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On the dynamics of semi-rigid chains

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ABSTRACT. The dynamics of a semi-rigid polymer chain is studied. The force structure of the chain is derived from the statistics generated through a Wiener measure whose end-to-end distance is that of a Kratky-Porod chain. Additionally, the dissipative terms in the equation of motion will contain, besides the usual Stokes' term, a non-local friction term (internal viscosity) which is quadratic in the normal mode q, in order to take into account the resistance to changes in curvature. The analytical shape of this term is the same as the one introduced by Edwards and Freed. We show that this model of stiff chain reproduces both asymptotic limits: the flexible and the rod limits for the elastic moduli. A form for the internal viscosity coefficient is deduced from a phenomenological approach, which has the right solvent viscosity dependency as obtained by MacInnes.

RESUMEN. Se ha obtenido la dinámica de una cadena semi-rígida, en donde la forma analítica para la fuerza fue obtenida estadísticamente a partir de una medida de Wiener, la cual tiene la propiedad de que la distancia extremo-extremo de la cadena corresponde exactamente al de una cadena de Kratky-Porod. Adicionalmente, los términos disipativos en la ecuación de movimiento contienen, además del término usual de Stokes, una contribución no-local a la fricción (llamada viscosidad interna) la cual es cuadrática en el modo normal q para tomar en cuenta la resistencia a los cambios de curvatura; la forma analítica de este término es la misma que la introducida por Edwards y Freed. Nosotros hemos mostrado que este modelo de cadena semi-rígida reproduce ambos límites asintóticos: los límites flexible y rígido para los módulos elásticos. Se deduce una forma para el coeficiente de viscosidad interna desde un punto de vista fenomenológico el cual tiene la propiedad de reproducir la dependencia en la viscosidad del medio obtenida por MacInnes.

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1. INTRODUCTION

There have been many theories in the past concerned with the dynamics of a polymer chain at a coarse grained level such as Rouse's theory [1] of viscoelasticity. In the case of flexible chains, many improvements have been made at this level of description, such as Zimm's theory [2], which correct Rouse's theory by including hydrodynamic interactions, and a Cerf-Peterlin theory [3-5], which corrects both theories in the high frequency region. On the other hand, there has been also work on the microscopic foundations of these theories such as Fixman and coworker's approach [6-10] and the work by Pugh and Jones [11], to the understanding of the high frequency viscosity limit, the Freed-Adelman's theory [12] and the de Gennes [13] approach for the internal viscosity. However, in the case of stiff chains, coarse grained theories such as Harris and Hearst's [14-17] have made poor predictions of the viscoelastic response of such systems and not many improvements at this level of description have been made. This level is relevant in problems where polymers interact as a whole such as in entanglements. Precisely in this type of applications, stiffness plays a major role since it is the natural cutoff to the degree of entanglement. In a recent paper [18], we have proposed a Wiener measure for semi-rigid chains which has the exact Kratky-Porod end-to-end distance. In this paper we intent to improve Harris and Hearst's theory for stiff chains by using the force terms, which are responsible for the structure of the molecule and by introducing a non-local friction coefficient in the equation of motion.

2. THE EQUATION OF MOTION

In the work of Harris and Hearst [14-17] or Saito *et al.* [19], the forces considered in establishing an equation of motion were, on the one hand, the average force on a monomer induced by the nearest neighbor interactions, and on the other, the friction that the fluid exerts on each monomer. In their considerations, the friction coefficient per monomer was independent of the stiffness of the chain. However, we know that the friction coefficient per monomer of a rigid rod is quite different from that of a flexible chain. This would imply a non-local character of the friction coefficient, since this depends on the structure of the whole polymer, that is, the friction force should look like

$$\text{Friction force} = -\int_0^L \xi(s-s')\frac{d\mathbf{R}(s',t)}{dt}\,ds', \tag{1}$$

where $\xi(s-s')$ is a non-local friction coefficient per unit length, $\mathbf{R}(s,t)$ is the position vector of the s-monomer at the time t, s is the arch length along the curve representing the polymer chain and L is the total length of the chain. For simplicity, we are using a continuous model for the polymer chain.

