ELSEVIER

Polymer 40 (1999) 565–568

polymer

Notes on the formulation of concentration fluctuation in moderately concentrated polymer solutions

Yoshiyuki Einaga[a,*], Hiroshi Fujita[b]

[a]Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan
[b]35 Shimotakedono-Cho, Shichiku, Kita-Ku, Kyoto 603, Japan

Received 16 January 1998; accepted 20 February 1998

Abstract

The dynamic structure factor of moderately concentrated polymer solutions is often multimodal, roughly consisting of fast and slow modes. Wang's formulation of concentration fluctuations predicts that the slow mode disappears when the polymer and solvent components have identical partial specific volumes, but the prediction is not supported by the formulation of Onuki (*J. Non-crystalline Solids*, 1994, **172–174**, 1151) and that of Doi and Onuki as well (*J. Phys.* II (Paris), 1992, **2**, 1631). The present paper shows that the primary origin of the disagreement is the difference in the basic equations of the two theories, in contrast to the prevailing notion that attributes it to the different constitutive equations assumed by the two theories for the partial stresses generated by concentration fluctuation. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Concentration fluctuation; Dynamic structure factor; Polymer solution

1. Introduction

The dynamic structure factor $S(q,t)$ (t is time and q the magnitude of the scattering vector) of moderately concentrated polymer solutions (including semi-dilute ones) is usually not a single mode. The slow mode (s) appearing subsequent to a fast mode has been the subject of considerable interest since the pioneering work of Brochard [1] and Adam and Delsanti [2] clarified that it reflects the viscoelastic deformation of a temporary polymer network due to the stress generated by concentration fluctuation. Recently, Wang [3–5] developed an elaborate theory of $S(q,t)$ and predicted that the slow mode disappears in a system where the partial specific volumes of the polymer and solvent components are identical. This prediction, however, was not supported by Onuki [6] (and Doi and Onuki [7] as well), who approached $S(q,t)$ by a formulation that differed from Wang's. It is the prevailing notion that the disagreement is due to the different assumptions taken by the two theories for the components of the stress. Thus, Wang [4,5] has claimed that the stress acting on the polymer is controlled by the gradient of the local-center-of-mass velocity, while Onuki and also Doi and Onuki have considered physically reasonable to relate it to the gradient of the local velocity of the polymer component. No decision of which method is right has been made yet.

The present paper aims to point out that the primary origin of the disagreement between Wang and Onuki is the difference in the basic equations of their formulations for the dynamics of concentration fluctuations, not the difference in the assumptions for the stresses. We believe this remark is of interest in relation to the current dispute on the interpretation of dynamic light scattering measurements on semidilute polystyrene solutions [8,9].

2. Basic relations

Though well-documented in existing literature [5], the basic relations needed for the subsequent analysis are enumerated here.

We consider concentration fluctuations that take place in an isothermal equilibrium binary solution consisting of a solvent (component 1) and a monodisperse polymer (component 2). For simplicity, we assume that the solution is incompressible and the partial specific volumes v_1 and v_2 of the components are independent of the composition.

---

* Corresponding author.

PII S0032-3861(98)00226-2

If the solution is viewed as a continuous fluid, the mass and momentum conservation laws give

$$\partial\rho/\partial t + \nabla\cdot(\rho\mathbf{u}) = 0 \tag{1}$$

$$\partial(\rho\mathbf{u})/\partial t + \nabla\cdot(\rho\mathbf{u}\mathbf{u} - \sigma) = 0 \tag{2}$$

Here, ρ denotes the local solution density, $\mathbf{u}$ the velocity of the local center of mass, and σ the local total stress tensor.

The mass conservation for each component is expressed by

$$\partial c_i/\partial t + \nabla\cdot(c_i\mathbf{u}_i) = 0 \ (i = 1, 2) \tag{3}$$

where c_i and $\mathbf{u}_i$ are the local mass concentration and the local velocity of component i, respectively. The local composition of the solution under consideration is uniquely determined by either c_1 or c_2. Here we choose the polymer concentration c_2 as the independent composition variable.

