LETTER TO THE EDITOR

The exponent z for the dynamics of polymer chains in the presence of hydrodynamic and excluded volume interactions

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Abstract. A new calculation is presented for the effect of excluded volume interactions on the critical exponent z for polymer dynamics.

For a polymer molecule in a good solvent all characteristic lengths ξ are expected to depend on the number of links N (and hence the molecular weight) as

$$\xi \sim N^{\nu}. \tag{1}$$

For the dynamical properties, describable in terms of a relaxation time τ, a new exponent z is introduced by

$$\tau \sim \xi^{z} \sim N^{\nu z}. \tag{2}$$

In terms of these exponents the macroscopic diffusion constant D can be shown (de Gennes 1976) to depend on N as

$$D \sim N^{(z-2)\nu}. \tag{3}$$

Debye and Bueche showed that from the point of view of the diffusional properties a single polymer molecule in a solvent behaves as a rigid sphere. Using Stokes' law in d dimensions a hydrodynamic radius R_H can be defined by

$$D \sim \frac{kT}{\eta R_H^{d-2}} \tag{4}$$

where η is the solvent viscosity. Combining (3) and (4) we see that the hydrodynamic radius depends on N as

$$R_H \sim N^{\nu(z-2)/(d-2)}. \tag{5}$$

For the original scaling hypothesis to be valid no new scaling lengths should be introduced and $R_H \sim N^{\nu}$ which implies that the dynamic exponent z is determined as

$$z = d. \tag{6}$$

Recently Moore and Jasnow (1977) have treated the effect of hydrodynamic and excluded volume interactions on the relaxational internal modes of a polymer chain. Their method uses the $\epsilon = 4 - d$ expansion and they found

$$z = 2 + (1/\nu) - \epsilon = 4 - (\epsilon/4) - \epsilon \neq d \tag{7}$$

and consequently they infer that R_H will not have the same exponent ν as the end-to-end vector. In their result the $(2 + (1/\nu))$ term is the effect of excluded volume in the absence of hydrodynamic interactions and agrees with an earlier conjecture of de Gennes (1976). The $(-\epsilon)$ in term in (7) comes from the hydrodynamic interactions calculated in the absence of the excluded volume effects. In this Letter we wish to show that the excluded volume effects also affect the friction coefficient and that it is possible to recover the $z = d$ result to at least $O(\epsilon^2)$. Alternatively a new exponent can be introduced to describe the molecular weight dependence of the friction coefficient and used to discuss the recent experimental results of Adam and Delsanti (1977).

We have shown elsewhere (Brereton and Rusli 1977) that the equation of motion for a polymer molecule can be written as

$$\ddot{r}_i(t) = -\sum_j \gamma_{ij}\dot{r}_j - \sum_j \Omega_{ij} r_j + \eta_i \tag{8}$$

where the γ_{ij} and Ω_{ij} may be regarded as generalisations of the usual friction and spring force constants of the Rouse model, and η_i represents only the fast processes affecting the motion of the ith monomer.

The γ_{ij} and Ω_{ij} are determined by the correlations of the random forces ξ_i and the polymer chain equilibrium conformation through the fluctuation dissipation relations

$$2\gamma_{ij}\delta(\tau) = kT\langle \eta_i(t) \cdot \eta_i(t+\tau)\rangle \tag{9}$$

$$\Omega_{ij} = kT\Gamma_{ij} \qquad \text{where } (\Gamma^{-1})_{ij} = \langle r_i \cdot r_j\rangle. \tag{10}$$

In particular the spring constant is determined entirely by the conformational correlation function $\langle r_i \cdot r_j\rangle$. If excluded volume effects are incorporated, then

$$\langle r_i \cdot r_j\rangle \sim l^2 |i-j|^{2\nu}$$

and this leads directly, through (10), to a mode-dependent spring constant Ω_n:

$$\Omega_n \sim kT\left(\frac{n}{N}\right)^{2\nu+1}$$

where

$$\Omega_n = \sum_{i,-j} \gamma_{i-j} \exp\left(-\frac{2\pi i}{N}n(i-j)\right). \tag{11}$$

