Osmotic compressibility of partially deuterated polymer solutions

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Elastic neutron scattering by partially deuterated polymer solutions has played an essential role in elucidating the large scale conformations in good solvents. The long wavelength limit of the structure factor yields the osmotic compressibility of the deuterated monomers (assuming that the data have been analysed in terms of the large deuteron coherent scattering). In this paper, we present a rather general theory of this deuterated monomer osmotic compressibility as a function of percentage deuteration for general interactions among monomers. This method yields known results for neutral excluded volume systems and some new predictions for polyelectrolytes.

INTRODUCTION

Elastic neutron scattering has proven to be a powerful tool for the investigation of the overall dimensions and internal structure of polymer solutions[1]. Furthermore, the large coherent scattering amplitude of deuterons (as compared to protons) has enabled the application of selective deuteration to provide some rather different and complementary information on polymer conformations to that obtained from completely deuterated samples. For example, with a low concentration of completely deuterated chains, the geometry of an isolated macromolecule in the presence of the other (protonated) polymers is investigated. Assuming that the deuteration has negligible effect on the monomer–monomer interaction, the concentration dependence of the conformation of an isolated chain is elucidated. In the limit of forward scattering, the elastic neutron scattering intensity is proportional to the compressibility of the main coherent scatterers. For example, in an entirely deuterated polymer solution (the solute molecules being deuterated), one measures the osmotic compressibility. For a partially deuterated sample, it is the osmotic compressibility associated with the labelled monomers that is determined.

The goal of the present study is to investigate the effect of the concentration of deuterated polymers on the observed form factors. We do this in two stages.

We proceed to calculate the dependence of the deuteron osmotic compressibility (*DOC*) on the concentration of deuterated monomers (c_D) embedded in a solution of overall monomer concentration c, and assuming that all polymers are either completely deuterated or completely protonated.

This information will be very useful in normalizing neutron scattering data on samples of various concentrations. Furthermore for polyelectrolytes[2] where the osmotic pressure is large, the corresponding weak density fluctuations produce weak scattering intensities requiring higher labelling concentrations than for neutral systems.

We shall present derivations of the *DOC* for a very general form of the monomer–monomer interaction. Then, we shall discuss this result in terms of the renormalized excluded volume interaction[1] appropriate for neutral polymers in good solvents. These ideas will then be extended to the case of polyelectrolytes in solutions of various ionic strengths. Both calculations assume that deuteration does not effect the monomer–monomer interaction.

To approach the problem from a different point of view, we set up self consistency equations relating the single chain correlation function to the deuteron correlation functions at finite concentrations. To simplify the expressions we neglect the small long wavelength fluctuations in the total density. The resulting expressions give the correct osmotic pressure for low deutron concentrations. They are different from the expressions of Daoud *et al.*[1] based on the work of Zimm[3]. We also believe the derivation has certain intuitive advantages in bringing out the role of the gyration radius (R_G) in problems of this type.

DEUTERON OSMOTIC COMPRESSIBILITY: GENERAL FORMULATION

We consider a monodisperse solution of polymers where some of the chains are completely deuterated[4]. The crucial assumption is that all interactions (other than the neutron coherent scattering amplitude) involving deuterated monomers are identical to those of the protonated species. If $c_i (i = p, d$ corresponding to the protonated and deuterated species respectively) is the monomer concentration of the i^{th} species, the energy associated with small concentration fluctuations is given by[5]

$$\delta G = \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 G}{\partial c_i \partial c_j} \right)_0 \delta c_i \delta c_j \tag{1}$$

where δc_i is the concentration fluctuation of the i^{th} species and G is the Gibbs energy per unit volume. For dilute solutions

$$G = G_0 + k_B T \Sigma_i (c_i/N) \ln (c_i/N) + U(c) \tag{2}$$

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where G_0 represents the solvent–solute interaction which is linear in the c_i, the second term is the contribution to the Gibbs energy associated with the translational entropy of macromolecules of polymerization index N, and the last term is the monomer–monomer interaction energy density which depends only on the total concentration $c = \Sigma_i c_i$. For the moment, this interaction term will be treated quite generally. We shall discuss specific cases later. The second derivatives in equation (2) are

