Alternative Theory of Hydrodynamic Interactions in Polymer Solutions

Igor P. Borodin, Teodor N. Khazanovich*

Kostroma State Technological University, Kostroma, 156005, Russia
*Semenov Institute of Chemical Physics RAS, Moscow, 117577, Russia

Summary: The model is presented for coarse grained dynamics of macromolecules in dilute solutions. The coarse graining is achieved by dividing the polymer chain into subchains, consisting of many monomers, and spatial averaging over lengths that are large compared to the mean-square end-to-end distance of subchains and small compared to macromolecule size. Kinetic equations of the model are derived from first principles of statistical mechanics under the assumption that subchain center of mass positions and solvent flow velocity field are the only slow variables of the system. In this approach hydrodynamic interactions result from the intercomponent friction forces between polymer and solvent instead of boundary conditions on the bead surfaces as in traditional theories. The integrodifferential diffusion equation is obtained for steady flows with the kernel involving the Oseen tensor multiplied by equilibrium distribution in the space of the subchain center of mass positions.

Introduction

The hydrodynamic interactions (HI) can have a dramatic effect on the transport processes and dynamics in dilute polymer solutions [1-5]. The most of existing theories of HI was developed by analogy with the theory of HI in hard sphere suspensions (see e.g. ref.[6]). The theories of HI in polymer solutions are based on the bead-spring or bead-rod models. For brevity, we restrict ourselves to dilute solutions of flexible polymers and to the bead-spring models. The Smoluchowski diffusion equation for distribution of bead positions $W(t,\mathbf{R}_N)$, where $\mathbf{R}_N = \{\mathbf{r}_1, \mathbf{r}_2,...\mathbf{r}_N\}$ is a point in the chain configuration space and N is a number of the beads in the chain, may be written most generally in the form

$$\frac{\partial W}{\partial t} + \sum_{m=1}^{N} \frac{\partial}{\partial \mathbf{r}_m}[\mathbf{v}_0(\mathbf{r}_m)W] = \sum_{m,n=1}^{N} \frac{\partial}{\partial \mathbf{r}_m}\mathbf{D}_{mn}W_0(\mathbf{R}_N)\frac{\partial}{\partial \mathbf{r}_n}\frac{W}{W_0} \tag{1}$$

where $\mathbf{v}_0(\mathbf{r})$ is the flow velocity in the point $\mathbf{r}$, unperturbed by the presence of the macromolecules, $W_0(\mathbf{R}_N)$ is the equilibrium distribution of the bead positions and the diffusion tensor

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$$\mathbf{D}_{mn} = D[\delta\delta_{mn} + (1 - \delta_{mn})\zeta\Omega(\mathbf{r}_m - \mathbf{r}_n)] \qquad (2)$$

where D is the bead diffusion coefficient, δ is the unit tensor, $\zeta = k_B T/D$ is the bead friction coefficient, k_B and T being the Boltzmann constant and the temperature, and the Oseen tensor

$$\Omega(\mathbf{r}) = \frac{1}{8\pi\eta r}(\delta + \frac{\mathbf{rr}}{r^2}) \qquad (3)$$

η being the solvent viscosity, describes the HI effects. Eqs. (2) and (3) had been obtained under assumptions that Navier-Stokes equation for steady solvent motion can be linearized and solved for the stick boundary conditions on the bead surfaces and that the beads are point particles. There are many drawbacks in this approach (see e.g. ref.[7]). The most serious among them lies in the fact that diffusion tensor (2) involving Oseen tensor (3) for small distances between beads, r, is actually not positive-definite 8), whereas the second law of thermodynamics demands it to be at least positive-semidefinite. Origin of this flaw is the assumption that beads are point particles. Taking into account the first nonvanishing term in the ratio of the bead radius to the distance r leads to substitution of Oseen tensor (3) in the eq. (2) by the Rotne-Prager-Yamakawa tensor 9,10). This substitution makes the diffusion tensor to be positive-definite. Even with the Oseen tensor solutions of eq. (1) is notoriously difficult, that have forced to introduce various uncontrollable approximations5). A more accurate description of the hydrodynamic interactions between the beads makes an initially complex problem significantly more complicated. Seemingly this way goes to a deadlock.

Here we propose an approach based on a spatial coarse graining which allows us to reject the hard sphere model (and accordingly boundary conditions on their surfaces). Our model assumptions will mainly be formulated with the use the language of slow and fast variables, i.e. using the language of nonequilibrium statistical thermodynamics.