As $\xi(s)$ should be related to the stiffness, the simplest choice of such functional dependence would be, in Fourier components,

$$\xi(\mathbf{q}) = \xi_0 + \tau_0 q^2, \tag{2}$$

where ξ_0 is the usual Stokes' friction coefficient per unit length and the second term corresponds to the internal viscosity, being τ_0 the internal viscosity coefficient. This term was originally introduced by Kuhn and Kuhn [20], from a phenomenological point of view, to take into account the internal forces that prevent the fast changes in the length of a monomer. This idea was modified by Cerf [3] to take into account the hydrodynamic friction due to the rotation of effective monomer segments; he predicted a linear dependence of the internal viscosity with q. The latter means that the force on one monomer is proportional to its relative velocity with respect to one of its neighbors; this implies that there should be a preferential direction along the polymer chain, which is not physically true [21]. Here, we are introducing a quadratic dependence of the internal viscosity with q. This dependence means that the force on one monomer depends on the relative velocities with respect to both neighbors. Therefore in this case, the force at any point of the chain depends on the rate of change of the curvature. This q dependence of the internal viscosity was assumed by Edwards and Freed [22], by Bazua *et al.* [23,24], and by MacInnes [25].

As far as the nearest neighbor interactions are concerned, we shall consider these in an average way, as most of the mesoscopic approaches to chain dynamics have been made since Rouse's theory. In a previous paper [18], we have proposed a Wiener measure for semi-rigid chains that has the exact Kratky-Porod ent-to-end distance; the partition function associated with this Wiener measure is

$$\exp - \left[\int_0^L (\alpha \dot{\mathbf{R}} + \beta \ddot{\mathbf{R}})^2 \, ds \right], \tag{3}$$

where $\dot{\mathbf{R}} = \frac{\partial \mathbf{R}}{\partial s}$, α and β are parameters related to the inextensibility and rigidity of the polymer molecules, respectively. Under an average inextensibility condition they are not independent, but they are related by the following relation:

$$\alpha\beta = \tfrac{3}{4}. \tag{4}$$

In this case the persistence length a is given by

$$a = \frac{\beta}{\alpha} = \frac{3}{4\alpha^2}. \tag{4'}$$

These relations are required to obtain for the polymer chain, the Kratky-Porod end-to-end distance.

The free energy of the chain at the time t will be then

$$H = kT \int_0^L \left[\alpha \dot{\mathbf{R}}(s,t) + \beta \ddot{\mathbf{R}}(s,t) \right]^2 ds. \tag{5}$$

Hence the average force per unit length on a point of the chain will be given by the following variational derivative:

$$\mathbf{F} = -\frac{\delta H}{\delta \mathbf{R}(s,t)}. \tag{6}$$

Therefore

$$\mathbf{F} = 2kT \left[\beta^2 \frac{\partial^4 \mathbf{R}}{\partial s^4} - \alpha^2 \frac{\partial^2 \mathbf{R}}{\partial s^2} \right]. \tag{7}$$

As a matter of fact, any homogeneous quadratic function in the variables $\dot{\mathbf{R}}$ and $\ddot{\mathbf{R}}$ for the partition function, will give exactly the same analytical expression for the force.

As in this paper we are only interested in how the viscoelastic response of the system depends on the structure of the polymer molecule, we will ignore the hydrodynamical interactions and the excluded volume effects. Hence, the Langevin equation of motion of the polymer chain will look like

$$\rho \frac{d^2 \mathbf{R}}{dt^2} = -\xi_0 \frac{d\mathbf{R}}{dt} + \tau_0 \frac{d}{dt} \left(\frac{\partial^2 \mathbf{R}}{\partial s^2} \right) + 2\beta^2 kT \left(\frac{\partial^4 \mathbf{R}}{\partial s^4} \right) - 2\alpha^2 kT \left(\frac{\partial^2 \mathbf{R}}{\partial s^2} \right) + \boldsymbol{\sigma}(s), \tag{8}$$

where ρ is the linear mass density of the chain and $\boldsymbol{\sigma}$ is a local random force whose average properties will be determined by the fluctuation-dissipation theorem.

