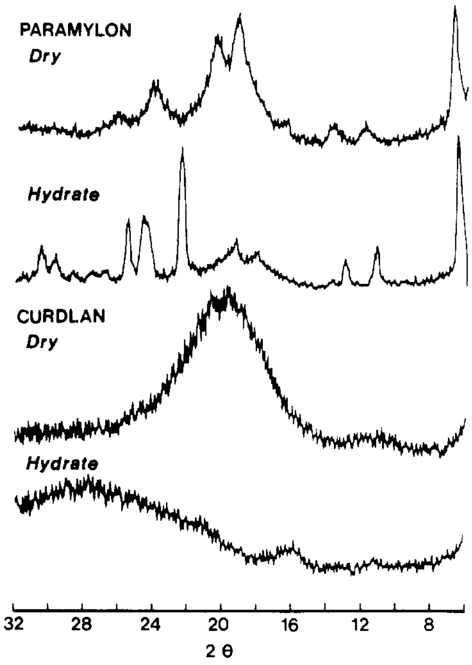

Figure 3. X-ray powder diffraction traces for paramylon and curdlan in the dry and hydrated forms.

The line broadening observed in the spectra of the dry polysaccharides is likely due in large part to distributions of chemical shifts for the individual resonances.[8] This type of line broadening results from a distribution of microenvironments within the solid sample. Hydration could alter this heterogeneity in a number of ways. X-ray diffraction studies of dry[9] and hydrated[10] (1→3)-β-D-glucans indicate that hydration is accompanied by lattice expansion, which allows water to enter the intertriplex spaces in these triple-helical solids. This lattice expansion may allow strain relief and removal of local defects in the solid. This treatment would yield a structure with greater conformational homogeneity, leading to smaller chemical shift distributions for the individual ^{13}C resonances.

Regardless of the detailed mechanism responsible for the observed spectral changes, it is seen that caution must be exercised in the interpretation of the ^{13}C spectra of these materials. Differences found in comparisons of spectra of related materials may be due only to differences in the degree of hydration of the materials. Hydration effects have been noted for another (1→3)-β-D-glucan (laminarin), (1→3)-β-D-xylan (C. A. Fyfe and P. J. Stephenson, unpublished results), cellulose[11] and oligomers of cellulose.[12] The ^{13}C spectra of other solid biopolymers may also depend strongly on hydration. Thus, the sample history with respect to exposure to water should be carefully controlled in solid-state ^{13}C NMR studies of these materials.

Registry No. Curdlan, 54724-00-4; paramylon, 51052-65-4.

References and Notes

(1) W. L. Earl and D. L. VanderHart, *J. Am. Chem. Soc.*, **102**, 3251-3252 (1980).
(2) W. L. Earl and D. L. VanderHart, *Macromolecules* **14**, 570-574 (1981).
(3) R. H. Atalla, J. C. Gast, D. W. Sindorf, V. J. Bartuska, and G. E. Maciel, *J. Am. Chem. Soc.*, **102**, 3249-3251 (1980).
(4) C. A. Fyfe, R. L. Dudley, P. J. Stephenson, Y. Deslandes, G. K. Hamer, and R. H. Marchessault, *J. Macromol. Sci., Rev. Macromol. Chem.*, in press.
(5) H. Saitô, R. Tabeta, and T. Harada, *Chem. Lett.*, 571-574 (1981).
(6) G. E. Maciel, W. L. Kolodziejski, M. S. Bertran, and B. E. Dale, *Macromolecules*, **15**, 686-687 (1982).
(7) F. Horii, A. Hirai, and R. Kitamaru, *Polym. Bull.*, **8**, 163-170 (1982).
(8) D. L. VanderHart, W. L. Earl, and A. N. Garroway, *J. Magn. Reson.*, **44**, 361-401 (1981).
(9) Y. Deslandes, R. H. Marchessault, and A. Sarko, *Macromolecules*, **13**, 1466-1471 (1980).
(10) C. T. Chuah, A. Sarko, Y. Deslandes, and R. H. Marchessault, *Macromolecules*, in press.
(11) D. L. VanderHart, National Bureau of Standards Report NBSIR 82-2534, 1982.
(12) R. L. Dudley, C. A. Fyfe, P. J. Stephenson, Y. Deslandes, G. K. Hamer, and R. H. Marchessault, *J. Am. Chem. Soc.*, **105**, 2469-2472 (1983).

Similarity Applied to the Statistics of Confined Stiff Polymers

THEO ODIJK

Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands. Received May 14, 1983

In a recent paper[1] we introduced a so-called deflection length for describing the statistical properties of wormlike chains trapped in pores. Scaling-type laws were derived for equilibrium as well as dynamical quantities, the latter pertaining to polymers confined in networks. Our results for the rotational diffusion coefficient agree with a somewhat different approach due to Doi,[2] who obtained some of the numerical coefficients as well. At present it is not known if the calculations outlined in ref 1 and 2 have any bearing on the modification of the dynamics of mutually entangled rodlike polymers.[3-6] There still seems to be a major missing link between experiment (e.g., ref 7) and theory (ref 3-6, 1, and 2).

