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Orientational mobility in uniaxially deformed polymer chains: a Brownian dynamics simulation study

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Various functions describing the anisotropy of segmental dynamics such as mean mobility-amplitude term, orientation-mobility correlation, directivity and sense of mobility are determined for chains with different degrees of extension using the results from Brownian dynamics simulation. Strong dependence of these properties on chain deformation is observed.

(Keywords: segmental orientation; uniaxially deformed networks; orientation-mobility amplitude correlation; directivity and sense of mobility; Brownian dynamics simulations)

Orientational motions of segments in polymers depend sensitively on both intra- and intermolecular configurational characteristics of the chains, and thus are of special interest for the understanding of polymer behaviour. In a previous work[1,2], results of Brownian dynamics (BD) simulations were used to study the orientational dynamics of deformed polyethylene model chains as a function of their end-to-end separation. On the basis of the cylindrical symmetry of polymers about the direction of extension, time-dependent joint probability functions expanded in terms of double spherical harmonics were developed. The anisotropy of segmental dynamics in terms of spherical harmonics was originally investigated by Tao[3] and Jarry and Monnerie[4] some years ago. These authors formulated the time-dependent orientational distribution for vectors affixed to chains in a form suitable for studying local chain dynamics by polarized fluorescence experiments. Recent developments in deuterium n.m.r. spectroscopy[5] have refocused interest on the problem of the anisotropy of local static and dynamic orientational correlations.

The initial orientation of a vector **m** rigidly affixed to the chain is described by the set $\Omega_0=\{\omega_0,\psi_0\}$, with respect to the laboratory fixed frame $0xyz$, as shown in *Figure 1a*. At time t, the orientation of **m** is given by $\Omega=\{\omega,\psi\}$. For spectroscopic reasons, the orientation of **m** at time t relative to its previous orientation may be desirable. This requires the introduction of an internal coordinate system, $0XYZ$, shown in *Figure 1a*. Following the definition of Jarry and Monnerie[4] the Z axis is chosen to coincide with the initial direction of **m**, thus making an angle ω_0 with the z axis. The intersection of the XZ plane with the xy plane makes an angle of ψ_0 with the x axis, and the Y axis always remains in the xy plane. The instantaneous orientation of **m** is shown in *Figure 1b* with the angles α and β denoting the polar and azimuthal angles, respectively, relative to the $0XYZ$ coordinate system.

The spherical harmonics[6] $Y_k^m(\Omega)$ appearing in the time-dependent joint distribution function[2] may be expressed in terms of the internal reorientation variables $\Gamma=\{\alpha,\beta\}$ by the use of Wigner rotation matrices $\bar{D}^k_{m\mu}(\Omega_0)$ as:

$$Y_k^m(\Omega)=\sum_{\mu=-k}^{+k}\bar{D}^k_{m\mu}(\Omega_0)Y_k^\mu(\Gamma) \quad (1)$$

These matrices are used[4] for the elimination of the set $\Omega=\{\omega,\psi\}$ in favour of $\Gamma=\{\alpha,\beta\}$ and $\Omega_0=\{\omega_0,\psi_0\}$. Four physically meaningful functions characterizing mobility result from this elimination:

1. The mean mobility-amplitude $M(t)$:

$$M(t)=\tfrac{1}{2}(3\langle\cos^2\alpha\rangle-1) \quad (2)$$

$M(t)$ is also referred to as the second orientational autocorrelation function of **m**. Time decay of $M(t)$ has been recently obtained[1] from BD simulations for polyethylene chains with the four different extension ratios, $\lambda=0.37$, 0.91, 1.38 and 2.00. Here, λ refers to the ratio of the deformed end-to-end distance of the chain to its root-mean-square value in the unperturbed state.