$$\left(\frac{\partial^2 G}{\partial c_i \partial c_j}\right)_0 = (k_B T/Nc_i)\delta_{ij} + \frac{\partial^2 U}{\partial c^2} \tag{3}$$

leading to

$$\delta G = \frac{1}{2}\left[\frac{k_B T}{Nc_p} + \frac{\partial^2 U}{\partial c^2}\right]\delta c_p^2 + \frac{1}{2}\left[\frac{k_B T}{Nc_d} + \frac{\partial^2 U}{\partial c^2}\right]\delta c_d^2 + \frac{\partial^2 U}{\partial c^2}\delta c_p \delta c_d \tag{4}$$

This quadratic form may easily be diagonalized to yield the mean square fluctuation in the deuterated monomer concentration which is directly related to the long wavelength limit of the neutron coherent scattering structure factor $S(q)$

$$\lim_{q\to 0} S(q) \simeq \langle \delta c_d^2 \rangle V = \frac{Nc_d\left[1 + \frac{\partial^2 U}{\partial c^2}\frac{Nc_p}{k_B T}\right]}{1 + \frac{\partial^2 U}{\partial c^2}\left[\frac{Nc}{k_B T}\right]} \tag{5}$$

The *DOC* (χ_d^d) is related to equation (5) by a standard thermodynamic relation

$$\langle \delta c_d^2 \rangle V = k_B T c_d^2 \chi_d \tag{6}$$

An alternate derivation of (5)–(6) is to assume that a small external pressure, π_d is applied that couples only to the deuterated monomers. Then the resulting modification of the densities of deuterated and protonated monomers are given by

$$\delta c_d / c_d = \chi_d^d \pi_d = \chi_d^0\left[\pi_d - \frac{\partial^2 U}{\partial c^2} c_d \delta c\right]$$

$$\delta c_p / c_p = \chi_p^d \pi_d = -\chi_p^0 \frac{\partial^2 U}{\partial c^2} c_p \delta c \tag{7}$$

On the right hand side of these expressions, χ_p^0, χ_d^0 are the compressibilities in the absence of any interactions ($\chi_{p,d}^0 = N/c_{p,d}k_B T$) and the term involving $\partial^2 U/\partial c^2$ is the effective field resulting from the change in concentration generated by π_d. Then writing $\delta c = (\chi_p^d + \chi_d^d)\pi_d$ and solving the resulting pair of coupled equations for χ_p^d and χ_d^d, (5) is immediately obtained. We shall now apply equation (5) to several cases of relevance to semi-dilute polymer solutions.

As an example of the application of equation (5), let us first consider a monodisperse solution of neutral flexible polymers in a good solvent where the interactions between monomers may be described by an excluded volume v. Then, the mean field form for the interaction energy density is

$$U(c) = \frac{1}{2} k_B T v c^2 \tag{8}$$

Using this expression in equation (5) we obtain

$$S(0) = Nc_d(1 + Nvc_p)(1 + Nvc)^{-1} \tag{9}$$

In semi-dilute solutions ($Nvc \gg 1$) and not too high deuterated monomer concentration ($Nvc_p \gg 1$), e.g. (9) reduces to the standard result[1]:

$$S(0) \cong Nc_d(c_p/c) \tag{10}$$

When all monomers are deuterated ($c_p = 0$),

$$S(0) = Nc(1 + Nvc)^{-1} \tag{11}$$

which is the random phase approximation result[6] for the excluded volume problem. In ref 1 it is argued that the excluded volume, v, should be renormalized and replaced in these expressions by[7]

$$\tilde{v} = v(vc)^{1/4} \tag{12}$$

POLYELECTROLYTES

We shall now discuss the osmotic compressibility for polyelectrolyte solutions. We focus on semi-dilute solutions, where the chains interpenetrate and we assume the isotropic model[2].

