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The Stokes resistance for a polymer chain

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Abstract. A flexible cylinder in a viscous fluid is used to model a dilute polymer solution, with a non-slip boundary condition between the polymer chain surface and fluid. The problem is solved using Green functions and a perturbation expansion. The lowest-order term in the expansion gives for the mean Stokes force

$$\langle \boldsymbol{F} \rangle = \frac{6\pi\eta \boldsymbol{v}^{\infty}(3\pi lL)^{1/2}}{12} \phi(\alpha^2/lL)$$

where $(\alpha^2/lL)^{1/2}$ is the ratio of the cylinder radius to the root-mean-square end-to-end distance and the function ϕ is given in the text. Our model generalizes that of Kirkwood and Riseman by having thickness, and avoids the friction coefficient they use.

1. Introduction

The Stokes resistance for particles of a variety of geometrical shapes has been much studied (Happel and Brenner 1965). In this paper we introduce a new geometrical shape: a cylinder of radius α, and whose axis takes a random flight trajectory, and the conformation of the axis changes in time due to Brownian motion. The usual non-slip boundary condition for the liquid-cylinder surface is assumed. This model is given some respectability as a representation of a macromolecule by a remark of Flory's (1953—p. 610). It should be noticed that a cylinder with a random flight axis is a rather peculiar object, we should rather have an axis which is a smooth curve with a maximum curvature of $1/\alpha$. The modification to our analysis is straightforward but leads to difficult quadrature. The first approximation to this modification, in a small parameter expansion, exists and corresponds to our random flight axis model.

Our model differs from that of Kirkwood and Riseman (1948—to be referred to as K & R) not only in that it is a continuous cylinder rather than a discrete chain of beads but more fundamentally in that we make no use of any friction coefficient and also our chain has a definite thickness. Hence, we have to solve a hydrodynamical boundary value problem.

Physically it is the hydrodynamic interactions between distant parts of the chain which give rise to the hydrodynamic properties of polymer solutions, this is why the friction coefficient does not appear in the physically significant part of the solution of K & R. They obtain for the mean drag on a polymer chain

$$\langle \boldsymbol{F} \rangle = f\eta(lL)^{1/2}\boldsymbol{v}^{\infty}\frac{x}{1+x} \tag{1.1}$$

where

$$f = \tfrac{1}{16}(6\pi)^{3/2}$$
$$x = \zeta(L/l)^{1/2}/f\eta l$$

ζ is the friction coefficient per chain link, l is the link length, L the chain length, η the solvent viscosity and $\boldsymbol{v}^\infty$ the velocity of the solvent relative to the chain far from the chain. Since $\zeta \simeq \eta l$, for long chains $x \gg 1$ and

$$\langle \boldsymbol{F} \rangle = f\eta(lL)^{1/2}\boldsymbol{v}^\infty = 6\pi\eta\boldsymbol{v}^\infty(6\pi lL)^{1/2}/16 \tag{1.2}$$

which is independent of ζ. Thus ζ is irrelevant to the problem, and our model has the advantage of doing without it.

In a previous paper by Edwards and Papadopoulos (1968) the Stokes resistance for a nearly spherical body has been studied. Here we set our problem up in the same manner and the reader should see that paper for more detail.

2. The model

The surface of the cylinder is given by

$$\boldsymbol{r} = \boldsymbol{R}(x, \theta)$$

where x and θ are the surface parameters. L is the length of the cylinder along its axis and xL gives the distance along the axis from one end, $0 \leqslant x \leqslant 1$. $\partial \boldsymbol{R}(x, \theta)/\partial x$

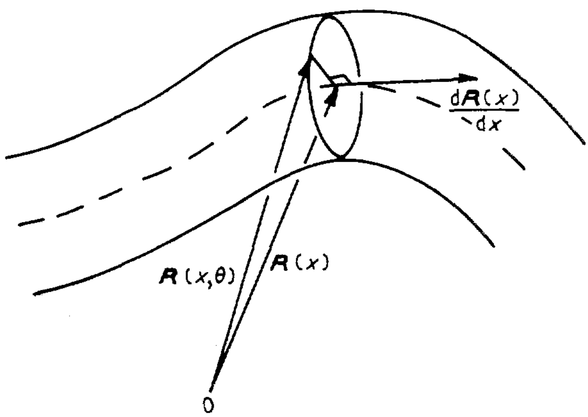

Figure 1

is the vector tangent to the axis at xL from one end. The plane perpendicular to this is cut by the cylinder in a circle, θ is the angle subtended by the point on the surface (x, θ) from some defined direction, $0 \leqslant \theta \leqslant 2\pi$ (see figure 1).

