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Normalized scaling relations as a natural classification of linear macromolecules according to size

This paper is dedicated to the memory of professor Sergey Yu Frenkel

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Abstract The scaling relationships (Mark–Kuhn–Houwink–Sakurada type) are considered for the following hydrodynamic values: intrinsic viscosity, velocity sedimentation coefficient and translational diffusion coefficient and the concentration sedimentation coefficient (Gralen coefficient). By also taking into account the mass per unit length we can obtain "normalized scaling plots" which provide a convenient way of representing the rigidity of linear polymers.

Key words Hydrodynamic values · Equilibrium rigidity · Scaling relationships

Introduction

Molecular hydrodynamics provides a powerful means for studying polymers and macromolecular systems. The principal experimental values we can measure are the coefficients of translational diffusion (D) and velocity sedimentation (s), which both manifest translational motion, and the intrinsic viscosity ($[\eta]$), which manifests the rotational motion. Fundamental relations exist which connect these values with the molecular weight (M) and the size of a polymeric chain (in terms of either $\langle h^2 \rangle$, the mean square end-to-end distance, or $\langle s^2 \rangle$, the mean square radius of gyration) are the well-known relations of Einstein–Stokes, Kirkwood–Riseman, Svedberg and Flory [1–5] which are, respectively

$$D = kT/f \tag{1}$$

$$f = P_0 \eta_0 \langle h^2 \rangle^{1/2} \tag{2}$$

$$s = (1 - v\rho_0)M/N_A f \tag{3}$$

$$[\eta] = \Phi_0 \langle h^2 \rangle^{3/2}/M \ . \tag{4}$$

In these relations, f is the translation frictional coefficient, η_0 the viscosity of solvent, T the temperature, N_A Avogadro's number, k the Boltzmann constant, Φ_0 and P_0 are dimensionless hydrodynamic parameters. These parameters (Φ_0 and P_0) are dependent on the relative contour length (L/A, where L is the contour length and A is the Kuhn segment length, see later), relative transverse dimension of the chain (d/A, where d is hydrodynamic diameter of the chain) and also on the thermodynamic quality of the solvent [6].

The key molecular parameters are the molecular weight and the size of the macromolecule. The molecular weight may be characterized by $M = M_L L$, where M_L is the molecular weight per unit length. This parameter is distinctive of a particular type of macromolecule.

The size is determined by the equilibrium rigidity, diameter of the chain and the excluded-volume effect. The equilibrium rigidity may be defined for sufficiently long linear chains in the θ condition (Gaussian statistics) as the ratio of the mean square end-to-end distance to the contour length $A = \langle h^2 \rangle/L$ [2, 6, 7]. This ratio is called the Kuhn segment length. Another characteristic of equilibrium rigidity is the persistence length, a, which is a half the Kuhn segment length: $A = 2a$ [2, 6, 7].

Molecular information is also contained in the first coefficients of the concentration expansion for these experimental values. For instance, the most widely known is that for the intrinsic viscosity $[\eta] \equiv k_1$, that is the first concentration coefficient in the expansion of the dynamic viscosity of a solution

$$\eta = \eta_0(1 + k_1 c + k_2 c^2 + \cdots) \tag{5}$$

$$k_1 \equiv [\eta] \equiv \lim(\eta - \eta_0)/\eta_0 c \tag{6}$$

with the concentration, c, in grams per cubic centimetre, and the intrinsic viscosity, $[\eta]$, in cubic centimetres per gram.

In some cases molecular information can also be obtained from comparison of s_0 with the concentration-dependence "Gralen" coefficient (k_s), [8–10] from the relation

$$s^{-1} = s_0^{-1}(1 + k_s c + \cdots) \ , \tag{7}$$

with k_s also in cubic centimetres per gram. In terms of molecular parameters

$$k_s = B\langle h^2 \rangle^{3/2}/M \ . \tag{8}$$

where B is a dimensionless parameter.

The values of $[\eta]$, s_0 and D_0 are also directly related to the molecular weight by the well known Mark–Kuhn–Houwink–Sakurada (MKHS) relationships [1, 2, 7]:

$$[\eta] = K_\eta M^{b_\eta} \tag{9}$$

$$s_0 = K_s M^{b_s} \tag{10}$$

$$D_0 = K_d M^{b_d} \tag{11}$$

These are often referred to as hydrodynamic "scaling relations". The additional scaling relations may be obtained for any pair of experimental values ($[\eta] \sim s_0^{b_{\eta s}}; s_0 \sim D_0^{b_{sD}}; k_s \sim s_0^{b_{ks}}$, etc). Particularly informative is the relation of k_s to s_0 ($k_s \sim s_0^{b_{ks}}$) since this relation can be obtained in a single series of sedimentation velocity experiments [9, 11].