The quantity $\mathbf{u}$ is expressed by

$$\rho\mathbf{u} = c_1\mathbf{u}_1 + c_2\mathbf{u}_2 \tag{4}$$

and the quantity σ by

$$\sigma = -p\mathbf{I} + \sigma_1 + \sigma_2 \tag{5}$$

where p is the pressure, $\mathbf{I}$ the unit tensor, and σ_i the contribution of the stress generated by concentration fluctuation to component i and often called the partial stress for component i.

The flux $\mathbf{j}_i$ of component i relative to the local center of mass is defined by

$$\mathbf{j}_i = c_i(\mathbf{u}_i - \mathbf{u}) \tag{6}$$

and obeys the relation

$$\mathbf{j}_1 + \mathbf{j}_2 = 0 \tag{7}$$

Hence it is sufficient for us to concern $\mathbf{j}_2$ only.

With the subscript zero attached to the quantities at the equilibrium state of the solution, we define $\delta\rho(\mathbf{r},t)$, $\delta c_i(\mathbf{r},t)$, $\delta p(\mathbf{r},t)$, $\delta\sigma(\mathbf{r},t)$, $\delta\mathbf{u}(\mathbf{r},t)$, $\delta\mathbf{u}_i(\mathbf{r},t)$ and $\delta\mathbf{j}_i(\mathbf{r},t)$ by

$$\rho(\mathbf{r},t) = \rho_0 + \delta\rho(\mathbf{r},t) \tag{8}$$

$$c_i(\mathbf{r},t) = c_{i0} + \delta c_i(\mathbf{r},t) \tag{9}$$

$$p(\mathbf{r},t) = p_0 + \delta p(\mathbf{r},t) \tag{10}$$

$$\sigma(\mathbf{r},t) = \sigma_0 + \delta\sigma(\mathbf{r},t) \tag{11}$$

$$\mathbf{u} = \mathbf{u}_0 + \delta\mathbf{u}(\mathbf{r},t) \tag{12}$$

$$\mathbf{u}_i = \mathbf{u}_{i0} + \delta\mathbf{u}_i(\mathbf{r},t) \tag{13}$$

and

$$\mathbf{j}_i = \mathbf{j}_{i0} + \delta\mathbf{j}_i(\mathbf{r},t) \tag{14}$$

Then these quantities signify the fluctuations of density, mass concentration of component i, pressure, total stress tensor, center-of-mass velocity, velocity of component i, and flux of component i at the position $\mathbf{r}$ and the time t. In what follows we take advantage of the fact that σ_0, $\mathbf{u}_0$, $\mathbf{u}_{i0}$ and $\mathbf{j}_{i0}$ are all zero.

As usual, we restrict ourselves to the situation where concentration fluctuations are so small that only linear terms of all δ-attached quantities may be retained. Then it follows from Eqs. (1) and (2) that

$$\partial\delta\rho/\partial t = -\rho_0\nabla\cdot\delta\mathbf{u} \tag{15}$$

$$\rho_0(\partial\delta\mathbf{u}/\partial t) = \nabla\cdot\delta\sigma \tag{16}$$

and from combination of Eqs. (3) and (6) that

$$\partial\delta c_2/\partial t = -\nabla\cdot\delta\mathbf{j}_2 \tag{17}$$

These three equations allow determination of $\delta c_2(\mathbf{r},t)$, $\delta\rho(\mathbf{r},t)$ and $\delta\mathbf{u}(\mathbf{r},t)$ when coupled with appropriate theories for $\mathbf{j}_i$ and σ.

