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Concentration dependent translational friction coefficient of cyclic polymers in dilute solutions

Jose Luis Alessandrini^{a)} and Alejandro Fatur

Laboratorio de Física Teórica, Departamento de Física, Universidad Nacional de La Plata, C. C. 67, (1900) La Plata, Argentina

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The leading concentration dependence of the translational friction coefficient of long cyclic polymers is evaluated in the framework of the cluster expansion method. It is found that excellent agreement is achieved with recent quasielastic light scattering experiments on linear and cyclic polystyrene macromolecules.

INTRODUCTION

The thermodynamic and hydrodynamic properties of dilute solutions of cyclic (ring) polymers have received considerable attention from the experimental point of view.¹⁻⁴ The controlled chemical synthesis of well defined cyclic macromolecules such as poly(dimethylsiloxanes) and polystyrenes make possible a systematic investigation of the theoretical predictions by experiments. Very recently, the results on the diffusion of linear and cyclic polystyrenes in dilute solutions have been reported¹ by using quasielastic light scattering. From the extrapolation to infinite dilution of the mutual diffusion coefficient $D(c)$ at concentration c for all cyclic and corresponding linear homologs, $D(0)$ was obtained. Using the known Stokes-Einstein formula, the ratio of the translational friction coefficients at infinite dilution in ϑ solvents was reported as $f_{i,C}^{(0)}/f_{i,L}^{(0)} = 1.12 \pm 0.06$, where the subscripts L and C refer to the linear and cyclic polymers, respectively. This universal quantity is in good agreement with the theoretical estimate 1.178 ($= 3\pi/8$), using the Kirkwood-Riseman method⁵ in the limit of infinite hydrodynamic interaction.

For very low polymer concentrations, the translational friction coefficient f_i of a polymer chain is written as

$$f_i(c) = f_i^{(0)}(1 + k_i c + \dots) \quad (1)$$

and k_i is also available in experiments from the slope of $f(c)$ vs c . Hadziioannou *et al.*¹ found the same power law $k_i \sim M^{0.5}$ for both polymer topologies, where M is the molecular weight of the macromolecules. This finding is consistent with the expected proportionality of k_i with the intrinsic viscosity $[\eta]_0$ or V_h/M , where V_h is some kind of hydrodynamic volume of the chain. Moreover, the reported values of k_i for cyclic polymers are "only slightly smaller" than those of the linear polymer of the same molecular weight. Since the ratio $[\eta]_{0,C}/[\eta]_{0,L} = 0.72$ in the Kirkwood-Riseman scheme,⁵ it follows that the proportionality factor between k_i and $[\eta]_0$ must depend upon the chain geometry, being considerably higher in the cyclic case.

The purpose of this paper is to report the calculated value of k_i for cyclic polymers in the frame of the cluster expansion for the friction coefficient developed by Muthukumar⁶ and applied to the linear case with the result k_i

$= 0.75 [\eta]_{0,L}$. We find here that $k_{i,C} = 0.96 [\eta]_{0,C}$, in good agreement with experiments.¹

In the next section we reproduce shortly the main equations of the theory to introduce the notation and display our final expressions for both topologies of the chain. We close the paper with a discussion of our results.

TRANSLATIONAL FRICTION COEFFICIENT

We assume the reader is familiar with the grounds of the theory as exposed in detail in the Ref. 6. The topology of the chain is incorporated in the theory throughout the (different) Gaussian distribution functions of the internal distances between beads. The popular preaveraged approximation is used throughout and hence, no distinction is made between the tracer and cooperative diffusion coefficients.⁶ Following the standard notation, we define I_i as the leading concentration dependent term for the translational friction coefficient $f_i(c) = f_i^{(0)} + I_i$, as

$$I_i = \frac{N}{V} \int \frac{d^3k}{(2\pi)^3} \left\langle \sum_{i,r} G^{-1}(\mathbf{s}_i, \mathbf{s}_r) e^{i\mathbf{k} \cdot \mathbf{s}_i} \right\rangle \times G(\mathbf{k}) X(\mathbf{k}) G(\mathbf{k}) \left\langle \sum_{j,l} G^{-1}(\mathbf{s}_j, \mathbf{s}_l) e^{-i\mathbf{k} \cdot \mathbf{s}_j} \right\rangle. \quad (2)$$

Here N is the number of macromolecules interacting in the solvent, each polymer composed of n beads, V is the volume and $G(\mathbf{r})$ is the Oseen tensor:

$$G(\mathbf{r}) = \int \frac{d^3k}{(2\pi)^3} G(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}} \quad (3a)$$

with

$$G(\mathbf{k}) = \frac{1}{\eta_0 k^2} (1 - k^{-2} \mathbf{k} \mathbf{k}). \quad (3b)$$

