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Registry No. (α,ω-Dihydroxypoly(propylene oxide))·(tris(isocyanatophenyl) thiophosphate) (copolymer), 88546-51-4; araldite CT 200, 25085-99-8.

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Model for the Clustering of Multiplets in Ionomers

Bernard Dreyfus

Groupe de Physico-Chimie Moléculaire, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, 38041 Grenoble Cédex, France.

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ABSTRACT: A new model for the clustering of charges in ionomers is presented. The basic idea is that, due to the strong electrostatic interactions, the multiplets of charges build a kind of structure, with a geometry that takes into account the presence of the polymeric material. The result is a cluster which, for a given material, is independent of the concentration of charges. It is shown that the multiplets are very likely quadruplets. It is also shown that the large cations produce bigger clusters. The state of the chains inside the matrix is discussed and it is suggested that the clusters are arranged in hypercrystallites, with a diamond structure. This allows for the interpretation of the central peak observed in diffraction experiments. A preliminary discussion of the first step of hydration is also presented.

1. Introduction

Ionomers are defined as copolymers containing predominantly linear nonpolar backbones and less than about 10 mol % of charged neutralizable side groups. Their properties are dominated by the existence of long linear polymeric chains which are strongly cross-linked by the electrostatic forces between the charged monomers. We exclude here materials such as "Nafions", perfluorinated ionomers where the charged units are at the end of rather long side pendant chains. In these materials the interaction between the electrical charges and the main chain is much weaker, and they may display structures differing from those discussed here.

In the last 15 years, many experimental studies have been conducted on ionomers. We refer the reader to three review articles[1-3a] and one recent paper devoted to the structure of the ionomeric membranes[3b] which give an extensive description of these works as well as the different models that have been proposed. The studies include a large variety of monomers (ethylene, butadiene, styrene, etc.) as well as charged acids (carboxylic, methacrylic, sulfonic, etc.) and neutralization cations (Na, Cs, Zn, Fe, ...). Although much progress has been made, it is generally accepted that the structure of these compounds is still poorly understood. The objective of this paper is to present a model which is mathematically simple and yet quantitatively predictive.

In a pioneer work Eisenberg[4] showed that the condensation of charges is a two-step process. The basic *ionic pairs* consisting of one anion (the acid) and a neutralizing charge (the cation) are associated with a few other pairs, more or less in contact, to form a *multiplet* resulting in strong cross-linking of different polymer chains, or different segments of one chain. We call the electric interaction responsible for the formation of the multiplets the *primary* electrostatic energy. This primary energy of interaction is an important fraction of the total energy of a basic pair. In a vacuum this energy is 100 kcal or 185 times k_BT at room temperature for two point charges 3 Å apart. Such a huge energy can easily stress the polymer chains during cross-linking since the energy needed to produce a strong deformation of one segment of a chain is a only a few k_BT. What limits the size of the multiplet is the steric hindrance since each ionic pair is coated by neutral monomers. This prevents the growth of the multiplet beyond a certain size, except in special cases, which will not be considered here, such as a lamella where a linear agglomeration of the basic pairs is possible. We shall call an object made of k basic pairs a "$2k$-plet". $k = 1$, the basic pair itself, is an electrical dipole; $k = 2$, corresponding to two basic pairs, is a quadrupole. Because of the steric hindrance, it is likely that in most ionomers k is a rather small number, probably smaller than 4, and most likely equal to 2 (dimerization). Being electrical $2k$-poles, coated with neutral materials, these multiplets still interact among themselves. We call this corresponding energy the *residual* energy of interaction. This energy can be larger than k_BT. For example, two basic dipoles, built with two unit charges distant of $d = 3$ Å, separated by $r = 8$ Å, have a dipolar energy of the order of $e^2d^2/r^3 \sim 9.8k_BT$. For two quadrupoles, with the same conditions, e^2d^4/r^5 is equal to $1.38k_BT$. An important remark will be made here; if a and b are the radii of the anion and the cation, the primary electrostatic energy varies like $(a + b)^{-1}$, and the residual energy, in the case of a dipole, like $(a + b)^2$, or for a $2k$-pole, like $(a + b)^{2k}$, so that the weaker the primary energy, the stronger is the residual energy.

This residual energy condenses the multiplets into aggregates which are called *clusters* in the nomenclature of Eisenberg. These clusters have been detected by many techniques, mainly by small-angle X-ray or neutron scattering. Their size is often in the range 10–30 Å in radii. Each cluster typically contains 50–100 basic pairs and the separation between adjacent clusters, D, is about 20–100 Å.

One wonders how such big objects, with such large and rather well-defined separation distances, can exist in a medium of random coils, carrying charges which are also distributed at random with a mean molar concentration c.

We also must decide whether the structure results from thermodynamic equilibrium or is just frozen in during sample preparation. Many existing data are in favor of the thermodynamic equilibrium assumption. For example, D increases progressively during hydration as much as a factor of 3 in some cases;[5] a similar trend is observed upon neutralization of the acid samples;[6] however, annealing well above T_g causes no change in D or the size of the clusters. These experiments suggest that the chains can glide along each other and adjust to the new conditions. Therefore, we will construct a clustering model which is consistent with equilibrium thermodynamics.

The three main energies that need to be considered during cluster formation are (1) the *residual* electrical energy between multiplets, (2) the steric (or hard-core) repulsion between monomers, and (3) the "entropic" energies needed to deform the coils from their free, natural configuration.

(1) The residual electrical energy between multiplets is much larger than k_BT when the multiplets are close to each other and approaches k_BT at a multiplet density that will be calculated later.

(2) The steric (or hard-core) repulsion between monomers prevents the sample from collapsing under the influence of the van der Waals or electrical forces. If one neglects thermal expansion, the monomers fill space in a compact way and the density of the material is constant.

(3) The "entropic" energies needed to deform the coils from their free, natural, configuration are identical with the usual "rubber elasticity". It is typically of a few k_BT.

In the next section we shall determine the structure of the cluster starting with the two energies which are predominant in its core, namely the residual electrical and hard-core energies.

2. Structure of the Clusters

In the core of a spherical cluster, the residual energy tends to compact the *multiplets* as densely as possible. However, since each $2k$-plet has $2k$ segments of chains emerging, there must be enough room in the more external shells of the cluster for these segments to escape the cluster. This will result in a decrease of the density of the multiplets when one moves away from the center. We introduce the following notation: c is the molar concentration (at most a few percent) of charged monomers. ρ is the distance from the center of the cluster. v is the volume of one monomer; for simplicity we consider that it is also the volume of one charged unit.

Table I

	v, Å^3	$v^{1/3}$, Å	l, Å	σ, Å^2	$\sigma^{1/2}$, Å
polyethylene	51	3.71	2.53	20	4.47
polystyrene	166	5.50	2.80	60	7.75

The chain is modeled as freely jointed rods (the monomers) each of length l and cross section σ. One has $v = \sigma l$; l can be determined from crystallographic data; σ is then calculated from the specific volume v.

