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The effect of entanglements on the viscosity of a polymer melt

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Abstract. This paper continues the work of the authors on the effect of entanglements on polymer melt properties. The gaussian chain model is used, together with the pipe constraint previously discussed, to calculate the viscosity of the melt. This is done employing a time correlation function which is derived from the Fokker-Planck equation of motion. The model predicts viscosity proportional to M , the molecular weight, below the entanglement point M_c , and M^3 above M_c . This compares reasonably with the $(M, M^{3.4})$ dependence observed experimentally. It is speculated that the remaining discrepancy may be related to a critical index phenomenon.

1. Introduction

This paper attempts to set up a statistical mechanical theory of the viscosity η of a polymer melt. Experimentally it is found that η depends on the molecular weight M in the following way,

$$\left. \begin{aligned} \eta &\propto M, & M < M_c \\ \eta &\propto M^{3.4}, & M \geq M_c \end{aligned} \right\} \quad (1.1)$$

where M_c is a molecular weight characteristic of the polymer, and represents the onset of entanglements. The situation has been reviewed by Porter and Johnson (1966).

This paper is an attempt to put entanglement effects on a more satisfactory basis, and continues the work of the preceding paper (Edwards and Grant 1973, to be referred to as I) in which the effects of topological constraints on diffusion were considered. Entanglements were studied in I (i) by assuming a pipe constraint and imposing self-consistency, and (ii) directly from the topological invariants (see Edwards 1967, 1968). Both methods give essentially the same results and we can write down Langevin and Smoluchowski-like equations to describe the diffusive motions.

For $M < M_c$, the Langevin equation is

$$v\dot{r}(s, t) - \epsilon r''(s, t) = \phi(s, t), \quad (1.2)$$

where $r(s, t)$ is a point on the chain, s represents an arc parameter, t the time. v is a friction coefficient and hence $v\dot{r}$ represents the friction of chains rubbing against one another. $\epsilon r''$ is the intramolecular entropy force $\epsilon = 3kT/2l$, and $\phi(s, t)$ is a random force arising from the microbrownian motion of the system. The inertial term has been neglected, the diffusional limit being presumed to hold. $r(s, t)$ is taken to be a continuous

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chain and the Wiener integral model is used. This can be written in Fourier transformed form

$$iE\nu r(\omega, E) + \epsilon\omega^2 r(\omega, E) = \Phi(\omega, E), \quad M < M_c, \quad (1.3)$$

where E is the Fourier conjugate of t , ω is the conjugate of s . $r(s, t)$ is really of finite length L , and as such we should have a Fourier series in n on s and not a transform, however the latter is more convenient and we use it provided we remember that by $L/2\pi \int d\omega$ we mean Σ_n and by ω , $2\pi n/L$.

For $M > M_c$, the Langevin equation is modified to

$$\{iE(\nu + \mu\tau(\omega)) + \epsilon\omega^2\}r(\omega, E) = \Phi(\omega, E), \quad (1.4)$$

where

$$\tau(\omega) = \frac{\nu}{2\epsilon\omega^2} \left\{ 1 + \left(1 + \frac{4\epsilon\omega^2}{\mu} \right)^{1/2} \right\} \quad (1.5)$$

and μ is a constant representing the strength of entanglements. In effect the entanglements increase the friction coefficient from ν to $\nu + \mu\tau(\omega)$. For ω large corresponding to short range motions between entanglements $\nu + \mu\tau(\omega) \rightarrow \nu$ for ω small, the long range modes have $\nu + \mu\tau(\omega) \simeq \mu\nu/\epsilon\omega^2$. The corresponding Smoluchowski equations are:

$$\left\{ \frac{\partial}{\partial t} - \frac{L}{2\pi} \int d\omega \frac{\delta}{\delta r(\omega)} \frac{kT}{\nu} \left(\frac{\delta}{\delta r(-\omega)} + \frac{3L}{2\pi l} \omega^2 r(\omega) \right) \right\} G(r, r', t, t') = \prod_{\omega} \delta(r(\omega) - r(\omega')) \delta(t - t') \quad (1.6)$$

and

$$\left\{ \frac{\partial}{\partial t} - \frac{L}{2\pi} \int d\omega \frac{\delta}{\delta r(\omega)} \frac{kT}{\nu + \mu\tau(\omega)} \left(\frac{\delta}{\delta r(-\omega)} + \frac{3L}{2\pi l} \omega^2 r(\omega) \right) \right\} G = \prod_{\omega} \delta(r(\omega) - r(\omega')) \delta(t - t'). \quad (1.7)$$

l is the effective monomer length and we note $\epsilon = 3kT/l$.

