

VISCOSITY OF THE DILUTE SOLUTION OF FLEXIBLE POLYMER MOLECULES

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In this paper the statistical theory of viscosity of the dilute solution of flexible polymer molecules is represented

In what follows we will consider the shear viscosity of the dilute solution of flexible polymer molecules. The shear viscosity coefficient is expressed by the time correlation function (TCF) of the microscopic shear stress tensor $\hat{\sigma}_{12}$ (see, for example [1, 2])

$$s = (\beta/V) \langle \hat{\sigma}_{12}(t) \hat{\sigma}_{12}(0) \rangle, \quad (1)$$

where V is volume of system, $\beta = (k_B T)^{-1}$.

The difficulty of calculation $s(t)$ is connected with a general difficulty evaluation TCF. The problems are appeared also of we make use of the method of kinetic equations.

Let me introduce the normalized TCF

$$c(t) = s(t) / s(0). \quad (2)$$

For calculation of $c(t)$ we will apply the method of the memory function due to Zwanzig–Mori and asymptotic approach [1, 2].

The complex shear stresses TCF is

$$c(\omega) = \int_0^{\infty} c(t) \exp(-i\omega t) dt = c''(\omega) - ic'(\omega). \quad (3)$$

Then the coefficient of shear viscosity defined by

$$\eta(\omega) = s(0) c''(\omega), \quad (4)$$

here ω is frequency.

For calculation the function $c(t)$ the Zwanzig–Mori equation is applied

$$\frac{dc(t)}{dt} = - \int_0^t M(t-\tau) c(\tau) d\tau, \quad (5)$$

where $M(t)$ is memory function.

In general case the microscopic stress tensor due to interaction between molecules define as [2]

$$\hat{\sigma}_{ij} = - \sum_{\nu, \mu} F_i^{\nu\mu} X_j^{\nu\mu}. \quad (6)$$

In order to overcome the difficulty calculation TCF $s(t)$ we will use the M.Doï and S. Edwards model for microscopic stress tensor in the case of chain molecules [3]

$$\hat{\sigma}_{ij} = K \sum X_i X_j, \quad K = \frac{3k_B T}{l_0^2}. \quad (7)$$

Here l_0 is the monomer length, $\mathbf{r}(X_i)$ is the bond vector directed along monomer, k_B is Boltzmann constant. In other words, we used the Gaussian bead–spring model.

In order to carry out the calculations we used the Fourier series for vector \mathbf{r} . The coefficients of the above mentioned series defined as [3, 4]

$$x_i(p) = \frac{1}{N} \int_0^N ds x_i(s, t) \cos \frac{\pi p s}{N}, \quad (8)$$

where N is the number monomers in molecule.

Then the microscopic stress tensor is

$$\hat{\sigma}_{ij} = K \sum_{p=1}^{\infty} \frac{2\pi^2 p^2}{N} x_i(p) x_j(p). \quad (9)$$

In the case of the shear viscosity

$$\hat{\sigma}_{12} = K \sum_p \frac{2\pi^2 p^2}{N} x_1(p) x_2(p). \quad (9')$$

We note that modes $x_i(p)$ are independent.

The formal solution of the equation (5) can be performed by means of the Fourier–Laplace transformation

$$c(x) = \int_0^{\infty} e^{-izt} c(t) dt, \quad z = \omega - i\varepsilon. \quad (10)$$

Then we find

$$c(z) = \frac{1}{iz + M(z)} \quad (11)$$

and for $z = \omega - i\varepsilon$ $\varepsilon \rightarrow 0$ we obtain

$$c(\omega) = \frac{1}{i\omega + M(\omega)}, \quad M(\omega) = \lim_{\varepsilon \rightarrow 0} M(\omega - i\varepsilon), \quad (12)$$

$$M(\omega) = \int_0^{\infty} e^{-i\omega t} M(t) dt = M''(\omega) - iM'(\omega). \quad (13)$$

In result we find

$$c''(\omega) = \frac{M''(\omega)}{(M''(\omega))^2 + (\omega - M'(\omega))^2}. \quad (14)$$

The memory function is defined the next model [5, 6]

$$M(t) = a \operatorname{sech} bt. \quad (15)$$

The evaluation of parameters a and b will be considered later on base of the asymptotic expression for $s(t)$ for case short times. With help (15) we find

$$M''(\omega) = \frac{\pi a}{2b} \operatorname{sech} \frac{\pi \omega}{2b}, \quad (16)$$

$$M'(\omega) = -\frac{ia}{2b} \left[\Psi \left(\frac{1}{4} + \frac{i\omega}{4b} \right) - \Psi \left(\frac{1}{4} - \frac{i\omega}{4b} \right) - \frac{\pi a}{2b} \tanh \frac{\pi \omega}{2b} \right], \quad (17)$$

where $\Psi(x)$ is the Euler psi-function.

