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DIFFUSION AND RELAXATION TIME OF POLYMERS IN DILUTE SOLUTIONS

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Résumé. — On montre que pour un polymère en solution diluée, le rayon hydrodynamique R_H et le rayon de gyration R_G obéissent à l'inégalité $R_H > CR_G$ où C est un nombre qui ne dépend pas de la longueur du polymère. R_H est ici défini par l'égalité $1/R_H = 6\pi\eta\beta D$ où D est la constante de diffusion et η la viscosité du solvant. Au point θ , pour de grandes masses, $C = 0,265$. Comme le temps de relaxation τ relatif aux déformations macroscopiques du polymère est proportionnel à R_G^2/D , l'inégalité montre que le rapport τ/R_G^3 ne peut tendre vers zéro quand la masse du polymère devient infinie.

Abstract. — It is shown that for a polymer in a dilute solution, the hydrodynamic radius R_H and the radius of gyration R_G obey an inequality of the form $R_H > CR_G$ where C is a number which does not depend on the length of the polymer. Here R_H is defined by the equality $1/R_H = 6\pi\eta\beta D$ where D is the diffusion constant and η the solvent viscosity. At the θ point for large masses, $C = 0.265$. As the relaxation time τ associated with macroscopic deformations of the polymer is proportional to R_G^2/D , the inequality shows that the ratio τ/R_G^3 cannot vanish when the mass of the polymer becomes infinite.

1. Introduction. — A polymer in a good solvent is usually considered as a ball of mean size R_G (radius of gyration) with $R_G \propto N^\nu$ (N = number of links of the polymer).

The velocity of the fluid inside the ball is not much perturbed by external motions of the fluid as shown by Debye and Bueche [1]. Thus as the mobility of a sphere of radius R is given by Stokes' law ($1/\mu = 6\pi\eta R$), we may write for a polymer

$$1/\mu = 6\pi\eta R_H \quad (1)$$

where R_H is by definition the hydrodynamic radius of the polymer. It is generally believed that

$$R_H \propto R_G \propto N^\nu \quad (2)$$

and since D is proportional to the mobility μ , then by Einstein's law, we have also

$$D = \mu/\beta \propto N^{-\nu} \quad (3)$$

On the other hand, scaling arguments [2] show that D^{-1} is proportional to a more fundamental quantity, namely the relaxation time τ associated with the macroscopic deformations of the polymer

$$\tau \propto R_G^2/D \propto R_H R_G^2 \quad (4)$$

and thus we obtain

$$\tau \propto N^{3\nu} \quad (5)$$

as predicted by de Gennes [3].

Recently, however, Adam and Delsanti [4] have measured D for very dilute solutions of polystyrene in benzene at room temperature by light scattering experiments, and they have found that, for large N ($250 < N < 6\,500$), the diffusion constant D can be represented by a law of the form

$$D = D_0 N^{-0.55 \pm 0.02} \quad (6)$$

The most recent and accurate calculations of ν made by Le Guillou and Zinn Justin [5] give

$$\nu = 0.5888 \pm 0.0010$$

a value which is in good agreement with the static measurements of ν by neutron diffraction [6] ($\nu = 0.595 \pm 0.020$).

Thus, these results seem incompatible with equation (6). In order to explain this discrepancy (which appears larger if we replace ν by the approximate Flory value $\nu_F = 0.6$), some physicists, including the author, have suggested the existence of dynamical indices for which a calculation has recently been attempted by Jasnow and Moore [7].

Our aim here is to show that such an assumption cannot explain this discrepancy.

In fact, we shall prove the inequality

$$R_H > CR_G,$$

where C does not depend on N for large N and depends only on the type of the chain (Brownian type or excluded volume type).

This result will be established by showing that the mobility has an upper bound. Thus, let us assume that the polymer is dragged with a constant force F along the Ox axis; the resulting velocity of the polymer along Ox , at time t will be v and its average will be $\langle v \rangle$.

The mobility is defined by

$$\mu = \langle v \rangle / F \quad \text{for small } v, \quad (7)$$

and the average dissipated energy is

$$F \langle v \rangle = \langle W(v) \rangle, \quad (8)$$

where $W(v)$ is the energy dissipated at time t .

Consequently, the mobility is given by

$$\mu = \frac{\langle v \rangle^2}{\langle W(v) \rangle} \leq \frac{\langle v^2 \rangle}{\langle W(v) \rangle}, \quad (9)$$

(this Schwartz inequality is a direct consequence of the inequality : $\langle W^{-1}[\langle W \rangle v - \langle v \rangle W]^2 \rangle \geq 0$).

