On the transition to the power law dependence of stiff and flexible macromolecules

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By means of a theoretical expression relating the average size of a chain and the characteristics of the interactions between the polymeric units, we explain the two different ways of approach to the power law dependence of flexible and stiff macromolecules.

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It is known that the power law region, where the various macroscopic properties of polymer chains depend on powers of their molecular weights, is the limiting region of very large molecular weights. A plot of the log of the limiting viscosity number $[\eta]$ of dilute solutions of polymers as a function of the log of their molecular weight M results in a graph of the form shown in *Figure 1*, where, regardless of the behaviour of smaller chains, limiting straight line dependences are obtained[1–15]. The gradients of such straight lines give the critical exponents which are universal numbers and characterize the states at which the macromolecules can exist.

A study of the large number of examples from the literature reveals that there are two different ways of approach to the power region of large molecular weights, as shown in *Figure 1*. One approach takes place from above, with larger values of $[\eta]$ at smaller molecular weights than those corresponding to the straight line of the pure power law. The second approach takes place from below, with smaller values of $[\eta]$ than those of the power law. A more detailed study of the two different classes of macromolecules reveals that the polymers approaching from above are those with flexible chains, with backbones of small diameter permitting closer approach of the chain units and greater flexibility[1–8]. The class of polymers approaching from below have more rigid chains with wider backbone diameters[9–15]. The two different behaviours may be explained by means of equation (3), which is based on recent techniques of statistical mechanics[16].

The analysis is based on the Flory–Fox equation:

$$[\eta]=\frac{\phi[\langle R^2\rangle]^{3/2}}{M} \tag{1}$$

where ϕ is a constant and M the molecular weight of the chain, which relates $[\eta]$ and the mean end-to-end square distance $\langle R^2\rangle$ of the chain[17]. $\langle R^2\rangle$ expresses the square of the linear size of the chain and can be calculated from molecular models of statistical thermodynamics. A knowledge of the dependence of $\langle R^2\rangle$ on various molecular parameters permits the study of $[\eta]$ as a function of these parameters by means of equation (1). Such parameters are the length L of the chain which is proportional to M, the length l of the chain unit and the intensity u_e of the interactions between the units of the chain. u_e is defined as the binary cluster integral:

$$u_e=\tfrac{1}{2}\int \mathrm{d}\boldsymbol{r}\left[1-\exp\left(-\frac{V(\boldsymbol{r})}{kT}\right)\right] \tag{2}$$

where $V(\boldsymbol{r})$ is the mean potential between any pair of chain units at the ends of the vector $\boldsymbol{r}$ and depends on the nature of the behaviour of the units in the environment of the solvent[18,19].

Working close to the critical dimensionality $d=4$ we have shown that first-order calculations and the knowledge of the fixed point value

$$u^*=\frac{\varepsilon}{16}\left[u=\left(\frac{d}{2\pi l^2}\right)^{d/2}u_e\right]$$

to first-order in $\varepsilon=4-d$ determine the critical exponents of the various properties to first order in ε. It was found, for example, that to first order in u:

$$\sqrt{\langle R^2\rangle}=l\sqrt{N}\,[1+u(\ln N-1)]$$

where $N=L/l$ is the number of units of the chain. By means of the fixed point value $u^*=\varepsilon/16$, we see that the critical exponent v of $\sqrt{\langle R^2\rangle}\approx N^v$ is equal to $v=(1/2)+(\varepsilon/16)$ to first order in ε (ref. 20). We have also shown, from higher order calculations, that an interesting

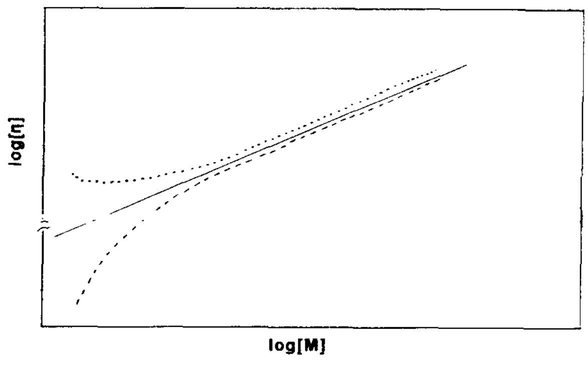

Figure 1 Plots of the log of the limiting viscosity numbers $[\eta]$ *versus* the log of the molecular weight M for flexible (· · ·) and stiff (– – –) macromolecules

