

## Dynamic Equations of Polymers with Deformations in Semidilute Regions

Akira ONUKI

*Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto 606*

(Received July 16, 1990)

We present fundamental dynamic equations describing collective diffusive motions of deformed polymers. If we incorporate Doi's recent idea on the polymer diffusion in flow, the equations turn out to be different from those previously proposed by the present author (Phys. Rev. Lett. **62** (1989) 2472). In the absence of flow, on the other hand, they are consistent with a theory of Brochard and de Gennes. A seriously ambiguous assumption in the derivation remains.

Two fluid models have been used to describe the dynamics of entangled polymer solutions in the semidilute regime.<sup>1)</sup> Such systems behave like elastic gels<sup>2)</sup> when the time scale of deformations is rapid compared to a rheological time  $\tau_d$ , while they behave like highly viscous fluids for slower deformations. Very recently, Doi employed a two-fluid model to predict inhomogeneity of the polymer concentration in the parallel plate geometry.<sup>3)</sup> He assumed the same form of dynamic equations for polymer solutions as those for gels<sup>4)</sup> except for the concrete expressions of the stress tensor. This is a rather drastic and problemistic assumption, while there seems to be no doubt on the validity of the dynamic equations in gels. The difference between gels and polymer solutions stems from whether entanglements are permanent or transient. In polymer solutions, it has been conceptually difficult to treat the effects of chain deformations on polymer diffusion. The aim of this letter is to derive Doi's result in another scheme and to develop a set of dynamic equations which allows us to analyze shear-induced phase separation<sup>5,6)</sup> in semidilute polymer solutions.

We introduce the polymer volume fraction  $\phi$  much smaller than 1, the two velocity fields  $v_p$  and  $v_s$  for polymers and solvents, and a conformation tensor  $W_{ij}$  to describe deformations of chains.<sup>6-8)</sup> We consider semidilute concentration regions with theta or poor solvents. The free energy for  $\phi$  and  $W_{ij}$  is of the form,

$$F = \int dr \left[ f(\phi) + f_{el}(\phi, \mathbf{W}) + \frac{1}{2} K_1 |\nabla\phi|^2 \right], \quad (1)$$

where  $f$  is the usual mixing free energy,  $f_{el}$  is

the elastic free energy, and the gradient term represents the increase of the free energy due to inhomogeneities of  $\phi$ . In the semidilute regime, we may assume the form

$$f_{el} = E(\phi) f_{el}^*(\mathbf{W}) \quad \text{with} \quad E(\phi) \propto \phi^{\hat{p}}, \quad (2)$$

where  $E(\phi)$  is the elastic shear modulus<sup>6)</sup> and  $\mathbf{W}$  is taken to be dimensionless. The exponent  $\hat{p}$  is 3 in theta solvents from the original scaling idea, but there is a theoretical possibility<sup>9)</sup> of  $\hat{p}=2$ . Experimentally, the exponent of the shear modulus was observed to be from 2 to 2.5 in theta solvents.<sup>10)</sup> For the time being, we neglect the gradient term until eq. (15) below. The total free energy  $F_T$  is the sum of  $F$  and the spaceintegral of  $\frac{1}{2}\rho_p v_p^2 + \frac{1}{2}\rho_s v_s^2$ . The two mass densities  $\rho_p$  and  $\rho_s$  are assumed to be simply proportional to  $\phi$  and  $1-\phi$ , respectively. Namely,  $\rho_p^0 \equiv \rho_p/\phi = \text{const.}$  and  $\rho_s^0 \equiv \rho_s/(1-\phi) = \text{const.}$  (the incompressibility assumption). Then it is convenient to introduce the following average velocity:

$$\mathbf{V} = \phi v_p + (1-\phi)v_s. \quad (3)$$

The conservations of  $\rho_p$  and  $\rho_s$  are compatible with the incompressibility condition only when