3. Wang's theory

Wang [3] started his formulation by choosing, for the $\mathbf{j}_i$, Onsager's flux equations familiar in the irreversible thermodynamics for multicomponent fluids. Thus, for the binary solution under consideration his starting equations were

$$-\mathbf{j}_1 = \Omega_{11}\nabla\mu_1 + \Omega_{12}\nabla\mu_2 \tag{18}$$

$$-\mathbf{j}_2 = \Omega_{21}\nabla\mu_1 + \Omega_{22}\nabla\mu_2 \tag{19}$$

where the Ω_{ij} are the Onsager phenomenological coefficients which obey the relations

$$\Omega_{11} = -\Omega_{12} = -\Omega_{21} = \Omega_{22} \equiv \Omega \tag{20}$$

and μ_i is the chemical potential of component i. Since $\mathbf{j}_i$ and $\nabla\mu_i$ are zero for the solution at equilibrium, it follows from Eqs. (18) and (19) that

$$-\delta\mathbf{j}_1 = \Omega_{11}\nabla\delta\mu_1 + \Omega_{12}\nabla\delta\mu_2 \tag{21}$$

$$-\delta\mathbf{j}_2 = \Omega_{21}\nabla\delta\mu_1 + \Omega_{22}\nabla\delta\mu_2 \tag{22}$$

To develop an analysis from these, we first use Eq. (20) to rewrite Eq. (22) as

$$\delta\mathbf{j}_2 = -\Omega(\nabla\delta\mu_2 - \nabla\delta\mu_1) \tag{23}$$

and utilize the fact that the Gibbs–Duhem relation at constant temperature $dp = c_1d\mu_1 + c_2d\mu_2$ gives

$$\delta\mu_1 - \delta\mu_2 = -(\delta p/c_{20}) + (\rho_0/c_{20})\delta\mu_1 \tag{24}$$

correct to the first order of fluctuations. According to the thermodynamics of incompressible systems at constant temperature, we have

$$\delta\mu_1 = v_1\delta p - v_1\Pi\delta c_2 \tag{25}$$

where Π stands for $(\partial\pi/\partial c_2)_{T,p}$, with π denoting the osmotic pressure of the solution and T the absolute temperature. Hence, Eq. (24) can be written

$$\delta\mu_1 - \delta\mu_2 = (v_1 - v_2)\delta p - (\rho_0 v_1\Pi/c_{20})\delta c_2 \tag{26}$$

If the result after inserting this into Eq. (23) is substituted into Eq. (17), it follows that

$$\partial\delta c_2/\partial t = D\nabla^2\delta c_2 - (v_1 - v_2)(c_{10}c_{20}/\rho_0\zeta, \nabla^2\delta p \tag{27}$$

where D is the (mutual) diffusion coefficient defined by

$$D = c_{10}v_1\Pi/\zeta \tag{28}$$

with the friction coefficient ζ related to Ω by

$$\zeta = c_{10}c_{20}/(\rho_0\Omega) \tag{29}$$

Wang [3] has introduced a dimensionless parameter β defined by

$$\beta \equiv (c_{20}/\rho_0)(\partial\rho_0/\partial c_{20})_{T,p} \tag{30}$$

which, under the assumption that both v_1 and v_2 are independent of the composition, gives

$$\beta = (c_{20}/\rho_0)(v_1 - v_2)/v_1 \tag{31}$$

Therefore, the coefficient of $\nabla^2\delta p$ in Eq. (27) may be written $-c_{10}v_1\beta/\zeta$, so that it is directly proportional to β.

Now we assume that the inertia effect may be neglected. Then, Eq. (16) gives $\nabla\cdot\delta\sigma = 0$, so that Eq. (5) yields

$$\nabla\delta p = \nabla\cdot\delta\sigma_1 + \nabla\cdot\delta\sigma_2 \tag{32}$$

This allows us to eliminate $\nabla\delta p$ from Eq. (27), giving

$$\partial\delta c_2/\partial t = D\nabla^2\delta c_2 - (c_{10}v_1\beta/\zeta)\nabla\cdot(\nabla\cdot\delta\sigma_1 + \nabla\cdot\delta\sigma_2) \tag{33}$$

where Eq. (31) has been used. This is the differential equation for $\delta c_2(\mathbf{r},t)$ from Wang's formulation. To solve it we need theoretical information about the $\nabla\cdot\delta\sigma_i$, which, however, is outside the scope of the present paper.