If the random forces are assumed to come entirely from the solvent then we can take $\gamma_{ij} \sim \gamma_0\delta_{ij}$ and the relaxation time for the nth normal mode is given by

$$\frac{1}{\tau_n} = \frac{\Omega_n}{\gamma_0} \sim \left(\frac{n}{N}\right)^{2\nu+1}$$

and so $z = 2 + (1/\nu)$ in agreement with an earlier conjecture by de Gennes. However, although excluded volume effects have been incorporated into the calculation of Ω_n, they were neglected when γ_{ij} was set equal to $\delta_{ij}\gamma_0$. We now show that they do in fact contribute to the friction coefficient in a very significant manner. If $V(r_i - r_j)$ is the interaction energy between monomers at r_i and r_j, the excluded volume force can be written as

$$f_i = -\frac{1}{2}\frac{d}{dr_i}\sum_j V(r_i - r_j) = -\frac{1}{2}\sum_{k,j} ikV(k)\exp[ik \cdot (r_i - r_j)]. \tag{12}$$

Using the projection operator technique of Mori (1965) we can project f_i onto the set of monomer coordinates r_m and write

$$f_i = -\sum_{m,j} r_m \Gamma_{mj} \langle r_j \cdot f_i \rangle + h_i \tag{13}$$

where Γ is already given by (10) and h_i is essentially defined by this equation.

If we denote by γ_0 and Ω_{ij}^0 the friction coefficient and spring constant in the absence of excluded volume respectively, then with the inclusion of excluded volume interactions the equation of motion (8) can still be written as

$$\ddot{r}_i = -\sum_j \gamma_{ij} \dot{r}_j - \sum_j \Omega_{ij} r_j + \zeta_i \tag{14}$$

where

$$\Omega_{ij} = \Omega_{ij}^0 + \sum_l \Gamma_{jl} \langle r_l \cdot f_i \rangle, \qquad \zeta_i = \eta_i + h_i \tag{15}$$

and

$$2\gamma_{ij} = \langle \zeta_i \cdot \zeta_j \rangle = 2\gamma_0 + \langle h_i \cdot h_j \rangle. \tag{16}$$

Using Gaussian statistics for the $\{r_i\}$, terms like $\langle r_j \cdot f_i \rangle$ which appear in (15) can be evaluated to give

$$\langle r_j \cdot f_i \rangle = \frac{1}{2} \sum_k V(k) \frac{6}{k^2 l^2} \exp\left(-\frac{k^2 l^2}{6}|i-j|\right). \tag{17}$$

In terms of the normal mode coordinates $\Omega_n = \Omega(p)$ where $p = n/N$:

$$\Omega(p) = \Omega^0(p)\left(1 + \sum_k V(k)\frac{1}{(l^2 k^2/6)^2 + p^2}\right). \tag{18}$$

For a delta function interaction $V(k) = V_0$ and in three dimensions, the corrections to Ω^0 go as $p^{-1/2}$, i.e. $N^{1/2}$, whereas in four dimensions the leading correction is logarithmic and we can write

$$\Omega(p) = \Omega^0(p)[1 - a \ln(N/n)] \sim N^{-2-a} \tag{19}$$

where a represents the conglomeration of a lot of constants, etc, including V_0. Following a regular procedure (Moore and Jasnow 1977) a is chosen so that in $d = 4 - \epsilon$ dimensions

$$\Omega(p) \sim p^{2\nu+1} \sim N^{-2\nu-1}$$

in agrement with (11), i.e.

$$a = 2\nu - 1. \tag{20}$$

Using essentially the same methods, the correlation function $\langle h_i \cdot h_j \rangle$, which determines the correction of the excluded volume effects to the friction coefficient, can be calculated. The result is, using (13) for h_i:

$$\langle h_i \cdot h_j \rangle = \langle f_i \cdot f_j \rangle - \sum_{\alpha,\beta} \langle f_i \cdot r_\alpha \rangle \Gamma_{\alpha\beta} \langle r_\beta \cdot f_j \rangle. \tag{21}$$