Discussion

Hydrodynamic theory of a wormlike chain with excluded-volume effect

A more complete interpretation of experimental hydrodynamic values (s_0 or D_0) and $[\eta]$ can be derived by applying the theories of the translational-friction coefficient [12] and intrinsic viscosity [13] for wormlike chains, after taking into account excluded-volume effects. In these theories [12, 13] the Porod statistic is applied for the neighbouring (adjacent) segments and the excluded-volume effects take into account the remote

segments by the parameter ε in the relations $\langle h^2 \rangle \sim N^{1+\varepsilon} \sim M^{1+\varepsilon}$ [14].

The analytical expression may be obtained [15, 16] only for translational friction on the basis of the theory [12]:

$$[s]PN_A = M[D]Pk^{-1} = Mf^{-1}\eta_0 P$$
$$= [3/(1-\varepsilon)(3-\varepsilon)](M_L^{(1+\varepsilon)/2}/A^{(1-\varepsilon)/2})M^{(1-\varepsilon)/2}$$
$$+ (M_L P/3\pi)[\ln A/d - d/3A - \varphi(\varepsilon)] \ . \tag{12}$$

The asymptotic limit ($M \to \infty$) for the purely nondraining case corresponds to

$$f = [\eta_0 P_0(1-\varepsilon)(3-\varepsilon)/3]A^{(1-\varepsilon)/2}M_L^{-(1+\varepsilon)/2}M^{(1+\varepsilon)/2} \ . \tag{13}$$

For the intrinsic viscosity only the asymptotic limit ($M \to \infty$) is currently known theoretically [13, 15, 17]:

$$[\eta] = \Phi(\varepsilon)A^{(3-3\varepsilon)/2}M_L^{-(3+3\varepsilon)/2}$$
$$\times [1 + (5/6)\varepsilon + (1/6)\varepsilon^2]^{-1}M^{(1+3\varepsilon)/2} \ . \tag{14}$$

In the case of $\varepsilon = 0$ these relations transform into the well-known Flory (intrinsic viscosity) and the Kirkwood–Riseman (translational friction) relations for nondraining Gaussian coils. Since $(1 + 2\varepsilon)/2 \equiv b_\eta$ and $b_d \equiv (1+\varepsilon)/2$ [14] Eqs. (13) and (14) reveal the physical sense of the MKHS parameters (K_η, K_d and K_s) and their correlations with the scaling indices become clear [15].

The analysis of these relations (Eqs. 12–14) allows us to enumerate the molecular parameters (except M) which underpin $[\eta]$, s_0 and other experimental hydrodynamic values such as

1. The Kuhn segment length (which characterizes the equilibrium rigidity of the chain).
2. M_L – the mass per unit length.
3. d – the hydrodynamic diameter of the chain.
4. ε – the thermodynamic quality of the polymer–solvent system.

MKHS relationships and fractal concept

The fulfilment of the MKHS relationships reflects the fundamental principle of scale invariance for polymeric molecules [18]. This principle applies not only to linear polymers, but also to branched polymers. The scale indices b_η, b_s and b_d are simply related to the fractal (scale) dimensionality of these particles (i.e. in this case, the macromolecules).

The "fractal" concept was introduced by Mandelbrot [19] and is now widely applied in physics [20, 21]. The physical fractal may be formed by the connection of the separate particles into a single loose integer, called a "cluster", which has, as a rule, a noninteger fractal dimension. This dimension may be determined from the

dependence of the number (N) of single particle clusters on the distance r on which the number is calculated:

$$N \sim r^{d_f} \ . \tag{15}$$

Since for identical particles N is directly proportional to the mass (weight) M, it is possible to give the weight distribution of clusters in terms of size:

$$M \sim r^{d_f} \ . \tag{16}$$

An individual macromolecule is regarded as a fractal object (cluster of connected repeat units, connected monomer cluster), which may be represented by the actual fractal dimension [19]. The relations (Eqs. 1–4, 8) and (Eqs. 9–11) provide us with the possibility of relating the fractal dimension to the scaling indices of MKHS relationships:

$$d_f = |b_d|^{-1} = (1 - b_s)^{-1}$$
$$= 3/(1 + b_\eta) = (b_{k_s} + 3)/(b_{k_s} + 1) \ . \tag{17}$$

This use of the fractal concept provides us with the possibility of relating completely different objects with the same fractal dimension or same scale invariance. From the point of view of molecular physics and molecular hydrodynamics the fractal concept is a more general one than is the simple use of particular properties of individual objects. Molecular hydrodynamics allows us in fact to estimate not only the scaling indicies (fractal dimension), but also to interpret at the molecular level parameters such as Φ_0, P_0, K_η, K_d and K_s [1–6].