This inequality will be used to find an upper bound for the mobility. Everything will be calculated at a given time t . No particular assumption will be made concerning the dynamics of the polymer and since we study a linear response, the result will depend only on the statistical properties of the polymer at equilibrium.

2. The dissipation energy. — The power dissipated in the solvent is given by [8]

$$W = \frac{\eta}{4} \int dV \sum_{ji} (\partial_i v_j + \partial_j v_i)^2, \quad (10)$$

The incompressibility condition is

$$\sum_i \partial_i v_i = 0. \quad (11)$$

For given boundary conditions (for $\mathbf{v}(\mathbf{r})$), a lower bound of the power dissipated in the solvent is obtained by minimizing $\left[W - \int dV p \sum_i \partial_i v_i \right]$ (here the pressure p acts as a Lagrange multiplier).

This minimization leads to the linearized hydrodynamic equations

$$\eta \Delta v_j - \partial_j p = 0 \quad (12)$$

which are valid everywhere in the fluid and from this equation we deduce

$$\Delta p = 0. \quad (13)$$

The polymer can be represented by a continuous curve $\mathbf{r}(\lambda)$ where λ is the length measured along the polymer ($0 < \lambda < L$, $L = Nl$, l = length of a segment).

The singularities of p and v_j are located on the

polymer and to solve equation (12), we must analyse them.

We note that a small ball (infinitesimally small) moving at the origin produces a velocity in the fluid of the form [9]

$$\mathbf{v}(\mathbf{r}) = \frac{\mathbf{a}}{r} + \frac{\mathbf{r}(\mathbf{a} \cdot \mathbf{r})}{r^3} \quad (\text{Stokes' and Oseen's law}) \quad (14)$$

where a is proportional to the velocity of the fluid. The corresponding pressure is (see Eq. (12))

$$p(\mathbf{r}) = \left(\frac{\mathbf{a} \cdot \mathbf{r}}{r^3} \right). \quad (15)$$

This remark shows that the pressure in the fluid is given by dipolar singularities located on the polymer :

$$p(\mathbf{r}) = 2\eta \int_0^L d\lambda \frac{\mathbf{a}(\lambda) \cdot (\mathbf{r} - \mathbf{r}(\lambda))}{|\mathbf{r} - \mathbf{r}(\lambda)|^3} \quad (16)$$

where $\mathbf{a}(\lambda)$ is a vectorial function defining the singularities. This function $p(\mathbf{r})$ is of course a solution of equation (13).

Now, the velocity can be written [10]

$$\mathbf{v}(\mathbf{r}) = \int_0^L d\lambda \left[\frac{\mathbf{a}(\lambda) + 2\mathbf{b}(\lambda)}{|\mathbf{r} - \mathbf{r}(\lambda)|} + \frac{[\mathbf{r} - \mathbf{r}(\lambda)][\mathbf{a}(\lambda) \cdot (\mathbf{r} - \mathbf{r}(\lambda))]}{|\mathbf{r} - \mathbf{r}(\lambda)|^3} \right]. \quad (17)$$

Here the vectorial function $\mathbf{b}(\lambda)$ defines charges located on the polymer.

No singularity of higher order may occur on the polymer because $\mathbf{v}(\mathbf{r})$ must be a rather smooth function of $\mathbf{r}$. Thus, the preceding expression can be considered as the general solution of equation (12).

Of course, boundary conditions have also to be taken into account and they will be introduced later.

The preceding formula can be used to calculate the velocity on the polymer. We shall use the notation

$$\begin{aligned} \mathbf{v}(\mathbf{r}(\lambda)) &= \mathbf{v}(\lambda) \\ \mathbf{r}(\lambda) - \mathbf{r}(\lambda') &= \mathbf{r}(\lambda, \lambda'). \end{aligned} \quad (18)$$

A cut-off can be introduced at small distances; this cut-off can be interpreted as the thickness of the polymer.