Typical values are given in Table I. k is the functionality of the $2k$-plet, i.e., the number of basic pairs; the number of segments of chains issuing from one $2k$-plet is $2k$.

$k = 2$ corresponds to dimers, $k = 4$ to tetramers; the degree of association of the charges is strongly influenced by the chemical structure of the material. We assume, for that reason, that all the multiplets have the same k, and the conclusion of section 3 will argue in favor of this assumption.

The volume of one k-plet is $kv(1 + \alpha)$. The dimensionless factor α could account for a structural difference between a charged and a neutral monomer. It will be assumed to be a constant throughout the sample; it is mainly introduced to discuss the influence of solvation. If the volume of one water (or polar) molecule is $\alpha_0 v$, and if there are ν such molecules solvating one cation, using a simple additive rule, one has $\alpha = \nu\alpha_0$ from simple volume addition. For dry material $\alpha = 0$.

We call $p(\rho)$ the number of $2k$-plets inside a sphere of radius ρ. The corresponding number of basic pairs is $kp(\rho)$ and the number of chain segments leaving the sphere would ideally be $2kp(\rho)$. However, some chains may participate in more than one multiplet within the cluster, so that the number of segments leaving the sphere is only $2ks(\rho)$, where $s(\rho) < p(\rho)$ (cf. Figure 1a).

These $2ks(\rho)$ segments need a certain minimum space in the shell between ρ and $\rho + \mathrm{d}\rho$. As they are mostly neutral monomers, the principle of dense packing of the multiplets implies that the segments would leave the ionic region as directly as possible. Therefore, we assume that they go out radially. In a length $\mathrm{d}\rho$, there are $\mathrm{d}\rho/l$ monomers for each segment and the minimum number of monomers that we have to place in the shell is

$$2ks(\rho)\ \mathrm{d}\rho/l \qquad (1)$$

Among these monomers, a proportion $(1 - c)$ is neutral with a specific volume v and the rest (c) is *charged* with a specific volume $v(1 + \alpha)$. The total volume is then

$$2ks(\rho)\frac{\mathrm{d}\rho}{l}[(1 - c) + c(1 + \alpha)]v \qquad (2)$$

Now, the remaining empty space in the shell is filled by a number $\mathrm{d}p'$ of *new* multiplets, and the equality of volumes leads to the first basic equation:

$$\mathrm{d}V = 4\pi\rho^2\ \mathrm{d}\rho = 2ks(\rho)(1 + \alpha c)(v/l)\ \mathrm{d}\rho + k(1 + \alpha)v\ \mathrm{d}p' \qquad (3)$$

We write the second basic equation by expressing the number of segments leaving the sphere ($\rho + \mathrm{d}\rho$) as equal to those entering, augmented by the number needed by the "new" $\mathrm{d}p'$ multiplets

$$s(\rho + \mathrm{d}\rho) = s(\rho) + \mathrm{d}p' \qquad (4)$$

or

$$\frac{\mathrm{d}s}{\mathrm{d}\rho} = \frac{\mathrm{d}p'}{\mathrm{d}\rho}$$

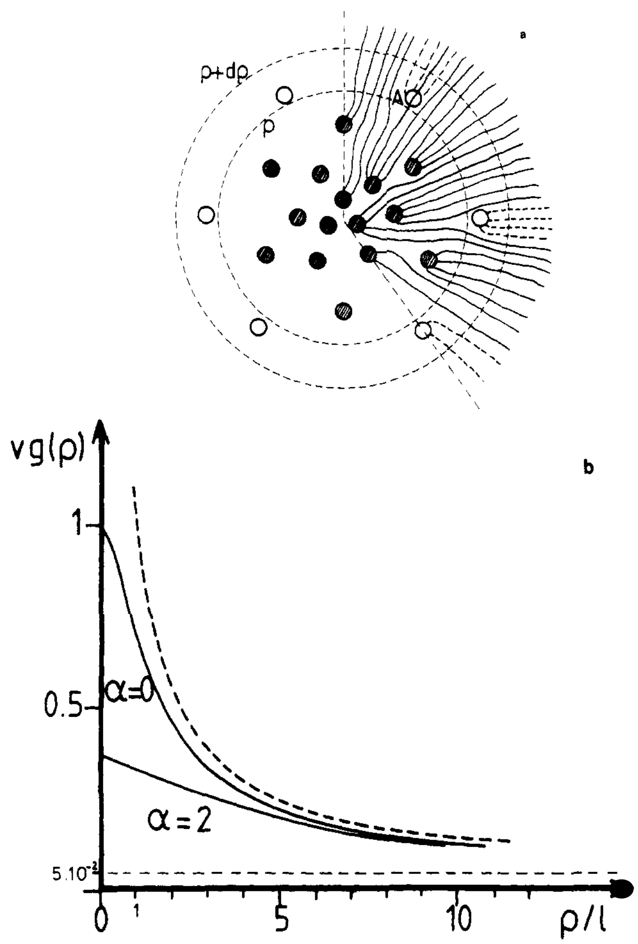

Figure 1. (a) Schematic two-dimensional view of a cluster. Cross-hatched circles are multiplets inside a circle of radius ρ. Four segments are shown outgoing from each multiplet and are represented by continuous lines without thickness. Open circles are the new multiplets in the shell between ρ, $\rho + \mathrm{d}\rho$. The "new" segments are represented by broken lines. At point A a "new" multiplet is located on a segment issuing from a more internal multiplet. (b) Density $vg(\rho)$ as a function of ρ/l, for $c = 5 \times 10^{-2}$, $\alpha = 0$, and $\alpha = 2$. In dashed line the approximation $vg = l/\rho$. Note that the solvation affects mainly the cluster's core.

Equations 3 and 4 are a pair of differential equations in $s(\rho)$ and $\mathrm{d}p'/\mathrm{d}\rho$; by elimination we get

$$\frac{4\pi}{kv}\rho^2 = \frac{2}{l}(1 + \alpha c)s(\rho) + (1 + \alpha)\frac{\mathrm{d}s}{\mathrm{d}\rho} \tag{5}$$

The integration is straightforward, with the limiting condition $s(0) = 0$ and $p(0) = 0$, it leads to

$$s(\rho) = \frac{2\pi l}{kv(1 + \alpha c)}\left[\rho^2 - \rho l\frac{1 + \alpha}{1 + \alpha c} + \frac{l^2}{2}\frac{(1 + \alpha)^2}{(1 + \alpha c)^2}\left(1 - \exp\left(-\left\{\frac{2\rho}{l}\,\frac{1 + \alpha c}{1 + \alpha}\right\}\right)\right)\right]$$

$$p(\rho) = \frac{2\pi l}{kv(1 + c)}\left[\frac{2c}{3l}\rho^3 + \rho^2\frac{1 - c}{1 + \alpha c} - \rho l\frac{(1 + \alpha)(1 - c)}{(1 + \alpha c)^2} + \frac{l^2(1 + \alpha)^2(1 - c)}{(1 + \alpha c)^3}\left(1 - \exp\left\{-\frac{2\rho}{l}\,\frac{1 + \alpha c}{1 + \alpha}\right\}\right)\right] \tag{6}$$

Here $p(\rho)$ is the *total* number of multiplets, issuing from (2) and (3).