We picture an idealized polyion as a polymer where each monomer carries a charge e which is compensated by hydrated counterions. The polymer is assumed to be perfectly flexible except for the Coulomb forces which tend to stretch the chains in dilute solutions. In semi-dilute solutions, the screening length (κ^{-1}) is sufficiently short that distant parts of one chain are effectively screened from one another. The stretched chain then collapses as a function of increasing concentration yielding a spherically symmetric conformation; this is the picture associated with the isotropic model. The interaction energy in this regime may be estimated by considering a segment of one chain of length κ_0^{-1}. On this scale the chain is stretched by the Coulomb forces with an energy per monomer

$$U \cong \frac{2e^2}{\epsilon a}\int_a^{\kappa_0^{-1}} \frac{dx}{x} \simeq -\frac{2e^2}{\epsilon a}\ln(\kappa_0 a) \tag{13}$$

or an energy density

$$U \cong -\frac{2ce^2}{\epsilon a}\ln(\kappa_0 a) \tag{14}$$

where ϵ is the dielectric constant of the solvent. The Debye screening length is given by

$$\kappa_0^2 = 4\pi c e^2/\epsilon k_B T \tag{15}$$

which yields

$$\frac{\partial^2 U}{\partial c^2} = \frac{3}{2} e^2(\epsilon ac)^{-1} \tag{16}$$

For completely deuterated samples this gives

$$S(0) \cong \frac{2}{3} c\epsilon k_B T/e^2 \tag{17}$$

in substantial agreement with de Gennes *et al.*[2]. In order to simplify the discussion, we define the characteristic length

$$l = e^2/\epsilon k_B T \tag{18}$$

which is typically of order a. This gives for the fully deuterated systems

$$S(0) \cong \frac{2}{3} c(a/l) \sim c \tag{19}$$

As the concentration of deuterated chains is diluted with protonated polymers, the low angle scattering intensity increases slowly and then crosses over to the typical low density regime equation (10) at

$$c_p \sim (c/N)\,(a/l) \sim c_D/N \tag{20}$$

Thus so long as a substantial fraction ($\gtrsim N^{-1}$) of the chains are protonated, the polyelectrolyte has the same *DOC* as neutral systems.

The preceding discussion of polyelectrolyte solutions assumed no saline screening. We shall now consider the case where a concentration of a monovalent salt (e.g. NaCl) is added to the solution, thereby decreasing the Debye screening length to

$$\kappa^2 \cong 4\pi(n + c)l = (1 + n/c)\kappa_0^2 \tag{21}$$

The interactions between monomers are then of the form of screened Coulomb potentials leading to an effective excluded volume parameter at zero momentum transfer

$$v(0) \simeq l/\kappa^2 \tag{22}$$

or a renormalized interaction (equation 12)

$$\tilde{v}(0) = (l/\kappa^2)\,(\kappa_0/\kappa)^{1/2} \tag{23}$$

For a completely deuterated sample this yields

$$S(0) = c(\kappa/\kappa_0)^{5/2} \simeq c(1 + n/c)^{5/4} \tag{24}$$

which scales properly between the excluded volume result ($c^{-1/4}$) for $n \gg c$ to the linear c dependence for low salt concentration. This result may also be obtained by the following argument. For completely deuterated excluded volume chains

$$S(0) \cong \tilde{v}^{-1} \tag{25}$$

In the presence of strong screening, a polyelectrolyte should behave as a chain of hard globules of radius κ^{-1}, each globule containing $(\kappa a)^{-1}$ monomers. Then

$$\tilde{v}^{-1} \cong \kappa^3(\kappa^3 c\kappa a)^{-1/4} \cong \kappa^3(\kappa/\kappa_0)^{1/2} \tag{26}$$

But, this is $S(0)$ per globule and to obtain $S(0)$ per monomer we must multiply by the number of monomers per globule $(\kappa a)^{-1}$ yielding

$$S(0) \simeq c(\kappa/\kappa_0)^{5/2} \tag{27}$$

in agreement with equation (24).

When some chains are protonated, $S(0)$ tends towards (10) when

$$c_D \approx (c/N)\,[1 + n/c]^{5/4} \tag{28}$$

These properties may be experimentally studied by coherent neutron scattering. Osmotic pressure studies using membranes permeable to the small ions may be used to investigate equation (24).

LABELLED CORRELATION FUNCTIONS

As above we consider a semi-dilute solution of total monomer concentration c of which c_p are protonated and c_d deuterated. We also assume that the chains, of length N, are either wholly protonated or deuterated. We wish to construct the correlation function for the deuterated species[8].