The single chain inverse operator $G^{-1}(\mathbf{s}_i, \mathbf{s}_p)$ is defined as

$$\sum_{p=1}^n G^{-1}(\mathbf{s}_i, \mathbf{s}_p) G(\mathbf{s}_p, \mathbf{s}_j) = \delta_{ij}, \quad (4)$$

where \mathbf{s}_i is the position vector of the i th bead with respect to the center of mass of the chain. Finally, $X(\mathbf{k})$ is given by $X(\mathbf{k}) = T_1 + T_2 + T_3$, with

^{a)} Member of Comision de Investigaciones Cientificas de la Provincia de Buenos Aires (CIC), Argentina.

$$\begin{aligned}
T_1 &= \left\langle \sum_{ij}^n G^{-1}(\mathbf{s}_i, \mathbf{s}_j) e^{-\mathbf{k} \cdot (\mathbf{s}_i - \mathbf{s}_j)} \right\rangle, \\
T_2 &= - \left\langle \sum_{ij, pp'} G^{-1}(\mathbf{s}_i, \mathbf{s}_p) g_i^{-1} G^{-1}(\mathbf{s}_p, \mathbf{s}_j) e^{-\mathbf{k} \cdot (\mathbf{s}_i - \mathbf{s}_j)} \right\rangle, \\
T_3 &= \left\langle \sum_{ij, pp'} G^{-1}(\mathbf{s}_i, \mathbf{s}_p) \times \mathbf{s}_p \cdot \mathbf{g}_r^{-1} \cdot \mathbf{s}_{p'} \right. \\
&\quad \left. \times G^{-1}(\mathbf{s}_{p'}, \mathbf{s}_j) e^{-\mathbf{k} \cdot (\mathbf{s}_i - \mathbf{s}_j)} \right\rangle.
\end{aligned} \quad (5)$$

The definition of g_i^{-1} and g_r^{-1} are given in Ref. 6. We are interested here only in their averaged expressions that are related to the various friction coefficients of a single chain at infinite dilution, as follows:

$$\begin{aligned}
\langle g_i^{-1} \rangle &= 1/f_i^{(0)}, \\
\langle g_r^{-1} \rangle &= 1/f_r^{(0)}.
\end{aligned} \quad (6)$$

All the summations are converted to integrals (large n limit) with the change of variables $x = (2i/n) - 1$, $y = (2j/n) - 1$ and we obtain, for instance

$$f_i^{(0)} = \left\langle \sum_{ij} G^{-1}(\mathbf{s}_i, \mathbf{s}_j) \right\rangle = \frac{n^2}{4} \int_{-1}^1 dx \int_{-1}^1 dy \langle G^{-1}(x, y) \rangle. \quad (7)$$

Expanding $\langle G^{-1}(x, y) \rangle$ in double Fourier series,

$$\langle G^{-1}(x, y) \rangle = \sum_{\mu=-\infty}^{\infty} \sum_{\mu'=-\infty}^{\infty} G_{\mu\mu'}^{-1} e^{-i\pi\mu x + i\pi\mu' y} \quad (8)$$

it follows that $f_i^{(0)} = n^2 G_{00}^{-1}$. The coefficients $G_{\mu\mu'}^{-1}$ are obtained inverting $G_{\mu\mu'}$ using Eq. (4). For ϑ conditions and cyclic polymers, $G_{\mu\mu'}$ are given by

$$G_{\mu\mu'} = \begin{cases} \pi\sqrt{2h}; & \mu = \mu' = 0 \\ \pi \frac{(-1)^\mu J_0(\pi\mu)}{2} \sqrt{2h} \delta_{\mu\mu'}; & \mu \neq 0 \end{cases} \quad (9)$$

where

$$h = \frac{1}{\eta_0 l (12\pi^3 n)^{1/2}} \quad (10)$$

and l is the Kuhn length. Replacing $G_{\mu\mu'}^{-1} = n^{-2} (G_{\mu\mu'})^{-1}$ from Eq. (4) in the expression for $f_i^{(0)}$, we obtain the known Kirkwood-Riseman result^{5,7}:

$$f_i^{(0)} = (G_{00})^{-1} = \frac{1}{\pi\sqrt{2h}}. \quad (11)$$

The previous formulas were reproduced in order to show that one difference with the linear chain case comes from the Fourier coefficients ($G_{\mu\mu'} = \sqrt{2h}/|\mu|^{1/2} \delta_{\mu\mu'}$, $G_{00} = 8\sqrt{2h}/3$,⁶) closely related to the averages of inverse interbead distances. Another one arises from the average of distances from the center of gravity $\langle s_i^2 \rangle$:

$$\begin{aligned}
\langle s_i^2 \rangle &= \frac{nl^2}{3} \left[1 - \frac{3i(n-i)}{n^2} \right] \quad (\text{linear}) \\
&= \frac{nl^2}{12} \quad (\text{cyclic})
\end{aligned} \quad (12)$$

in Eqs. (5), for instance, with $\langle \exp i\mathbf{k} \cdot \mathbf{s}_i \rangle = \exp(-k^2 \langle s_i^2 \rangle / 6)$.