Our derivation of the deflection length was very heuristic. Hence, we would like to point out in this Note that it can be obtained much more rigorously from the partition function by a similarity analysis.[8]

Consider a wormlike chain of contour length L trapped in a infinitely long, cylindrical pore of diameter D. In our Cartesian coordinate system (x, y, z) the axis of the pore is along the z direction. The canonical variable is $\vec{u}(s) = \partial\vec{r}(s)/\partial s$ with $\vec{u}^2 = 1$. Here, $\vec{r}(s)$ is the radius vector of a point of the coil at a contour distance s from one end to that point. The partition function is given formally by the following path integral:[9]

$$Z(\vec{u}(0),\vec{u}(L),P,L,D) = \int_{\substack{\vec{u}(0)\text{ fixed}\\ \vec{u}^2(s)=1}}^{\vec{u}(L)\text{ fixed}} \mathcal{D}[\vec{u}(s)]\exp\left\{-\tfrac{1}{2}P\int_0^L\left(\frac{\partial\vec{u}}{\partial s}\right)^2 \mathrm{d}s\right\} \quad (1)$$

with the additional restriction

$$\left[r_x(0) + \int_0^s u_x(t)\,\mathrm{d}t\right]^2 + \left[r_y(0) + \int_0^s u_y(t)\,\mathrm{d}t\right]^2 \le \tfrac{1}{4}D^2 \quad \text{for all } s \quad (2)$$

Here, P is the persistence length. Now, if $D \ll P$, the chain cannot fold along the z axis (see ref 1). Furthermore, $u_x(s) \ll 1$ and $u_y(s) \ll 1$. In that case, eq 1 can be rewritten as follows:

$$Z(u_x(0),u_y(0),u_x(L),u_y(L),P,L,D) = \int_{u_x(0),u_y(0)}^{u_x(L),u_y(L)} \mathcal{D}[u_x(s)]\mathcal{D}[u_y(s)] \times \exp\left\{-\tfrac{1}{2}P\int_0^L\left[\left(\frac{\mathrm{d}u_x}{\mathrm{d}s}\right)^2 + \left(\frac{\mathrm{d}u_y}{\mathrm{d}s}\right)^2\right]\mathrm{d}s\right\} \quad (3)$$

Although eq 3 is not exact, we can make it as exact as we want to by letting DP^{-1} become smaller and smaller.

Next, we introduce the dimensionless variables s', u_x', u_y', r_x', r_y', and L' as well as two scales λ (dimension length) and α (dimensionless), defined in the following way: $s = \lambda s'$, $u_x(s) = \alpha u_x'(s')$, $u_y(s) = \alpha u_y'(s')$, $r_x(0) = \alpha\lambda r_x'(0)$, $r_y(0) = \alpha\lambda r_y'(0)$, $L = \lambda L'$. Accordingly, eq 2 and 3 become

$$Z(u_x'(0),u_y'(0),u_x'(L'),u_y'(L'),P,L,D) = S(\alpha,L') \int_{u_x'(0),u_y'(0)}^{u_x'(L'),u_y'(L')} \mathcal{D}[u_x'(s')]\mathcal{D}[u_y'(s')] \times \exp\left\{-\frac{P\alpha^2}{2\lambda}\int_0^{L'}\left[\left(\frac{\mathrm{d}u_x'}{\mathrm{d}s'}\right)^2 + \left(\frac{\mathrm{d}u_y'}{\mathrm{d}s'}\right)^2\right]\mathrm{d}s'\right\} \tag{4}$$

$$\left[r_x'(0) + \int_0^{s'} u_x'(t',L')\,\mathrm{d}t'\right]^2 + \left[r_y'(0) + \int_0^{s'} u_y'(t',L')\,\mathrm{d}t'\right]^2 \le \frac{D^2}{4\alpha^2\lambda^2} \tag{5}$$

where $S(\alpha,L')$ is a function of α and L' on which we shall remark later on.

It is now expedient to choose α and λ as follows: $\alpha = D/\lambda$; $\lambda^3 = D^2P$. One then sees immediately that the following two relevant dimensionless groups remain, viz., $L' = L\lambda^{-1}$ and $\alpha = D\lambda^{-1}$; i.e., we can write

$$Z(\phi_i(L'),\alpha,L') = S(\alpha,L') \int_{\phi_i(L')} \mathcal{D}[u_x'(s')]\mathcal{D}[u_y'(s')] \times \exp\left\{-\frac{1}{2}\int_0^{L'}\left[\left(\frac{\mathrm{d}u_x'}{\mathrm{d}s'}\right)^2 + \left(\frac{\mathrm{d}u_y'}{\mathrm{d}s'}\right)^2\right]\mathrm{d}s'\right\} \tag{6}$$

($\phi_i(L')$ represent the angular restrictions), with the constraint

$$\left[r_x'(0) + \int_0^{s'} u_x'(t',L')\,\mathrm{d}t'\right]^2 + \left[r_y'(0) + \int_0^{s'} u_y'(t',L')\,\mathrm{d}t'\right]^2 \le 1/4 \tag{7}$$

From eq 6 and 7 we can discern the following.