The viscosity can be calculated by a time correlation function technique. For a system of particles the viscosity is given by the formula,

$$\eta = \frac{1}{VkT} \int_0^{\infty} \langle J^{xy}(t) J^{xy}(0) \rangle dt, \quad (1.8)$$

where

$$J^{xy} = \sum_i m_i \dot{x}_i \dot{y}_i + \sum_i y_i F_i^{(x)}. \quad (1.9)$$

The i th particle has mass m_i , velocity components \dot{x}_i and \dot{y}_i , and is acted on by the x component of force $F_i^{(x)}$, the time correlation function is over an equilibrium ensemble, and the system is undergoing steady shear. This result has been derived from Liouville's equation by Mazo (1967) and has been used in the case of a dilute polymer solution by Stockmayer *et al* (1970). However Liouville's equation applies to a system of particles without any non-conservative forces such as friction acting between them. In the polymer case, we are dealing with long chain molecules which are certainly acted upon

by interchain frictional forces. It is possible to obtain a correlation function formula for η , but we must start not from Liouville's equation, but from the Fokker-Planck equation over position and velocity space. This equation is

$$\begin{aligned} & \left\{ \frac{\partial}{\partial t} - \frac{L}{2\pi} \int d\omega \frac{\delta}{\delta \mathbf{v}(\omega)} \frac{kT}{mL} \left(\frac{\delta}{\delta \mathbf{v}(-\omega)} + \frac{m\mathbf{v}(\omega)L}{kT2\pi} \right) \right. \\ & \quad \left. - \frac{L}{2\pi} \int d\omega \left(\frac{\delta}{\delta \mathbf{v}(\omega)} \frac{3kT}{l} \omega^2 \mathbf{r}(\omega) + \frac{\delta}{\delta \mathbf{r}(\omega)} \mathbf{v}(-\omega) \right) \right\} G(\mathbf{r}, \mathbf{r}', \mathbf{v}, \mathbf{v}', t, t') \\ & = \prod_{\omega} \delta(\mathbf{r}(\omega) - \mathbf{r}(\omega')) \delta(\mathbf{v}(\omega) - \mathbf{v}(\omega')) \delta(t - t'), \end{aligned} \quad (1.10)$$

where

$$\begin{aligned} \mathbf{v}' &= \mathbf{v} && \text{for } M < M_c \\ &= \mathbf{v} + \mu\boldsymbol{\tau}(\omega) && \text{for } M \geq M_c. \end{aligned}$$

This has the equilibrium distribution

$$\mathcal{N} \exp \left(- \frac{3L}{2\pi 2l} \int |\mathbf{r}(\omega)|^2 \omega^2 d\omega - \frac{mL}{2kT2\pi} \int |\mathbf{v}(\omega)|^2 d\omega \right). \quad (1.11)$$

Equation (1.10) can be derived from the Langevin equation with the inertia term included, namely:

$$m\ddot{\mathbf{r}}(\omega, t) + \mathbf{v}'\dot{\mathbf{r}}(\omega, t) + \epsilon\omega^2 \mathbf{r}(\omega, t) = \boldsymbol{\Phi}(\omega, t), \quad (1.12)$$

where $\epsilon = 3kT/l$ by the standard theory of brownian motion, or alternatively can be checked by integrating over velocity space along the line

$$\mathbf{r} + \mathbf{v} \frac{\mathbf{v}'}{m} = \text{constant} = \mathbf{r}_0. \quad (1.13)$$

This then recovers the Smoluchowski equations (1.6) and (1.7). This scheme of obtaining a Smoluchowski equation from a Fokker-Planck equation is given by Chandrasekhar (1943) and the reader is referred there for details.