$$\nabla \cdot \mathbf{V} = 0. \quad (4)$$

From the definition, it follows that

$$\frac{\partial}{\partial t} \phi = -\nabla \cdot (\phi v_p). \quad (5)$$

Let  $v_p$  and  $v_s$  obey

$$\frac{\partial}{\partial t} (\rho_p v_p) + \nabla \cdot (\rho_p v_p v_p) = F_p, \quad (6)$$

$$\frac{\partial}{\partial t} (\rho_s \mathbf{v}_s) + \nabla \cdot (\rho_s \mathbf{v}_s \mathbf{v}_s) = -\nabla \cdot \Pi - \mathbf{F}_p, \quad (7) \quad \rho_p \mathbf{v}_p \mathbf{v}_p + \rho_s \mathbf{v}_s \mathbf{v}_s. \text{ The equation for } W_{ij} \text{ is very ambiguous theoretically, but it is first assumed to be given by}$$

where  $\Pi$  is the total stress tensor subtracted by

$$\frac{\partial}{\partial t} W_{ij} + (v_p \cdot \nabla) W_{ij} - \sum_l \left( \frac{\partial}{\partial x_l} v_{pl} \right) W_{lj} - \sum W_{il} \left( \frac{\partial}{\partial x_l} v_{pj} \right) = - \sum_{k,l} \Gamma_{ijkl} \hat{W}_{kl}, \quad (8)$$

where the left-hand side is the so-called upper convected time derivative.<sup>11)</sup> Thus, (i)  $\mathbf{W}$  is convected by  $\mathbf{v}_p$ , and (ii)  $\mathbf{W}$  is affinely deformed by the gradients of  $\mathbf{v}_p$ , where the second assumption is ambiguous (see eq. (24) below). The right-hand side of (8) represents the relaxation and

$$\hat{W}_{ij} = \frac{\delta}{\delta W_{ij}} F = \left( \frac{\partial}{\partial W_{ij}} f_{el} \right)_\phi. \quad (9)$$

The  $\Gamma_{ijkl}$  are the kinetic coefficients. The stress tensor due to chain deformations is then given by  $-\sigma_p$ , where<sup>7)</sup>

$$\sigma_{pij} = 2 \sum_l W_{il} \hat{W}_{lj}. \quad (10)$$

In the following, we suppose isothermal processes neglecting temperature variations.

Now the problem is to determine the explicit expressions for  $\mathbf{F}_p$  and  $\Pi$ . To this end, we use the principle of positive entropy production,<sup>12)</sup> which is equivalent to requiring  $dF_T/dt < 0$  in our scheme. Using eqs. (5)–(8), we find after some calculations

$$\begin{aligned} \frac{d}{dt} F_T = \int d\mathbf{r} [ & (\mathbf{v}_p - \mathbf{v}_s) \cdot \{ (1 - \phi)(\nabla \pi - \nabla \cdot \sigma_p) + \phi \nabla \cdot \Pi + \mathbf{F}_p \} + \mathbf{V} \cdot (\nabla \pi - \nabla \cdot \sigma_p - \nabla \cdot \Pi) \\ & - \sum_{i,j,k,l} \hat{W}_{ij} \Gamma_{ijkl} \hat{W}_{kl} ]. \end{aligned} \quad (11)$$

Here  $\mathbf{V}$  is defined by (3) and the osmotic pressure  $\pi = \pi_\phi + \pi_{el}$  arises from the mixing free energy and the elastic free energy as

$$\pi_\phi = \left( \phi \frac{\partial}{\partial \phi} - 1 \right) f, \quad \pi_{el} = \left( \phi \frac{\partial}{\partial \phi} - 1 \right) f_{el} = \left( \phi \frac{\partial E}{\partial \phi} - E \right) f_{el}^*, \quad (12)$$

the derivative  $\partial/\partial\phi$  being taken with  $\mathbf{W}$  held fixed. The negative definiteness of eq. (11) leads to