The position vector of the axis at x is clearly

$$\boldsymbol{R}(x) = \frac{1}{2\pi}\int_0^{2\pi} \boldsymbol{R}(x, \theta)\, \mathrm{d}\theta$$

so that the equation for the axis is

$$\boldsymbol{r} = \boldsymbol{R}(x).$$

This equation for the axis with the condition for constant radius

$$|\boldsymbol{R}(x,\theta)-\boldsymbol{R}(x)| = \alpha, \qquad \text{all } \theta$$

together define the cylinder with surface S.

The differential of surface area is

$$\mathrm{d}S = \left|\frac{\partial \boldsymbol{R}(x,\theta)}{\partial x}\times\frac{\partial \boldsymbol{R}(x,\theta)}{\partial \theta}\right| \mathrm{d}x\,\mathrm{d}\theta$$

$$= \left|\frac{\partial \boldsymbol{R}}{\partial x}\right| \left|\frac{\partial \boldsymbol{R}}{\partial \theta}\right| \mathrm{d}x\,\mathrm{d}\theta$$

since the vectors are perpendicular.

$|\partial \boldsymbol{R}/\partial\theta| = \alpha$ for a cylinder of radius α. $|\partial \boldsymbol{R}/\partial x| = L$ for a completely inextensible chain; for the measure we use in averaging over chain conformations, Weiner measure, this is not strictly true and we should leave $\mathrm{d}S$ as a function of $|\partial \boldsymbol{R}/\partial x|$. However, an expansion about the value L can be made though we shall follow previous work using Weiner measure and simply take the first term in this expansion. Thus we shall take

$$\mathrm{d}S = \alpha L\,\mathrm{d}\theta\,\mathrm{d}x. \tag{2.1}$$

$\boldsymbol{R}(x)$ will be treated as a stochastic variable, its distribution will be taken to be the Weiner measure with the centroid of the chain at the origin,

$$W[\boldsymbol{R}(x)] = \mathcal{N}\exp\left(-\frac{3}{2lL}\int_0^1\left|\frac{\mathrm{d}\boldsymbol{R}(x)}{\mathrm{d}x}\right|^2\mathrm{d}x\right)\delta\left\{\int_0^1 \boldsymbol{R}(x)\,\mathrm{d}x\right\}$$

lL is the mean square end-to-end distance of the chain. Thus the axis takes up random flight conformations. Averages will be indicated by angular brackets.

Using this measure to obtain ensemble averages over all possible random flight conformations should give a good representation of the Brownian motion of the chain at the theta temperature since

(i) The theta temperature is defined as that at which random flight statistics are a good representation of flexible macromolecule conformation statistics.

(ii) By the ergodic hypothesis, the average over all available conformations (on the appropriate time-scale) should simulate the thermal motion of the chain.

(iii) Though one chain will not have available to it all random flight conformations, because in some approximate sense its topology will be fixed (how much depends on the time-scale), experimentally one has a system with many chains which means one is averaging over topologies. Thus the measure $W[\boldsymbol{R}(x)]$ is an appropriate one.

The object of this paper is to solve Stokes' equations

$$\eta\Delta\boldsymbol{v}-\nabla p = \boldsymbol{0}$$

$$\nabla\cdot\boldsymbol{v} = 0$$

with the boundary conditions

$$\boldsymbol{v}\{\boldsymbol{R}(x,\theta)\} = 0, \qquad \text{all } (x,\theta) \tag{2.2}$$

and, at infinity

$$\lim \boldsymbol{v}(\boldsymbol{r})_{r\to\infty} = \boldsymbol{v}^{\infty}.$$

The Stokes resistance is obtained from the solution as

$$\boldsymbol{F} = \int_{S_R} [-p\boldsymbol{I}+\eta\{\nabla \boldsymbol{v}+(\nabla \boldsymbol{v})^+\}] \,.\, \mathrm{d}\boldsymbol{S} \tag{2.3}$$

where $\boldsymbol{I}$ is the unit tensor, $(\ )^+$ indicates transposition, the surface S_R is a sphere of radius R drawn around the origin and enclosing the chain. For details see Landau and Lifshitz (1959). The mean Stokes resistance is obtained by averaging (2.3) using the measure $W[\boldsymbol{R}(x)]$, as this is spherically symmetric the friction tensor will be isotropic and the mean force will be along $\boldsymbol{v}^\infty$.