In the following section, we derive the correlation function formula and then in the third section we use it to calculate the viscosity.

2. The correlation function formula

The Fokker-Planck equation (1.10) can be modified to include all the chains in volume V ,

$$\begin{aligned} & \left[\frac{\partial}{\partial t} - \sum_{\text{chains}} \frac{L}{2\pi} \int d\omega \left\{ \frac{\delta}{\delta \mathbf{v}(\omega)} \frac{kTv'}{m} \left(\frac{\delta}{\delta \mathbf{v}(-\omega)} + \frac{L}{2\pi} \frac{m\mathbf{v}(\omega)}{kT} \right) \right. \right. \\ & \quad \left. \left. + \frac{\delta}{\delta \mathbf{v}(\omega)} \frac{3kT}{l} \omega^2 \mathbf{r}(\omega) - \frac{\delta}{\delta \mathbf{r}(\omega)} \mathbf{v}(\omega) \right\} \right] f = 0, \end{aligned} \quad (2.1)$$

where f is the (separable) distribution function of all the chains in volume V . This can be written as

$$\frac{i\partial f}{\partial t} = L_{rp}f, \quad (2.2)$$

where

$$L_{rp} = -i \sum_{\text{chains}} \left[\frac{L}{2\pi} \int d\omega \left\{ \frac{\delta}{\delta \mathbf{v}(\omega)} \frac{kTv'}{m} \left(\frac{\delta}{\delta \mathbf{v}(-\omega)} + \frac{L}{2\pi} \frac{m\mathbf{v}(\omega)}{kT} \right) + \frac{\delta}{\delta \mathbf{v}(\omega)} \frac{3kT}{l} \omega^2 \mathbf{r}(\omega) - \frac{\delta}{\delta \mathbf{r}(\omega)} \mathbf{v}(\omega) \right\} \right]. \quad (2.3)$$

The advantage of this notation is that we can write a formal solution,

$$f(\{\mathbf{r}\}, \{\mathbf{v}\}, t) = \exp(-iL_{rp}t)f(\{\mathbf{r}\}, \{\mathbf{v}\}, 0). \quad (2.4)$$

In equilibrium at temperature T , (2.1) has the solution,

$$f = \prod_{\text{chains}} \mathcal{N} \exp\left(-\frac{3L}{2\pi 2l} \int \omega^2 |\mathbf{r}(\omega)|^2 d\omega - \frac{mL}{2kT 2\pi} \int |\mathbf{v}(\omega)|^2 d\omega\right) \quad (2.5)$$

where \mathcal{N} is a normalization constant.

We consider the system to undergo simple shear on the xy plane, with macroscopic velocity,

$$\mathbf{V} = (gy, 0, 0). \quad (2.6)$$

g being the constant shear rate; it is in a non-equilibrium state and is trying to relax to equilibrium. We consider f to be,

$$f(t_0 + b) = f_0(t_0) + f_1(t_0 + b) \quad (2.7)$$

at time $t_0 + b$, where f_0 is the local equilibrium distribution function,

$$f_0 = \prod_{\text{chains}} \mathcal{N} \exp\left\{-\frac{3L}{2\pi 2l} \int \omega^2 |\mathbf{r}(\omega)|^2 d\omega - \frac{mL}{2\pi 2kT} \int |(\mathbf{v}(\omega) - \mathbf{V})|^2 d\omega\right\}, \quad (2.8)$$

where \mathbf{r}, \mathbf{V} are at time t_0 . We require the correction term, $f_1(t_0 + b)$, since the local equilibrium function f_0 cannot yield any shear stress. Since $f(t_0 + b)$ must satisfy (2.1)

