Mean Relaxation Times in Quasi-Elastic Light Scattering

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ABSTRACT: Mean relaxation times are introduced and calculated for the complicated autocorrelation function of the pearl-necklace model. They are compared with those for a homogeneous sphere and a rod. The procedure of comparing these with mean relaxation times measured by heterodyne and homodyne detection is given.

When using model calculations for the interpretation of quasi-elastic light scattering, one often gets complicated autocorrelation functions consisting of a superposition of many terms, as for instance the autocorrelation function of the pearl-necklace model calculated by Pecora[1,2] (eq 3 of this paper). In cases like this, it is impossible to fit directly the experimental curves to the calculated autocorrelation functions in the entire angular range for numerical and computational reasons.

Many authors tried to test the necklace model in the following way: at sufficiently small angles the experimental curves were fitted to the translational diffusion term according to Pecora's theory; then they extracted additional information from a certain small range of higher angles, where the superposition of only two terms, the translational diffusion term and the term of the segmental motion with the longest relaxation time, is predicted by the theory. This method has the disadvantage that the information given by the autocorrelation functions of all the other angles is not used and therefore it might be expected that many models would fit the results of the measurements within the experimental uncertainties.

The present treatment introduces mean relaxation times T^* and T^{**}, which can be determined analytically from model calculations and can be measured directly and precisely. Using these parameters the model can be tested over the whole angular range.

In addition, when the coil dimensions are very large, even at very low angles the translational diffusion term is superimposed on the terms of segmental motion. In this case the translational diffusion coefficient D can no longer be extracted directly from measurements in the low-angle region. But by introducing T^* and T^{**} the model can be tested over the entire angular range and D is determined from this fit.

The mean relaxation times T^* and $\tilde{T}$ can be defined as was done formerly by Schwarz[3] for kinetic investigation of reaction systems. (The definition of T^{**} will follow later.)

$$\frac{1}{T^*} = -\lim_{t\to 0} \frac{\mathrm{d}P(\varkappa,t)}{\mathrm{d}t} \qquad (1)$$

and

$$\tilde{T} = \int_0^\infty P(\varkappa,t)\mathrm{d}t \qquad (2)$$

where $P(\varkappa,t)$ = autocorrelation function; $\varkappa$ = scattering parameter ($\varkappa = (4\pi n/\lambda_0)\sin\vartheta/2)$; λ_0 = wavelength of light in vacuum; n = index of refraction; ϑ = scattering angle. The values of T^* and $\tilde{T}$ are easily extracted from experimental curves.

T^* is often used in polydispersity problems in quasi-elastic light scattering and $\tilde{T}$ could also easily be introduced in that field. However, in the case of the pearl-necklace model it seems to be impossible to obtain $\tilde{T}$ from the model calculation analytically.

Therefore, in the following section only T^* is introduced into the theory of the pearl-necklace model and the T^* function deduced will be subsequently compared with the corresponding simply calculated functions for rods and spheres.

Calculation of T^* for the Pearl-Necklace Model

The mean relaxation times for the pearl-necklace model will now be derived from eq 8 given in the paper of Pecora[2] for the free-draining case:

$$P(\varkappa,t) = \exp(-D\varkappa^2 t)z^{-2} \sum_{j=0}^{z}\sum_{l=0}^{z} \exp\left[1/6(-\varkappa^2) \times \left\{ \sum_{k=1}^{z} \langle \mu_k{}^2\rangle_\mathrm{e}[Q_{jk}{}^2 + Q_{lk}{}^2 - 2Q_{lk}Q_{jk}\exp(-t/\tau_k)] \right\} \right] \qquad (3)$$

where D = translational diffusion coefficient; z = number of segments; $\langle \mu_k{}^2\rangle_\mathrm{e}$ = mean-squared equilibrium length of the kth normal mode coordinate; τ_k = relaxation time of the kth normal mode. The following two expressions for the relaxation times τ_k of segmental motion have been given:

$$\tau_k = 6M\eta_\mathrm{s}[\eta]/\pi^2k^2RT \qquad (4)$$

$$\tau_k = \langle l^2\rangle_\mathrm{e}/(3\pi^2k^2D) \qquad \text{for} \qquad k \ll z \qquad (5)$$

where η_s = solvent viscosity; $[\eta]$ = viscosity number; R = gas constant; T = absolute temperature; M = molecular weight; $\langle l^2\rangle_\mathrm{e}$ = equilibrium mean-squared end-to-end distance of the chain.

It is possible to express both relaxation times in the form

$$\tau_k = 1/Ak^2 \qquad (6)$$

with A independent of index k.