(a) The variable α appears only in a front factor in eq 6 and does not occur at all in eq 7. Hence, the probability of some path ($u_x'(s')$, $u_y'(s')$) does not depend on α, even implicitly. It is in this sense that we have similarity. Suppose we compare the behavior of two stiff polymers (with P_1,L_1 and P_2,L_2) each within their respective thin tube (with D_1 and D_2). Furthermore, let $L_1\lambda_2 = L_2\lambda_1$. The statistical properties of $u_1\alpha_1^{-1}$ are then identical with those of $u_2\alpha_2^{-1}$. Note that these results hold only if λ and α are chosen as above.

(b) A further implication is that $S(\alpha,L')$ must be of the form

$$S(\alpha,L') = \alpha^{g(L')} \tag{8}$$

where $g(L')$ represents the number of degrees of freedom. The latter are to be determined from physical arguments.

(c) If $L' \gg 1$, we expect $\ln Z_{\text{tot}}$ to be "extensive"[10] (Z_{tot} is the partition function without any restrictions on the chain ends). It does not matter in a calculation of the free energy whether we cut a very long chain in half because the end effects are entirely negligible as $L' \to \infty$.

$$F_c/k_BT = -\ln Z_{\text{tot}} = L'f(\alpha') \qquad (L' \gg 1) \tag{9}$$

Here, k_B is Boltzmann's constant and T the temperature. In other words, we have

$$g(L') = c_1L' \qquad (L' \gg 1) \tag{10}$$

and also

$$Z_{\text{tot}} = \alpha^{c_1L'}e^{-c_2L'} \qquad (L' \gg 1) \tag{11}$$

where c_1 and c_2 are numerical constants.

(d) Let us consider the behavior of Z/S given by eq 6 and 7. For $L' \ll 1$, $(u_x',u_y') = \mathcal{O}(1/L')$ from eq 7. Moreover, as $L' \to 0$, we are in the WKBJ limit[9] so all fluctuations away from the rod limit become smaller and smaller. Now an integration over $\phi_i(L')$ yields solely a constant factor. Hence, we end up with

$$Z_{\text{tot}}/S = \mathcal{O}(1/L')$$

or

$$Z_{\text{tot}} = c_3D/L \qquad (L' \ll 1) \tag{12}$$

where c_3 is a numerical factor of order unity.

When $L' \gg 1$, u_x' and u_y' as well as their derivatives with respect to s' must be $\mathcal{O}(1)$. Any other choice would not make $\ln Z$ extensive. However, it then follows from eq 7 that u_x' and u_y' must be, in the main, oscillating functions with a dimensionless period of order unity; i.e., the actual period is λ. Accordingly, the latter may be called a deflection length. Brownian motion causes appreciable wriggling (but no folding) of the stiff chain. Near a wall the entropy of the polymer is greatly decreased so the pore walls exert an effective repulsive force deflecting the stiff coil once every λ on the average.

These results coincide with our rather different, more intuitive analysis outlined in ref 1. In particular, eq 11 and 12, to leading order, are identical with, respectively, eq 18 and 9 of ref 1.

Acknowledgment. The author thanks R. C. Ball and S. F. Edwards for a discussion that led to an improvement in the presentation of this Note.

References and Notes

(1) Odijk, T. *Macromolecules*, **1983**, *16*, 1340.

(2) Doi, M. "Effect of the Chain Flexibility on the Dynamics of Rodlike Polymers in the Entangled State", preprint.

(3) Doi, M. *J. Phys.* (*Paris*) **1975**, *36*, 607.

(4) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 560.

(5) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 918.

(6) Edwards, S. F.; Evans, K. E. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 113.

(7) Zero, K. M.; Pecora, R. *Macromolecules* **1982**, *15*, 87.

(8) Barenblatt, G. I. "Similarity, Self-Similarity and Intermediate Asymptotics"; Consultants Bureau: New York, 1979. It is perhaps worthwhile to comment on some often-heard, misinformed opinions concerning scaling. Scaling as used in the theory of phase transitions is what Barenblatt calls similarity of the second kind. This is more restrictive than similarity in its general sense. However, nowadays, one often uses the term scaling even then. In that case it can be applied to situations without critical points. There may even be a large number of competing length scales. Our application is a typical example.

(9) Yamakawa, H. *Pure Appl. Chem.* **1976**, *46*, 135.

(10) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.