Omitting the tedious algebra and calling $v^2 = k^2 nl^2 / 6$, we obtain

$$\begin{aligned}
T_1 &= 1f_i^{(0)} \left\{ P_0(v) + \sum_{\mu=1}^{\infty} c_\mu P_\mu(v) \right\}, \\
T_2 &= -1f_i^{(0)} A(v), \\
T_3 &= -1f_r^{(0)} k^2 A(v) / 6,
\end{aligned} \quad (13)$$

where the functions $P_0(v)$, $P_\mu(v)$, $A(v)$, the coefficients c_μ and the infinite dilution rotatory friction coefficient $f_r^{(0)}$ are collected in the Appendix for both linear and cyclic polymers.

The general expression for I_t is obtained performing the angular integrations in Eq. (2):

$$I_t = c[\eta]_0 f_r^{(0)} \frac{2\pi^{3/2} q^2}{p} (Q_1 + Q_2), \quad (14)$$

where p and q are defined in the equations below:

$$\begin{aligned}
f_i^{(0)} &= q \frac{1}{\sqrt{2h}}, \\
[\eta]_0 &= p \frac{1}{\sqrt{2h}} \frac{N}{cv} \frac{(nl^2)}{6\eta_0\pi^2}
\end{aligned} \quad (15)$$

with values $q_L = 3/8$, $p_L = \zeta(3/2)$, and $q_C = 1/\pi$, $p_C = A_0/\sqrt{2\pi}$ ($A_0 = 8.398$) for the linear and cyclic cases, respectively. Moreover,

$$\begin{aligned}
Q_1 &= \int_0^\infty \frac{dv}{v^2} A(v) [P_0(v) - A(v)], \\
Q_2 &= \int_0^\infty \frac{dv}{v^2} A(v) \left[\sum_{\mu=1}^{\infty} c_\mu P_\mu(v) - D_\mu(v) A(v) \right],
\end{aligned} \quad (16)$$

where $D_\mu(v)$ is also defined in the Appendix.

The resulting one-dimensional integrals were performed numerically:

$$\begin{aligned}
Q_1 &= 7.14 \times 10^{-3}, \\
Q_2 &= 0.953
\end{aligned} \quad (17)$$

and our final result is

$$I_t = 0.96[\eta]_0 f_i^{(0)} c \quad (18)$$

for the cyclic chain.

DISCUSSION

The deficiencies of older approaches to deal with the concentration dependence of the frictional properties of long polymer chains in dilute solutions have been reviewed by Muthukumar.⁶ The cluster expansion developed by him appears as the only available theory to be compared quantitatively with experiments. Nevertheless, to date only results within the preaveraged approximation in ϑ solvents are at our disposal. Hence, we expect that the errors introduced in the various approximations cancel when appropriate ratios are compared with experiments. This feature seems to be present in our result [Eqs. (14)–(18)], since the ratio of slopes:

$$\frac{I_{t,C}}{I_{t,L}} = \frac{0.96[\eta]_{0,C}}{0.75[\eta]_{0,L}} = 0.92 \quad (19)$$

reproduce the relative behavior of $f_t(c)$ vs c for linear and cyclic polystyrenes, as shown in Fig. 7 of Ref. 1. There,

$I_{t,C}/I_{t,L} \approx 0.95$, in excellent agreement with our theoretical prediction.

Finally, we mention that our Eq. (14) factorizes explicitly the effects of the topology of the chain for the first time and is clearly applicable to branched polymers with appropriate coefficients too. These systems are currently under investigation.

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APPENDIX

Below we collect the definition of the several quantities that appear in the text [Eqs. (13)–(16)] for both linear and cyclic chains.

	Linear	Cyclic
$P_0(v)$	$\frac{2}{v^4} [v^2 - 1 + e^{-v^2}]$ (Debye function)	$\frac{2}{v} e^{-v^2/4} \int_0^{v/2} e^{t^2} dt$ (Casassa function)
$P_\mu(v)$	see Eq. (3.30), Ref. 6	$(-1)^\mu e^{-v^2/4} Q_\mu(v)$ $Q_\mu(v) = \int_0^1 \cos \pi \mu y e^{u^2 y^2/4} dy$ $e^{-v^2/6}$
$A(v)$	$\frac{\pi}{v^2} e^{-v^2/6} \left[\operatorname{erf} \left(\frac{v}{2} \right) \right]^2$	
C_μ	$\frac{1}{3} \mu ^{1/2}$	$\frac{4(-1)^\mu}{J_0(\pi\mu)}$
$D_\mu(v)$	$\frac{16}{6\pi^2} \frac{v^2}{\mu^{3/2}}$	$\frac{1}{\pi^2} \frac{(-1)^\mu v^2}{\mu^2 J_0(\pi\mu)}$
$f_r^{(0)}$	$\frac{16}{9} \frac{n l^2}{\pi^2} \zeta(3/2) f_i^{(0)}$	$\frac{2}{3\pi^2} \frac{n l^2}{\sqrt{2}} f_i^{(0)}$

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