3. The solution of Stokes' equations

In this section we shall generalize the boundary condition at infinity to

$$\lim \boldsymbol{v}(\boldsymbol{r})_{r\to\infty} = \boldsymbol{v}^\infty(\boldsymbol{r}). \tag{3.1}$$

To ease the handling of the boundary conditions on the chain surface Lagrange multipliers are used (Edwards and Papadopoulos 1968). Stokes' equations are modified to

$$\eta\Delta \boldsymbol{v} - \nabla p + \int_S \boldsymbol{\xi}(x, \theta)\delta\{\boldsymbol{R}(x, \theta)-\boldsymbol{r}\}\,\mathrm{d}S = 0 \tag{3.2}$$

$$\nabla \,.\, \boldsymbol{v} = 0 \tag{3.3}$$

where $[\boldsymbol{\xi}(x, \theta)]$ will be chosen to satisfy the surface boundary condition (2.2).

Take the divergence of (3.2) and use (3.3) to obtain an equation for the pressure. The Green function is well known and one obtains

$$p(\boldsymbol{r}) = p^\infty(\boldsymbol{r})+\frac{1}{4\pi}\int_S \mathrm{d}S\,\frac{\{\boldsymbol{r}-\boldsymbol{R}(\sigma)\}}{|\boldsymbol{r}-\boldsymbol{R}(\sigma)|^3}\,.\,\boldsymbol{\xi}(\sigma) \tag{3.4}$$

where $p^\infty(\boldsymbol{r})$ is the pressure at infinity, and for brevity we write σ for the pair (x, θ). Substituting (3.4) in (3.2) gives an equation for the velocity which is solved in the same manner. The solution is

$$\boldsymbol{v}(\boldsymbol{r}) = \boldsymbol{v}^\infty(\boldsymbol{r})+\frac{1}{4\pi\eta}\int_S \boldsymbol{K}\{\boldsymbol{r}-\boldsymbol{R}(\sigma)\}\,.\,\boldsymbol{\xi}(\sigma)\,\mathrm{d}S \tag{3.5}$$

where

$$\boldsymbol{K}(\boldsymbol{r}) = \frac{r^2\boldsymbol{I}+\boldsymbol{r}\boldsymbol{r}}{2r^3}.$$

The Lagrange multipliers $[\boldsymbol{\xi}(\sigma)]$ are obtained by applying the boundary conditions (2.2).

$$\boldsymbol{0} = \boldsymbol{v}^\infty\{\boldsymbol{R}(\sigma')\}+\frac{1}{4\pi\eta}\int_S \boldsymbol{K}\{\boldsymbol{R}(\sigma')-\boldsymbol{R}(\sigma)\}\,.\,\boldsymbol{\xi}(\sigma)\,\mathrm{d}S. \tag{3.6}$$

It is now assumed that the inverse to $\boldsymbol{K}\{\boldsymbol{R}(\sigma')-\boldsymbol{R}(\sigma)\}$ exists, it is defined by

$$\int_S \boldsymbol{K}^{-1}(\sigma'', \sigma')\,.\,\boldsymbol{K}\{\boldsymbol{R}(\sigma')-\boldsymbol{R}(\sigma)\}\,\mathrm{d}S' = \boldsymbol{I}\delta(\sigma''-\sigma)$$

where $\delta(\sigma''-\sigma)$ is an appropriately defined delta function. Clearly, from the definition of $\boldsymbol{K}(\boldsymbol{r})$,

$$\boldsymbol{K}^{-1}(\sigma'', \sigma) = \boldsymbol{K}^{-1}(\sigma, \sigma'').$$

Multiply (3.6) by $\boldsymbol{K}^{-1}(\sigma'', \sigma')$ and integrate over σ', then

$$\boldsymbol{\xi}(\sigma) = -4\pi\eta \int_S \boldsymbol{K}^{-1}(\sigma, \sigma') \,.\, \boldsymbol{v}^{\infty}\{\boldsymbol{R}(\sigma')\}\, \mathrm{d}S'.$$

