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Velocity Autocorrelation Function for the Motion of Long-Chain Molecules in the Free Draining Limit

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The thermal motion of a long-chain molecule dispersed in a solvent is examined in terms of the velocity autocorrelation, in a reference frame attached to a subunit of the chain.

KEY WORDS: Polymers; Brownian motion; velocity autocorrelation; short-range interactions; quasielastic broadening for incoherent neutron scattering.

The velocity autocorrelation function has proved to be an appropriate representation in the study of liquid dynamics.$^{(1)}$ It reflects the dynamic behavior both in the collision and collisionless regime. It is directly related to such observables as the incoherent neutron scattering law$^{(2)}$

$$\lim_{q\to 0} \frac{\omega^2 S_{\text{inc}}(q, \omega)}{q^2} = \frac{2}{\pi} \int_0^\infty \cos \omega t \langle v(0)\, v(t)\rangle \, dt \tag{1}$$

In an earlier paper Jannink and Saint-James$^{(3)}$ used the Rouse model to calculate the mean square displacement function (MSD) for the slow motion

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of long-chain molecules in solution. In this model the random forces which act upon the subunits are not correlated. Motion of simple liquids⁽¹⁾ is, however, interpreted in terms of a strong correlation of the random forces. Polar diatomic molecules also show preferential orientations in the rotation motion.⁽⁴⁾ We examine here the effect of random force correlation on the velocity autocorrelation for long-chain molecules and discuss the value of the parameters for certain types of solvent–solute systems.

As in Ref. 3, a system of coupled Langevin equations will be taken as interpolation model⁽⁵⁾ for the motion of the solute molecules

$$\ddot{q}_j + \int_{t_0}^{t} \gamma(t - t')\, \dot{q}_j(t')\, dt' + \omega_j^2 q_j = F(t), \qquad j = 1,\ldots, N \tag{2}$$

In this equation, written in normal coordinates, q_j is the normal displacement of mode j. The frequency distribution is

$$\omega_j^2 = \frac{2\alpha}{m}\left(1 - \cos\frac{2\pi j}{N}\right), \qquad j = 1,\ldots, N \tag{2'}$$

where $\alpha = 3k_BT/l^2$ is the force constant. There are N statistical subunits, of mass m and mean square length l^2 per chain The time-dependent damping factor $\gamma(t)$ is directly related to the random force autocorrelation:

$$k_BT \int_0^\infty e^{-i\omega t}\gamma(t)\, dt = (1/m) \int_0^\infty e^{-i\omega t}\langle F(0)\, F(t)\rangle\, dt \tag{3}$$

When $\gamma(t)$ reduces to $\gamma_0\delta(t)$ the model is equivalent to the Rouse treatment. We shall study the function

$$z(\omega) = \frac{1}{N} \sum_{p=1}^{N} z_p(\omega) = \lim_{q\to 0} \omega^2 \sum_{p=1}^{N} \frac{S_p(p, \omega)}{q^2} \tag{4}$$

where $S_p(p, \omega)$ is the scattering law of the pth subunit in a reference frame attached to the first subunit. The function $z_p(\omega)$ is related to the velocity autocorrelation spectrum $f_p(\omega)$:

$$z_p(\omega) = \langle v^2\rangle f_p(\omega) = \operatorname{Re} \lim_{\lambda\to i\omega} (2/\pi) \int_0^\infty e^{\lambda t}\langle v_p(0)\, v_p(t)\rangle\, dt \tag{5a}$$

and to the mean square displacement:

$$z_p(\omega) = -(\omega^2/2\pi) \operatorname{Re} \int_{-\infty}^{+\infty} e^{i\omega t}\langle (X_p(t) - X_p(0))^2\rangle\, dt \tag{5b}$$

where X_p is the displacement of the pth subunit in the above-mentioned reference frame. Expression (5b) was calculated in Ref. 3 as

$$z_p(\omega) = \underset{\lambda\to i\omega}{\mathrm{mli}} \frac{-\omega^2}{2\pi} \frac{8l^2}{3} \operatorname{Re} \frac{\sinh(p\beta/2)\sinh[(N-p)\beta/2]}{\lambda \sinh\beta \sinh(N\beta/2)} \tag{6}$$

where

$$\sinh\beta = \left(\frac{m}{\alpha}\lambda[\lambda+\gamma(\lambda)]\left\{1+\frac{m}{4\alpha}\lambda[\lambda+\gamma(\lambda)]\right\}\right)^{1/2} \tag{7}$$

In this equation $\gamma(\lambda)$ is the Laplace transform of $\gamma(t)$. For the Rouse model $\gamma(\lambda) = \gamma_0$ and in the limit $N \to \infty$ one has the following result:

$$\lim_{p\to\infty} z_p(\omega) = -\frac{\omega^2}{2\pi}\frac{8l^2}{3}\frac{\cos\varphi}{\omega^{1/2}(\omega^2+\gamma_0{}^2)^{1/4}[(\omega_{N/2}^2+\gamma_0{}^2)^2+\gamma_0{}^2\omega^2]^{1/4}} \tag{8}$$

where

$$\varphi = \frac{1}{2}\left[\frac{3\pi}{2} + \tan^{-1}\frac{\omega}{\gamma_0} + \tan^{-1}\frac{2\omega}{\gamma_0+(\gamma_0{}^2-\omega^2)^{1/2}} + \tan^{-1}\frac{2\omega}{\gamma_0-(\gamma_0{}^2-\omega^2)^{1/2}}\right]$$

$$\gamma_0 \geqslant 2\omega_{N/2}$$

Returning to the finite case, addition of the signal over all subunits yields the simplified expression

$$z(\omega) = -\frac{\omega^2}{2\pi}\frac{8l^2}{3}\lim_{\lambda\to i\omega}\operatorname{Re}\frac{\coth(N\beta/2)-(1/N)\coth(\beta/2)}{2\lambda\sinh\beta} \tag{9a}$$