The first term on the right-hand side of Eq. (33) represents the rate of change in polymer concentration fluctuation due to diffusion and the second term the one due to the deformation of polymer chains by partial stresses. The latter vanishes at $\beta = 0$, so that Eq. (33) predicts that no viscoelastic slow mode appears in $S(q,t)$ when the two components have identical partial specific volumes. This is just Wang's prediction. Importantly, it is the consequence from the choice of Onsager's flux equations for the $\mathbf{j}_i$ and holds having nothing to do with the constitutive equations for the partial stresses.

4. Onuki's theory

Onuki's formulation [6] differs from Wang's in that it starts from the equations of motion for the respective components. In the approximation of neglecting inertia effects, they read

$$-c_1\nabla\mu_1 - \zeta_v(\mathbf{u}_1 - \mathbf{u}_2) + \nabla\cdot\sigma_1 = 0 \tag{34}$$

$$-c_2\nabla\mu_2 - \zeta_v(\mathbf{u}_2 - \mathbf{u}_1) + \nabla\cdot\sigma_2 = 0 \tag{35}$$

where ζ_v denotes the friction coefficient between the two components per unit volume of the solution. It follows from these equations that

$$\delta\mathbf{u}_2 - \delta\mathbf{u}_1 = \zeta^{-1}[\nabla\delta\mu_1 - \nabla\delta\mu_2 - (\nabla\cdot\delta\sigma_1/c_{10}) + (\nabla\cdot\delta\sigma_2/c_{20})] \tag{36}$$

correct to the first order of fluctuations, where

$$\zeta \equiv \rho_0\zeta_v/(c_{10}c_{20}) \tag{37}$$

Onuki neglected density fluctuation due to composition fluctuation, which, according to Wang's definition of β, means to assume $\beta = 0$ or $v_1 = v_2$. Apparently, this approximation is neither realistic nor desirable.

As shown below, we can carry through the analysis without it. To this end we utilize the relation

$$\mathbf{j}_2 = (c_1c_2/\rho)(\mathbf{u}_2 - \mathbf{u}_1) \tag{38}$$

which can be derived from Eqs. (4) and (6). Combining this with Eq. (36) gives

$$\delta\mathbf{j}_2 = -(c_{10}c_{20}/\rho_0\zeta)[\nabla\delta\mu_2 - \nabla\delta\mu_1 - (\nabla\cdot\delta\sigma_2/c_{20}) + (\nabla\cdot\delta\sigma_1/c_{10})] \tag{39}$$

In the same way as reaching Eq. (33) from Eq. (23), it is possible to derive the following from this equation:

$$\partial\delta c_2/\partial t = D\nabla^2\delta c_2 - (c_{10}v_1\beta/\zeta)\nabla\cdot(\nabla\cdot\delta\sigma_1 + \nabla\cdot\delta\sigma_2) + (c_{20}v_2/\zeta)\nabla\cdot(\nabla\cdot\delta\sigma_1) - (c_{10}v_1/\zeta)\nabla\cdot(\nabla\cdot\delta\sigma_2) \tag{40}$$

which corresponds to Eq. (33) from Wang's formulation. It is seen that Eq. (40) contains two more terms on the right-hand side than Eq. (33). Noticing that $(v_1 - v_2)c_{10}$ and $(v_1 - v_2)c_{20}$ are the same order as ρ_0v_1 and ρ_0v_2, we find that these additional terms are comparable in order with the second term in Eq. (40) [or Eq. (33)] for either $\nabla\cdot(\nabla\cdot\delta\sigma_1)$ or $\nabla\cdot(\nabla\cdot\delta\sigma_2)$. Thus, Eq. (40) predicts that, when $\beta = 0$ at which the second term vanishes, the rate of change in polymer momentum has contributions from the partial stresses that cannot be neglected. Therefore, $S(q,t)$ may exhibit a viscoelastic slow mode in systems where v_1 and v_2 have identical values. In other words, Onuki's formulation does not support Wang's prediction. This conclusion is the direct consequence from Onuki's basic equations of motion and bears no relation to the constitutive equations for the partial stresses.