Normalized scaling relations

It is possible to eliminate from our consideration the effects of different M_L values by using the corresponding normalized scaling relations.

We will consider the dependence of the terms $[\eta]M_L$, $[s]/M_L$ and $[D]$ on the contour length of the molecules $L = M/M_L$ and $k_s M_L$ on $[s]/M_L$ on a double-logarithmic scale, where $[s] \equiv s_0\eta_0/(1-\upsilon\rho_0)$ and $[D] \equiv D_0\eta_0/T$. In these cases the terms $[\eta]M_L$, $[s]/M_L$, $[D]$ and $k_s M_L$ following Eqs. (1)–(4) and Eq. (8) will depend first of all on the size of the coil in the solution. The normalized MKHS plot is shown in Fig. 1. In this plot all possible conformations of linear macromolecules are repres-ented.

We have now found that the normalized (reduced) scaling relations allow the classification of polymers according to the size of the molecules, which will depend in the main on the equilibrium rigidity of the chain. This preliminary classification of the macromolecules on the basis of their rigidity (extra rigid, rigid, semiflexible, flexible) is important for the choice of the corresponding theory for the interpretation of hydrodynamic data (with or without the excluded-volume effects).

The same principles underlie the plot of $k_s M_L$ versus $[s]/M_L$ (Fig. 2) as discussed by us earlier [22]. It is clear
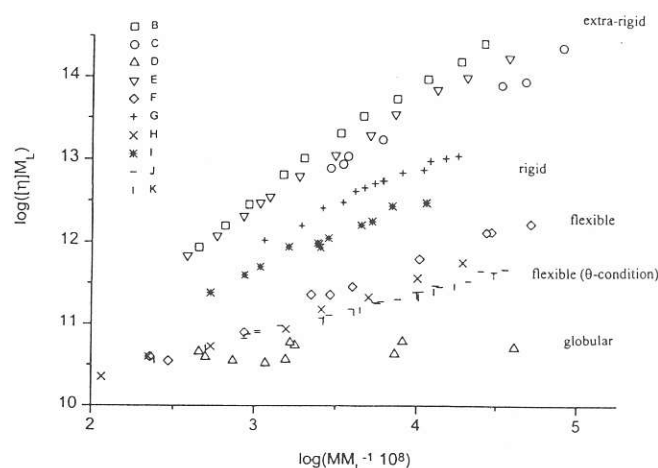

Fig. 1 Normalized double-logarithmic plot of $[\eta]M_L$ against MM_L^{-1} for the following polymer–solvent systems: B – schizophylan in water [26], C – DNA in aqueous buffer [27–30], D – globular proteins in aqueous buffer [1, 31], E – xanthan in 0.1 M NaCl [32], F – poly(1-vinyl-2-pyrrolidone) in 0.1 M sodium acetate [15], G – cellulose nitrate in ethylacetate [33], H – pullulan in water [34–38], I – methylcellulose in water [39], J – poly-α-methylstyrene in cyclohexane (θ condition) [40–43] and in *trans*-decalin (θ condition) [43], K – polystyrene in cyclohexane (θ condition) [42, 44]
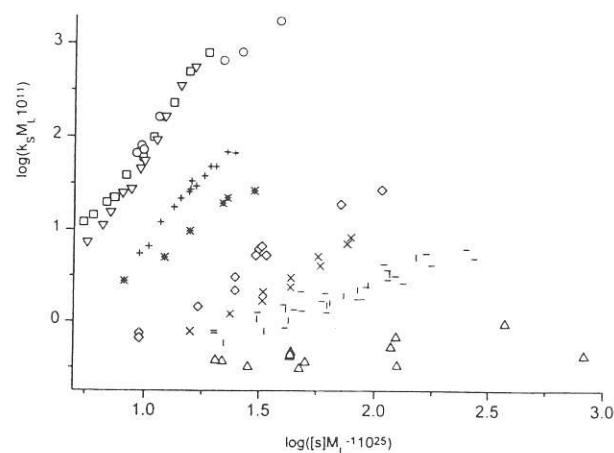

Fig. 2 Normalized double-logarithmic plot of $k_s M_L$ against $[s]M_L^{-1}$ for the same polymer–solvent systems as shown in Fig. 1

evidence of the usefulness of a direct comparison of the values for k_s and s_0, determined from a single series of experiments.