Substituting this back in (3.4) and (3.5) gives

$$\boldsymbol{v}(\boldsymbol{r}) = \boldsymbol{v}^{\infty}(\boldsymbol{r}) - \int_S \mathrm{d}S \int_S \mathrm{d}S' \boldsymbol{K}\{\boldsymbol{r}-\boldsymbol{R}(\sigma')\} \,.\, \boldsymbol{K}^{-1}(\sigma', \sigma) \,.\, \boldsymbol{v}^{\infty}\{\boldsymbol{R}(\sigma)\} \tag{3.7}$$

and

$$p(\boldsymbol{r}) = p^{\infty}(\boldsymbol{r}) - \eta \int_S \mathrm{d}S \int_S \mathrm{d}S' \frac{\{\boldsymbol{r}-\boldsymbol{R}(\sigma)\}}{|\boldsymbol{r}-\boldsymbol{R}(\sigma)|^3} \,.\, \boldsymbol{K}^{-1}(\sigma, \sigma') \,.\, \boldsymbol{v}^{\infty}\{\boldsymbol{R}(\sigma')\}. \tag{3.8}$$

4. Application to the Stokes resistance problem

The solutions (3.7) and (3.8) for the velocity and pressure fields are appropriate to the Stokes resistance problem if in (3.1) $\boldsymbol{v}^{\infty}(\boldsymbol{r}) = \boldsymbol{v}^{\infty}$, a constant vector, and $p^{\infty}(\boldsymbol{r}) = p^{\infty}$, a constant. These solutions inserted in (2.3) give the drag on the chain for the chain conformation $[\boldsymbol{R}(\sigma)]$. Equation (2.3) holds for arbitrary R, provided the sphere encloses the chain, therefore only terms of order $1/r$ in the velocity and $1/r^2$ in the pressure contribute to the integral. From (3.7) and (3.8) we have

$$\boldsymbol{v}(\boldsymbol{r}) = \boldsymbol{v}^{\infty} - \boldsymbol{K}(\boldsymbol{r}) \,.\, \int_S \mathrm{d}S \int_S \mathrm{d}S' \boldsymbol{K}^{-1}(\sigma, \sigma') \,.\, \boldsymbol{v}^{\infty} + \mathrm{O}(r^{-2})$$

$$p(\boldsymbol{r}) = p^{\infty} - \eta \frac{\boldsymbol{r}}{r^3} \,.\, \int_S \mathrm{d}S \int_S \mathrm{d}S' \boldsymbol{K}^{-1}(\sigma, \sigma') \,.\, \boldsymbol{v}^{\infty} + \mathrm{O}(r^{-3}).$$

Using the symmetry of $\boldsymbol{K}^{-1}$ we can write (2.3) as

$$\begin{aligned} F_i &= -\eta v_k^{\infty} \int_S \mathrm{d}S \int_S \mathrm{d}S' K_{kl}^{-1}(\sigma, \sigma') \int_{S_R} \left(\frac{r_l}{r^3}\,\delta_{ij} + \frac{\partial K_{li}}{\partial x_j} + \frac{\partial K_{lj}}{\partial x_i}\right) \mathrm{d}S_j \\ &= 4\pi\eta v_k^{\infty} \int_S \mathrm{d}S \int_S \mathrm{d}S' K_{ki}^{-1}(\sigma, \sigma'). \end{aligned} \tag{4.1}$$

Define the friction tensor $\boldsymbol{\Phi}$ by

$$\boldsymbol{F} = \boldsymbol{\Phi} \,.\, \boldsymbol{v}^{\infty}$$

then

$$\boldsymbol{\Phi} = 4\pi\eta \int_S \mathrm{d}S \int_S \mathrm{d}S' \boldsymbol{K}^{-1}(\sigma, \sigma')$$

which is a functional of $[\boldsymbol{R}(\sigma)]$.