With these exact expressions, we can check that there is no inconsistency in the model: $s(\rho)$, $p(\rho)$, $\mathrm{d}s/\mathrm{d}\rho$, and $\mathrm{d}p/\mathrm{d}\rho$ are all positive, and the cross section needed for the $2ks(\rho)$ segments to leave the sphere is less than the surface offered:

$$2ks(\rho)\sigma < 4\pi\rho^2$$

We recall that α is at most a few units, c of the order of a few percent or less, so that we can safely put $1 - c$ and $1 + \alpha c$ equal to unity.

We introduce the volume density of charges (or rather of basic pairs) $g(\rho)$

$$g(\rho) = \frac{k\,\mathrm{d}p}{4\pi\rho^2\,\mathrm{d}\rho} \tag{6'}$$

and obtain, with the above approximations

$$vg(\rho) = c + \frac{l}{\rho} - \frac{l^2}{2\rho^2}(1 + \alpha)\left(1 - \exp\left[-\left\{\frac{2\rho}{l(1 + \alpha)}\right\}\right]\right) \tag{7}$$

This function is drawn in Figure 1b for $\alpha = 0$ and $\alpha = 2$. For $\rho = 0$ its value is $(1 + \alpha)^{-1}$. It is the sum of the nominal constant molar density c of the sample plus a term in ρ^{-1}; the last term, which is the only one depending explicity upon α, is rapidly vanishing with respect to the second term (as soon as ρ/l is of the order of a few units). The dotted lines are the part corresponding to the first two terms.

In the same manner, we have

$$kp(\rho) = \frac{2\pi}{\sigma}\left[\frac{2c}{3l}\rho^3 + \rho^2 - \rho l(1 + \alpha) + \frac{l^2}{2}(1 + \alpha)^2\left(1 - \exp\left(-\left\{\frac{2\rho}{l(1 + \alpha)}\right\}\right)\right)\right] \tag{8}$$

The extreme limit of validity of the simple, and in some sense brutal, arguments that we have used is for

$$\rho_1 = lc^{-1} \tag{9}$$

In that limit, the excess density of the cluster is equal to the weak nominal density c, and it is no longer realistic to say that the neutral monomers have to be strongly ejected from the ionic region; then eq 3 becomes invalid. Fortunately ρ_1 is very large; for polyethylene and $c = 3 \times 10^{-2}$, ρ_1 is about 80 Å, which is much bigger than the clusters that we have to deal with.

An exact expression of $g(\rho)$ is unimportant near the origin, as it is weighted by the geometrical factor $4\pi\rho^2$. Therefore, we can use simplified expressions for the dry cluster (although precise enough in the useful range of ρ), for the density, and for the number of charges:

$$vg(\rho) = l/\rho \tag{10}$$

$$n(\rho) = kp(\rho) = (2\pi/\sigma)\rho^2 \tag{11}$$

For a hydrated sample, we need the next significant terms:

$$vg(\rho) = \frac{l}{\rho} - \frac{l^2}{2\rho^2}(1 + \alpha) \tag{12}$$

$$n(\rho) = (2\pi/\sigma)(\rho^2 - \rho l(1 + \alpha)) \tag{13}$$

3. Radius ρ_c of the Clusters

The multiplets k are built from k basic pairs which we think are in close contact with one another. The residual electrostatic energy is the interaction energy of electrical $2k$-poles. For $k = 1$ one has a dipole, for $k = 2$ a quadrupole, for $k = 4$ an octupole, ..., but only if a proper symmetry is maintained. For example, if $k = 3$, one may have two dipoles up and one down in a linear arrangement, and the field would be the sum of a dipole plus a quadrupole, rather than a hexapole. These multipoles have interaction energies which have an angular dependence. The first task should be to determine the minimum-energy configuration consistent with the distribution law (6). That would be very difficult, even in the case of dipoles, and one is not even sure that the multiplets have enough freedom of orientation to minimize the energy. However, we can say that, if d is the distance between the ions of the basic pairs, the electrostatic energy varies like[7] $e^2d^2/\epsilon u^{2k+1}$ with some numerical coefficient, where e is the unit electronic charge, u is the distance between the $2k$-poles, and ϵ is the dielectric constant of the medium.

When a multiplet is attracted toward the surface of a cluster of radius ρ, it gains an energy of the order of

$$|W| = \frac{e^2}{\epsilon d}\left(\frac{d}{u}\right)^{2k+1} \tag{14}$$

where u is the mean distance between the multiplets at ρ. We can compute u from (10); since the mean volumic density of the multiplets is $(kg(\rho))^{-1}$, the mean volume occupied by one cluster, at the distance ρ from the origin, is

$$u^3 = kv\rho/l \tag{15}$$

The decrease in the interaction energy is opposed by a decrease of the entropy (the rubber elasticity) of the chains within the matrix, which we have to estimate.

One may say that when one multiplet is fixed on the surface of the cluster, certain degrees of freedom have been frozen. The orientational entropy of one monomer is equal to $k_BLn(z-1)/e$ where z is the coordination number of the Flory–Huggins lattice;[8] such a term gives a contribution to the free energy of the order of k_BT. One could also say that the entropy of a Gaussian segment of end-to-end normal length R, when extended to a length L, varies like $-{}^3/_2k_BL^2/R^2$; if the variation of L is the order of R (we shall return to this point in the next section) that variation of entropy again leaves a term of the order of k_BT. We are led to the following expression for the free energy of fixation of a multiplet:

$$G \cong -|W| - k_BT \tag{16}$$

To be rigorous we need the free energy of the multiplet before its condensation. It comes from the matrix where the charge concentration is much less than c and the chains are not subject to the same stress as in a cluster; therefore, (16) is a reasonable approximation for the *variation* of G during the fixation.

At equilibrium ($\rho = \rho_c$) we have $G = 0$, and this gives a determination of ρ_c.