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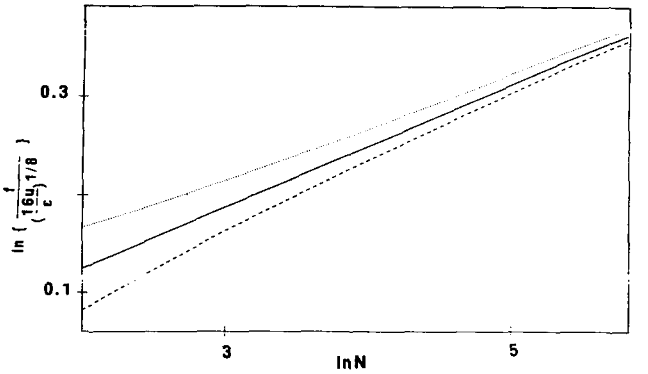

Figure 2 The dependence of $\ln[f/(16u/\varepsilon)^{1/8}]$ on $\ln N$ based on equation (3). For $u=\varepsilon/16$ the pure power law (——) is obtained while for u larger or smaller than this characteristic value graphs approaching from above (···) or below (− − −) are obtained, respectively

closed form can be given of the structure:

$$\sqrt{\langle R^2\rangle}=l\exp(-u)\sqrt{N}f$$
$$f=\left(1-\frac{16u}{\varepsilon}+\frac{16}{\varepsilon}uN^{\varepsilon/2}\right)^{1/8} \tag{3}$$

where $\ln(N)$ is replaced with $(2/\varepsilon)(N^{\varepsilon/2}-1)$ which is its limit for $\varepsilon\to 0$ (ref. 16). This closed form, which can be determined from second-order calculations in u and verified from third-order calculations, describes the macroscopic behaviour of the size of the chain in a large range of values of u and N. It proves, first of all, the existence of a power law in a larger range of N and u, which is the region where the combination $uN^{\varepsilon/2}$ dominates over the terms of f. It explains the existence of the fixed point value $u^*=\varepsilon/16$ which is that value of u which makes equation (3) an exact power law to first order ε. It describes the chain under Θ conditions where $u=0$ and also describes the beginning of the shrinkage of the chain where u obtains small negative values.

It is interesting that since equation (3) describes the size of the chain in a larger range of positive u values, it can also be used in studying the approach to the power law region in good solvents. When the constant $1-(16u/\varepsilon)$ of equation (3) is positive, which means that $u<\varepsilon/16$ to first order in ε, a transition from above takes place, while for $u>\varepsilon/16$ the transition to the power law takes place from below. These two kinds of behaviour are shown in *Figure 2*, where the basic function

$$f=\left(1-\frac{16u}{\varepsilon}+\frac{16u}{\varepsilon}N^{\varepsilon/2}\right)^{1/8}$$

appears, which determines the power law dependence. We plot the function

$$\ln f-\tfrac{1}{8}\ln\left(\frac{16u}{\varepsilon}\right)$$

as a function of $\ln N$ which approaches the power law behaviour

$$\ln f-\tfrac{1}{8}\ln\left(\frac{16u}{\varepsilon}\right)\to\frac{\varepsilon}{16}\ln N$$

and does not depend on the parameter u which characterizes the quality of the solvent. A quantitative explanation of the experimental observations can be pursued further by calculating u_e in terms of characteristic molecular parameters. Using the hard core potential $V(\rho)$ ($\rho=|\boldsymbol{r}|$) with an attractive well shown in *Figure 3* we can calculate:

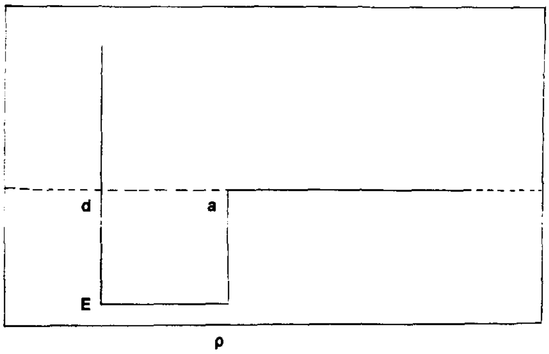

Figure 3 Potential $V(\rho)$ between the polymeric units with a hard core diameter d, an attractive well E and a range of attractions a

$$u_e=\tfrac{2}{3}\pi d^3\exp\left(\frac{E}{kT}\right)+\tfrac{2}{3}\pi a^3\left[1-\exp\left(\frac{E}{kT}\right)\right] \tag{4}$$

which shows the dependence of u_e on the hard core diameter d, on the attractive energy E and the temperature T, and on the range a of the attractions. With increasing d, u certainly increases and the behaviour of the linear size $\sqrt{\langle R^2\rangle}$ of the chain goes from that of flexible chains approaching from above the power law to that of more rigid chains approaching from below.

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