The mean drag is simply $\boldsymbol{F}$ in (4.1) averaged over all conformations as described in § 2. Thus

$$\langle \boldsymbol{F} \rangle = \langle \boldsymbol{\Phi} \rangle \,.\, \boldsymbol{v}^{\infty}. \tag{4.2}$$

Since $\mathrm{d}S$ is not a function of $\boldsymbol{R}(x, \theta)$ in our approximation, equation (2.1), we have

$$\left\langle \int_S \mathrm{d}S \int_S \mathrm{d}S' \boldsymbol{K}^{-1}(\sigma, \sigma') \right\rangle = \int_S \mathrm{d}S \int_S \mathrm{d}S' \langle \boldsymbol{K}^{-1}(\sigma, \sigma') \rangle$$

and the problem is reduced to obtaining

$$\langle \boldsymbol{\Phi} \rangle = 4\pi\eta \int_S \mathrm{d}S \int_S \mathrm{d}S' \langle \boldsymbol{K}^{-1}(\sigma, \sigma') \rangle. \tag{4.3}$$

5. An expansion for K^{-1}

In order to obtain an expression for $\langle \boldsymbol{K}^{-1} \rangle$ we shall make an expansion about the mean $\langle \boldsymbol{K}\{\boldsymbol{R}(\sigma) - \boldsymbol{R}(\sigma')\} \rangle^{-1}$. Write

$$\boldsymbol{K}\{\boldsymbol{R}(\sigma) - \boldsymbol{R}(\sigma')\} \equiv \langle \boldsymbol{K}\{\boldsymbol{R}(\sigma) - \boldsymbol{R}(\sigma')\} \rangle - \boldsymbol{V}(\sigma, \sigma')$$

which defines $\boldsymbol{V}$. It is convenient to write

$$\langle \boldsymbol{K}\{\boldsymbol{R}(\sigma) - \boldsymbol{R}(\sigma')\} \rangle \equiv \boldsymbol{Q}^{-1}(\sigma, \sigma')$$

then

$$\boldsymbol{K}^{-1}(\sigma, \sigma') = \boldsymbol{Q}(\sigma, \sigma') + \int_S \mathrm{d}S'' \int_S \mathrm{d}S''' \boldsymbol{Q}(\sigma, \sigma'') \cdot \boldsymbol{V}(\sigma'', \sigma''') \cdot \boldsymbol{K}^{-1}(\sigma''', \sigma') \tag{5.1}$$

where $\boldsymbol{K}^{-1}$ is, of course, a functional of $[\boldsymbol{R}(\sigma)]$, $\boldsymbol{Q}$ is defined by

$$\int_S \mathrm{d}S'' \boldsymbol{Q}(\sigma, \sigma'') \cdot \boldsymbol{Q}^{-1}(\sigma'', \sigma') = \boldsymbol{I}\delta(\sigma - \sigma') \tag{5.2}$$

which is analogous to the defining equation for $\boldsymbol{K}^{-1}$. Equation (5.1), when iterated, gives an expansion for $\boldsymbol{K}^{-1}$ in $\boldsymbol{V}$.

$\boldsymbol{Q}^{-1}$ is evaluated in Appendix 1 and is given by (A1.4):

$$\boldsymbol{Q}^{-1}(\sigma, \sigma') = \boldsymbol{I} \frac{2|x - x'|^{1/2}}{3\lambda\alpha} \int_0^{\gamma/\alpha} \operatorname{Erf}(u)\, \mathrm{d}u$$

where

$$\gamma/\alpha = (lL/12\alpha^2)^{1/2} |x - x'|^{1/2}, \qquad \lambda \equiv (12\alpha^2/lL)^{1/2}.$$

This is substituted in (5.2) and since

$$\int \delta(\sigma - \sigma')\, \mathrm{d}S' = 1$$

and $\mathrm{d}S = \alpha L\, \mathrm{d}\theta\, \mathrm{d}x$ we write

$$\delta(\sigma - \sigma') = (1/\alpha L)\delta(\theta - \theta')\delta(x - x').$$

(5.2) reduces to

$$(2\pi\alpha L)^2 \int_0^1 \mathrm{d}x'' Q(x, x'') Q^{-1}(x'', x') = \delta(x - x')$$

where $\boldsymbol{Q}$ has been written as $Q\boldsymbol{I}$.

This equation is solved in Appendix 2 where the solution is obtained in the form of a Fourier series. g is the periodic extension of Q, and

$$g(x - x'') = \sum_{m=-\infty}^{\infty} f_m^{-1} \exp\{2\pi i m(x - x'')\}$$

with the coefficients given in (A2.2).