In dimensionless terms we get

$$\frac{\rho_c}{l} = \left(\frac{e^2}{\epsilon d}\frac{1}{k_BT}\right)^{3/(2k+1)}\frac{d^3}{kv} \tag{17}$$

and for the number of basic pairs inside the cluster

$$n_c = kp(\rho_c) = \frac{2\pi d^6}{k^2\sigma^3}\left(\frac{e^2}{\epsilon d}\frac{1}{k_BT}\right)^{6/(2k+1)} \tag{18}$$

It is clear that our estimation of G (eq 16) is very crude, but as W is a rapidly varying function of u, or ρ, the effect of neglected terms on ρ_c is certainly small. We now apply eq 17 and 18 to polyethylene and polystyrene for $k = 1$, 2, or 4, for $d = 3$ or 4.5 Å. (See Table II.)

Table II shows that, for polyethylene, $k = 1$ gives unrealistically large values; this is not surprising as $k = 1$ corresponds to the case of isolated basic pairs in which the chains are not cross-linked. On the other hand, $k = 4$ (octuplets) gives unrealistically small values. Finally, $k = 2$ (quadruplets) gives ρ_c and n_c which are in an acceptable range.

Table II

k	ρ_c, Å	n_c[a]
Polyethylene, $v = 51$ Å^3, $\sigma = 20$ Å^2, $l = 2.53$ Å		
$d = 3$ Å		
1	125.3	4965
2	10.7	33
4	1.52	0.74
$d = 4.5$ Å		
1	281.9	25125
2	28.3	231
4	4.5	6.4
Polystyrene, $v = 166$ Å^3, $\sigma = 60$ Å^2, $l = 2.8$ Å		
$d = 3$ Å		
1	42.4	189.9
2	3.46	1.2
4	0.52	0.03
$d = 4.5$ Å		
1	95.4	931
2	9.16	8.6
4	1.53	0.24

[a] $n_c = kp(\rho_c)$.

One can draw similar conclusions for polystyrene, except that the agreement is not as good. Even for $k = 2$, ρ_c and n_c are a bit too low. It must be noted that in that case $\sigma = 60$ Å^2 is a mean average cross section of the tube associated with the main chain. In reality the benzene rings are quite anisotropic and are highly likely to arrange their planes in parallel. Therefore, among the first neighbors of a quadruplet, two benzene rings are probably much closer than $\sigma^{1/2}$, increasing the electrostatic energy, ρ_c and n_c.

We also repeat here what has already been stated before: if the $2k$-plet is not in the maximum symmetry state, it provides a multipolar field of order less than $2k$. Anyway, we can conclude that the residual electrostatic interaction in a cluster is very likely quadrupolar and therefore originating from a quadruplet of charges (two basic pairs). For a family of *similar* structures but limited to $k = 2$, we can extract from (17) and (18) the scaling laws:

$$\rho_c \sim d^{2.4}\sigma^{-1} \tag{19}$$

$$n_c = kp_c \sim d^{4.8}\sigma^{-3} \tag{20}$$

Returning to eq 10, and since $vg(\rho_c)$ is the molar concentration of surface charges on a cluster, we write

$$vg(\rho_c) = l/\rho_c = c_0 \tag{21}$$

This concentration is characteristic of a given ionomer and independent of its nominal concentration c. Experimentally $\rho_c/l \lesssim 10$ and therefore c_0 is of the order of 0.1 or larger; anyway c_0 is beyond the limit of c for which the present model is still valid.

Before closing this section we have to consider the question of the *absolute stability* of the cluster. We have so far let the cluster grow as long as it could fix the quadruplets of the matrix on its surface. However, due to its special structure, we also need to address the question of whether the cluster is stable against splitting into two smaller clusters. For a droplet of homogeneous fluid, the volume density of energy is constant and the surface energy is proportional to the surface so that a splitting into two smaller droplets is energetically unfavorable. Here the situation is quite different. The volume energy density is (in absolute terms) larger in the core than near the surface because of the higher density of the multiplets. Therefore, the system should prefer splitting into two smaller clusters. There is however a threshold below which this splitting cannot occur: in the limit of a cluster containing only one multiplet, the residual electrostatic energy vanishes. Evidently the ratio of first-neighbor bonds to the number of multiplets is low in small clusters.

The splitting of a cluster of 100 basic pairs or 50 quadruplets would produce two clusters of 25 quadruplets each, and we estimate that the gain in energy due to the higher concentration is compensated by the rapid decrease in the number of bonds. Nevertheless, we cannot exclude completely the possibility of such a splitting. When that happens, c_0 (the concentration on the surface) would no longer be obtained by eq 17 and 21, but be determined by stability considerations. Most conclusions should remain valid, but the dependence of the size of the cluster upon d, which controls the strength of the interaction, should be reexamined. We can be sure that at least the huge clusters obtained for $k = 1$ (Table II) are unstable.

4. Cluster Ordering

The fact that we have calculated, from first principles, the structure, size, and capacity of the clusters is not enough to prove their existence; one must also check that the state of the chains in the matrix, between the clusters, is compatible with their known properties.

We first have to determine the spatial arrangement of the clusters. As we shall show below, in order to deposit their charges inside the clusters, the segments of the chains have to be somewhat extended. One minimizes this constraint by choosing a structure where the distance between first neighbors is the smallest for a given density of lattice points. An inspection of some simple lattices show that this condition is realized by the diamond structure. In that structure each cluster has $z = 4$ first neighbors at a distance D. The 12 second nearest neighbors are at a distance $1.6330D$. The volume occupied by one cluster is $(8/3^{3/2})D^3 = 1.5396D^3$. The total number of basic pairs within this volume is $1.5396cD^3/v$ (we recall that v is the volume of one monomer).

We know the number n_c of pairs in one cluster. What would be needed is the average concentration c' of the multiplets in the space between the clusters. This cloud of quadruplets is in thermodynamic equilibrium with the surface of the cluster. The approximate expression for G (eq 16) is too inaccurate for an absolute determination of c'; anyway we expect that the majority of the charges condense in the clusters, and we shall take as a first approximation $c' = 0$. Although this approximation will give a reasonably good value for D, it may need further analysis.

The conservation of charges leads to

$$n_c = 1.5396dD^3/v \qquad (22)$$

$$D = (2\pi/1.5396)^{1/3}(\rho_c{}^2l)^{1/3}c^{-1/3} = 1.60(\rho_c{}^2l)^{1/3}c^{-1/3} \qquad (23)$$

In this section and the following we consider only dry samples ($\alpha = 0$).

As ρ_c is constant and independent of c, it follows immediately that D, identified with the ionomer peak (cf. section 5), varies like $c^{-1/3}$. Such a law has been observed in ethylene- and butadiene–methacrylic ionomers,[9] and in other cases such as pentenamer sulfonate,[6] it is compatible with data within the precision of measurements.

Conversely, a law of the type of (23) cannot be explained in the absence of clusters whose capacity is independent of c, and if such clusters do exist they should have a well-defined structure, such as the one described in the present work.