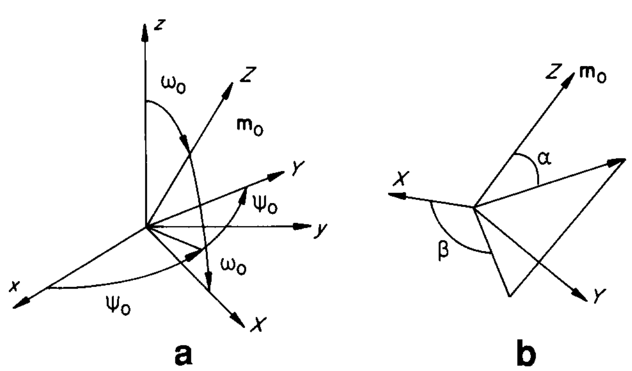

Figure 1 Coordinate systems defining the orientation of $\mathbf{m}_0$. $0xyz$ is the laboratory-fixed frame with the z axis along the direction of uniaxial deformation. The frame $0XYZ$ defines the internal reorientation of **m**, in terms of the polar and azimuthal angles α and β, respectively, as shown in (b). The Z axis is directed along $\mathbf{m}_0$ and makes an angle ω_0 with the z axis. The intersection of the XZ plane with the xy plane makes an angle of ψ_0 with the x axis, and the Y axis always remains in the xy plane

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2. The orientation-mobility amplitude correlation $C(t)$:

$$C(t)=\tfrac{1}{4}\langle(3\cos^2\omega_0-1)(3\cos^2\alpha-1)\rangle \qquad (3)$$

This function reflects the correlations between the original orientation of **m** and its mobility. At long times, the two terms in parentheses become independent and $C(t)$ may therefore be written as a product of two functions. Thus, the orientation-mobility correlations may be described in terms of the difference $R(t)$:

$$R(t)=C(t)-\tfrac{1}{4}\langle(3\cos^2\omega_0-1)\rangle\langle(3\cos^2\alpha-1)\rangle \qquad (4)$$

If $R(t)=0$, the mobility of **m** is uncorrelated with its direction. If directions parallel to **r** have less mobility than the perpendicular directions, then $R(t)>0$. Otherwise $R(t)$ is negative. In *Figure 2*, the time dependences of $R(t)$ calculated from BD simulations are shown for four different extension ratios. For very short times ($\leqslant 0.01$ ns) $R(t)$ is negative and therefore the bonds along directions perpendicular to **r** are relatively more mobile. For the highly compressed chain with $\lambda=0.37$, $R(t)$ remains negative for all times. For the chain with $\lambda=0.91$, which is closest to the unperturbed state, $R(t)$ rapidly becomes zero and oscillates about this value. $R(t)$ is positive for all times, for $\lambda=1.38$ and 2.00.

3. The directivity of mobility $D(t)$:

$$D(t)=\tfrac{3}{4}\langle\sin^2\omega_0\sin^2\alpha_0\cos 2\beta\rangle \qquad (5)$$

This function may best be described following Jarry and Monnerie, in terms of two planes P and P' shown in *Figure 3a*. $D(t)$ differentiates between motions contained in such planes. The P plane is defined as the plane that contains $\mathbf{m}_0$ and the laboratory-fixed z axis. Motions of **m** with $\beta=0$ or π are confined to this plane. The P' plane contains $\mathbf{m}_0$ and is perpendicular to the P plane. Motions of **m** with $\beta=-\pi/2$ or $\pi/2$ are confined to this plane. If the vector moves in the P plane, $\cos 2\beta=1$ and $D(t)$ is positive. If it moves in the P' plane, $\cos 2\beta=-1$ and $D(t)$ is negative.