$$\frac{i\partial f_1}{\partial b} + L_{rp}f_1 = -L_{rp}f_0 \quad (2.9)$$

giving the solution which vanishes at t_0 ,

$$f_1(t) = i \int_{t_0}^t \exp\{-i(b-t)L_{rp}\} L_{rp}f_0 db. \quad (2.10)$$

Now

$$L_{rp}f_0 = \sum_{\text{chains}} \frac{L}{2\pi} \int d\omega \left\{ \frac{m\mathbf{v}(\omega)}{kT} \frac{\delta}{\delta \mathbf{r}(\omega)} \{(\mathbf{v}(\omega) - \mathbf{V}) \cdot \mathbf{V}\} - \frac{\epsilon}{kT} \omega^2 \mathbf{r}(\omega) \mathbf{v}(\omega) + \frac{kTv'}{m} \left(\frac{m}{kT} - m^2 \frac{(\mathbf{v}(\omega) - \mathbf{V})^2}{(kT)^2} \right) - \frac{kTv'}{m} \left(\frac{m}{kT} - m^2 \frac{\mathbf{v}(\omega)(\mathbf{v}(\omega) - \mathbf{V})}{(kT)^2} \right) \right\}. \quad (2.11)$$

If we are considering only a small velocity gradient, we can neglect the terms in V^2 , and the last two terms of (2.11) cancel leaving

$$L_{\text{cp}} f_0 = \sum_{\text{chains}} \frac{L}{2\pi} \int d\omega \left(\frac{m\mathbf{v}(\omega)}{kT} \frac{\delta}{\delta \mathbf{r}(\omega)} (\mathbf{v}(\omega) \cdot \mathbf{V}) + \frac{3\omega^2}{l} \mathbf{r}(\omega) \mathbf{v}(\omega) \right) = \frac{\mathbf{g}}{kT} J^{xy}(\mathbf{r}, \mathbf{v}), \quad (2.12)$$

where

$$\begin{aligned} J^{xy} &= \sum_{\text{chains}} \frac{L}{2\pi} \int d\omega (m v^x(\omega) v^y(\omega) + \epsilon \omega^2 x(\omega) y(\omega)) \\ &= \sum_{\text{chains}} \int_0^L ds (m v^x(s) v^y(s) - \epsilon x''(s) y(s)). \end{aligned} \quad (2.13)$$

This is related to the stress tensor as can be seen from the following argument. Consider the average of a , where

$$a = \frac{L}{2\pi} \int d\omega \sum_{\text{chains}} m \mathbf{v}(\omega) \delta(\mathbf{R} - \mathbf{r}(\omega)) \quad (2.14)$$

against the Fokker–Planck equation; this will lead to the equation of momentum transport. Using the notation,

$$\langle a | f \rangle = \int a(\{\mathbf{r}\}, \{\mathbf{v}\}; t) f \prod d\mathbf{r} d\mathbf{v} \quad (2.15)$$

and noting that a does not depend explicitly on time t ,

$$\begin{aligned} \left\langle a \left| \frac{\partial f}{\partial t} \right. \right\rangle &= \frac{\partial}{\partial t} \langle a | f \rangle = - \sum_{\text{chains}} \left\langle a \left| \frac{L}{2\pi} \int d\omega \left\{ \frac{\delta}{\delta \mathbf{v}(\omega)} \frac{kT v'}{m} \right. \right. \right. \\ &\quad \left. \left. \left. \times \left(\frac{\delta}{\delta \mathbf{v}(-\omega)} + \frac{L m \mathbf{v}(\omega)}{2\pi kT} + \frac{\delta}{\delta \mathbf{v}(\omega)} \epsilon \omega^2 \mathbf{r}(\omega) - \frac{\delta \mathbf{v}(\omega)}{\delta \mathbf{r}(\omega)} \right) \right\} f \right. \right\rangle. \end{aligned} \quad (2.16)$$

Integrating by parts and assuming that the surface terms in position and velocity space either vanish or are negligible, we obtain

$$\begin{aligned} -\frac{\partial}{\partial t} \langle a | f \rangle &= \sum_{\text{chains}} \left\langle \int \frac{L}{2\pi} d\omega \frac{v' kT}{m} \frac{\delta^2}{\delta \mathbf{v}(\omega)^2} a \middle| f \right\rangle + \left\langle \frac{L}{2\pi} \int d\omega \frac{L}{2\pi} v' \mathbf{v}(\omega) \frac{\delta}{\delta \mathbf{v}(\omega)} a \middle| f \right\rangle \\ &\quad - \left\langle \epsilon \omega^2 \mathbf{r}(\omega) \frac{\delta}{\delta \mathbf{v}(\omega)} a \middle| f \right\rangle + \left\langle \mathbf{v}(\omega) \frac{\delta}{\delta \mathbf{r}(\omega)} a \middle| f \right\rangle. \end{aligned} \quad (2.17)$$