$$\mathbf{F}_p = -\nabla \pi + \nabla \cdot \sigma_p + \phi (-\nabla p + \eta_0 \nabla^2 \mathbf{V}) - \zeta (\mathbf{v}_p - \mathbf{v}_s), \quad (13)$$

$$\Pi_{ij} = (p + \pi) \delta_{ij} - \sigma_{pij} - \eta_0 \left( \frac{\partial}{\partial x_i} V_j + \frac{\partial}{\partial x_j} V_i \right), \quad (14)$$

where the higher-order gradients of  $\mathbf{v}_p - \mathbf{v}_s$  and  $\mathbf{V}$  have been omitted. The friction coefficient  $\zeta$  is of order  $6\pi\eta_s\xi^{-2}$  in theta solvents,<sup>9)</sup> where  $\eta_s$  is the solvent viscosity and  $\xi \propto 1/\phi$  is the blob size.<sup>1,13)</sup> The viscosity  $\eta_0$  in eq. (13) is of order  $\eta_s$ . A pressure  $p$  is needed to assure the condition  $\nabla \cdot \mathbf{V} = 0$ . If the gradient term in  $F$  is recovered in the above calculation, we notice that  $\nabla \pi_\phi$  in eqs. (11), (13) and (14) is replaced by  $\nabla \cdot \Pi_\phi$  with<sup>4)</sup>

$$\Pi_{\phi ij} = \left[ \phi f' - f - \frac{1}{2} \nabla \cdot (K_1 \phi \nabla \phi) - \frac{1}{2} \phi K_1 \nabla^2 \phi \right] \delta_{ij} + K_1 \frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_j}. \quad (15)$$

The last term in eq. (15) can be crucial with the appearance of interfaces giving rise to the surface tension force. Notice  $K_1 \propto 1/\phi$  from the scaling theory<sup>13)</sup> and

$$\nabla \cdot \Pi_\phi + \nabla \pi_{el} = \phi \nabla \frac{\delta F}{\delta \phi} - \sum_{i,j} \hat{W}_{ij} \nabla W_{ij} = \phi \nabla \frac{\delta F}{\delta \phi} - E \nabla f_{el}^*. \quad (16)$$

In most physical processes in polymer solutions, the time scale is very slow and the inertia effect is negligible, so that we may set the left-hand side of eq. (6) equal to zero to have  $F_p = 0$  or

$$\mathbf{v}_p - \mathbf{v}_s = -\zeta^{-1}[\nabla \cdot \Pi_\phi + \nabla \pi_{el} - \nabla \cdot \sigma_p - \phi(\nabla p - \eta_0 \nabla^2 V)] \approx -\zeta^{-1}[\nabla \cdot \Pi_\phi + \nabla \pi_{el} - \nabla \cdot \sigma_p]. \quad (17)$$

Here the gradient term has been recovered and the second line is obtained from  $\phi \ll 1$ . If we neglect  $\pi_{el}$  (or include it into the definition of  $\sigma_p$ ) and set  $\Pi_{\phi ij} = \pi_\phi \delta_{ij}$ , the second line coincides with Doi's result.<sup>3)</sup> From  $\mathbf{v}_p - \mathbf{V} = (1 - \phi)(\mathbf{v}_p - \mathbf{v}_s)$  and eq. (3), we find

$$\frac{\partial}{\partial t} \phi + \nabla \cdot (\phi \mathbf{V}) \approx \nabla \cdot \left( \frac{\phi}{\zeta} \right) \cdot [\nabla \cdot \Pi_\phi + \nabla \pi_{el} - \nabla \cdot \sigma_p]. \quad (18)$$

