

Addendum to the paper "On the dynamics of polyelectrolyte solutions"

M. Benmouna, A. Z. Akcasu,^{a)} and B. Hammouda^{b)}
Institut of Sciences, Physics Department, Tlemcen B. P. 119, Algeria

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In a recent paper¹ to which we shall refer here as I, we have developed a general formalism for studying the dynamic scattering from polymer solutions based on the projection operator technique. One of main quantities obtained was the first cumulant matrix Ω which is useful to recall in this note:

$$\Omega(q) = \frac{q^2 k_B T}{S_{11}S_{22} - S_{12}S_{21}} \times \begin{bmatrix} \mu_{11}S_{22} - \mu_{12}S_{21} & \mu_{12}S_{11} - \mu_{11}S_{12} \\ \mu_{21}S_{22} - \mu_{22}S_{21} & \mu_{22}S_{11} - \mu_{21}S_{12} \end{bmatrix}. \quad (1)$$

All quantities appearing in this note have their usual meaning and they were defined explicitly in I. It is also useful to recall the expression of $S_{ij}(q)$ which was obtained in I using the Debye-Hückel approximation:

$$S_{ij}(q) = (N_i N_j)^{1/2} \left[\delta_{ij} + (-1)^{i+j+1} \frac{k_i k_j}{q^2 + k^2} \right] \quad (i, j = 1, 2), \quad (2)$$

where k is the total inverse Debye screening length:

$$k^2 = k_1^2 + k_2^2 = \frac{4\pi}{\epsilon_0 k_B T} \left[\frac{N_1}{V} (Z_1 e)^2 + \frac{N_2}{V} (Z_2 e)^2 \right]. \quad (3)$$

The aim of this note is to correct some typographical mistakes in Eqs. (27) of I, and more importantly to add missing terms in the calculation of Ω_{ij} with hydrodynamic interaction, which were left out essentially because of an erroneous statement that for point particles μ_{11} and μ_{22} are not affected by the hydrodynamic interaction. We also take this opportunity to include some new discussions of the results obtained in I.

First we rewrite Eqs. (27) of I in the corrected form:

$$\frac{\partial}{\partial t} C_1(q, t) = -D_1(q^2 + k_1^2)C_1(q, t) + D_1 k_2^2 C_2(q, t), \quad (4a)$$

$$\frac{\partial}{\partial t} C_2(q, t) = D_2 k_1^2 C_1(q, t) - D_2(q^2 + k_2^2)C_2(q, t) \quad (4b)$$

which are identical to Berne-Pecora equations for point particles in the free draining limit.

In the presence of hydrodynamic interaction, it is clear, of course, that all mobilities $\mu_{ij}(q)$ ($i, j = 1, 2$) should be reexamined, even in the case of point particle description where, using the Oseen tensor description:

$$\mu_{ij} = (N_i N_j)^{1/2} \left[\delta_{ij} D_{ij} / k_B T + (-1)^{i+j+1} \frac{k_i k_j F(q/k)}{8\pi\eta_0 q} \right], \quad (5)$$

where $D_{ii} = D_i$ ($i = 1, 2$) is the diffusion coefficient of particle i and $F(x)$ was defined in I.

Substituting Eqs. (2) and (5) into Eq. (1) yields

$$\Omega_{11}(q) = D_1(q^2 + k_1^2) - \frac{k_B T}{8\pi\eta_0} \frac{k_1^2 (q^2 + k^2) F(q/k)}{q}, \quad (6)$$

$$\Omega_{12}(q) = -D_1 k_2^2 + \frac{k_B T}{8\pi\eta_0} \frac{k_2^2 (q^2 + k^2) F(q/k)}{q}. \quad (7)$$

Similar expressions can be written for $\Omega_{22}(q)$ and $\Omega_{21}(q)$ by interchanging the proper indices. Comparison of these equations with Eqs. (32a) and (32b) of I indicates the implications of the error made in assuming μ_{11} and μ_{22} independent of hydrodynamic interaction. This correction also affects the results concerning the eigenmodes Γ_1 and Γ_2 which characterize the relaxation in time of the measurable intermediate scattering function $S(q, t)$:

$$S(q, t) = A_1(q) e^{-\Gamma_1 t} + A_2(q) e^{-\Gamma_2 t}, \quad (8)$$

where the amplitudes $A_1(q)$ and $A_2(q)$ of these two modes are given explicitly in I.