On substituting for a , the first two terms vanish, leaving

$$\begin{aligned} \frac{\partial}{\partial t} (\rho V) &= \sum_{\text{chains}} \frac{L}{2\pi} \int d\omega \\ &\quad \times \left(\frac{\delta}{\delta \mathbf{r}(\omega)} \langle m \mathbf{v}(\omega) \mathbf{v}(-\omega) \delta(\mathbf{r}(\omega) - \mathbf{R}) \middle| f \rangle + \langle \epsilon \omega^2 \mathbf{r}(\omega) \delta(\mathbf{r}(\omega) - \mathbf{R}) \middle| f \rangle \right). \end{aligned} \quad (2.18)$$

Now to a first approximation,

$$\epsilon\omega^2\mathbf{r}(\omega)\delta(\mathbf{r}(\omega)-\mathbf{R}) \simeq \frac{\delta}{\delta\mathbf{r}(-\omega)}\epsilon\omega^2\mathbf{r}(\omega)\mathbf{r}(-\omega)\delta(\mathbf{r}(\omega)-\mathbf{R}). \quad (2.19)$$

If we ignore derivatives of the delta function, then

$$\begin{aligned} \frac{\partial}{\partial t}(\rho V) = \sum_{\text{chains}} \frac{L}{2\pi} \int d\omega \frac{\delta}{\delta\mathbf{r}(\omega)} \langle m\mathbf{v}(\omega)\mathbf{v}(-\omega) \delta(\mathbf{r}(\omega)-\mathbf{R}) \\ + \epsilon\omega^2\mathbf{r}(\omega)\mathbf{r}(-\omega) \delta(\mathbf{r}(\omega)-\mathbf{R}) | f \rangle. \end{aligned} \quad (2.20)$$

Thus

$$\frac{\partial}{\partial t}(\rho V) = \nabla\sigma, \quad (2.21)$$

where

$$\sigma = \sum_{\text{chains}} \frac{L}{2\pi} \int d\omega \langle m\mathbf{v}(\omega)\mathbf{v}(-\omega) \delta(\mathbf{r}(\omega)-\mathbf{R}) + \mathbf{r}(\omega)\epsilon\omega^2\mathbf{r}(-\omega) \delta(\mathbf{r}(\omega)-\mathbf{R}) | f \rangle. \quad (2.22)$$

(2.21) is the linearization of

$$\frac{\partial}{\partial t}(\rho V) + \nabla(\rho V \cdot V) = \nabla \cdot \sigma \quad (2.23)$$

and is consistent with ignoring the difference between \mathbf{v} and $\mathbf{v} - V$ as in (2.12).

If we define $J(\mathbf{r}, \mathbf{v}, \mathbf{R})$,

$$J(\mathbf{r}, \mathbf{v}, \mathbf{R}) = \sum_{\text{chains}} \frac{L}{2\pi} \int d\omega (m\mathbf{v}(\omega)\mathbf{v}(-\omega) \delta(\mathbf{r}(\omega)-\mathbf{R}) + \epsilon\omega^2\mathbf{r}(\omega)\mathbf{r}(-\omega) \delta(\mathbf{r}(\omega)-\mathbf{R})), \quad (2.24)$$

the relationship between $J(\mathbf{r}, \mathbf{v}, \mathbf{R})$ and $J(\mathbf{r}, \mathbf{v})$ is apparent. Thus

$$\sigma(\mathbf{R}) = \langle \mathbf{J}(\mathbf{r}, \mathbf{v}, \mathbf{R}) | f_0 \rangle + \langle \mathbf{J}(\mathbf{r}, \mathbf{v}, \mathbf{R}) | f_1 \rangle \quad (2.25)$$