Model

As it is traditional in kinetic polymer theories we divide the polymer chain into N subchains consisting of M monomers. Both numbers M and N obey the inequalities

$$N \gg 1, \qquad M \gg 1. \qquad (4)$$

Our model is based on the following assumptions. (i) The positions of subchain centers of mass and solvent flow velocity field are the only slow variables of the system. In other words, the system equilibrates in time so short that positions of subchain centers of mass do not change significantly. (ii) Microscopic densities of mass, momenta and fluxes are introduced using coarse grained δ-functions which deviate from zero over lengths that are large compared to the subchain mean-square end-to-end distances and small compared to macromolecule size. Such δ-functions are supposed to be real singular δ-functions in final expressions after statistical averaging. This process can be called as spatial coarse graining. (iii) The all interactions between monomers and between solvent molecules and between monomers and solvent molecules are short range two-body interactions. For covalently bonded monomers the last statement means the interaction potential tends to infinity at the distances comparable to the length of C-C bond.

(iv) The diffusion coefficient of the oligomer chain of M monomers in the solution of the same mass concentration as our polymer solution in the same solvent scales as

$$D = D_0/M \qquad (5)$$

This assumption of oligomer free-draining put in second upper bound for the M. For example, Paul and Mazo¹¹⁾ have considered a great number of the diffusion coefficient data of normal alkanes and have shown that eq. (5) is valid for $M < 20$. (v) The polymer density inside the coils is small as compared to the solvent density. This assumption is valid for good and θ-solvent⁴⁾. (vi) The time dependent cross-correlation functions between forces exerted on the centers of mass of different subchains from solvent or monomers can be neglected.

(vii) The solvent is incompressible:

$$\partial \mathbf{v}/\partial \mathbf{r} = 0. \qquad (6)$$

Let us note that assumptions (iii) - (vii) are introduced for simplicity of presentation.

Kinetic equations

The model assumptions (i) - (iv) make polymer solutions to be very similar to the system of inelastic Brownian particles in a nonequilibrium bath, which were treated from first principles of statistical mechanics by Shea and Oppenheim (SO)¹²⁾. Center of mass coordinates of their spherical Brownian particles correspond to subchain center of mass positions. SO Brownian particles contain internal modes which in polymer chain have a counterpart in the position and momenta of monomers relative their subchain center of mass. However in contrast with SO we have no translational invariance in our system, that is, a permutation of positions of two subchains strongly change the system state. If temperatures and pressures of Brownian particles, internal modes and solvent are equal then the spatial coarse graining (assumption (ii)) permits not to consider internal modes explicitly and thus effaces the difference between inelastic and elastic systems of Brownian particles, the latter being analyzed be Shea and Openheim earlier$^{13)}$.

SO derived the Fokker-Planck equations for the systems of inelastic and elastic Brownian particles$^{12,13)}$. Accordingly to model assumption (i) we must eliminate fast variables (momenta in the frame moving with the solvent) from the Fokker-Planck equations and obtain the Smoluchowski diffusion equation:

$$\frac{\partial W(t,XN)}{\partial t} + \sum_{m=1}^{N} \frac{\partial}{\partial \mathbf{x}_m} [\mathbf{v}(\mathbf{x}_m, t) W(t, \mathbf{X}_N)] = D \sum_{m=1}^{N} \frac{\partial}{\partial \mathbf{x}_m} \cdot W_0 \frac{\partial}{\partial \mathbf{x}_m} \frac{W(t, \mathbf{X}_N)}{W_0(\mathbf{X}_N)} \qquad (7)$$

where $\mathbf{X}_N = \{\mathbf{x}_1, \ldots. \mathbf{x}_N\}$ and $\mathbf{x}_m$ being the position of m*th* subchain center of mass, $\mathbf{v}(\mathbf{x}_m)$ is the solvent velocity in the point $\mathbf{x}_m$, D is the subchain diffusion coefficient given by eq. (5).

There are two apparent distinctions between eqs. (1) and (7). Firstly, the drift terms in eq. (7) involve velocity field perturbed by presence of polymer, whereas eq. (1) involve only nonperturbed velocity field. Secondly, the right-hand side (RHS) of eq. (7) involves scalar diffusion coefficient, whereas eq. (1) involve the diffusion tensor (2). Absence of the direct hydrodynamic interactions in RHS of eq. (7) is due to assumptions (iv) and (vi).

Evidently eq. (7) have to be completed by the equation for solvent velocity $\mathbf{v}(t,\mathbf{x})$. The spatial coarse-graining (assumption (ii)) permit to consider a polymer coil as a mixture of two fluids consisting of a solvent and subchains. Bearman and Kirkwood$^{14)}$ introduced two-fluid hydrodynamics in which equation for the solvent velocity may be written in the form

$$\rho_s (\partial \mathbf{v}/\partial t + \mathbf{v} \cdot \nabla \mathbf{v}) = - \nabla p_s + \eta \Delta \mathbf{v} + \mathbf{F}_{sp} \qquad (8)$$

where ρ_s and p_s are the density and pressure of the solvent and the $\mathbf{F}_{sp}$ is the force of intercomponent friction. The equation for bath velocity by SO$^{13)}$ after some approximations following from the model assumptions also can be reduced to the form (8) and the intercomponent friction force takes the form

$$\mathbf{F}_{sp}(t,\mathbf{x}) = - k_B T \int d\mathbf{X}_N \sum_{m=1}^{N} \delta(\mathbf{x}_m - \mathbf{x}) \, W_0(\mathbf{X}_N) \frac{\partial}{\partial \mathbf{x}_m} \frac{W(t,\mathbf{X}_N)}{W_0(\mathbf{X}_N)} \qquad (9)$$

In equilibrium the intercomponent friction vanishes.