Table III

ρ_c, Å	n_c	D, Å $c = 0.01$	 $c = 0.02$	 $c = 0.05$
10	31	60.8	48.2	35.6
15	71	76.6	60.8	44.8
20	126	96.5	76.6	56.4

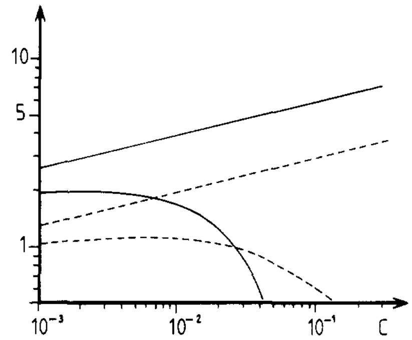

Figure 2. Plots of $D/\bar{R}$ (straight lines) and $(D - 2\rho_c)/\bar{R}$ (curves) as a function of c. Full lines $c_0 = 0.1$. Dashed lines $c_0 = 0.3$.

When the cations are substituted, resulting in a change of d, at constant c from eq 19 and 23 D changes like

$$D \sim d^{1.6} \qquad (24)$$

This law explains why the ionomer peak appears at lower **Q**, the scattering vector, for Cs cations than for Li[10] as well as in many other neutralization experiments,[10,11] if one accepts that the acid has a smaller dipole moment than the salts, due to the small size of H^+.

A numerical application of (22) of polyethylene gives D for different values of c and ρ_c. (See Table III).

Now we come to the important question of the *state of tension* of the chains between the clusters, as it can be calculated from the present model (bear in mind that the system will try to rearrange to decrease the tension or increase the entropy). However, as we are in the k_BT range of energies, the theory of these rearrangements would need a precise expression for the thermodynamic functions of a very complex system and we are only able to give some general insights into these possible rearrangements.

The segments between two consecutive charges containing, on the average, c^{-1} monomers have a "free" end-to-end length R

$$R = c^{-1/2}l \qquad (25)$$

A more sophisticated expression, using the Poisson's distribution law for the length ν of the segments

$$\bar{\omega}(\nu) = ce^{-\nu c} \qquad (26)$$

gives an average end-to-end length

$$\bar{R} = (\pi/2)c^{-1/2}l = 0.886c^{-1/2}l \qquad (27)$$

which is only slightly different from (25).

The distance between the centers of the clusters is D. The shortest distance that must be covered by the segments from one cluster to another is $D - 2\rho_c$; we can get an idea of the relative tension of the chains by comparing these quantities to $\bar{R}$. The ratios $D/\bar{R}$ and $(D - 2\rho_c)/\bar{R}$ are plotted in Figure 2 as a function of c, for two values of c_0. The relative tension of a chain connecting two adjacent clusters is certainly intermediate between the two ratios. It is largest for the strongest residual interaction ($c_0 = 0.1$ $\rho_c = 10l$). $(D - 2\rho_c)/\bar{R}$ is a rather flat function in the useful range of c. The strong decrease for $c = 0.51c_0$ indicates that, at this concentration, the clusters enter into contact.

$D/\bar{R}$ is slowly increasing as $c^{1/6}$. It is of the order of a few units. Our conclusion is that the chains are clearly *extended* but not too excessively.

Let us consider ways that the system can decrease this tension. First, it can allow some multiplets to stay in the space between the clusters, functioning as bridges, for the most extended segments. Then it can "select" its segments, using the shortest (the ones where the charges are the closest) inside the clusters, or for segments which turn back to the originating cluster. We can estimate the first of these two effects, by noting that the proportion Φ of the matter inside the cluster is

$$\Phi = \frac{4}{3}\pi \rho_c{}^3/1.5396D^3 = \frac{2}{3}\,\frac{c}{c_0} \tag{28}$$

If we assume that it is constituted of the shortest segments, up to a number ν_0 of monomers, we have for ν_0 the equation

$$\int_0^{\nu_0} \nu\bar{\omega}(\nu)\;\mathrm{d}\nu = (1/c)\Phi = {}^2\!/_3c_0 \tag{29}$$

or

$$\nu_0 \sim \frac{1}{c}\left(\frac{4}{3}\,\frac{c}{c_0}\right)^{1/2} \tag{30}$$

From a well-known property of Poisson's law, the average number of monomers for the remaining segments is $\nu_0 + 1/c$, and of course this "selection" increases the value of $\bar{R}$. A calculation shows that this can account for a reduction of the relative extension by a factor of about 30% for $c = 10^{-2}$, or 10% for $c = 10^{-3}$ and $c_0 = 0.1$, and less for smaller c's or bigger c_0's.

We examine now the question of the segments which come back to the same cluster. The most important physical fact to take into account is that before clustering the cross-linked network of chains is *three-dimensional.* The multiplets will ultimately coalesce on clusters in a "diamond" lattice, each situated at the center of a polyhedron (the first Brillouin zone) that will be approximated, for simplicity, by a sphere of radius δ with the same volume

$$\delta = \left(\frac{3}{4} \times 1.5396\right)^{1/3} D = 0.7163D \tag{31}$$

In the clustering process, we do not expect the multiplets to move over considerable distances, so we assume that a given multiplet A will move toward the center of the "Brillouin sphere" in which it is initially located.[12] Let us now consider a multiplet B, first neighbor of A on one polymeric chain which may (or may not) lie in the same sphere. If it does not, it will coalesce into a different cluster, leading to a segment connecting two different clusters.

The problem reduces to finding the probability P that B, being connected to A by a Gaussian probability law, will find itself in the same sphere while A is uniformly distributed over the sphere (δ). This calculation is done in the Appendix, where

$$\rho^2/2 = 3\delta^2/\nu l^2 \tag{32}$$

Of special interest is the average value of ν, $\nu = 1/c$ for which $\rho^2/2$ is equal to 18.29 or 8.49, respectively, for $c = 10^{-2}$ or $c = 10^{-3}$ ($c_0 = 0.1$). This gives probabilities $P = 0.74$ or $P = 0.60$. For a larger c_0, these quantities would be smaller. The conclusions are as follows: more than one-half of the segments would return to the originating cluster; the shorter the segments (ρ large) the greater the probability of returning; the proportion of connecting segments decreases when c increases. This last property shows that when the capacity n_c of one cluster is varied continuously, for example by a partial neutralization of the acid, the rearrangement of the order is a delicate process in which not only the extension of the segments can be modified but also the proportion of connecting segments. We also note that this effect is selective, in the sense that there is a smaller proportion of connecting segments with small values of ν. This selective effect is strongest at low c, where the slope $\mathrm{d}P/\mathrm{d}\rho$ is large. It will also contribute somewhat to the reduction in tension of the segments.