Since the scope of the present work is addressed to the low-intermediate frequency range, the inertial term can be neglected, and the equation of motion will reduce to

$$2\beta^2 kT\left(\frac{\partial^4 \mathbf{R}}{\partial s^4}\right) - 2\alpha^2 kT\left(\frac{\partial^2 \mathbf{R}}{\partial s^2}\right) + \tau_0 \frac{d}{dt}\left(\frac{\partial^2 \mathbf{R}}{\partial s^2}\right) - \xi_0 \frac{d\mathbf{R}}{dt} = -\boldsymbol{\sigma}. \tag{9}$$

The Green's function for this equation can be easily calculated and is given by

$$\mathbf{G}(s-s', t-t') = \frac{\xi_0^{-1}}{2\pi}\int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}} \frac{\exp[-iq(s-s') - \omega_0(t-t')]}{[1+\xi_0^{-1}\tau_0 q^2]}\Theta(\Delta t)\, dq, \tag{10}$$

where Θ is a step function, l represents the length of a monomer and ω_0 is defined as

$$\omega_0 = \frac{2kT\xi_0^{-1}(\beta^2 q^4 + \alpha^2 q^2)}{(1+\xi_0^{-1}\tau_0 q^2)}. \tag{11}$$

The relaxation times for this system will then be

$$\tau_q = \frac{1}{\omega_0} = \frac{(1+\xi_0^{-1}\tau_0 q^2)}{2kT\xi_0^{-1}(\beta^2 q^4 + \alpha^2 q^2)}. \tag{12}$$

If we do not consider the non-local term, Eq. (12) reduces to Harris and Hearst's relaxation times

$$\tau_{q,\mathrm{H-H}} = \frac{1}{2kT\xi_0^{-1}(\beta^2 q^4 + \alpha^2 q^2)}. \tag{13}$$

3. THE DYNAMIC INTRINSIC VISCOSITY

Edwards and Freed [22] have provided a general expression for the dynamical intrinsic viscosity which in this case reduces to

$$[\eta(\omega)] = \frac{N_{\mathrm{A}}}{2\eta_0 M}\int_0^\infty d\Delta t\, e^{i\omega\Delta t}\int_0^L ds\int_0^L ds'\, \Delta(s,t)\mathbf{G}(s-s', t-t')\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle, \tag{14}$$

where N_{A} is Avogadro's number, η_0 is the viscosity of the solvent, M is the molecular weight of the polymer and Δ is, in our case, the following differential operator:

$$\Delta = \tau_0 \frac{d}{dt}\left(\frac{\partial^2}{\partial s^2}\right) + 2\beta^2 kT\left(\frac{\partial^4}{\partial s^4}\right) - 2\alpha^2 kT\left(\frac{\partial^2}{\partial s^2}\right) \tag{15}$$

In order to calculate $\langle[\mathbf{R}(s,t)-\mathbf{R}(s',t')]^2\rangle$, we have to evaluate $\mathbf{R}(s,t)$ subject to the condition that for $t=t'$ we should get the Kratky-Porod end-to-end distance. Assuming that the correlation between different parts of the polymer molecule depends only on $s-s'$ and $t-t'$ we can write

$$\mathbf{B}(\Delta s,\Delta t)=\langle[\mathbf{R}(s,t)-\mathbf{R}(s',t')]^2\rangle, \tag{16}$$

such that for $t=t'$

$$\mathbf{B}(\Delta s,0)=\frac{3\beta}{2\alpha^3}\left[\frac{\alpha}{\beta}\Delta s-1+\exp\left\{-\frac{\alpha}{\beta}\Delta s\right\}\right], \tag{17}$$

which is the Kratky-Porod end-to-end distance.