Assume there is a deuterated monomer at the origin. Up to a correlation distance ξ all monomers then belong to the same chain and are therefore also deuterated. Beyond this one has two contributions. There is the contribution of monomers belonging to the original chain described by the single chain correlation function $g_{sc}(r)$. All these monomers are deuterated. This creates a correlation hole in the density of the monomers belonging to other chains $[c_o(r)]$ since the total density must add up to c:

$$c_o(r) = c - g_{sc}(r) \tag{29}$$

If these other chain monomers were independent of each other one would have an additional density of deuterons $c_d/c \cdot c_o(r)$ and

$$g_d(r) = g_{sc}(r) + \frac{c_d}{c}\,[c - g_{sc}(r)]$$

$$= c_p/c g_{sc}(r) + c_d$$

This is, however, inconsistent in the correlated region where $g_{sc}(r) \neq 0$ because each additional chain carries with it a locally enhanced deuteron density $[g_d(r) - c_d]$. We therefore have to compute $g_d(r)$ in a self-consistent way.

$$g_d(r) = g_{sc}(r) + \frac{c_d}{Nc}\int \mathrm{d}r'\,[c - g_{sc}(r')]\;[g_d(r - r') - c_d] \tag{30}$$

We emphasize two points: the integral (dr') is, in essence, an integral over additional chains. Hence the factor $1/N$. Each chain has a form factor

$$\hat{g}_d(r) = g_d(r) - c_d$$

describing the local enhancement in deuterated density due to the fact that a deuterated chain is known to be there.

It is convenient to subtract c_d from equation (30). This leads to a self-consistent equation for $\hat{g}_d(r)$:

$$\hat{g}_d(r) = g_{sc}(r) - c_d/Nc \int \mathrm{d}\mathbf{r}' g_{sc}(r') g_d(\mathbf{r} - r') \qquad (32)$$

Finally, Fourier transforming equation (5), one finds:

$$\hat{g}_d(q) = g_{sc}(q)/[1 + (c_d/Nc)g_{sc}(q)] \qquad (33)$$

where $g(q)$ is the Fourier transform of $g(r)$.

In the limit $q \rightarrow 0$ this becomes

$$\lim_{q \to 0} \hat{g}_d(q) = N/(1 + c_d/c) \qquad (34)$$

where we have used $g_{sc}(0) = N$.

It can be seen that this coincides with our result for the deuterated osmotic pressure [equations (9), (10)] to lowest order in c_d/c.

The reason for this discrepancy is that we have effectively assumed the total density to be constant while treating the deuterated chains as an ideal gas. This neglects the fact that the total and relative densities are not completely decoupled as we showed previously. In practice this is, however, always a small correction even for flexible chains where the osmotic pressure is relatively low. In our derivation here the approximation comes in because we have neglected the fact that the self consistency equation (32) only applies for distances ($\mathbf{r}$, $|\mathbf{r} - \mathbf{r}'|$) large compared to the correlation length ξ. We have disregarded this in deriving equation (33).

Finally we note that equation (33) implies that the observed correlation functions are very insensitive to the deuterium concentration and essentially equal to the single chain form factor $g_{sc}(r)$. The correction term in the denominator becomes significant only when

$$\hat{g}_{sc}(q) \approx N$$

i.e., for $qR_G \lesssim 1$ where R_G is the single chain radius.

Since expressions for $g_{sc}(r)$ have been derived for flexible chains in ref 1 and for polyelectrolytes in ref 2 we shall not discuss $g_d(q)$ in detail here.

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4 Actually, partially deuterated chains are also used, e.g., deuterated end groups. The theoretical techniques employed here are very easily extended to such cases

5 See, for example, Landau, L. D. and Lifshitz, Statistical Physics Pergamon Press, London, 1958, Chapter XII

6 Edwards, S. F. *Proc. Phys. Soc. London* 1966, **88**, 265

7 The consequences of using $\tilde{v}$ in place of v in equation 2 are fully discussed in ref 1

8 The related problem of the correlation function for the labels on chains labelled at a single point has been discussed by de Gennes