \frac{5}{32\xi} + \frac{25}{64\xi^2}} \quad (4\text{-}4d)$$

To see the difference quickly, let us examine the limit of small ξ.

$$S_{EXACT} = S_{NEW} = S_{HL} = \frac{3}{5}\xi \text{ for small } \xi \quad (4\text{-}5a)$$

$$\text{but } S_D = \xi \text{ for small } \xi \quad (4\text{-}5b)$$

New clousure gives the exact limit for small ξ. On the other hand for the limit of large ξ, the decoupling closure gives the exact solution and also we can make the new closure give the exact limit up to order of $1/\xi$ by choosing f = 6/5. It can be compared with the S_{H-L} which understimates S a little. Detailed values of S as a function of ξ is shown in Fig. 1 in which one can see the difference between three closure approximations.

$$S_{EXACT} = S_D = 1 - \frac{1}{3\xi} \text{ for large } \xi \quad (4\text{-}6a)$$

$$S_{NEW} = 1 - \frac{5}{(3+10f)\xi} \text{ for large } \xi \quad (4\text{-}6b)$$

$$S_{H-L} = 1 - \frac{5}{7\xi} \text{ for large } \xi \quad (4\text{-}6c)$$

Then from eq(3-11b), the extensional viscosity is given by

$$\mu_e - 3\mu_s = [T_{11} - T_{22}]/\dot{\epsilon} = \frac{3}{2}ckT[S + S\xi + \xi] \quad (4\text{-}7a)$$

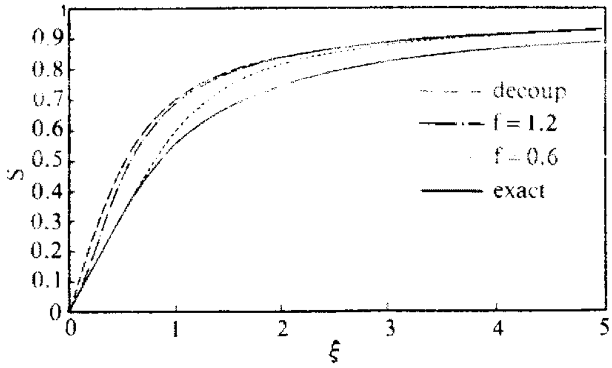

Fig. 1. Orientational parameter S as a function of ξ. From the top in the region of small ξ, Decoupling closure (eq. 4-4c), new closure (eq. 4-4a) with f = 1.2, exact solution (eq. 4-4b), and new closure with f = 0.6.

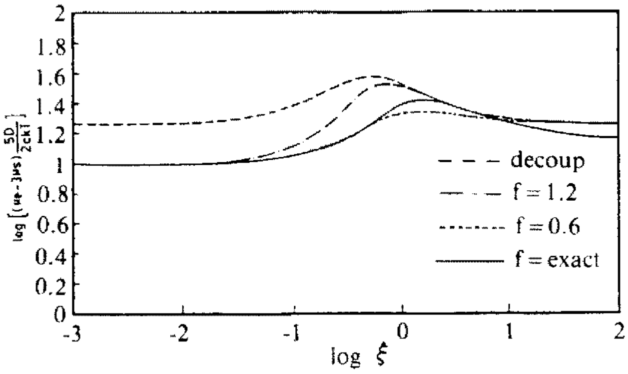

Fig. 2. Extensional viscosity as a function of ξ. From the top in the region near $\xi = 0$, decoupling closure, new closure with f = 1.2, exact solution, and new closure with f = 0.6.

The extensional viscosity is predicted to be constant for both small and large ξ.

$$\text{As } \xi \to 0,\ \mu_e - 3\mu_s \to \frac{2ckT}{5D} \quad (4\text{-}7b)$$

$$\text{As } \xi \to \infty,\ \mu_e - 3\mu_s \to \frac{ckT}{2D} \quad (4\text{-}7c)$$

The exact extensional viscosity is known as

$$\mu_e - 3\mu_s = \frac{ckT}{24D}\frac{\int_0^1 (\frac{2}{\xi} + 3t^2 - 1)(3t^2 - 1)\exp[\frac{9}{2}\xi t^2]dt}{\int_0^1 dt\,\exp[\frac{9}{2}\xi t^2]} \quad (4\text{-}8)$$

With this exact value, three different approximated cases are compared in Fig.2.

As seen in the region of small ξ, new approximation gives us pretty good results regardless of value (f = 0.6, f = 1.2). On the other hand, decoupling approximation gives us a wrong result.

For large ξ, every approximation slightly overestimate including the decoupling one. Therefore it is hard to tell that the decoupling approximation is truely valid near the strong alignment. The reason is that even for the strong alignment it is always necessary to have 4th order orientational parameter along with the 2nd order orientational parameter S.

Every approximation described here is essentially 2nd order approximation, so that it is not enough to describe the exact behavior in the region of large ξ. And also it is one of the reasons why f = 0.6 is chosen in the new approximation. As you see in eq(3-1b), it is the only way to have proper limit of 4th moment when the rod aligns strongly along a unidirectional vector n_i. The case of f = 0.6 gives us best results over a wide range of ξ as shown in Fig. 2.