However, this cut-off is unimportant. In the asymptotic limit, the polymer cannot be considered as a smooth curve and for small values of $|\lambda - \lambda'|$, $\mathbf{r}(\lambda, \lambda')$ is proportional to $|\lambda - \lambda'|$ and not to $|\lambda - \lambda'|$. Consequently, the velocity on the polymer is given by the following convergent integral

$$\mathbf{v}(\lambda) = \int_0^L d\lambda' \left\{ \frac{\mathbf{a}(\lambda) + 2\mathbf{b}(\lambda)}{r(\lambda, \lambda')} + \frac{\mathbf{r}(\lambda, \lambda') [\mathbf{a}(\lambda) \cdot \mathbf{r}(\lambda, \lambda')]}{r^3(\lambda, \lambda')} \right\}. \quad (19)$$

The dissipated power W can also be expressed in terms of $\mathbf{a}(\lambda)$ and $\mathbf{b}(\lambda)$. In equation (19), we replace

$\mathbf{v}(\mathbf{r})$ by its explicit value (Eq. (17)) and, after integrating, we obtain

$$\frac{W}{8\pi\eta} = \frac{1}{2} \int_0^L d\lambda \int_0^L d\lambda' \left\{ \frac{[\mathbf{a}(\lambda) + \mathbf{b}(\lambda)][\mathbf{a}(\lambda') + \mathbf{b}(\lambda')] + 2\mathbf{b}(\lambda)\mathbf{b}(\lambda')}{r(\lambda, \lambda')} + \frac{[(\mathbf{a}(\lambda) + \mathbf{b}(\lambda)) \cdot \mathbf{r}(\lambda, \lambda')][(\mathbf{a}(\lambda') + \mathbf{b}(\lambda')) \cdot \mathbf{r}(\lambda, \lambda')] - 2[\mathbf{b}(\lambda) \cdot \mathbf{r}(\lambda, \lambda')][\mathbf{b}(\lambda') \cdot \mathbf{r}(\lambda, \lambda')]}{r^3(\lambda, \lambda')} \right\}. \quad (20)$$

However, in order to calculate $\text{Min } W(v)$ for a given v , one must introduce realistic boundary conditions for $v_j(r)$. It is difficult to take all these conditions into account, but we may impose only some of them and minimize W . In this way, we shall not obtain $\text{Min } W(v)$ but a lower bound $W_m(v)$ and this is all that we need here.

Now let us discuss the boundary conditions.

We may decide that the mean velocity of the polymer along the axis Ox has a given value v

$$\int_0^L d\lambda v_x(\lambda) = vL. \quad (21)$$

On the other hand, let us consider the quantity

$$\varphi(\mathbf{r}) = \sum_i \partial_i v_i(\mathbf{r})$$

where $v_i(r)$ is given by equation (17).

We know that everywhere in the fluid

$$\Delta\varphi = 0. \quad (22)$$

On the surface of the polymer, the function φ should vanish. However, since φ obeys equation (22) its extrema are located on the boundary. But φ vanishes at infinity; thus, if $\varphi = 0$ on the polymer, $\varphi = 0$ everywhere. Thus the incompressibility requirements can be reduced to the conditions

$$\varphi(\mathbf{r}(\lambda)) = 0. \quad (23)$$

In order to calculate $\text{Min } W(v)$, one should take equations (21) and (23) into account. However, since we need only a lower bound $W_m(v)$, we may ignore equation (23) and calculate $W_m(v)$ by minimizing W and keeping equation (21). We obtain the equations

$$\begin{aligned} \frac{\partial}{\partial a_j(\lambda)} \left[W/8\pi\eta - A \int_0^L d\lambda v_x(\lambda) \right] &= 0 \\ \frac{\partial}{\partial b_j(\lambda)} \left[W/8\pi\eta - A \int_0^L d\lambda v_x(\lambda) \right] &= 0 \end{aligned} \quad (24)$$

where A is a Lagrangian multiplier.

By writing these equations explicitly and adding them, we get :

$$2v_j(\lambda) = A \int_0^L \frac{d\lambda'}{r(\lambda, \lambda')} \left[3\delta_{xj} + \frac{r_x(\lambda, \lambda')r_j(\lambda, \lambda')}{r^2(\lambda, \lambda')} \right]. \quad (25)$$

Let us put $j = x$ and integrate with respect to λ with the help of equation (21); we get

$$\begin{aligned} A &= 2vL/u \\ u &= \int_0^L d\lambda \int_0^L d\lambda' \left[\frac{3}{r(\lambda, \lambda')} + \frac{r_x^2(\lambda, \lambda')}{r^3(\lambda, \lambda')} \right]. \end{aligned} \quad (26)$$