When (5.1) is iterated we obtain, schematically,

$$K^{-1} = Q + Q\,.\,V\,.\,Q + Q\,.\,V\,.\,Q\,.\,V\,.\,Q + \ldots.$$

It is the mean of this that is required. From the properties already given of the quantities on the right hand side we have

$$\langle K^{-1} \rangle = IQ + \mathrm{O}(V^2)$$

Integrating $\langle K^{-1} \rangle$ and inserting in (4.3) the mean of the friction tensor is

$$\begin{aligned}\langle \Phi \rangle &= 4\pi\eta \int_S \mathrm{d}S \int_S \mathrm{d}S' \langle K^{-1}(\sigma, \sigma') \rangle \\ &= I\left(4\pi\eta \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}x' \sum_{m=-\infty}^{\infty} f_m^{-1} \exp\{2\pi i m(x-x')\} + \mathrm{O}(V^2)\right) \\ &= I\{4\pi\eta f_0^{-1} + \mathrm{O}(V^2)\}. \end{aligned} \tag{5.3}$$

6. Conclusions

From (4.2) and (5.3) we have

$$\langle F \rangle = 4\pi\eta f_0^{-1}(\lambda) v^{\infty} + \mathrm{O}(V^2).$$

Since our model has meaning only for $\lambda \gg 1$, $f_0^{-1}(\lambda)$ can be expanded, from (A2.3)

$$\langle F \rangle = 6\pi\eta v^{\infty} \frac{(3\pi l L)^{1/2}}{12}\left\{1 + \frac{4\pi}{3}\left(\frac{\alpha^2}{lL}\right)^{1/2} + \frac{4\pi - 6}{3}\frac{\alpha^2}{lL} + \ldots\right\} + \mathrm{O}(V^2). \tag{6.1}$$

It should be noticed that $\mathrm{O}(V^2)$ contains correction terms of all orders in λ, so that we are unable to estimate the accuracy of (6.1). The correction terms are not difficult to evaluate in as much as they present functional problems, but the resulting functions give exceedingly complicated integrals.

The ratio of the first term in (6.1) to the result of K & R quoted in (1.2) is $2^{3/2} : 3$, that is approximately 0·95.

The form of our result differs from that of K & R (1.1). The reason for this is that we have treated the diagonal terms of K on an equal footing with the off-diagonal terms, whereas K & R treat them unequally. They account for the intrachain interactions using the formula of Oseen (their T, our K) as we do, but whereas we also use this to account for the diagonal terms they introduce a friction coefficient to avoid this. The same formulae result for the reasons stated in § 1. The method of this paper can therefore claim to be more consistent as there is no reason for treating the diagonal terms as special since the singularity in $\langle K \rangle$ (see (A1.4)) goes like $|x-x'|^{-1/2}$ and can be easily dealt with.

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Appendix 1. Evaluation of $\langle K \rangle$

Notice that

$$K\{R(\sigma) - R(\sigma')\} = \frac{1}{2\pi^2} \int \mathrm{d}^3 q \frac{Iq^2 - qq}{q^4} \exp[-\mathrm{i}q\,.\,\{R(\sigma) - R(\sigma')\}] \tag{A1.1}$$

and write

$$\exp[-i\boldsymbol{q}\,.\,\{\boldsymbol{R}(\sigma)-\boldsymbol{R}(\sigma')\}] = \exp[-i\boldsymbol{q}\,.\,\{\boldsymbol{R}(x)-\boldsymbol{R}(x')\}] \times \exp[-i\boldsymbol{q}\,.\,\{\boldsymbol{R}(\sigma)-\boldsymbol{R}(x)\}]\exp[i\boldsymbol{q}\,.\,\{\boldsymbol{R}(\sigma')-\boldsymbol{R}(x')\}]. \tag{A1.2}$$

Thus finding the mean of $\boldsymbol{K}$ can be reduced to finding the mean of (A1.2).

We perform the average over all chain conformations in two parts. First keeping $\boldsymbol{R}(x)$ and $\boldsymbol{R}(x')$ fixed we average over all possible remaining conformations. Secondly we average over all possible $\boldsymbol{R}(x)$ and $\boldsymbol{R}(x')$, subject only to the centre of mass of the chain being held at the origin.