There are some experiments, where the radius of gyration R_g of the chains has been measured, by neutron small-angle scattering, on deuterated probes. The results are contradictory. In one experiment no increase in R_g has been found,[13] and in another[14] an increase of 40% in R_g was observed when the concentration of charges in a sulfonated polystyrene is increased from 1.9×10^{-2} to 8.5×10^{-2}. In this last experiment the reality of the effect is questionable as the molecular weight of the diffracting object increased simultaneously by 80%. The present model predicts a moderate variation of $R_g{}^2$. If, for example, we take 65% of the segments returning to the originating cluster, with an end-to-end distance equal to zero, and 35% with an extension of a factor of 2, we should get an increase of $R_g{}^2$ equal to (0.35)(4) = 1.4 or an increase in R_g of about 20%. This effect, if it exists, is not expected to vary simply with c and should not disappear for a concentration of the order of 1×10^{-2} or 2×10^{-2}. More experiments are needed to clarify the situation.

5. Scattering Laws

In X-ray or neutron diffraction experiments the scattered intensity along the wave vector $\mathbf{Q}$ ($Q = (4\pi/\lambda)\sin(\theta/2)$) is given by

$$I(Q) = KF(Q)^2S(Q) \tag{33}$$

where K is a numerical factor which depends upon the contrast of the scattering object; $F(Q)$ is the structure factor of one isolated object, here a cluster; and $S(Q)$ is an interference term, which takes into account the spatial arrangement of the clusters.

In the case of X-ray scattering, the scattering is mainly due to the cations which are usually much heavier than all other atoms in the matrix. However, since a weak diffusion has been observed even with light cations such as Li, one can argue that inside a cluster the density of the material is greater than between the clusters due to the electrostatic interactions.

In the case of neutron scattering, the sample is wet, usually with deuterated water which gives the contrast and thus the scattering.

In any case, we shall assume the scattering amplitude is proportional to the density of multiplets inside the cluster as given by eq 6 or 10, as the terms in c and c^2 are negligible in $F(Q)^2$. We shall assume that the water content is low enough that we can use the structure of the dry cluster; we shall return to this point in the last section.

The structure factor is then given by

$$F(Q) = \int_0^{\rho_c} 4\pi\rho^2 g(\rho)\frac{\sin Q\rho}{Q\rho}\;\mathrm{d}\rho \tag{34}$$

or

$$F(Q) = \frac{l\rho_c{}^2}{v}\,\frac{1 - \cos x}{x^2} \qquad \text{where } x = Q\rho_c$$

$$F(Q) \sim n_c\left(\frac{\sin(x/2)}{x/2}\right)^2 \tag{35}$$

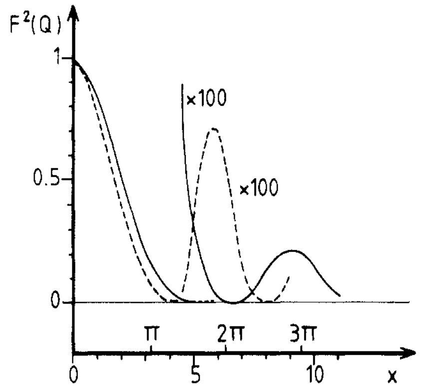

Figure 3. Plots of the structure factor $F^2(Q)$ for a cluster with a density in ρ^{-1} (full line) and for a constant density, with the same radius ρ_c (dashed line). In the region of the secondary maximum, the ordinates have been multiplied by 100. $x = Q\rho_c$.

which has to compared with the structure factor of a sphere of constant density.

$$F(Q) \sim 3n_c\left(\frac{\sin x - x\cos x}{x^3}\right) \tag{36}$$

The two functions $F(Q)^2$ are plotted in Figure 3. The main differences are that the cluster in ρ^{-1} has a larger central peak, because its radius of gyration is less than that for a homogeneous sphere. The ratio of the widths is $(6/5)^{1/2} \sim 1.09$. The first secondary maximum of eq 35 occurs at $x \sim 3\pi$ (for the homogeneous sphere $x \sim 2\pi$) and its intensity relative to the central peak is $\sim 2 \times 10^{-3}$ (for the homogeneous sphere $\sim 7 \times 10^{-3}$).

Let us now consider the interference term $S(Q)$. In the analysis of the so-called "ionomer peak", the clusters have been considered as forming a *random* gas with a hard-core repulsion potential whose range is D, the closest distance between two clusters. This method allows a reasonable analysis of the ionomer peak[11] but leaves aside the existence of a strong central peak, which is also observed. We propose a different approach, which basically takes into account a *local order* of the clusters. Although the clusters are separated by a distance D so large that no significant potential can have an influence on their positions, they are still linked by many segments. These segments have an average length and cannot be extended easily to accommodate large changes in D. The nonconnecting segments give rise to a kind of ball which coats the cluster. The rubber elasticity of this ball also resists deformation. All this results in an "entropic interaction" which holds the clusters close to a regular lattice. We have already argued in favor of a diamond type lattice and we suggest that the clusters form a *hypercrystal* of this type with a parameter $a = 4D/3^{1/2}$. Of course, in an amorphous material with random coils and random distribution of charges one does not expect that the range of the order can be very long. We imagine the structure, as "*hypercrystallites*" with finite crystal size Δ ($\Delta > D$). Typically if D is in the range of a few tens of angstroms, Δ is to be found in the range of 100 Å or more.

As an illustration of the possibilities of the model we have plotted in Figure 4 the interference term of a small crystallite of 17 clusters (1 central cluster, 4 first neighbors, and 12 second neighbors) which has an overall diameter $\Delta = 4(2/3)^{1/2}D = 3.26D$. $S(Q)$ shows clearly a central peak, with a width of the order of Δ^{-1}; $S(Q)$ is normalized in such a way that it oscillates around 1 for large Q's. $S(0)$ is equal to 17, the number of clusters. There are seconary peaks at $x \sim 4.7, 7.2, \ldots$. The resultant $I(Q)$ is also plotted for $\rho_c = 0.2D$ and $\rho_c = 0.4D$.

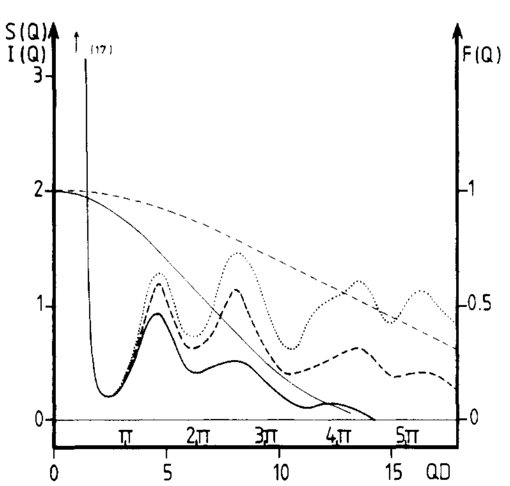

Figure 4. Interference term for a block of 17 clusters. $(\sin x)/x = A(x)$, $x = QD$, $17S(Q) = 17 + 32A(x) + 84A((4/6^{1/2})x) + 48A((11/3)^{1/2})x) + 24A((4/3^{1/2})x) + 24A((19/3)^{1/2}x) + 48A(2(2^{1/2})x) + 12A([4(2^{1/2})/3]x)$: (···) $S(Q)$, (– – –) structure factor for $\rho_c = 0.2D$, (- - -) $I(Q) = F^2(Q)S(Q)$ ($\rho_c = 0.2D$), (—) structure factor for $\rho_c = 0.4D$, (—) $I(Q)$ ($\rho_c = 0.4D$).