The formal solution of the equation of motion is

$$\mathbf{R}(s,t)=-\frac{\xi_0^{-1}}{2\pi}\int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}}\int_0^{\infty}\frac{\boldsymbol{\sigma}(q,\omega)\exp\{-i(qs+\omega t)\}}{[i\omega(1+\xi_0^{-1}\tau_0q^2)+2kT\xi_0^{-1}(\beta^2q^4+\alpha^2q^2)]}\,d\omega\,dq. \tag{18}$$

From this equation we can write $\mathbf{R}(q,\omega)$ as

$$\mathbf{R}(q,\omega)=-\frac{\xi_0^{-1}\boldsymbol{\sigma}(q,\omega)}{[2kT\xi_0^{-1}(\beta^2q^4+\alpha^2q^2)+i\omega(1+\xi_0^{-1}\tau_0q^2)]}. \tag{19}$$

Using the fact that $\mathbf{B}(\Delta s,\Delta t)$ is only a function of the difference $s-s'$ and $t-t'$, we obtain the following expression:

$$\mathbf{B}(\Delta s,\Delta t)=\frac{2}{(2\pi)^2}\int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}}\int_0^{\infty}[1-\cos(q\Delta s+\omega\Delta t)]\langle|(\mathbf{R}(q,\omega))|^2\rangle\,d\omega\,dq. \tag{20}$$

By means of the fluctuation-dissipation theorem, we can evaluate $\langle|(\boldsymbol{\sigma}(q,\omega))|^2\rangle$ obtaining finally for $\mathbf{B}(\Delta s,\Delta t)$

$$\mathbf{B}(\Delta s,\Delta t)=\frac{3}{\pi}\int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}}\frac{[1-\cos(q\Delta s)\exp\{-\omega_0|\Delta t|\}]}{(\beta^2q^4+\alpha^2q^2)}\,dq. \tag{21}$$

If we substitute this result and the Eqs. (10) and (15) into Eq. (14) we get the final expression for the dynamical intrinsic viscosity:

$$[\eta(\omega)]=\frac{lN_{\mathrm{A}}kT}{\pi M\eta_0\xi_0^2}\int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}}\frac{[\omega_0^2(1+\xi_0^{-1}\tau_0q^2)+\omega^2\xi_0^{-1}\tau_0q^2+i\omega\omega_0]}{\omega_0(1+\xi_0^{-1}\tau_0q^2)[\omega^2+\omega_0^2]}\,dq. \tag{22}$$

Using the definitions of the relaxation moduli

$$[G'(\omega)] = c\eta_0\omega \operatorname{Im}[\eta(\omega)] \tag{23}$$

and

$$[G''(\omega)] = \eta_0\omega + c\eta_0\omega \operatorname{Re}[\eta(\omega)], \tag{24}$$

we get for these the following relations:

$$[G'(\omega)]_R = \int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}} \frac{\omega^2\, dq}{(1+\xi_0^{-1}\tau_0 q^2)[\omega^2+\omega_0^2]} \tag{25}$$

and

$$[G'(\omega) - \omega\eta_0]_R = \int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}} \frac{[\omega_0^2(1+\xi_0^{-1}\tau_0 q^2) + \omega^2\xi_0^{-1}\tau_0 q^2]}{\omega_0(1+\xi_0^{-1}\tau_0 q^2)[\omega^2+\omega_0^2]}\, dq, \tag{26}$$

where the subindex R means that the moduli are expressed in natural units.

We can write Eqs. (25) and (26) in terms of the relaxation times of the system τ_q and the Harris and Hearst relaxation times $\tau_{q,\mathrm{HH}}$ respectively as

$$[G'(\omega)]_R = \int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}} \frac{(\omega\tau_{q,\mathrm{HH}})^2}{(1+\omega^2\tau_q^2)}\, dq \tag{27}$$

and

$$[G'(\omega) - \eta_0\omega]_R = \int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}} \frac{(\omega\tau_{q,\mathrm{HH}})[(1+\omega^2\tau_q(\tau_q - \tau_{q,\mathrm{HH}}))]}{(1+\omega^2\tau_q^2)}\, dq. \tag{28}$$

These expressions have the same analytical form than those obtained by Peterlin [4,5] for the bead and spring model modified by an internal viscosity term.

