Reanalysis of $D_{app}(q)$ of Polystyrene Latex Spheres in Terms of the Extended Coupled Mode Model

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Introduction. In their study of polystyrene latex spheres (PLS), Petsev and Denkov[1] fitted the apparent diffusion coefficient, $D_{app}(q)$, obtained by quasi-elastic light scattering methods to an empirical equation of the form,

$$D_{app}(q) = D_c + Aq^2 + Bq^4 \tag{1}$$

where the scattering vector is defined as $q = (4\pi n/\lambda)\sin(\theta/2)$, n is the index of refraction, λ is the wavelength of incident light, and θ is the scattering angle. It is shown in this paper that the small ion–polyion coupled mode model (CMM) of Lin, Lee, and Schurr[2] as extended to arbitrary q-values[3,4] (extended CMM, denoted by XCMM) gives a very good quantitative interpretation of the coefficients A and B as well as the $q = 0$ value D_c, provided that an appropriate number of terms are used in the empirical power series fit.

Theory. The CCM model[2] is based on three ionic components (component 1, the polyion; component 2, the counterion; component 3, the co-ion) with the approximations $D_2 = D_3 = D_s$ and $Z_2 = -Z_3$. With this formulation $D_{app}(q)$ is computed from the second root (R_2) of the 3 × 3 frequency matrix $\Omega(q)$, which has the elements,

$$[\Omega(q)]_{ij} = D_j^\circ[q^2\delta_{ij} + (Z_i/Z_j)\kappa_j^2] \tag{2}$$

where D_j° is the self-diffusion coefficient, δ_{ij} is the Dirac delta function, $\kappa_j^2 = 4\pi\lambda_B Z_j^2\langle n_j\rangle_u$ is the partial screening parameter of the jth species with a charge magnitude (and sign) Z_j and uniform concentration $\langle n_j\rangle_u$, and $\lambda_B = e^2/\epsilon k_B T$ is the Bjerrum length, with e being the proton charge, ϵ the dielectric constant of the medium, k_B Boltzmannn's constant, and T the absolute temperature.

Mathematica (Wolfram Research) was used[4] to obtain the roots (R_k) of the XCMM for arbitrary q with the result for $D_{app}(q)$,

$$D_{app}(q) = \frac{R_2(q)}{q^2} = \frac{X(q) - \{-4q^2D_1D_s(q^2 + \kappa_{tot}^2) + X(q)^2\}^{1/2}}{2q^2} \tag{3}$$

where $X(q) = D_1(q^2 + \kappa_1^2) + D_s(q^2 + \kappa_2^2 + \kappa_3^2)$ and $\kappa_{tot}^2 = \kappa_1^2 + \kappa_2^2 + \kappa_3^2$ is the total screening parameter. *Mathematica* was also used to represent eq 3 as a power series in q, viz.,

$$D_{app}(q) = \sum_{j=0}^{m} W_{2j}q^{2j} \tag{4}$$

where m can have the values 0, 1, 2, 3, ... The first three coefficients of the XCMM were given as

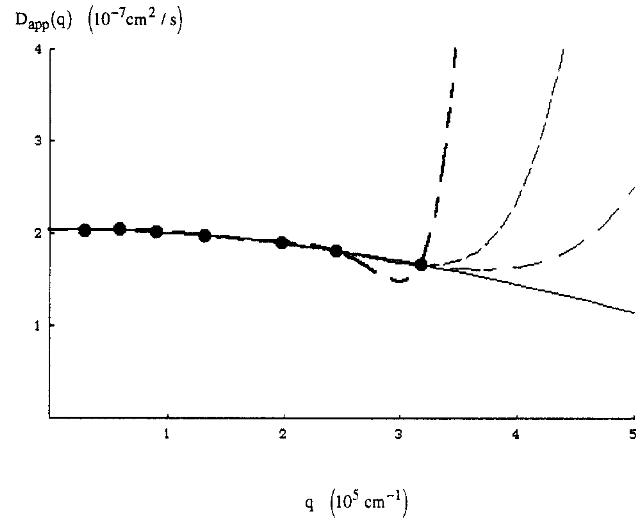

Figure 1. Power series fit to the PLS data for $\phi_1 = 1 \times 10^{-4}$ and [NaCl] = 1 × 10^{-4} M: (●) data of Petsev and Denkov;[1] (—) $D_{app}(q) = W_0 + W_2q^2 + W_4q^4$; (– -) $D_{app}(q) = W_0 + W_2q^2 + W_4q^4 + W_6q^6$; (- - -) $D_{app}(q) = W_0 + W_2q^2 + W_4q^4 + W_6q^6 + W_8q^8$; (– - –) $D_{app}(q) = W_0 + W_2q^2 + W_4q^4 + W_6q^6 + W_8q^8 + W_{10}q^{10}$. The values of the coefficients W_{2j} are given in Table 1.