Most often, in order to increase the contrast, the experiments are performed on rather highly concentrated samples; in that case the clusters are not far from being in contact. Then the structure factor damps rapidly the oscillations of $S(Q)$, and only one secondary peak is clearly observable at $QD \sim 4.7$ and can be identified as the "ionomer peak". At smaller concentration c, when ρ_c/D is smaller, another peak could be observed at $QD \sim 7.2$. We note also that we have identified the scattering function of the whole sample as the scattering function of an isolated crystallite. This raises the difficult problem of matching the different crystallites and distributing them in space. We think that the handling of these problems can only have an influence at smaller Q's than those considered in the above discussion. In other words, we can say that if the clusters are well ordered on a local scale, fluctuations (of orientation or concentration) remain with a wavelength of the order of Δ, which are responsible for the increase of the scattering at low Q.

Δ, the size of hypercrystallites, is not as well-defined as ρ_c and D, and one expects a distribution of Δ, which should appear in a Guinier-plot analysis of the central peak. The perfection of the hypercrystal of clusters can be influenced by the kinetic approach to equilibrium, and be sample dependent. It can also be linked to the number N of monomers of the chains since $N^{1/2}l$ is a characteristic distance over which the memory of the chains is lost.

6. Solvation

Ionomers are well-known for their capacity to absorb water, or other polar solvents. In fact, many of their industrial utilizations are related to this property.

The absorption of water is generally thought to occur in two steps. In the first step, a few polar molecules ($\nu \lesssim$ 4–6) are fixed on the cation, building the so-called "solvation shell".[3b] In that process, the existence of the basic ion pair is maintained, as well as that of the multiplets which cross-link the chains. The material keeps most of its qualitative features, and the preceding model can be useful to explore some consequences of hydration. In the second step, which occurs often, but not for all ionomers, additional free water molecules are absorbed. The mixture of ions and water is probably like a concentrated solution, where the individuality of the basic ionic pairs and of the multiplets is lost. The cross-linking between chains becomes labile, and the principles on which the present model relies are no longer valid. In this section, we deal only with the first step, that of solvation. We shall make the assumption that α is constant throughout the sample. This assumption may be unrealistic since the very first polar molecule should have a preference for the cations either in the core or on the surface of the cluster, and one should determine the function $\alpha(\rho)$ through the equilibrium of the chemical potentials. However, many experiments show that there is a discontinuity in hydration, at the end of the solvation step; one may assume that all the cations complete their solvation shell before absorbing additional free water molecules; at this stage, α is constant.

Another assumption is the simple additive rule for the volume of the hydrated sample: each water molecule occupies a volume $\alpha_0 v$ (about 30 Å^3). This rule works quite well for a lot of crystalline organic materials as well as for ionomers.

Most of the scattering experiments show that D, the intercluster distance, has a tendency to *increase* with the content of water and we shall examine the influence of α on the different parameters.

The first effect to be examined is the *macroscopic expansion* of the sample. The volume of the dry material is multiplied by $1 + \alpha c$; if the capacity of the cluster was *frozen* (n_c constant), this would imply an increases in D by a factor of $(1 + \alpha c)^{1/3}$. For polyethylene $\alpha_0 \sim 0.6$, with four molecules of water per cation and $c = 5 \times 10^{-2}$, this gives an increases of D of 3.8%; the detection of such a small variation would be difficult because of uncertainty in the position of the ionomer peak.

The second effect to be envisaged is the variation of cluster structure. We have plotted in Figure 1b the density of multiplets for $\alpha = 0$ and $\alpha = 2$. The density is more decreased in the center than in the external shells. This is simple to understand: the proportion of inert material (neutral monomers) increases with ρ and the mean volume u^3, occupied by one charge, is less and less affected by solvation when one moves off the center. If we suppose first that the quadrupolar moment is unchanged, then c_0 remains constant. To calculate the new radius ρ_c' of the cluster we use eq 12 with the corrective term in α; to first order in $(l/\rho)(1 + \alpha)$, we write

$$vg(\rho) = \frac{l}{\rho} - \frac{l^2}{2\rho^2}(1 + \alpha) \simeq \frac{l}{\rho + (l/2)(1 + \alpha)} = \frac{l}{c_0} \qquad (37)$$

from which we obtain

$$\rho_c' = \rho_c - \frac{l}{2}\alpha \quad \text{or} \quad \frac{\Delta\rho}{\rho} = -c_0\alpha = -\frac{l}{\rho_c}\alpha \qquad (38)$$

The decrease in n_c can be calculated with eq 13; to the same approximation

$$\frac{n_c' - n_c}{n_c} = -2c_0\alpha = -2\frac{l}{\rho_c}\alpha \qquad (39)$$

This is indeed a large variation, especially when ρ_c is small, for weak residual interactions. In fact, even for $c_0 = 0.1$, with $\alpha = 2.4$, this corresponds to a diminution of n_c by 48%. Of course, this effect implies a *decrease* in D (of 13% with the numbers quoted). This effect, which is a consequence of the model, exceeds the macroscopic expansion of the sample and leads to a decrease in D, contrary to the experimental results.

One still has to envisage the variation of the electrical quadrupolar moment of the multiplet. The effect of water is very likely to *weaken* the attraction between the anion and the cation, with the consequence of an increase in d. From eq 20, we know that $n_c \sim d^{4.8}$; an increase of d of only 15% would give a doubling of n_c. We lack an expression for $d(\nu)$, but we think that this effect is very probably the dominant one, leading to a global increase in D.

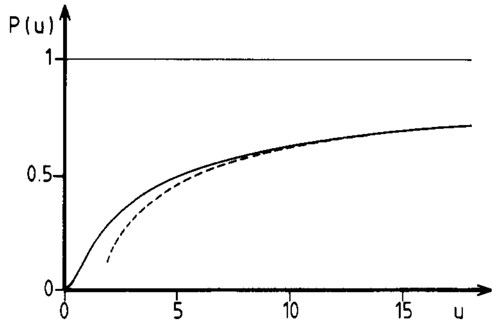

Figure 5. (—) $P(u)$; $u = 3R^2/\nu l^2$. (---) The approximation $P(u) = 1 - 1.197/u^{1/2}$.

If one takes into account only this last effect, we have the scaling laws

$$\rho_c \sim d^{2.4} \qquad n_c \sim d^{4.8} \qquad D \sim d^{1.6} \qquad (40)$$

from which it follows that ρ_c *increases more rapidly than* D.