The structure of τ_0 can be obtained phenomenologically by demanding that the moduli given by (27) and (28) satisfy the asymptotic limits of Kirkwood-Auer [26] and Rouse [1] for the rod and flexible chains respectively.

The elastic moduli, also in natural units, for a rigid -rod molecules are

$$[G'(\omega)]_R = \left[\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right] \tag{29}$$

and

$$[G'(\omega) - \omega\eta_0]_R = \omega\tau\left[1 + \frac{3}{(1+\omega^2\tau^2)}\right], \tag{30}$$

where

$$\tau = \frac{\pi \eta_0 L^3}{18kT \ln\left(\frac{L}{l}\right)}. \tag{31}$$

In order to obtain this limit, the relaxation times τ_q and $\tau_{q,\mathrm{HH}}$ given by Eqs. (12) and (13) must satisfy the relationship

$$\tau_{q,\mathrm{HH}} = \tfrac{3}{4}\tau_q. \tag{32}$$

With this requirement, the analytical expressions for the elastic moduli given by Eqs. (27) and (28) become

$$[G'(\omega)]_R = \int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}} \left[\frac{\omega^2 \tau_q^2}{1+\omega^2\tau^2}\right] dq \tag{33}$$

and

$$[G'(\omega) - \eta_0\omega]_R = \int_{\frac{2\pi}{L}}^{\frac{2\pi}{l}} (\omega\tau_q) \left[1 + \frac{3}{(1+\omega^2\tau_q^2)}\right] dq. \tag{34}$$

The structure of the largest relaxation time can be obtained by substituting Eqs. (13),(4) and (4′) into Eq. (32), and for ξ_0 its corresponding rod value. After doing this we get

$$\tau_{\max} = \frac{\eta_0 L^3}{6\pi^3 kT \left(\frac{a}{L}\right) \ln\left(\frac{L}{l}\right)}. \tag{35}$$

In this limit, the largest relaxation time is the only term contributing in Eqs. (33) and (34). Therefore, in the rod limit, our elastic moduli have the same analytical shape as the ones obtained by Kirkwood-Auer.

On the other hand, for a random coil molecule (Rouse's limit), the elastic moduli have the following expression:

$$[G'(\omega)]_R = \sum_q \left[\frac{\omega^2\tau_q^2}{(1+\omega^2\tau_q^2)}\right], \tag{36}$$

$$[G''(\omega)]_R = \sum_q \left[\frac{\omega\tau_q}{(1+\omega^2\tau_q^2)}\right], \tag{37}$$

$$\tau_q = \frac{6M\eta_0[\eta]}{\pi^2 RTq^2}. \tag{38}$$

In order to obtain these expressions, it is necessary that $\tau_q = \tau_{q,\mathrm{HH}}$. The latter is satisfied when

$$\xi_0^{-1}\tau_0 q^2 \ll 1. \tag{39}$$

Additionally, since Rouse's theory is valid for low values of q, Eq. (39) should be satisfied for small values of q.

In the flexible limit, the only rigidity left is the one coming from segmental nearest neighbors interactions. This means that τ_0 should only depend on the smallest spatial scale that in the flexible limit is the monomer length. That is, if $\tau_0 \cong \frac{l^2}{\xi_0^{-1}}$ then Eq. (39) will be satisfied.