Table 1. *Mathematica* Power Series Fit to PLS Data for Which $\phi_1 = 1 \times 10^{-4}$ and [NaCl] = 1 × 10^{-4} M[a]

$W_0 \times 10^7$ (cm^2/s)	$W_2 \times 10^{19}$ (cm^4/s)	$W_4 \times 10^{31}$ (cm^6/s)	$W_6 \times 10^{41}$ (cm^8/s)	$W_8 \times 10^{52}$ (cm^{10}/s)	$W_{10} \times 10^{61}$ (cm^{12}/s)
2.051	−3.980	+1.383			
2.046	−3.025	−25.61	+1.795		
2.049	−3.917	+28.02	+8.093	+5.379	
2.037	+2.865	−714.5	+261.4	−375.2	+1.784

[a] Series expansion is given by eq 4.

$$W_0 = \frac{D_1 + D_s}{2} + \frac{(D_1 - D_s)(D_s\kappa_2^2 + D_s\kappa_3^2 - D_1\kappa_1^2)}{2(D_1\kappa_1^2 + D_s\kappa_2^2 + D_s\kappa_3^2)} \tag{5}$$

$$W_2 = -\frac{D_1D_s(D_1 - D_s)^2\kappa_1^2(\kappa_2^2 + \kappa_3^2)}{(D_1\kappa_1^2 + D_s\kappa_2^2 + D_s\kappa_3^2)^3} \tag{6}$$

and

$$W_4 = \frac{D_1D_s(D_1 - D_s)^3\kappa_1^2(\kappa_2^2 + \kappa_3^2)(D_s\kappa_2^2 + D_s\kappa_3^2 - D_1\kappa_1^2)}{(D_1\kappa_1^2 + D_s\kappa_2^2 + D_s\kappa_3^2)^5} \tag{7}$$

Discussion. The total concentration of small ions ($2C_s$) in these calculations is given by $2C_s = 2C_{add} + |Z_1|C_1$, where $Z_2 = +1$, $|Z_1|C_1$ is the molar concentration of released counterions, and $C_2 = |Z_1|C_1 + C_3$ (electrical neutrality requirement). Calculations were carried out with the reported[1] values of ϕ_1 (the volume fraction), $Z_1 = -40$, and $D_1^\circ(20^\circ) = 1.86 \times 10^{-7}$ cm^2/s. The value $D_s = 2 \times 10^{-5}$ cm^2/s was assumed. The PLS concentrations were calculated from the relationship $C_1 = (4000\pi R_1^3/3N_A)\phi_1$, where the radius R_1 was computed from $D_1^\circ(20^\circ)$.

For the purpose of visualization of the quality of the expansion fits, data for [NaCl] = 1 × 10^{-4} M and $\phi_1 = 1 \times 10^{-4}$ reported by Petsev and Denkov[1] are shown in Figure 1 along with the *Mathematica* empirical fit using the power series of eq 4 with m = 2, 3, 4, or 5. The numerical values for W_0 through W_{10} are listed in Table 1, where the plus signs are included for emphasis.

Errors can sometimes occur in the process of extracting numerical values from a published plot. Comparison of

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Table 2. Comparison of A and B with W_2 and W_4 for the Extended Coupled Mode Model[a]

$\phi_1 \times 10^4$	1	2	4	6
$A \times 10^{19}$ (cm⁴/s)	−3.94	−7.37	−13.9	−17.8
$W_2 \times 10^{19}$ (cm⁴/s)	−3.45	−6.79	−13.2	−19.1
$B \times 10^{31}$ (cm⁶/s)	+1.39	+19.7	+50.6	+61.9
$W_4 \times 10^{31}$ (cm⁶/s)	−31.4	−61.1	−116.0	−165.2

[a] A and B were reported for the PLS data by Petsev and Denkov.[1] W_2 and W_4 were computed from eqs 6 and 7, respectively, with the reported values of $D_1^\circ = 1.86 \times 10^{-7}$ cm²/s, $Z_1 = -40$, and ϕ_1 (hence C_1) with an assumed value of $D_s = 2 \times 10^{-5}$ cm²/s.

the Petsev–Denkov[1] values of A and B in the first column of Table 2 with the *Mathematica* empirical values of W_2 and W_4 in the first row of Table 1 indicates that the set of data points extracted from the literature are accurate. It is evident from these empirical fits that the parameter W_0 is quite reliable, varying by less than 1%. The parameter W_2 is likewise assumed stable to within 25% provided that one does not "overfit" the curve, as indicated by the "oscillation" for the expansion to the q^{10}th term in Figure 1.

Attention is now directed to the model-dependent calculations of W_2 and W_4 in Table 2 for eqs 6 and 7, respectively. Since the values of D_1°, Z_1, and ϕ_1 (hence C_1) in these calculations were those reported by Petsev and Denkov,[1] the agreement between the values of A and W_2 is quite remarkable. The discrepancies between B and W_4, even with regard to the sign, may be due to the premature truncation of the empirical fit of the data to only the q^4 term. An empirical fit of the data to the q^6 term results in much better agreement of W_4 between the empirical fit value ($W_4 = -25.61 \times 10^{-31}$ cm⁶/s in Table 1) and the XCMM calculation ($W_4 = -31.4 \times 10^{-31}$ cm⁶/s in Table 2).

It can be concluded that the expansion coefficients W_2 and W_4 obtained from the extended CMM are consistent with the curve-fitting parameters of the $D_{app}(q)$ versus q data for PLS particles, provided that the expansion is not prematurely truncated to the q^4th term or "overfitted" to higher powers of q. The agreement between the empirical fit coefficients and the XCMM expressions strongly supports the notion that the original CMM and that the Drifford and co-workers[5,6] modification of the theory to include arbitrary values of D_2, D_3, Z_2, Z_3, and hydrodynamic interactions are valid for *dilute* colloidal systems.

While, in principle, hydrodynamic interactions can be included in the XCMM approach to the q-dependent diffusion coefficient, this has not yet been formally achieved as in the theory of Drifford and co-workers[5,6] for $D_{app}(q=0)$. It is anticipated that inclusion of the hydrodynamic interactions will further increase the magnitude of Z_1 in the XCMM characterization of the data. Proof of this conjecture awaits further experimental data on highly charged spherical particles in the very dilute concentration regime for both the added electrolyte and polyion.

References and Notes

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