Simple shear flow

In this case,

$$e_{ij}=\dot{\gamma}/2\,(\delta_{i1}\delta_{j2}+\delta_{i2}\delta_{j1}) \tag{4-9a}$$

$$\omega_{ij}=\dot{\gamma}/2\,(\delta_{i1}\delta_{j2}-\delta_{i2}\delta_{j1}) \tag{4-9b}$$

It is natural that we have only S_{11}, S_{22}, S_{12} ($=S_{21}$) and S_{33}. All other terms are zero.

Since $S_{33}=-(S_{11}+S_{22})$, only 3 nonlinear equations should be solved for the orientation tensor.

$$S_{11}=\xi\{(\frac{4}{5}+\frac{2}{3}f)-2fS_{11}\}S_{12} \tag{4-10a}$$

$$S_{22}=\xi\{(-\frac{6}{5}+\frac{2}{3}f)-2fS_{22}\}S_{12} \tag{4-10b}$$

$$S_{12}=\xi\{\frac{1}{5}+(f-\frac{13}{10})S_{11}+(f+\frac{7}{10})S_{22}-2fS_{12}^2\} \tag{4-10c}$$

where $\xi=\dot{\gamma}/6D$.

It is easy to eliminate S_{11} and S_{22} from these three equations.

$$S_{12}=\frac{\xi}{5(1+2f\xi S_{12})}+\frac{[\frac{4}{3}(f-\frac{3}{10})^2-1]\xi^2 S_{12}}{(1+2f\xi S_{12})^2} \tag{4-11}$$

Then S_{11} and S_{22} can be obtained respectively once S_{12} is determined. Then the shear viscosity can be given as follows.

$$\mu-\mu_s=\frac{ckT}{2D}\left[\frac{S_{12}}{\xi}+\frac{1}{15}+(\frac{2}{5}-\frac{f}{2})(S_{11}+S_{22})+fS_{12}^2\right] \tag{4-12}$$

In the limit of small ξ,

$$S_{12}=\frac{1}{5}\xi \tag{4-12a}$$

$$S_{11}=(\frac{4}{25}+\frac{2}{15}f)\xi^2 \tag{4-12b}$$

$$S_{22}=(-\frac{6}{25}+\frac{2}{15}f)\xi^2 \tag{4-12c}$$

Therefore the shear viscosity and first normal stress difference coefficient are obtained as constants.

$$\mu-\mu_s=\frac{2ckT}{15D} \tag{4-13a}$$

$$\psi_1=\frac{ckT}{30D^2} \tag{4-13b}$$

It turns out to be equal to the rigorous values [2] as expected.

For comparison, the exact numerical shear viscosity is plotted in Fig. 3 with the approximate viscosity obtained in this analysis. The detailed procedure to obtain the exact numerical value is well explained in Stewart and Sorensen [7]. Once the orientation distribution function is obtained, contribution of polymer chain in the shear viscosity can be obtained by averaging over this distribution.

$$(\mu-\mu_s)\,(\frac{15D}{2ckT})=\frac{15}{4\xi}\langle u_1u_2\rangle+\frac{15}{4}\langle u_1^2u_2^2\rangle \tag{4-14}$$

As shown in Fig. 3, our approximate result is well representing the exact behavior until log ξ is 0.5. On the other hand, the approximate result from decoupling closure is not good at all except the nature of shear thinning in the large ξ region.

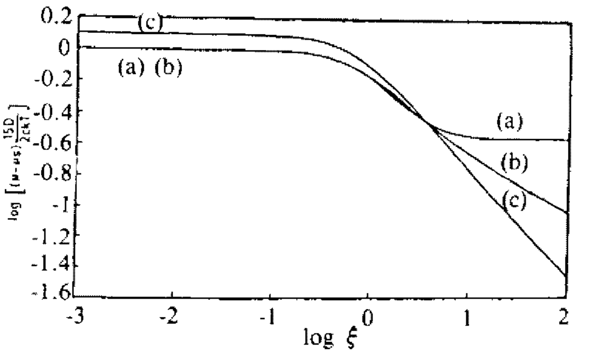

Fig. 3. Shear viscosity as a function of ξ. Upper one (c) is from decoupling approximation, lower one (a) from new closure with f = 0.6, and (b) from numerical solution in the region of small ξ.

CONCLUSION

The newly developed closure approximation is applied for the dynamics of dilute solution of rigid macromolecules to show the satisfactory results for wide range of flow strength. It is clear that it may be good for dynamics of polymer liquid crystals where we have two sources of fourth order tensors. For example, if we deal with a highly ordered polymer liquid crystal with weak flow condition, the newly developed closure will be a better one than the simple decoupling one. This is a subject of next paper which is under consideration in our laboratory. In the case of shear flow, the new closure is fairly good for weak flow but not satisfactory for strong flow, for which other closure is definitely necessary.

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