Equations 1 and 3 give the mean reciprocal relaxation time:

$$\frac{1}{T^*} = D\varkappa^2P(\varkappa) - z^{-2} \times \left\{ \sum_{j=0}^{z}\sum_{l=0}^{z} \exp\left[1/6(-\varkappa^2) \sum_{k=1}^{z} \langle \mu_k{}^2\rangle_\mathrm{e}[Q_{jk} - Q_{lk}]^2 \right] \times \left(1/6(-\varkappa^2) \sum_{k=1}^{z} \langle \mu_k{}^2\rangle_\mathrm{e} 2Q_{lk}Q_{jk}/\tau_k \right) \right\} \qquad (7)$$

where $P(\varkappa)$ is Debye's scattering formula for flexible Gaussian coils[6]

$$P(\varkappa) = \frac{2}{x^2}(e^{-x} - 1 + x) \qquad (8)$$

with $x = R_\mathrm{G}{}^2\varkappa^2$ and R_G = radius of gyration.

By using the formulas of Peterlin and Reinhold[5] for Q_{jk} the following expression is derived:

$$\frac{1}{T^*} = D\varkappa^2P(\varkappa) + z^{-2}\left\{ \sum_{j=0}^{z}\sum_{l=0}^{z} e^{-x(|j-l|/z)} \sum_{k=1}^{z} \frac{2xA}{\pi^2} \times \left(\cos\frac{\pi k(l+j)}{z} + \cos\frac{\pi k(j-l)}{z} \right) \right\} \qquad (9)$$

It is seen that the sum

$$S_{l,j} = \sum_{k=1}^{z} \cos\frac{\pi k(l+j)}{z} + \cos\frac{\pi k(j-l)}{z} \qquad (10)$$

can be simplified in the following way: for $l = 0$ and $j = 0$, $S_{0,0} = 2z$; for $l = j$, $S_{l,l} = z$; for all l, j with $|l - j|$ equal to an odd number, $S_{l,j} = -2$; for all l, j with $|l - j|$ equal to an even number and $l \neq j$, $S_{l,j} = 0$.

Now eq 9 can be rewritten as follows

$$\frac{1}{T^*} = D\varkappa^2 P(\varkappa) + \frac{2xA}{\pi^2 z^2} 2z + \frac{2xA}{\pi^2 z^2} z^2 - z^{-2} \left\{ \sum_{j=0}^{z} \sum_{l=0}^{z} e^{-x(|j-l|/z)(2xA/\pi^2)} (1 - \cos(\pi|j - l|)) \right\} \quad (11)$$

The factor $(1 - \cos(\pi|j - l|))$ is introduced to give a value of 0 or 2 for $|j - l|$ even or odd, respectively.

The last term in eq 11 can be converted into an integral form:

$$z^{-2}\{\ldots\} = \frac{2xA}{\pi^2} P(\varkappa) - \frac{4xA}{\pi^2 z^2} \times \int_0^z (z - p + 1)e^{-xp/z} \cos(\pi p)\, \mathrm{d}p \quad (12)$$

By integration it is seen that the second term on the right-hand side of eq 12 vanishes for large z.

Therefore the final expression for eq 11 is:

$$\frac{1}{T^*} = P(\varkappa)\left\{D\varkappa^2 - \frac{2xA}{\pi^2}\right\} + \frac{2xA}{\pi^2} \quad (13)$$

This is the general formula for the pearl-necklace model applying to both relaxation times τ_k. Introducing $A = 3\pi^2 D/\langle l^2\rangle_e$, derived from eq 5 and the relation $x = \varkappa^2\langle l^2\rangle_e/6$, into eq 13, a very simple expression for $1/T^*$ is found:

$$1/T^* = \varkappa^2 D \quad (14)$$

Discussion

In order to compare T^* of the pearl-necklace model with that of a sphere and a rod let us derive the T^* functions for these models. The autocorrelation function for a homogeneous sphere in the Rayleigh-Debye region is

$$P(\varkappa,t) = P(\varkappa)e^{-\varkappa^2 Dt} \quad (15)$$

with[6]

$$P(\varkappa) = \left[\frac{3}{u^3}(\sin u - u \cos u)\right]^2 \quad (16)$$

$$u = R\varkappa \quad (17)$$

where R = radius of the sphere and T^* is given by

$$1/T^* = \varkappa^2 DP(\varkappa) \quad (18)$$

According to Cummins et al.[7] the autocorrelation function for a rod is

$$P(\varkappa,t) = e^{-\varkappa^2 Dt} \sum_{\substack{l=0\\ \text{even}}}^{\infty} B_l e^{-l(l+1)D_R t} \quad (19)$$

where[9]

$$B_l = (2l + 1)\left[\frac{1}{h}\int_0^h j_l(w)\, \mathrm{d}w\right]^2$$

It follows that

$$\frac{1}{T^*} = \varkappa^2 DP(\varkappa) + D_R \sum_{\substack{l=0\\ \text{even}}}^{\infty} B_l l(l + 1) \quad (20)$$

with

$$P(\varkappa) = \frac{1}{h}\int_0^{2h} \frac{\sin w}{w}\, \mathrm{d}w - \left(\frac{\sin h}{h}\right)^2 \quad (21)$$

and

$$h = (L/2)\varkappa \quad (22)$$

where L = length of the rod.