In the limit $N \to \infty$

$$z(\omega) = -\frac{\omega^2}{2\pi}\frac{8l^2}{3}\lim_{\lambda\to i\omega}\operatorname{Re}\frac{1}{2\lambda\sinh\beta} \tag{9b}$$

Using reduced variables $y = \omega/\omega_{N/2}$, $c = \gamma_0\omega_{N/2}$, where $\omega_{N/2}$ is given by (2′), we finally have

$$z(y) = \frac{l^2\omega_N}{3\pi}\left| Im\left\{\frac{y}{(y-ic)[y(y-ic)-1]}\right\}^{1/2}\right| \tag{10}$$

The effect of parameter c is seen in Fig. 1, where the function $H(y) = (3\pi/l^2\omega_{N/2})\, z(y)$ is plotted against y for several values of c. The motion is overdamped for $c > 2$, which is the case of interest. A maximum appears at $y = 1$. The $y^{1/2}$ behavior in the interval (0, 1) reflects the square root time dependence of the MSD.(6) We now introduce the random force correlation and assume a time dependence of the form

$$\gamma(t) = \mu\gamma_0 e^{-\mu t} \tag{11a}$$

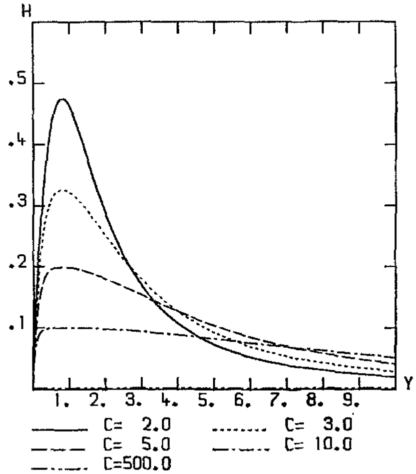

Fig. 1. Reduced velocity autocorrelation spectrum $H(y) = (3\pi/l^2\omega_{N/2})z(\omega)$ for several values of the damping $c = \gamma_0/\omega_{N/2}$ [Eq. (10)]. The value $c = 2$ is the lower limit for the overdamped motion.

This yields

$$\gamma(\lambda) = \mu\gamma_0/(\lambda + \mu) \tag{11b}$$

In reduced variables one has

$$c(y) = \frac{\gamma_0/\omega_{N/2}}{1 + iyR}, \qquad R^{-1} = \frac{\mu}{\omega_{N/2}}$$

The parameter c is now replaced by $c(y)$ in Eq. (10). The function $H(y)$ for $\gamma_0/\omega_{N/2} = 5$ and several values of R is shown in Fig. 2. The time dependence in the damping produces a second resonance at $y > 1$. Such a pattern is also found in the interpretation of the velocity autocorrelation in simple liquids.[6] We notice that maximum shifts toward $y = 1$ as R increases. The "memory" parameter R will then modify the velocity autocorrelation function in the interval (0, 1). The latter was seen to reflect the diffusive conformational motions. A finite values of R tends to decrease the characteristic frequencies of this motion in the vicinity $y = 1$. Our interpolation model is of course questionable beyond $y = 1$. In this region many degrees of freedom will contribute to the velocity autocorrelation, for which Eq. (10) may be representative. We single out the solvent–solute interaction due to the dipole distribution along the chain. The reorientation of the dipole is known to depend strongly on the type of (nonpolar) solvent.[4] Also the dipole moment

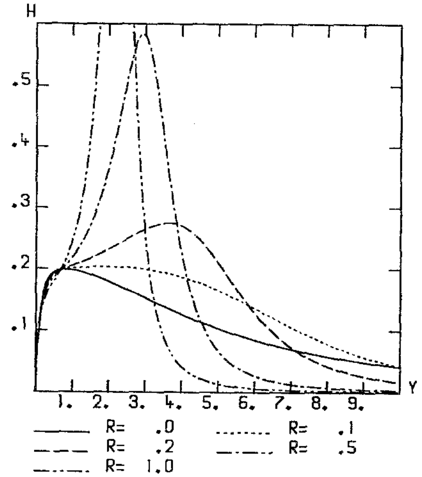

FIG. 2. Reduced velocity autocorrelation spectrum $H(y)$ (as in Fig. 1) for several values of the random force correlation constant R. The damping "intensity" corresponds to $c = 5$ in Fig. 1.

per repeat unit can be easily controlled in such polymers as polyesters. It would therefore be possible to determine experimentally the velocity autocorrelation (from a neutron inelastic scattering experiment) for several solvent–solute systems and to interpret the variations of the parameter R in terms of solute dipole moment and electric field induced by the solvent.

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