This equation is similar to that of Helfand and Fredrickson<sup>5)</sup> if  $\pi_{el}$  is neglected. On the other hand,  $\mathbf{V}$  defined by eq. (3) approximately obeys

$$\rho_0 \frac{\partial}{\partial t} \mathbf{V} \approx \nabla \cdot (-\Pi_\phi + \sigma_p) - \nabla(\pi_{el} + p) + \eta_0 \nabla^2 \mathbf{V}, \quad (19)$$

where  $\rho_0$  is the average density and  $p$  assures eq. (4). Now with eqs. (18), (19) and (8), we have obtained the closed set of equations for the three gross variables,  $\phi$ ,  $\mathbf{V}$  and  $W_{ij}$ ,<sup>6,7)</sup> where  $\mathbf{v}_p - \mathbf{v}_s$  has been coarse-grained owing to eq. (17).

As a direct application, we examine the above equations around equilibrium (without shear) to reproduce Brochard and de Gennes' result<sup>9)</sup> for dynamic light scattering. Namely, all the deviations are small and depend on space and time as  $\exp(i\mathbf{q} \cdot \mathbf{r} + i\omega t)$ . Then eqs. (8)~(10) yield<sup>6)</sup>

$$\sigma_{vij} \approx \frac{G^*(\omega)}{i\omega} \left[ \frac{\partial}{\partial x_i} v_{pj} + \frac{\partial}{\partial x_j} v_{pi} - \frac{2}{3} \delta_{ij} (\nabla \cdot \mathbf{v}_p) \right], \quad (20)$$

where  $G^*(\omega)$  is the complex shear modulus<sup>14)</sup> and use has been made of  $\langle W_{ij} \rangle \propto \delta_{ij}$  in equilibrium.\* In the single-relaxation-time

approximation, we have  $G^*(\omega) = i\omega(\Delta\eta)/[1 + i\omega\tau_d]$ , where  $\Delta\eta (\gg \eta_s)$  is the zero-shear-limit viscosity due to entanglements. The right-hand side of (20) has been made traceless because we expect that  $W_{ij} - 1/3\delta_{ij}(Tr\mathbf{W})$  relaxes with  $\tau_d$  and  $Tr\mathbf{W}$  relaxes much more rapidly. This corresponds to the rapid contour-length relaxation in Doi-Edwards' theory<sup>14)</sup> if  $\mathbf{W}$  is defined as in ref. 6. It is crucial here that the gradients of  $\mathbf{v}_p$  appear in (20) as was also expected by Doi.<sup>3)</sup> Then, from  $\nabla \cdot \mathbf{v}_p = -i\omega\phi/\phi$ ,  $\delta\phi$  being the deviation of the volume fraction, we find

$$\sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j} \sigma_{pij} = \frac{4}{3} G^*(\omega) q^2 \left( \frac{\delta\phi}{\phi} \right). \quad (21)$$

The linearized form of eq. (18) becomes  $i\omega\delta\phi = -\Lambda(q, \omega)\delta\phi$  with

$$\Lambda(q, \omega) = \zeta^{-1} q^2 \left[ \phi \frac{\partial \pi}{\partial \phi} + (\phi^2 K_1) q^2 + \frac{4}{3} G^*(\omega) \right]. \quad (22)$$

The one-sided Fourier transform of  $S_q(t) = \langle \phi_q(t) \phi_q(0)^* \rangle$  may be expressed as

$$\int_0^\infty dt e^{-i\omega t} S_q(t) = [i\omega + \Lambda(q, \omega)]^{-1} S_q(0). \quad (23)$$

As a very feasible result,  $G^*(\omega) \approx E$  for  $\omega\tau_d \gg 1$ ,  $E$  being the shear modulus appearing in eq. (2), while  $G^*(\omega) \approx i\omega(\Delta\eta)$  for  $\omega\tau_d \ll 1$ . The high-frequency behavior represents gellike behavior. Notice that the diffusion constant in gels is known to be  $\zeta^{-1}(\phi\partial\pi/\partial\phi + 4/3\mu)$  in accord with eq. (22),  $\mu$  being the shear modulus.<sup>2)</sup>