$$= -p(\mathbf{R})\mathbf{1} + \langle \mathbf{J}(\mathbf{r}, \mathbf{v}, \mathbf{R}) | f_1 \rangle, \quad (2.26)$$

where $p(\mathbf{R})$ is the isotropic pressure. Only f_1 contributes to σ^{xy} . Thus

$$\sigma^{xy}(\mathbf{R}) = \int J^{xy}(\mathbf{r}, \mathbf{v}, \mathbf{R}) \sum_{\text{chains}} \frac{L}{2\pi} \int d\omega f_1 \delta(\mathbf{r}(\omega)-\mathbf{R}') \prod d\mathbf{r} d\mathbf{v} d\mathbf{R}'. \quad (2.27)$$

Substituting for f_1 from (2.10) and (2.12)

$$\sigma^{xy}(\mathbf{R}) = \int J^{xy}(\mathbf{r}, \mathbf{v}, \mathbf{R}) \int_{t_0}^t \exp\{i(b-t)L_{\text{fp}}\} db J^{xy}(\mathbf{r}, \mathbf{v}, \mathbf{R}') f_0 \prod d\mathbf{r} d\mathbf{v} d\mathbf{R}'. \quad (2.28)$$

Since e^{-ibL} is the time propagation operator taking a function $\phi(\mathbf{r}, \mathbf{v})$ to $(\mathbf{r}_b, \mathbf{v}_b)$ where $(\mathbf{r}_b, \mathbf{v}_b)$ is the phase evolving from (\mathbf{r}, \mathbf{v}) in time b ,

$$\sigma^{xy}(\mathbf{R}) = \int \int_0^\tau \langle J^{xy}(\mathbf{r}_\lambda, \mathbf{v}_\lambda, \mathbf{R}) J^{xy}(\mathbf{r}, \mathbf{v}, \mathbf{R}') | f_0 \rangle d\mathbf{R}' d\lambda, \quad (2.29)$$

where $t = t_0 + \tau$, $b = t_0 + b'$ and $b - t = b' - \tau = \lambda$.

We assume that there is no correlation between the J^{xy} in different volume elements, and that any correlation exists over macroscopically small distances, so we can write,

$$\langle J^{xy}(r_\lambda, v_\lambda, \mathbf{R}) J^{xy}(r, v, \mathbf{R}') | f_0 \rangle = \delta(\mathbf{R} - \mathbf{R}') \frac{1}{V} \langle J^{xy}(r_\lambda, v_\lambda) J^{xy}(r, v) \rangle \quad (2.30)$$

and hence

$$\eta = \frac{\sigma^{xy}}{g} = \frac{1}{VkT} \int_0^\tau \langle J^{xy}(t) J^{xy}(0) \rangle dt. \quad (2.31)$$

It would appear that η depends on τ . This is illusory since the time correlation $\langle J^{xy}(t) J^{xy}(0) \rangle$ is assumed to decay to zero in a time short compared to the time necessary for momentum fluxes to develop in a local equilibrium ensemble, which in turn is short in comparison to the time over which macroscopic variables change appreciably. Thus we may set $\tau = \infty$ giving

$$\eta = \frac{1}{VkT} \int_0^\infty \langle J^{xy}(t) J^{xy}(0) \rangle dt \quad (2.32)$$

with (2.13) defining J^{xy} .

In reality the chain monomers have only two degrees of freedom rather than three, corresponding to the fact that the monomers are linked together to form a chain. This point is discussed by Edwards and Goodyear (1972). All this will do is alter the coefficients in the Fokker-Planck equation, but the analysis will follow through in the same way except that we should define J^{xy} as,

$$\begin{aligned} J^{xy} &= \sum_{\text{chains}} \frac{L}{2\pi} \int d\omega \left(mv^x(\omega)v^y(-\omega) + \frac{2kT}{l} \omega^2 x(\omega)y(-\omega) \right) \\ &= \sum_{\text{chains}} \int_0^L ds \left(mv^x(s)v^y(s) - \frac{2kT}{l} x''(s)y(s) \right), \end{aligned} \quad (2.33)$$

the coefficient of the latter term being reduced by a factor of $\frac{2}{3}$. We will work with the form of (2.33), in the calculation of η .