We have already noted that the formulas of section 3 predict that the dry clusters enter into contact when $c \sim c_0$. If the sample is hydrated, this contact will take place for a smaller value of c. It is even certain that the clusters will "fuse" together by capillarity force before this physical contact is reached. In the case of liquid droplets of radius ρ, distributed regularly on a line with a spacing D, a cylindrical tube of liquid is more stable than separated droplets when $2\rho/D > {}^2/_3$. Because of the inhomogeneous structure of the cluster, as we have already discussed, the "fusion" of the clusters will happen at a smaller value of $2\rho/D$. One sees here the strong tendency of the clusters, favored by hydration, above a certain concentration c of charges, to collapse into *channels*, which in the present model would be along the tetrahedral bonds of the diamond lattice, building a three-dimensional network, along which the cations could more easily move. This of course is of fundamental importance to explain the transport properties of ionomers. A similar structure has already been envisaged[15] for ionomers in a different context. It is beyond the scope of the present paper to discuss the modifications implied by the existence of these channels, as well as what happens when the content of water continues to increase.

7. Conclusions

The model presented in this paper can be qualified as "quasi-crystalline" for two of its features: the cluster presents an order, like a small crystal, the organization of which is affected by the presence of the chains; the clusters themselves are ordered in a hypercrystal with a large cell, the cohesion being maintained by forces of entropic origin. The idea of introducing such an order in materials made of amorphous coils with a random distribution of charges may, at first sight, looks surprising, but in fact appears quite naturally as we have tried to convince the reader.

The author is well aware of the necessity of a more detailed comparison with experiments and a more careful theoretical analysis, but it is hoped that, because of its simplicity, this model can be useful at least as a guide for the experimentalists.

Acknowledgment. It is a pleasure to thank Dr. M. Pineri and F. Volino from Grenoble, and Professor A. Eisenberg from McGill University, Montreal. I was initiated to the field of ionomers through discussions with them. I am also grateful to G. Bassi for the computation of the integral in the Appendix.

Appendix

We look for the probability that a multiplet A, uniformly distributed over a sphere (Σ) of radius R, has a first-neighbor multiplet B within the same sphere. A and B are linked by a freely jointed chain with ν monomers, each of length l.

The distribution function of B, with coordinates X, Y, Z relative to A, is

$$\left(\frac{3}{2\pi a^2}\right)^{3/2} \exp\left[-\frac{3}{2a^2}(X^2 + Y^2 + Z^2)\right] \qquad \text{(A1)}$$

with $\langle r^2 \rangle = a^2 = \nu l^2$.

The Fourier transform of (A1) is

$$\exp(-Q^2a^2/6) \qquad \text{(A2)}$$

The distribution function of A in the sphere is a constant $(^4/_3\pi R^3)^{-1}$ and its Fourier transform is

$$3(\sin QR - QR\cos QR)/(QR)^3 \qquad \text{(A3)}$$

The convolution product of the two distributions is the product of their Fourier transforms, and the inverse Fourier transform of this product gives the probability Π of finding B at the point of coordinates xyz, relative to the center of the sphere.

$$\Pi(xyz) = \frac{3}{(2\pi)^3}\int \mathrm{d}^3Q \exp(-iQr) \times \exp\left(-\frac{Q^2a^2}{6}\right)\frac{\sin QR - QR\cos QR}{(QR)^3} \qquad \text{(A4)}$$

A further integration of Π, over Σ, gives the probability P that B lies in the sphere

$$P = \frac{6}{\pi R^3}\int_0^\infty \mathrm{d}Q \exp\left(-\frac{Q^2a^2}{6}\right)\frac{(\sin QR - QR\cos QR)^2}{Q^4} \qquad \text{(A5)}$$

$$= 3\int_0^\infty \frac{\mathrm{d}Q}{Q}\exp\left(-\frac{Q^2a^2}{6}\right)[J_{3/2}(QR)]^2 \qquad \text{(A6)}$$

where J is the usual symbol of Bessel functions. P can be transformed to

$$P(\rho) = 3\int_0^\infty \frac{\mathrm{d}x}{x}\exp\left(-\frac{x^2}{\rho^2}\right)[J_{3/2}(x)]^2 \qquad \text{(A7)}$$

where

$$\rho^2 = 6R^2/a^2 \qquad \text{(A8)}$$

The derivative $\mathrm{d}P/\mathrm{d}\rho$ is related to the integral (16):

$$\int_0^\infty \mathrm{d}x\, x \exp(-x^2/\rho^2)[J_{3/2}(x)]^2 = \frac{\rho^2}{2}\exp(-\rho^2/2)J_{3/2}(\rho^2/2) \qquad \text{(A9)}$$

Since $P(0) = 0$, by integration one gets

$$P(\rho) = 3\int_0^\rho (1/\rho)\exp(-\rho^2/2)I_{3/2}(\rho^2/2)\,\mathrm{d}\rho$$

$$P(\rho) = {}^3/_2\int_0^{\rho^2/2}\frac{\mathrm{d}x}{x}\exp(-x)I_{3/2}(x) \qquad \text{(A10)}$$

where I is now the usual modified Bessel function.

One checks easily that if $R \to \infty$, $\rho \to \infty$, $P(\infty) = 1$. P has been computed and it is plotted in Figure 5 as a function of

$$u = \frac{\rho^2}{2} = \frac{3R^2}{\nu l^2} \qquad \text{(A11)}$$

An interesting approximation for u large is obtained from the asymptotic form of $I_{3/2}$

$$P(u) = 1 - \frac{3}{2\pi}\frac{1}{u^{1/2}} = 1 - \frac{1.197}{u^{1/2}} \qquad \text{(A12)}$$

Notation

k_B	Boltzmann's constant
k	number of chains linked by a multiplet; $2k$ is the number of outgoing segments
d	distance between the positive and negative charges in a basic pair
D	distance between the clusters
c	molar concentration of the charged monomers
v	volume of one monomer
v_0	volume of one water molecule
ρ	distance from the center of the cluster
σ	cross section of one monomer
l	length of one monomer
α	ratio v_0/v
$p(\rho)$	number of multiplets inside a sphere of radius ρ
$2k\cdot s(\rho)$	number of segments leaving a sphere of radius ρ
$g(\rho)$	volume density of charges
ρ_c	equilibrium radius of one cluster
$n(\rho)$	number of charges inside a sphere of radius ρ
ϵ	dielectric constant of the matrix
n_c	total number of charges inside a cluster
c_0	limiting molar concentrations of charges on the surface of a cluster
R, $\bar{R}$	free end-to-end distance of a segment of polymer between two consecutive charges
δ	radius of the sphere occupied by one cluster
$\mathbf{Q}$	scattering vector
ν	number of water molecules per cation

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