Now let us consider the operator

$$\Theta = \sum_j \int_0^L d\lambda \left[a_j(\lambda) \frac{\partial}{\partial a_j(\lambda)} + b_j(\lambda) \frac{\partial}{\partial b_j(\lambda)} \right]. \quad (27)$$

Homogeneity considerations show that

$$2W = \Theta W \quad v_x(\lambda) = \Theta v_x(\lambda). \quad (28)$$

Combining these relations and equation (24), we obtain for $W(v)$ the lower bound

$$\frac{W_m(v)}{4\pi\eta} = AvL. \quad (29)$$

Then using equation (26), we obtain the final answer

$$\text{Min } W(v) > W_m(v) = \frac{8\pi\eta L^2 v^2}{u}. \quad (30)$$

3. A property of the hydrodynamic radius. — Let us reconsider equation (9). With the help of equation (30) we find for the mobility the upper bound

$$\mu < \langle u \rangle / 8\pi\eta L^2 \quad (31)$$

and for the hydrodynamical radius R_H defined by equation (1)

$$R_H > 4L^2/3 \langle u \rangle \quad (32)$$

where $\langle u \rangle$ is the mean value of the random variable u (see Eq. (26)) over all configurations of the chain

$$\langle u \rangle = \frac{10}{3} \int_0^L d\lambda \int_0^L d\lambda' \left\langle \frac{1}{r(\lambda, \lambda')} \right\rangle. \quad (33)$$

Now scaling arguments and the fact that, owing to excluded volume effects, central parts of the chain should be proportionally more stretched than the chain itself show that

$$\left\langle \frac{1}{r(\lambda, \lambda')} \right\rangle \leq \frac{L^v}{|\lambda - \lambda'|^v} \left\langle \frac{1}{r(0, L)} \right\rangle. \quad (34)$$

Thus equations (33) and (34) give

$$\langle u \rangle < \frac{20 L^2}{3(1-\nu)(2-\nu)} \left\langle \frac{1}{r(0, L)} \right\rangle. \quad (35)$$

Combining this inequality with equation (32), we obtain

$$R_H > \frac{1}{5} (1-\nu)(2-\nu) \left[\left\langle \frac{1}{r(0, L)} \right\rangle \right]^{-1}. \quad (36)$$

The well known properties [11] of the probability law $P(L, r)$ of the random variable $r(0, L)$ show that $\langle 1/r(0, L) \rangle$ is bounded and given by simple scaling laws (the cut-off can be ignored).

Thus we may write, and this is a crucial point,

$$\left\langle \frac{1}{r(0, L)} \right\rangle = \frac{\sigma}{R_G}, \quad (37)$$

where σ is a number which for a chain with excluded volume (in the asymptotic limit) is universal.

We obtain finally

$$R_H > \frac{(1-\nu)(2-\nu)}{5\sigma} R_G. \quad (38)$$

In a θ solvent, the chains are asymptotically Brownian; in this case, $\sigma = \pi^{-1/2}$ and we obtain

$$R_H > \frac{3}{20} \pi^{1/2} R_G > 0.265 R_G. \quad (39)$$

Incidentally, we note that the classical Kirkwood Riseman theory would give [12] in this case

$$R_H/R_G = \frac{3}{8} \pi^{1/2} \quad (40)$$

a result which is less reliable but (perhaps) more accurate.

4. Conclusion. — The preceding inequalities have been derived under very general conditions; no assumption has been made concerning the flexibility and the motions of the polymer, the derivation is valid when the hydrodynamic equations contain time derivatives of the velocity.

These inequalities show that, for very long chains, D cannot be given by equation (6).

Equations (38) and (4) also show that the ratio (τ/R_G^3) cannot vanish when the number of links of the polymer becomes infinite. In spite of this contradiction, the experimental results concerning solutions of polystyrene in benzene do not seem incompatible with our inequalities. For a polymer of large mass $M_w = 6.1 \times 10^5$, we have according to Adam and Delsanti [4]

$$R_H \simeq 239 \text{ \AA}.$$

For a polymer of the same mass, we have according to the results of Decker-Freyss [13]

$$R_G \simeq 401 \text{ \AA}.$$

Therefore for this large mass

$$(R_H/R_G)_{\text{exp}} = 0.596.$$

However, the experiments dealing with dynamical properties of polymers reveal anomalies which have to be explained [14]. We have only shown here that these anomalies cannot be simply explained by assuming the existence of an anomalous dynamical index.

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