On the other hand, to comply with Eq. (32) in the rod limit, τ_0 should adopt the form $\tau_0 = \frac{L^2}{12\pi^2\xi_0^{-1}}$. In the intermediate case, τ_0 should depend on the effective monomer length, which depends on the persistence length a. Therefore, to satisfy both expressions we may write

$$\tau_0 = \frac{l'^2}{12\pi^2\xi_0^{-1}}, \tag{40}$$

where l' is the effective monomer length of a Kratky-Porod chain:

$$l' = 2a\left\{1 - \frac{a}{L}\left[1 - \exp\left(-\frac{L}{a}\right)\right]\right\}. \tag{41}$$

In this way the definition of τ_0 given by Eq. (40) reflects the minimum "bendable" length scale.

Eq. (40) has the additional property that the internal viscosity coefficient is proportional to the solvent viscosity, which was predicted theoretically by MacInnes [25].

4. CONCLUSIONS

We have shown that a simple model for a semi-rigid chain has the correct rod and flexible limits as long as the internal viscosity coefficient depends as the square of the effective monomer length, and is proportional to the friction coefficient associated with such effective monomer length. In this model, the intramolecular force at any point in the chain is calculated from a Wiener measure whose associated statistics has an exact Kratky-Porod end-to-end distance and the friction coefficient at any point in the chain has a non-local character with a quadratic dependence in q.

REFERENCES

1. P.E. Rouse, *J. Chem. Phys.* **21** (1953) 1972.
2. B.H. Zimm, *J. Chem. Phys.* **24** (1956) 269.

3. R. Cerf, *Chem. Phys. Lett.* **16** (1972) 42; **22** (1973) 613.
4. A. Peterlin, *J. Polym. Sci.* **A25** (1967) 179.
5. A. Peterlin, *J. Polym. Sci.* **B10** (1972) 101.
6. M. Fixman, J. Kovac, *J. Chem. Phys.* **61**, No. 12 (1974) 4939.
7. M. Fixman, J. Kovac, *J. Chem. Phys.* **61**, No. 12 (1974) 4950.
8. J. Kovac, M. Fixman, *J. Chem. Phys.* **63**, No. 2 (1975) 935.
9. M. Fixman, G.T. Evans, *J. Chem. Phys.* **64**, No. 8 (1976) 3474.
10. M. Fixman, G.T. Evans, *J. Chem. Phys.* **68,** No. 1 (1977) 195.
11. D. Pugh, D.A. Jones, *Polymer* **19** (1978) 1008.
12. S.A. Adelman, K.F. Freed, *J. Chem. Phys.* **67**, No. 4 (1977) 1380.
13. P. De Gennes, *J. Chem. Phys.* **66** (1977) 5825 and *Scaling Concepts in Polymer Physics*, Cornell University Press (1979).
14. J.E. Hearst, *J. Chem. Phys.* **37** (1962) 2547.
15. R.A. Harris, J.E. Hearst, E. Beah, *J. Chem. Phys.* **45** (1966) 2595.
16. J.E. Hearst, R.A. Harris, E. Beah, *J. Chem. Phys.* **45** (1966) 3106.
17. J.J. Hearst, F. Beals, R.A. Harris, *J. Chem. Phys.* **48** (1968) 5371.
18. R. Alexander-Katz, R. Rodríguez, *Rev. Mex. Fís.* **35** No. 4 (1989) 603.
19. N. Saito, K. Takahashi, Y. Yunoki, *J. Phys. Soc. Japan* **22** (1967) 219.
20. W. Kuhn, H. Kuhn, *Helv. Chim. Acta* **28** (1945) 1533; **29** (1946) 72.
21. G. Allegra, *J. Chem. Phys.* **61** (1974) 4910.
22. S.F. Edwards, K.F. Freed, *J. Chem. Phys.* **61** (1974) 1189.
23. E. Bazua, M.C. Williams, *J. Chem. Phys.* **59** (1973) 2858.
24. E. Bazua, M.C. Williams, *J. Polym. Sci.* **12** (1974) 825.
25. D.A. MacInnes, *J. Polym. Sci.* **15** (1977) 465; **15** (1977) 657; *Polymer* **18** (1977) 505.
26. J.G. Kirkwood, P.L. Auer, *J. Chem. Phys.* **19** (1951) 281.