3. The calculation of η

The correlation function for the viscosity η can be expressed in the form,

$$\eta = \left(\frac{N_A \rho}{MkT} \right) \int_0^\infty \langle J^{xy}(t) J^{xy}(0) \rangle dt, \quad (3.1)$$

where N_A is Avogadro's number, M is the polymer molecular weight, ρ the density of the system and J^{xy} is defined for one chain,

$$J^{xy}(t) = \int_0^L m\dot{x}(s, t)\dot{y}(s, t) ds - \int_0^L \gamma(s, t) \frac{2kT}{l} x''(s, t) ds. \quad (3.2)$$

Since we are dealing with the diffusional limit and $m\dot{r} \ll \epsilon r''$, $\dot{v}r$ we can ignore the inertial term and approximate,

$$J^{xy}(t) \simeq - \int_0^L \gamma(s, t) \frac{2kT}{l} x''(s, t) ds, \quad (3.3)$$

and we can perform the average of (3.1) purely over configuration space, the integrals over the velocity space contributing a factor unity, because of the normalization. We can write

$$J^{xy}(t) = \frac{2kT}{l} \frac{L}{2\pi} \int d\omega \omega^2 x(\omega)y(-\omega) d\omega \quad (3.4)$$

giving

$$\langle J^{xy}(t)J^{xy}(0) \rangle = \left(\frac{2kT}{l}\right)^2 \left(\frac{L}{2\pi}\right)^2 \int d\omega d\omega' \omega^2 \omega'^2 x(\omega, t)x(\omega', 0)y(-\omega, t)y(-\omega', 0). \quad (3.5)$$

We only get contributions from $\omega' = -\omega$ in the averaging over the equilibrium distribution. Thus

$$\langle J^{xy}(t)J^{xy}(0) \rangle = \left(\frac{2kT}{l}\right)^2 \frac{L}{2\pi} \int d\omega \omega^4 \langle x(\omega, t)x(-\omega, 0) \rangle \langle y(\omega, t)y(-\omega, 0) \rangle. \quad (3.6)$$

The averages can be separated in this way only because we are dealing with gaussian distributions. The factor outside the integral contains $L/2\pi$ and not $(L/2\pi)^2$ because we are really dealing with an infinite Fourier series rather than a Fourier integral.

$$\sum_n \sum_{n'} \rightarrow \sum_n \Rightarrow \left(\frac{L}{2\pi}\right)^2 \int d\omega d\omega' \rightarrow \left(\frac{L}{2\pi}\right) \int d\omega, \quad (3.7)$$

where $\omega = 2\pi n/L$, the corresponding contributions only occurring for $n' = n$.

We must now calculate the correlations $\langle x(\omega, t)x(-\omega, 0) \rangle$ and $\langle y(\omega, t)y(-\omega, 0) \rangle$. For a free chain $v' = v$ and

$$\langle x(\omega, t)x(-\omega, 0) \rangle = \langle y(\omega, t)y(-\omega, 0) \rangle = l \int \frac{d\omega}{\omega^2} \exp\left(-\frac{\epsilon\omega^2}{v}t\right) \quad (3.8)$$

giving

$$\langle J^{xy}(t)J^{xy}(0) \rangle = \left(\frac{2kT}{l}\right)^2 \frac{Ll^2}{2\pi} \int d\omega \exp\left(-\frac{2\epsilon\omega^2}{v}t\right) \quad (3.9)$$

and hence

$$\int \langle J^{xy}(t)J^{xy}(0) \rangle dt = \frac{2kT}{3} \frac{Llv}{2\pi} \int \frac{d\omega}{\omega^2}. \quad (3.10)$$

Reverting to discrete notation it is clear that by $L/2\pi \int d\omega/\omega^2$ we understand

$$\sum_{n=1}^{\infty} \frac{1}{n^2} \frac{L^2}{4\pi^2}$$

giving the result

$$\eta = \frac{N\rho v l L^2}{M6\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2}, \quad (3.11)$$

identical to that obtained by Rouse, except that the sum is an infinite one, rather than cut off at N , the number of gaussian submolecules. This predicts $\eta \propto M$ in agreement with experiment since $L \propto M$.