Consider (A1.2) and the first part of the averaging. The vectors $\boldsymbol{R}(\sigma)-\boldsymbol{R}(x)$ and $\boldsymbol{R}(\sigma')-\boldsymbol{R}(x')$ both have magnitude α and are uncorrelated in direction as may be seen by inspection of the measure $W[\boldsymbol{R}(\sigma)]$. Thus, on averaging, each takes up all possible directions with equal weight; write $\boldsymbol{\alpha}(\Omega) = \boldsymbol{R}(\sigma)-\boldsymbol{R}(x)$, then

$$\frac{1}{4\pi}\int d\Omega\exp\{-i\boldsymbol{q}\,.\,\boldsymbol{\alpha}(\Omega)\} = \tfrac{1}{2}\int_{-1}^{1} d(\cos\theta)\exp\{-iq\alpha\cos\theta\} = \frac{\sin\alpha q}{\alpha q}.$$

Hence we have for the first part of the averaging for (A1.2)

$$\left(\frac{\sin\alpha q}{\alpha q}\right)^2\exp\{-i\boldsymbol{q}\,.\,(\boldsymbol{r}-\boldsymbol{r}')\} \tag{A1.3†}$$

where $\boldsymbol{r}$ and $\boldsymbol{r}'$ are the fixed values of $\boldsymbol{R}(x)$ and $\boldsymbol{R}(x')$.

For the second part of the averaging, the probability for finding $\boldsymbol{R}(x)$ at $\boldsymbol{r}$ and $\boldsymbol{R}(x')$ at $\boldsymbol{r}'$ is required. This is

$$p(\boldsymbol{r},\boldsymbol{r}') = \int\delta[\boldsymbol{R}(x)]\delta\{\boldsymbol{r}-\boldsymbol{R}(x)\}\delta\{\boldsymbol{r}'-\boldsymbol{R}(x')\}W[\boldsymbol{R}(x)].$$

Thus

$$\begin{aligned}\langle\exp[-i\boldsymbol{q}\,.\,\{\boldsymbol{R}(\sigma)-\boldsymbol{R}(\sigma')\}]\rangle &= \left(\frac{\sin\alpha q}{\alpha q}\right)^2\int d^3r\int d^3r'p(\boldsymbol{r},\boldsymbol{r}')\exp\{-i\boldsymbol{q}\,.\,(\boldsymbol{r}-\boldsymbol{r}')\}\\ &= \left(\frac{\sin\alpha q}{\alpha q}\right)^2\int\exp[-i\boldsymbol{q}\,.\,\{\boldsymbol{R}(x)-\boldsymbol{R}(x')\}]W[\boldsymbol{R}(x)]\\ &\quad\times\delta[\boldsymbol{R}(x)].\end{aligned}$$

This functional integral is evaluated by expanding $\boldsymbol{R}(x)$ in a Fourier series

$$\boldsymbol{R}(x) = \sum_{n=0}^{\infty}\boldsymbol{R}_n\cos n\pi x.$$

Then

$$W[\boldsymbol{R}(x)] = \delta(\boldsymbol{R}_0)\prod_{n=1}^{\infty}\left(\frac{3\pi n^2}{2lL}\right)^{3/2}\exp\left(-\frac{3\pi^2n^2}{2lL}|\boldsymbol{R}_n|^2\right)$$

and hence

$$\langle\exp[-i\boldsymbol{q}\,.\,\{\boldsymbol{R}(\sigma)-\boldsymbol{R}(\sigma')\}]\rangle = \left(\frac{\sin\alpha q}{\alpha q}\right)^2\exp(-\gamma^2q^2)$$

where $\gamma^2 \equiv \frac{1}{12}lL|x-x'|$.

† We wish to acknowledge the assistance of Dr Davies in obtaining this result.

Combining this with (A1.1) and performing the angular part of the integration

$$\langle \boldsymbol{K}\{\boldsymbol{R}(\sigma)-\boldsymbol{R}(\sigma')\}\rangle = \boldsymbol{I}\frac{4}{3\pi}\int_0^\infty \mathrm{d}q\frac{\sin^2 \alpha q}{q^2}\exp(-\gamma^2 q^2).$$