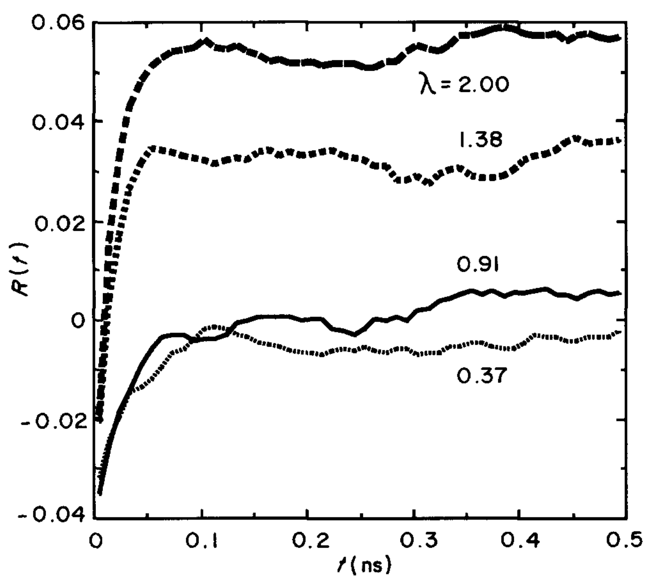

Figure 2 Time dependence of $R(t)$, defined by equation (4), for chains with the indicated extension ratios. $R(t)$ describes the orientation-mobility amplitude correlations $C(t)$ of bond vectors in deformed chains relative to the case of chains in which the original orientation of bond vectors is independent of their motion amplitude

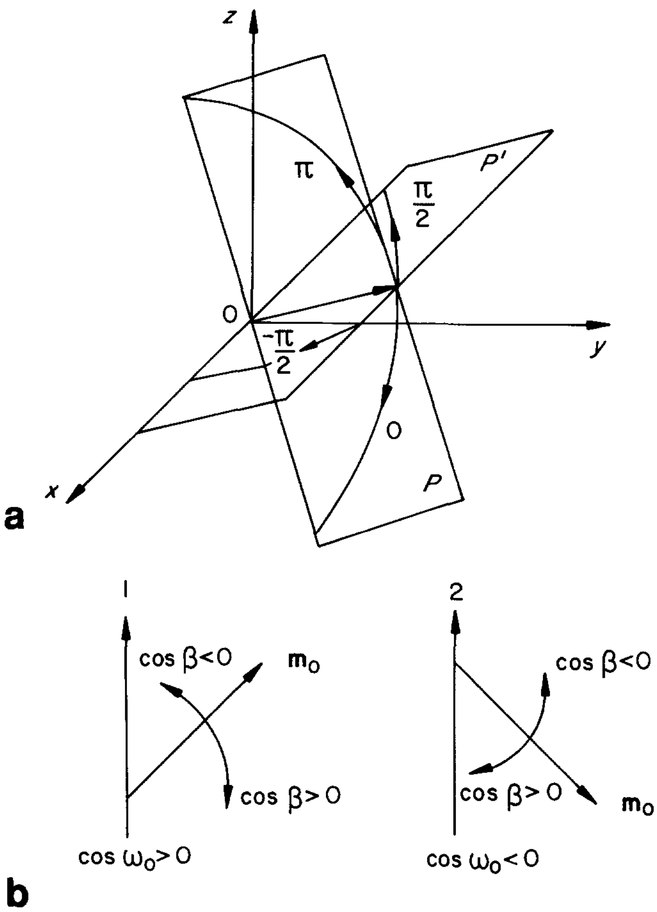

Figure 3 (a) Definition of planes P and P'. The P plane is defined as the plane that contains $\mathbf{m}_0$ and the laboratory-fixed z axis. The P' plane contains $\mathbf{m}_0$ and is perpendicular to the P plane. (b) Diagrams 1 and 2 illustrate the movements leading to positive or negative values for the terms involved in equation (4) defining the sense $S(t)$ of mobility