It is worth noting that the behaviour represented in Figs. 1 and 2 is similar in several important ways. First of all the terms $[\eta]M_L$ and $k_s M_L$ and the slopes of their dependencies are greater for more-rigid polymers. This is because the terms $[\eta]M_L \sim k_s M_L \sim \langle h^2 \rangle^{3/2}/L \sim V/L$ follow from Eqs. (4) and (8), where V is the volume occupied by macromolecule and L is its contour length. This ratio characterises the volume occupied per unit length of macromolecule (it is easy to choose the length
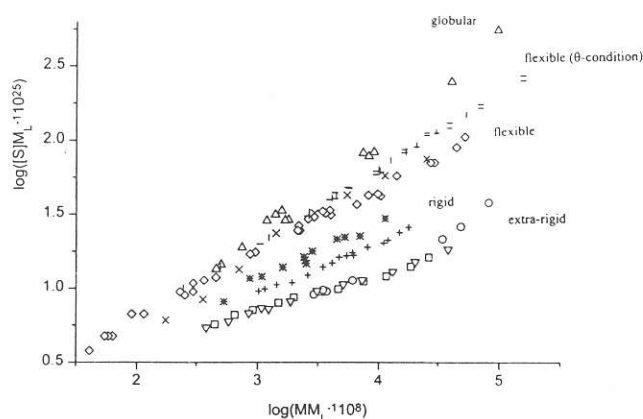
Fig. 3 Normalized double-logarithmic plot of $[s]M_L^{-1}$ against MM_L^{-1} for the same polymer–solvent systems as shown in Fig. 1

Fig. 4 Double normalized double-logarithmic plot of $[\eta]M_L/A^2$ against $MM_L^{-1}A^{-1}$ (master curve) for the same polymer systems as shown in Fig. 1

of a repeat unit in this case). Obviously these values are greater for rigid polymers, and small for the compact molecules (e.g. globular proteins or dendrimers [23, 24]). By contrast the dependence of $[s]M_L^{-1}$ versus MM_L^{-1} (Fig. 3) reveals the opposite tendency because $[s]/M_L \sim L/\langle h^2 \rangle^{1/2}$, and this ratio characterises the degree of coiling or the contraction of a macromolecule; this ratio is obviously greater for small and compact molecules and smaller for rigid ones. In this way the sedimentation coefficient is more sensitive to changes in molecular weight for compact molecules and is smaller for rigid ones [25]. Similar arguments may be applied to the $[D] \sim MM_L^{-1}$ plot.

We can now see how it is possible, using the equilibrium rigidity parameter, to develop the concept of a "master curve", bringing together all types of polymer conformation. The plot required is one in which $[\eta]M_L/A^2$ is plotted as a function of $M/M_L A$ (Fig. 4). This dependence, which follows directly from Eq. 4, shows that polymers whose equilibrium rigidities vary
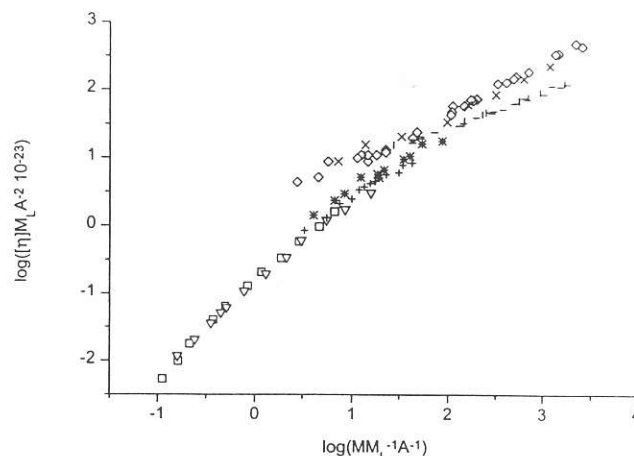
by up to about 200 fold [from flexible chains such as pullulan, poly(vinyl pyrrolidine) and poly(styrene) to extra-rigid rods such as shizophylan and xanthan)] all follow the same trend when represented in this way. There are small deviations from this curve, which in the upper region may be attributed to the excluded-volume effect, and in the lower region to the influence of the diameter of the chain, decreasing the draining of the macromolecules. In this new approach we have developed (and intend in the future to develop further) a formalism which allows the well-known MKHS relationships to be alternatively described in terms of the fractal dimension associated with the polymer, in particular with the equilibrium rigidity parameter of the linear polymer chain. It is clear that this newly derived relationship enables us to give, over a very wide range of solution types and parameters, an integrated description of polymer hydrodynamic behaviour.

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