Write the sine factor in terms of Bessel functions using

$$\frac{\sin^2 \alpha q}{q} = \frac{\pi\alpha}{2}\mathrm{J}^2_{1/2}(\alpha q)$$

then

$$\begin{aligned}\langle \boldsymbol{K}\{\boldsymbol{R}(\sigma)-\boldsymbol{R}(\sigma')\}\rangle &= \boldsymbol{I}\tfrac{2}{3}\alpha^{-1}\int_0^\infty \mathrm{d}q\, q^{-1}\mathrm{J}^2_{1/2}(\alpha q)\exp(-\gamma^2 q^2)\\ &= \boldsymbol{I}\tfrac{2}{3}\pi^{-1/2}\gamma^{-1}{}_3F_3(1,\tfrac{3}{2},\tfrac{1}{2};\tfrac{3}{2},\tfrac{3}{2},2;\,-\alpha^2/\gamma^2)\end{aligned}$$

from Erdélyi (1953—§ 7.7(21)). Writing the expansion for ${}_3F_3$ this is easily seen to be

$$\boldsymbol{I}\tfrac{1}{3}\frac{\gamma}{\alpha^2}\int_0^{(\alpha/\gamma)^2}\mathrm{Erf}(z^{1/2})z^{-1/2}\,\mathrm{d}z$$

from which by a change of variable we obtain

$$\langle \boldsymbol{K}\{\boldsymbol{R}(\sigma)-\boldsymbol{R}(\sigma')\}\rangle = \boldsymbol{Q}^{-1}(x,x') = \boldsymbol{I}\tfrac{2}{3}(\gamma/\alpha^2)\int_0^{\alpha/\gamma}\mathrm{Erf}(u)\,\mathrm{d}u. \qquad \text{(A1.4)}$$

Appendix 2. Evaluation of Q

We have to solve

$$(2\pi\alpha L)^2\int_0^1 \mathrm{d}x\, Q(x-x'')Q^{-1}(x''-x') = \delta(x-x')$$

for Q, $\boldsymbol{Q}^{-1} = \boldsymbol{I}Q^{-1}$ is given in equation (A1.4). This equation is to be interpreted in terms of generalized functions (see Lighthill 1958).

Define the periodic extensions of Q^{-1} and Q as f and g respectively, then we have to solve

$$(2\pi\alpha L)^2\int_{-\infty}^{\infty}\mathrm{d}x'' f(x-x'')g(x''-x')U(x''-\tfrac{1}{2}) = \sum_{k=-\infty}^{\infty}\delta(x-x'-k) \qquad \text{(A2.1)}$$

where $U(x)$ is the unitary function.

Now expand f and g in Fourier series

$$f(x-x'') = \sum_{n=-\infty}^{\infty} f_n \exp\{2\pi \mathrm{i}n(x-x'')\}$$

$$g(x''-x') = \sum_{m=-\infty}^{\infty} g_m \exp\{2\pi \mathrm{i}m(x''-x')\}.$$

Substituting in (A2.1) and integrating leads to

$$(2\pi\alpha L)^2 f_n g_n = 1$$

therefore

$$g(x''-x') = \frac{1}{(2\pi\alpha L)^2}\sum_{m=-\infty}^{\infty} f_m^{-1}\exp\{2\pi \mathrm{i}m(x''-x')\}$$

with

$$f_m = \int_{-\infty}^{\infty} f(x)U(x)\exp(-2\pi imx)\,dx$$
$$= \frac{2}{3\lambda\alpha}\int_0^1 dx\, x^{1/2}\exp(-2\pi imx)\int_0^{\lambda/x^{1/2}} \text{Erf}(u)\,du \qquad \text{(A2.2)}$$

where $\lambda/x^{1/2} \equiv \alpha/\gamma$. In particular

$$f_0 = \frac{2}{3\lambda\alpha}\int_0^1 dx\, x^{1/2}\int_0^{\lambda/x^{1/2}} \text{Erf}(u)\,du$$
$$= \frac{2}{3\alpha}\left(\text{Erf}(\lambda) - \frac{2}{3\pi^{1/2}}\frac{1-e^{-\lambda^2}}{\lambda} + \frac{2\lambda}{3\pi^{1/2}}e^{-\lambda^2} - \frac{2\lambda^2}{3} + \frac{2\lambda^2}{3}\text{Erf}(\lambda)\right).$$

Expanding we have

$$f_0(\lambda) = \frac{4\lambda}{3\alpha\pi^{1/2}}\left(1 - \frac{\pi^{1/2}}{3}\lambda + \frac{\lambda^2}{6}\right) + O(\lambda^4)$$

hence

$$f_0^{-1}(\lambda) = \frac{3\alpha\sqrt{\pi}}{4\lambda}\left(1 + \frac{\sqrt{\pi}}{3}\lambda + \frac{2\pi-3}{18}\lambda^2\right) + O(\lambda^3). \qquad \text{(A2.3)}$$

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