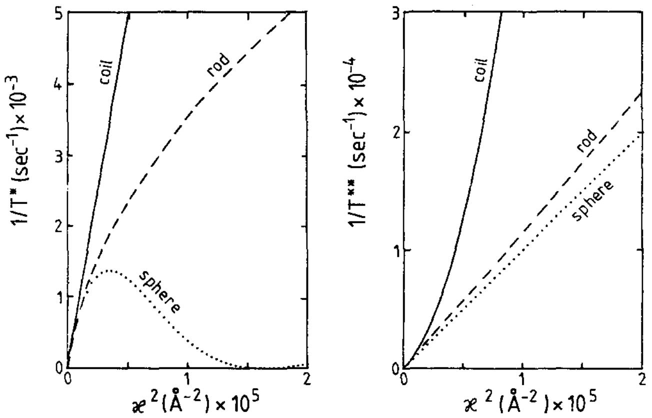

Figure 1. Comparison of $1/T^*$ and $1/T^{**}$ for coil, rod, and sphere. The rod has a length L of 3000 Å and the sphere a radius of 1118 Å in order to give in each case the same radius of gyration (R_G = 866 Å) as was given to the coil. D was in all cases 10^{-7} cm^2 s^{-1} and D_R for the rod was 300 s^{-1}.

In practice, as outlined by Cummins and Swinney,[8] there are two methods to obtain $P(\varkappa,t)$, namely heterodyne and homodyne detection. Neglecting the shot noise and the direct current, it is found that in the case of heterodyne detection $P(\varkappa,t)$ is directly measured, whereas in the case of homodyne detection the square of $P(\varkappa,t)$ is found. In order to compare the initial slopes of the experimental autocorrelation functions in the homodyne case directly with those obtained from model calculations, the following expression has to be used

$$\left(\frac{1}{T^*}\right)_{\text{hom}} = -\lim_{t\to 0} \frac{\partial}{\partial t} P^2(\varkappa,t) = 2P(\varkappa)\frac{1}{T^*} \quad (23)$$

It is clear that a plot of $1/T^*$ or $(1/T^*)_{\text{hom}}$ against $\varkappa$ gives all the information accessible to elastic and quasi-elastic light-scattering experiments. In practice, however, one is often only interested in the dynamic aspects of the sample and it is not necessary to have the ratios of the amplitudes of the autocorrelation functions for different $\varkappa$ values. This means that the amplitudes of the measured autocorrelation functions need not be calibrated. To get reasonable results in these cases each initial slope must be divided by the uncalibrated amplitude of the corresponding autocorrelation function (and in the homodyne case also by 2, according to eq 23) to obtain what may be termed the reduced reciprocal mean relaxation time $1/T^{**}$. In model calculations $1/T^{**}$ is found in the following way:

$$\frac{1}{T^{**}} = \frac{1}{T^*}\frac{1}{P(\varkappa)} \quad (24)$$

$$\frac{1}{T^{**}} = \left(\frac{1}{T^*}\right)_{\text{hom}} \frac{1}{2P^2(\varkappa)} \quad (25)$$

Figure 1 gives a comparison of model calculations of $1/T^*$ and $1/T^{**}$ for the pearl-necklace model, the rod, and the sphere. With L = 3000 Å for the length of the rod and R = 1118 Å for the radius of the sphere, both have a radius of gyration R_G of 866 Å, the same as was given to the coil. The translational diffusion coefficient was 10^{-7} cm^2 s^{-1} for all models. D_R, the rotational diffusion constant, had a value of 300 s^{-1}.