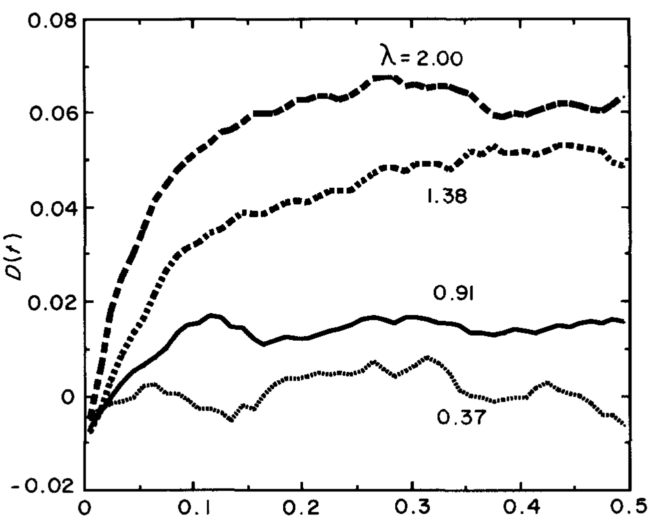

Figure 4 Time dependence of directivity of mobility $D(t)$ of **m** for chains with different extension ratios

Results of calculations for $D(t)$ based on BD simulations[1,2] are presented in *Figure 4*. For the chain with $\lambda=0.37$, $D(t)$ is close to zero or slightly negative, indicating the absence of a strongly preferred directivity. For $\lambda=0.91$, $D(t)$ remains small but positive

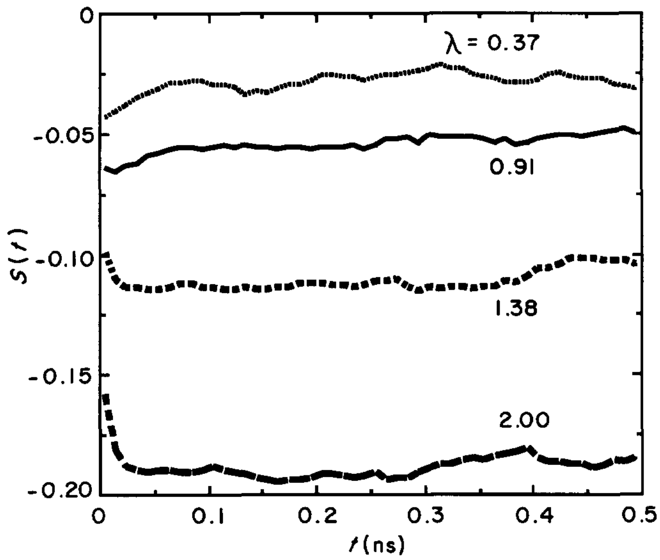

Figure 5 Time dependence of sense of mobility $S(t)$ of **m** for chains with different extension ratios

for all times, indicating that motions in planes containing the fixed end-to-end vector are more intense than those in other planes. Upon further stretching of the chain, $D(t)$ becomes strongly positive and motions in the P plane dominate.

4. Sense of mobility, $S(t)$:

$$S(t) = 3\langle \sin\omega_0 \cos\omega_0 \sin\alpha \cos\alpha \cos\beta \rangle \qquad (6)$$

This function distinguishes between motions of **m** towards the direction of stretch or away from it. The sign of $S(t)$ depends on the signs of $\cos\omega_0$ and $\cos\beta$. The latter is positive if $\mathbf{m}_0$ rotates away from the laboratory-fixed z axis and is negative otherwise, as shown in *Figure 3b*. Similarly, $\cos\omega_0$ is positive if $\mathbf{m}_0$ makes an angle of $<90°$ with **r** and is negative otherwise.

In *Figure 5* values of $S(t)$ calculated from BD simulations are presented for the four different values of the extension ratio. For all extensions $S(t)$ is negative and this negativity becomes more pronounced as the chain is stretched. Since bonds making an angle of $<90°$ with the z axis are more populated, the $\cos\omega_0$ term will contribute to $S(t)$ with a positive sign. One may conclude from this, therefore, that $\cos\beta$ should be negative, i.e. motions of the bonds directed towards the z axis are more intense than those away from it. This tendency is weakest in the case of compressed chains.

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