5. Remarks

The above analysis has proved that the disagreement between Wang and Onuki as to the prediction for the slow mode of $S(q,t)$ primarily arises from the difference in the starting equations of their formulations. To account for this difference we consider Eqs. (34) and (35) from which the $\nabla\cdot\sigma_1$ and $\nabla\cdot\sigma_2$ terms are removed. Then, in place of Eq. (39), we can derive

$$\delta\mathbf{j}_2 = -(c_{10}c_{20}/\rho_0\zeta)(\nabla\delta\mu_2 - \nabla\delta\mu_1) \tag{41}$$

which agrees with Eq. (23) because ζ is related to Ω by Eq. (29). This indicates that Wang's theory corresponds to Onuki's theory subject to the assumption that the gradient of the partial stress has no effect on the rate of change in momentum for each component. We believe, this assumption is physically inadequate for entangled polymer solutions.

Onuki [6] has not described how to derive his equations of motion, so that some may question their theoretical significance. In this connection, it is relevant to remark that they are equivalent to Bearman–Kirkwood partial equations of motion, simplified by neglecting the nonlinear and inertia terms [10]. Thus, the validity of Onuki's theory depends on that of the Bearman–Kirkwood theory [10]. Bearman's flux equations [11] are another deduction from the latter. Therefore, it is not surprising that their use as the starting equation for the formulation of concentration fluctuations leads to the same results as Onuki's theory does (see Appendix A).

Appendix A

Bearman's flux equations for the binary solution under consideration read

$$-\mathbf{j}_1 = \Omega_{11}\mathbf{Z}_1 + \Omega_{12}\mathbf{Z}_2 \tag{A1}$$

$$-\mathbf{j}_2 = \Omega_{21}\mathbf{Z}_1 + \Omega_{22}\mathbf{Z}_2 \tag{A2}$$

where, in the approximation neglecting both inertia and nonlinear effects, $\mathbf{Z}_i (i = 1, 2)$ is given by

$$\mathbf{Z}_i = \nabla\mu_i - (1/c_i)\nabla\cdot\sigma_i \tag{A3}$$

According to Bearman, the $\mathbf{Z}_i$ satisfy the relation

$$c_1\mathbf{Z}_1 + c_2\mathbf{Z}_2 = -\nabla\cdot\sigma \tag{A4}$$

Substitution of Eq. (A3) gives

$$c_1\nabla\mu_1 + c_2\nabla\mu_2 = \nabla p \tag{A5}$$

Though not shown here, this equation holds even when $\mathbf{Z}_i$ is not simplified by the approximation mentioned earlier. Thus we see that the Gibbs–Duhem relation is valid within the framework of the Bearman–Kirkwood theory.

Applying Eqs. (A2) and (A3) to fluctuations, with Eqs. (20) and (29) taken into account, we get

$$\delta\mathbf{j}_2 = (c_{10}c_{20}/\rho_0\zeta)[\nabla\delta\mu_1 - \nabla\delta\mu_2 - (\nabla\cdot\delta\sigma_1/c_{10}) + (\nabla\cdot\delta\sigma_2/c_{20})] \tag{A6}$$

This agrees with Eq. (39), leading to the conclusion that choosing Bearman's flux equations for the formulation of concentration fluctuations is equivalent to starting from Onuki's equations of motion, Eqs. (34) and (35).

References

[1] Brochard FJ. J Phys (Paris) 1983;44:39.
[2] Adam M, Delsanti M. Macromolecules 1985;18:1760.
[3] Wang CH. J Chem Phys 1991;95:3788.
[4] Wang CH. J Chem Phys 1995;102:6537.
[5] Wang CH. J Non-Equilib Thermodyn 1995;20:274.
[6] Onuki AJ. Non-Crystalline Solids 1994;172-174:1151.
[7] Doi M, Onuki A. J Phys II (Paris) 1992;2:1631.
[8] Brown W, Stepanek P. Macromolecules 1994;26:6884.
[9] Sun Z, Wang CH. Macromolecules 1994;27:4840.
[10] Bearman RJ, Kirkwood JG. J Chem Phys 1958;28:136.
[11] Bearman RJ. J Chem Phys 1959;31:751.