References and Notes

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(9) The integral $\int_0^h j_l(w)\,\mathrm{d}w$ can be transformed into the following sum that converges quickly:

$$\int_0^h j_l(w)\,\mathrm{d}w = \frac{(2l+3)}{(l+1)} j_{l+1}(h) + \sum_{k=1}^{\infty} \frac{(2l+3+4k)}{(l+1+2k)} \left(\prod_{i=1}^{k} \frac{l+2i}{l+2i-1} \right) j_{l+1+2k}(h)$$

Effect of Cation Size on Heats of Dilution of Aqueous Solutions of Alkaline Poly(styrenesulfonates)

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ABSTRACT: Intermediate heats of dilution at 25 °C have been measured for salt-free aqueous solutions of poly(styrenesulfonic acid) and its alkaline salts and for *p*-toluenesulfonic acid and its lithium and rubidium salts in the moderate concentration range (up to 15% by weight). Dilution for all the monomers and the polyacid and its lithium salt is exothermic over the entire concentration range covered in this investigation. The other polymeric salts give endothermic heats of dilution at moderate concentration; as concentration decreases, dilution becomes exothermic. Results are discussed in terms of the Eigen and Wicke theory on moderately concentrated electrolyte solutions, underlying hydration phenomenon as a criterion to distinguish between site binding and ionic atmosphere binding. The chemical model describing ion hydration is used to explain some of the results obtained for the polymeric and monomeric salts.

Polyelectrolytes combine the many problems of ionic interactions in solution and all those of ordinary polymers. Many experimental techniques have been used in the physical chemistry of polyelectrolyte solutions and some of the problems have been partly solved.[1] Among those techniques, heats of dilution measurement is very useful since a large concentration range can be investigated and some interesting results have already been published.[2–8]

It has been shown[9,10] that poly(styrenesulfonic acid) is completely ionized in aqueous solution and it is believed that the same is true for all strong polyelectrolytes. However, their transport properties and the osmotic coefficient of the counterions indicate that only a small fraction of them are free to move in solution.[1] To explain these experimental facts, many authors[11,12] have suggested the existence of two types of binding as usually found in moderately concentrated simple strong electrolyte solutions. One type of interaction between the charged sites on the polyion and the counterions is due to electrostatic attraction between opposite charges; this type of interaction is sometimes called ionic atmosphere binding or physical association. The second type of ionic association is believed to be due to specific interaction between the counterions and the charged sites on the polyelectrolyte chain; this type of interaction is called "site binding" or chemical association and is described in terms of a chemical equilibrium and results in a simultaneous decrease of the actual charge born by the polyion and the concentration of free counterions. Manning's treatment[13] suggests that even for a very dilute polyelectrolyte solution many counterions will condense on the polyion and that the mobile ions may be treated in the Debye–Hückel approximation.

Positive evidence for site binding is based on many experimental grounds[12,14,15] and it seems that it is accompanied by the release of water molecules from the solvation shells of the participating species. So, dehydration would serve as a criterion to distinguish between site binding and ionic atmosphere binding since solvation shells are kept untouched in the second type of ion binding. Dehydration of large alkali metal ions such as Cs^+ and Rb^+ upon formation of site binding may be said to be almost complete but the site binding of smaller ions such as H^+ and Li^+ may occur without complete dehydration.

On the basis of what has been mentioned above, the dilution of a moderately concentrated aqueous solution of a strong polyelectrolyte may be accompanied by many phenomena. Dilution effects may be regarded under two different aspects which are intimately correlated, the ionic aspect and the molecular aspect of dilution. The first effect of dilution will be the release of site bound counterions and that will involve a great amount of energy. This endothermic effect will be immediately followed by hydration of charged species which is essentially an exothermic phenomenon. Enthalpy of hydration[16] of H^+ is -1092×10^3 J mol^{-1} and that of alkali metal ions ranges between -209×10^3 and -469×10^3 J mol^{-1} from Cs^+ to Li^+. However, if only large cations are believed to be almost completely dehydrated when site bound, freeing of partly dehydrated counterions such as H^+ and Li^+ will be less endothermic since they are loosely bound to the sites on the chain due to the screening effect of the water molecules still attached to cations and negative sites. Also, hydration upon freeing of large cations should be relatively more important than that of hydrogen and lithium ions.

Hydration is not as simple a phenomenon as it appears at first sight. Hydration mechanism is believed to differ from one group of ions to another and the change in molecular structure of water due to the presence of charges will then be different for each group of ions.[17–19] According to the chemical model, each ion is embodied in cospheres made of water molecules leading to hydration of the first and of the second kind. Small cations having negative second cosphere entropy values (K^+, Rb^+, Cs^+) are called structure-breaking ions and this effect on water structure surely contributes to the heat of dilution.

In the absence of added salt, intra- and intermolecular repulsions between charged sites set free by the diffusion of some counterions out of the immediate vicinity of the polyion are increasing as dilution of a concentrated solution increases. The dilution of repulsive charges (counterions and charged sites) leads to an exothermic effect.

Finally, dilution of a moderately concentrated polyelectrolyte solution will produce some changes in the conformation of the chains. At a given concentration, polyelectrolyte mol-