Eqs. (7) - (9) are closed system of equations which can be named as the kinetic equations of the model proposed. The essential difference between the traditional theories and theory presented here is in the form of eq. (9). To make comparison more explicit we assume that flow is steady and the Navier-Stokes equation (8) can be linearized. Next we write the flow velocity as a sum of nonperturbed velocity and perturbation

$$\mathbf{v}(\mathbf{x}) = \mathbf{v}_0(\mathbf{x}) + \mathbf{v}_1(\mathbf{x})$$

and assume that

$$\Delta \mathbf{v}_0(\mathbf{x}) = 0. \tag{10}$$

This condition permits to write eq (8) in the form:

$$\nabla p_s = \eta \Delta\, \mathbf{v}_1(\mathbf{x}) + \mathbf{F}_{sp} \tag{11}$$

The perturbation $\mathbf{v}_1(\mathbf{x})$ have to go to zero at infinity. It is known that solution of eq. (11) vanishing at infinity may be written in the form

$$\mathbf{v}_1(\mathbf{x}) = \int d\mathbf{x}'\Omega(\mathbf{x} - \mathbf{x}')\, \mathbf{F}_{sp}(\mathbf{x}') \tag{12}$$

where $\Omega(\mathbf{x})$ is the Oseen tensor (3) (see e.g. eq. (3.III.4) from ref$^{1)}$). Substitution of eq. (12) into eq. (7) gives

$$\sum_{m=1}^{N} \frac{\partial}{\partial \mathbf{x}_m} [\mathbf{v}_0(\mathbf{x}) W(X_N)] = \tag{13}$$

$$D \sum_{m=1}^{N} \frac{\partial}{\partial \mathbf{x}_m} \cdot W_0(X_N) \frac{\partial}{\partial \mathbf{x}_m} \frac{W(X_N)}{W_0(X_N)} - \sum_{m=1}^{N} \frac{\partial}{\partial \mathbf{x}_m} W(X_N) \int d\mathbf{x}'\Omega(\mathbf{x}_m - \mathbf{x}')\, \mathbf{F}_{sp}(\mathbf{x}')$$

Since the intercomponent friction force (9) involve function $W(\mathbf{X}_N)$, eq. (13) is non-linear. However only terms linear in v_0 are needed for calculations of the transport properties. Linearized equation (13) takes the form

$$\sum_{m,n=1}^{N} \frac{\partial}{\partial \mathbf{x}_m} \int d\mathbf{X}_N' \mathbf{D}_{mn}(\mathbf{X}_N,\mathbf{X}_N') \frac{\partial U(\mathbf{X}_N')}{\partial \mathbf{x}_n'} = \sum_{m=1}^{N} \frac{\partial}{\partial \mathbf{x}_m} [\mathbf{v}_0(\mathbf{x}) W_0(\mathbf{X}_N)]. \qquad (14)$$

where

$$\mathbf{D}_{mn}(\mathbf{X}_N, \mathbf{X}_N') = D\delta\delta_{mn}\delta(\mathbf{X}_N - \mathbf{X}_N') + k_B T W_0(\mathbf{X}_N)\Omega(\mathbf{x}_m - \mathbf{x}'_n) W_0(\mathbf{X}_N') \qquad (15)$$

and $U(\mathbf{X}_N) = W(\mathbf{X}_N)/W_0(\mathbf{X}_N) - 1$ is the deviation of distribution from equilibrium.

To evaluate the rheological properties one must calculate the stress tensor of polymer solution. It follows from Irving-Kirkwood formula, SO analysis and the model assumptions (i) - (iii) that polymer contribution into stress tensor component has the form:

$$\sigma_{\alpha\beta} = n_p \int d\mathbf{X}_N \; W(t,\mathbf{X}_N) \sum_{m=1}^{N} \frac{\partial A}{\partial x_{m\alpha}} x_{m\beta} \qquad (16)$$

where n_p is the number of macromolecules in unit volume and the "entropic" potential

$$A(\mathbf{X}_N) = - k_B T \, ln \, W_0(\mathbf{X}_N). \qquad (17)$$

In fact, eq. (16) has the same form as the known Kramers expression$^{1,3,5)}$ for the bead-spring model.

Conclusion

Comparing of eqs. (1) - (3) and eqs. (14) and (15) one can conclude that kinetic equations of the bead-spring model differ from those introduced here. We hope that microscopic foundations of the spatial coarse graining are more justified. The problem now is comparison with experiment.

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