We note that a different set of equations is obtained if  $\mathbf{W}$  in eq. (8) is deformed by gradients of another velocity.<sup>8)</sup> To show this, we rewrite eq. (8) as

$$\frac{\partial}{\partial t} W_{ij} + \mathbf{v}_p \cdot \nabla W_{ij} = \sum_l \left[ \left( \frac{\partial}{\partial x_l} \tilde{v}_i \right) W_{lj} + W_{il} \left( \frac{\partial}{\partial x_l} \tilde{v}_j \right) \right] - \sum_{k,l} \Gamma_{ijkl} \hat{W}_{kl}, \quad (24)$$

where  $\tilde{\mathbf{v}}$  is a linear combination of  $\mathbf{v}_p$  and  $\mathbf{v}_s$ ,

$$\tilde{\mathbf{v}} = \alpha \mathbf{v}_p + (1 - \alpha) \mathbf{v}_s. \quad (25)$$

Then  $\tilde{\mathbf{v}} = \mathbf{v}_p$ ,  $\mathbf{V}$ , and  $\mathbf{v}_s$  for  $\alpha = 1$ ,  $\phi$ , and 0, respectively. The principle of  $dF_T/dt < 0$  yields, instead of eq. (13),

$$F_p = -\nabla \pi + \alpha \nabla \cdot \sigma_p + \phi(-\nabla p + \eta_0 \nabla^2 V) - \zeta(\mathbf{v}_p - \mathbf{v}_s). \quad (26)$$

\* In ref. 6, the equilibrium average was subtracted in the definition of  $W_{ij}$ .

The expression for  $\Pi$ , eq. (15), is unchanged. The counterpart of the first line of eq. (17) becomes

$$v_p - v_s = -\zeta^{-1}[\nabla \cdot \Pi_\phi + \nabla \pi_{el} - \alpha \nabla \cdot \sigma_p + \phi(\nabla p - \eta_0 \nabla^2 V)]. \quad (27)$$

If  $\alpha \ll 1$ , we have  $v_p - v_s = -\zeta^{-1} \nabla \pi$  as in the case of usual binary mixtures and the results in ref. 6 remain essentially valid. Following Doi, let us consider steady flows in which  $v_p - v_s = 0$  and  $\nabla^2 V = 0$ , as those in cone plates or capillary tubes. Then eqs. (19) and (27) yield

$$\nabla(\pi + p) = \nabla \cdot \sigma_p, \quad (28)$$

$$\nabla \pi + \phi \nabla p = \alpha \nabla \cdot \sigma_p, \quad (29)$$

where  $\pi = \pi_\phi + \pi_{el}$  and we have neglected the gradient free energy supposing macroscopic spatial variations. These two relations yield  $(1 - \alpha) \nabla \pi = (\alpha - \phi) \nabla p$  and

$$\nabla \pi_\phi = f'' \nabla \phi = -\nabla \pi_{el} + \frac{1}{3} \left( \frac{\alpha - \phi}{1 - \phi} \right) \nabla(\text{Tr } \sigma_p) + \frac{\alpha - \phi}{1 - \phi} \nabla \cdot \sigma_{pD}, \quad (30)$$

where  $\sigma_{pD} = \sigma_p - 1/3(\text{Tr } \sigma_p)\mathbf{I}$  is the deviatoric part and may be expressed in terms of the normal stress differences,  $N_1$  and  $N_2$ .<sup>11</sup> Doi's result is obtainable if only the last term is retained and  $\alpha = 1$ . To see the implication of eq. (30) more clearly, we note that the ratios,  $A_{el} \equiv \pi_{el}/N_1$ ,  $A_t = 1/3(\text{Tr } \sigma_p)/N_1$ , and  $A_2 = N_2/N_1$ , should all be nearly constant, independent of  $\phi$  and the shear\* from scaling considerations. Then, particularly for a Poiseuille flow through a circular tube, eq. (30) becomes