The frequency-dependent coefficient of shear viscosity defined as

$$\eta(\omega) = s(0) \tau \operatorname{sech} \frac{\pi \omega}{2b} \left[\left(\operatorname{sech} \frac{\pi \omega}{2b} \right)^2 + \zeta^2(\omega) \right]^{-1}, \quad \tau = \frac{2b}{\pi a}. \quad (18)$$

At $\omega \rightarrow 0$ we find the low-frequency viscosity coefficient

$$\eta(0) = s(0) \tau. \quad (19)$$

Now we proceed to the calculation of the coefficients a and b . For this end we will use the short-time expression of the quantity $s(t)$. Above mentioned asymptotical expansion has the form

$$s(t) = s(0) - \frac{t^2}{2!} s_2 + \frac{t^4}{4!} s_4. \quad (20)$$

Here $s(0) = \frac{\beta}{V} \langle \hat{\sigma}_{12}(0) \hat{\sigma}_{12}(0) \rangle$ is shear modulus.

$$s_2 = \frac{\beta}{V} \langle \dot{\hat{\sigma}}_{12}(0) \dot{\hat{\sigma}}_{12}(0) \rangle, \quad s_4 = \frac{\beta}{V} \langle \ddot{\hat{\sigma}}_{12}(0) \ddot{\hat{\sigma}}_{12}(0) \rangle. \quad (21)$$

The parameters a and b defined as

$$a = s_2 / s_0, \quad b = \sqrt{\frac{s_4 - s_2}{s_2 - s_0}}, \quad (22)$$

In (18) and (19)

$$\tau = 2b / \pi a. \quad (23)$$

The quantity τ is time of correlation for TCF $s(t)$. For evaluation s_0 , s_2 and s_4 we used expression (9') for stress tensor.

Taking into account the independence of modes $x_i(p)$, we obtain

$$s_0 = \frac{\beta}{V} \langle \hat{\sigma}_{12}(0) \hat{\sigma}_{12}(0) \rangle = \frac{\beta}{V} K^2 \sum_p \left(\frac{2\pi^2 p^2}{N} \right)^2 \langle x_1^2(p) \rangle \langle x_2^2(p) \rangle. \quad (24)$$

But

$$\langle x_1^2(p) \rangle = \langle x_2^2(p) \rangle = \frac{N}{\beta 2\pi^2 p^2 K}. \quad (25)$$

and there fore

$$s_0 = nk_B T, \quad (26)$$

where n is the density number for molecules.

In what follows we shall consider the separate mode with number p . For evaluation $s_2 = (\beta/V)\langle\dot{\hat{\sigma}}_{12}(0)\dot{\hat{\sigma}}_{12}(0)\rangle$ we must at first find

$$\dot{\hat{\sigma}}_{12} = K \frac{2\pi^2 p^2}{N} (\dot{x}_1(p)x_2(p) + x_1(p)\dot{x}_2(p)). \quad (27)$$

Take into account that

$$\begin{aligned} \dot{x}_1(p) &= \frac{1}{N} \int_0^N ds v_1(s,t) \cos \frac{\pi s p}{N}, \\ \dot{x}_2(p) &= \frac{1}{N} \int_0^N ds v_2(s,t) \cos \frac{\pi s p}{N}, \end{aligned} \quad (28)$$

where v_1 and v_2 is components of the vector $\mathbf{v} = \dot{\mathbf{r}}$, which is the relative velocity the two adjacent beads. Bearing in mind that

$$\langle v_1^2 \rangle = \langle v_2^2 \rangle = \frac{k_B T}{\mu}, \quad (29)$$

where μ is the reduced mass of the beads, we obtain

$$s_2 = \frac{6n\pi^2 (k_B T)^2 p^2}{N\mu l_0^2}. \quad (30)$$

In a similar way we find

$$s_4 = (\beta/V)\langle\ddot{\hat{\sigma}}_{12}(0)\ddot{\hat{\sigma}}_{12}(0)\rangle$$

At first we write

$$\ddot{\hat{\sigma}}_{12} = K \frac{2\pi^2 p^2}{N} [2\dot{x}_1(p)\dot{x}_2(p) + \ddot{x}_1(p)x_2(p) + x_1(p)\ddot{x}_2(p)], \quad (31)$$

$$\begin{aligned} \ddot{x}_1(p) &= \frac{1}{N} \int_0^N ds \dot{v}_1(s,t) \cos \frac{\pi p s}{N}, \\ \ddot{x}_2(p) &= \frac{1}{N} \int_0^N ds \dot{v}_2(s,t) \cos \frac{\pi p s}{N}. \end{aligned} \quad (32)$$

For evaluation \dot{v}_i we use relation

$$\dot{v}_i = -(\zeta/\mu)v_i, \quad (33)$$

where ζ is the friction coefficient. Besides, we take into account that the members with ζ are considerably greater than ones without ζ .

In result we obtained the next expression

$$s_4 = \frac{6n(k_B T)^2 \pi^2 p^2 \zeta^2}{l_0^2 N^2 \mu^3}. \quad (34)$$

The quantities a and b defined as

$$a = \frac{6p^2 \pi^2 (k_B T)}{N^3 \mu l_0^2}, \quad b = \frac{\zeta}{\mu}. \quad (35)$$

The correlation time for p – mode is

$$\tau_p = \frac{2b}{\pi a} = \frac{2\zeta l_0^2 N}{6\pi^3 (k_B T) p^2}. \quad (36)$$

After summation over p with taking account that $\sum p^{-2} = \pi^2 / 8$, we obtain

$$\tau = \frac{1}{24} \frac{\zeta l_0^2 N}{(k_B T) \pi}. \quad (37)$$

Then we used the next expression for the friction coefficient ζ due to Zimm (η_s is the solvent viscosity) [3, 4]

$$\zeta = \frac{3}{8} (6\pi^3)^{1/2} \eta_s l_0 \sqrt{N}. \quad (38)$$

As the important result we find that

$$\tau \sim N^{3/2} \sim M^{3/2}.$$

The dependence of this quantity on the molecular weight agrees with experiments.

According to (37) and (38) the correlation time is proportional to the $N^{3/2}$ (N is number of monomers in molecule). This dependence is important because due to increase N the viscosity coefficients increases essentially.

References

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