For an entangled chain with the pipe constraint with $\tau(\omega)$ given by (1.5)

$$\begin{aligned} \langle y(\omega, t)y(-\omega, 0) \rangle &= \langle x(\omega, t)x(-\omega, 0) \rangle \\ &= \frac{L}{2\pi} \int \int_{-\infty}^{\infty} \frac{\langle \phi_x(\omega, E)\phi_x^*(\omega, E) \rangle e^{iEt} d\omega dE}{E^2(v + \mu\tau(\omega))^2 + \epsilon^2\omega^4}, \end{aligned} \tag{3.12}$$

where to satisfy the random walk condition

$$\langle (r(s, t) - r(s', t))^2 \rangle = |s - s'| \tag{3.13}$$

$$\langle \phi_x(\omega, E)\phi_x^*(\omega, E) \rangle = \frac{2\epsilon(v + \mu\tau(\omega))l}{3L}. \tag{3.14}$$

Thus

$$\langle y(\omega, t)y(-\omega, 0) \rangle = \frac{l}{\omega^2} \exp\left(-\frac{2\epsilon\omega^2 t}{v} \left[1 + \frac{\mu}{2\epsilon\omega^2} \left\{1 + \left(1 + \frac{4\epsilon\omega^2}{\mu}\right)^{1/2}\right\}\right]^{-1}\right) \tag{3.15}$$

is obtained on substituting (3.14) into (3.12), integrating over E and substituting for $\tau(\omega)$. (3.8) was obtained in a similar way with $\mu\tau(\omega) = 0$. Hence

$$\langle J^{xy}(t)J^{xy}(0) \rangle = \frac{2kT}{3} \frac{ILv}{2\pi} \int \frac{d\omega}{\omega^2} \left[1 + \frac{\mu}{2\epsilon\omega^2} \left\{1 + \left(1 + \frac{4\epsilon\omega^2}{\mu}\right)^{1/2}\right\}\right]. \tag{3.16}$$

Thus for L large, the small ω modes dominate the integral and hence the right-hand side can be approximated by

$$\frac{2}{3} kTlv \frac{L}{2\pi} \int \frac{d\omega\mu}{\epsilon\omega^4}. \tag{3.17}$$

Substituting into (3.1) gives

$$\eta = \frac{2}{3} \frac{N_A \rho l \mu v}{M} \sum_{n=1}^{\infty} \frac{1}{n^4} \left(\frac{L}{2\pi}\right)^4 \tag{3.18}$$

on re-expressing as a series. Thus,

$$\eta \propto \mu v M^3 \tag{3.19}$$

since $M \propto L$. Thus our model predicts

$$\left. \begin{aligned} \eta &\propto M, & M < M_c \\ \eta &\propto M^3, & M \geq M_c \end{aligned} \right\} \tag{3.20}$$

in comparison with the experimental

$$\left. \begin{aligned} \eta &\propto M, & M < M_c \\ \eta &\propto M^{3.4}, & M \geq M_c \end{aligned} \right\} \tag{3.21}$$

No account was taken of excluded volume in this calculation. If the dynamical friction term $k(\omega)$ in I were included and were a possible non-analyticity to arise in $h(\omega)$, these will lead to a higher power, but that needs a further and more difficult calculation before it can be claimed to be the source of the 0.4 discrepancy in the power.

4. Conclusions

The model of a gaussian chain with entanglements incorporated via a pipe constraint proved useful in the calculation of viscosity. The behaviour obtained is qualitatively in agreement with experiment. It remains to incorporate excluded volume, chain stiffness and polydispersity into the model. Of these only excluded volume effects are felt to be the cause of the difference between the 3.0 power of M in theory and 3.4 experimentally. The correlation function technique has been put on a firmer basis for the polymer case, by its derivation from the Fokker–Planck equation rather than merely taking over the result *ad hoc* from the theory of particles.

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