$$f'' r \frac{\partial}{\partial r} \phi = - \left[ A_{el} + \frac{\alpha - \phi}{1 - \phi} \left( \frac{1}{3} - A_t - \frac{2}{3} A_2 \right) \right] r \frac{\partial}{\partial r} N_1 + \frac{\alpha - \phi}{1 - \phi} N_2, \quad (31)$$

where all the quantities depend on the radius  $r$  from the center of the tube. Interestingly, eq. (31) shows that Doi's prediction  $\delta \pi_\phi \sim -\delta N_1$  can be obtained for any value of  $\alpha$  between 1 and 0 (even from the equations in ref. 6). Here we expect (i)  $A_{el} > 0$ , which follows from (12) if  $f_{el}^* > 0$ , and (ii)  $(1/3) - A_t - (2/3)A_2 > 0$ . It should be noted that confirmation of his effect cannot be a direct test of  $\alpha = 1$  or  $\tilde{v} = v_p$  in view of the uncertainty of  $A_{el}$ .

The present author cannot find any compelling reason for  $\tilde{v} = v_p$  at present. Hence this work still does not constitute a real derivation of the new dynamic equations with a firm basis. A more fundamental approach of statistical physics is strongly needed to express  $v_p - v_s$  in terms of the other slow gross variables and to confirm or correct eq. (17). Experimentally, the scattering amplitude in shear will provide us useful information on the form of the dynamic equations.<sup>15</sup>

### Acknowledgments

This work would have not been completed

\* This holds at least in the Newtonian case. Furthermore, in any case,  $A_{el} \sim 1$  if the deformations are described by a conformation tensor and  $\sigma_p$  is defined as eq. (10).

without severe but friendly criticisms by M. Doi. Thanks are also due to G. H. Fredrickson, E. Helfand, R. G. Larson, T. Hashimoto, D. Pine, X. Wu, and D. Lhuillier for valuable discussions.

### References

- 1) P. G. de Gennes: *Macromolecules* **9** (1976) 594.
- 2) T. Tanaka, L. Hocker and G. Benedik: *J. Chem. Phys.* **59** (1973) 5151.
- 3) M. Doi: in *Dynamics and Patterns in Complex Fluids: New Aspects of Physics and Chemistry Interfaces*, ed. A. Onuki and K. Kawasaki (Springer, 1990).
- 4) A. Onuki: *J. Phys. Soc. Jpn.* **57** (1988) 699.
- 5) E. Helfand and G. H. Fredrickson: *Phys. Rev. Lett.* **62** (1989) 2468.
- 6) A. Onuki: *Phys. Rev. Lett.* **62** (1989) 2472.
- 7) M. Grmela: *Phys. Lett. A.* **130** (1988) 81.
- 8) D. Lhuillier: *J. de Physique* **44** (1983) 303.
- 9) F. Brochard and P. G. de Gennes: *Macromolecules* **10** (1977) 1157; F. Brochard: *J. Phys. (Paris)* **44** (1983) 39.
- 10) M. Adam and M. Delsanti: *J. Phys. (Paris)* **45** (1984) 1513; Y. Takahashi, I. Noda and M. Nagasawa: *Macromolecules* **18** (1985) 2220 and references quoted therein.
- 11) R. G. Larson: *Constitutive Equations for Polymer Melts and Solutions* (Butterworths, Boston, 1988).
- 12) I. M. Khalatonikov: *An Introduction to the Theory of Superfluidity* (Benjamin, New York, 1965).
- 13) P. G. de Gennes: *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, NY, 1979).
- 14) M. Doi and S. F. Edwards: *The Theory of Polymer Dynamics* (Oxford Univ. Press, Oxford, 1986).
- 15) A. Onuki: *J. Phys. Soc. Jpn.* **59** (1990) 3427.