Since this work is merely an addendum to Ref. 1, we would like to reexamine the same example as in I, in the light of the corrections made above, although perhaps the assumptions used in this example such as point particles limit, $D_1 = D_2 = D$ and the neglect of memory effects are not all realistic. Nevertheless, we think that the forms of the final results are suggestive and illustrate simply but clearly the phenomenon under investigation. Therefore, in this case, we obtain

$$\Gamma_1 = \left[D - \frac{k_B T}{8\pi\eta_0} \frac{k^2 F(q/k)}{q} \right] * [q^2 + k^2] \quad (9)$$

and

$$\Gamma_2 = D q^2. \quad (10)$$

It is interesting to note that, whereas the second mode is an ordinary diffusion mode of Rouse type, the first mode presents several specific features. First, an apparent q -dependent diffusion coefficient emerges:

$$D_{\text{app}} = D - \frac{k_B T}{8\pi\eta_0} \frac{k^2 F(q/k)}{q}, \quad (11)$$

where the second term in the right-hand side produces a decrease in D and appears as a correction due to the cloud of particles that surrounds each charge in the system. The reason why this correction is strongly q dependent is clear since the cloud is deformed as it "follows" the moving particle, and hence it is entirely due to hydrodynamic interaction. This observation is to be compared with that of Drifford and

co-workers for similar systems.^{2,3}

The more general case where one considers the dynamics of particles with different sizes, and different diffusion coefficients is certainly important from an experimental point of view and is now under investigation. But from the above formalism, one can of course immediately relax the condition of equal diffusion coefficients and let $D_1 \neq D_2$. For simplicity, we reproduce the results in the limiting regions of q values only: (i) In the small q region, $F(q/k) \rightarrow \frac{4}{3}(q/k)$, and we obtain

$$\Gamma_1 = \left(D_1 - \frac{k_B T}{6\pi\eta_0 k^{-1}} \right) k_1^2 + \left(D_2 - \frac{k_B T}{6\pi\eta_0 k^{-1}} \right) k_2^2 \quad (12)$$

and $\Gamma_2 = 0$. This constant limit of Γ_1 when $q \rightarrow 0$ was already obtained in I and characterized as a plasmon-like mode.

(ii) in the high q limit, one obtains as in I, a dynamic decoupling between the two species, i.e.,

$$\Gamma_1 = D_1 q^2, \quad \Gamma_2 = D_2 q^2. \quad (13)$$

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^{a)} Department of Nuclear Engineering, the University of Michigan, Ann Arbor, Michigan 48109.

^{b)} Research Reactor Facility, the University of Missouri, Columbia, Missouri 65211.

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ERRATA

Erratum: Thermal lens spectroscopic studies of radiationless processes in NO₂ [*J. Chem. Phys.* **79**, 3201(1983)]

Totaro Imasaka, Katsuhiko Shimano, and Nobuhiko Ishibashi
Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka 812, Japan

Due to an absorbance unit error we performed, the quantum yields of radiationless transition for NO₂ were incorrectly reported. The equations should be corrected to

$$\Theta \equiv \frac{2.303P}{\lambda k} \cdot \left(\frac{dn}{dT} \right) \cdot A, \quad (2)$$

$$\frac{I_0 - I_\infty}{I_0} = 0.524\Theta \equiv 1.207 \cdot \frac{P}{\lambda k} \cdot \left(\frac{dn}{dT} \right) \cdot A. \quad (3)$$

The calculated quantum yields from these equations are much lower than unity (0.45, 0.48). We repeated the experimental study, but the result was identical to the previous one within an experimental error. However, we found that the observed signal intensity was apparently lower than the theoretical intensity even for the nonfluorescent sample, which was ascertained by using a Co(II) aqueous solution. The ratio of the experimental and theoretical values were 0.36–0.42, which might be due to poor accuracy of theoretical prediction or experimental artifact coming from poor beam quality of the laser. Then, we divided the observed quantum yields by these correction factors. The obtained quantum yields were 1.01 at 514.5 nm and 1.11 at 488.0 nm. These results show that the quantum yields are unity in this wavelength region and electronic energies are completely converted to heat. Therefore, the conclusion was unchanged despite the above error.