The second term of (21) leads to a mode-p-dependent friction coefficient, which is not

of immediate concern here. For the slowest normal modes $p \sim 0$ and the first term dominates and is given by

$$\langle f_i \cdot f_j \rangle = \left(\frac{6V_0}{k^2 l^2}\right)^2 \sum_k \left[4 - \exp\left(-\frac{k^2 l^2}{6}|i-j|\right)\left(\frac{22}{9} + \frac{2}{3}\frac{k^2 l^2}{6}|i-j|\right) + \frac{4}{9}\exp(-\frac{2}{3}k^2 l^2|i-j|)\right]. \tag{22}$$

Again the leading corrections are of order $\ln N$ in four dimensions and the mode-dependent friction coefficient $\gamma(p)$ can be written as

$$\gamma(p) = \gamma_0(1 + b \ln N) + \text{terms in } (p^2). \tag{23}$$

Again b contains constants including V_0^2/γ_0. For the lowest-order modes the relaxation time is given by

$$\frac{1}{\tau(p)} = \frac{\Omega(p)}{\gamma(p)} = \frac{\Omega^0(p)}{\gamma_0}\frac{1 - a \ln N}{1 + b \ln N}.$$

If the denominator is expanded to give

$$\frac{1}{\tau(p)} = \frac{\Omega^0}{\gamma_0}[1 - (a+b)\ln N + (b^2 + ab)\ln^2 N - \ldots] \tag{24}$$

then in the same spirit that the value for a was chosen, we choose b so that this series can be more accurately resummed to give

$$\exp[-(a+b)\ln N] = N^{-(a+b)}. \tag{25}$$

For this to be so, we need $b = a$, therefore we have that in the presence of excluded volume interactions

$$\tau(p) \sim N^{2+a+b} = N^{2(1+a)}. \tag{26}$$

As we have already determined $a = 2\nu - 1$ (equation (20)), we have that $\tau(p) \sim N^{4\nu}$ giving for the dynamical exponent $z = 4$, i.e. to order ϵ^2, z retains its value at $z = d = 4$. This can now be combined with the effects of hydrodynamic interactions which have been calculated by Moore and Jasnow in the absence of excluded volume effects to give

$$z = 4 - \epsilon = d. \tag{27}$$

Thus the second, and more important, conjecture of de Gennes that $z = d$ is verified to order ϵ and consequently the hydrodynamic radius R_H (equation (5)) depends on N in the same way as the end-to-end vector is dependent as N^ν. Thus no new length scale needs to be introduced and the scaling laws proposed by de Gennes remain valid.

However if the experimental results of Adam and Delsanti (1977) and the analysis of Daoud and Jannik (1978) are accepted then they give

$$z = 2 \cdot 85 \pm 0 \cdot 05 \tag{28}$$

for a good solvent. This suggests that instead of expanding the denominator as in (24) we write

$$\gamma(p) \sim N^{b(\epsilon)}, \tag{29}$$

so that

$$\tau(p) \sim N^{2+a+b(\epsilon)}. \tag{30}$$

The exponent a is still given by equation (20) and so we obtain for z in the presence of hydrodynamic interactions

$$z(\epsilon) = \frac{2\nu + 1 + b(\epsilon)}{\nu} - \epsilon. \tag{31}$$

In three dimensions ($\epsilon = 1$) we use $\nu = 0 \cdot 6$ and if we set $z = 2 \cdot 85$, we get

$$b = 0 \cdot 11. \tag{32}$$

The alternative procedure of setting $b = a$, gives

$$b = a = \epsilon/8 = 0 \cdot 125. \tag{33}$$

From either point of view our analysis suggests that excluded volume interactions also 'renormalise' the friction coefficient which now becomes weakly dependent on the molecular weight as M^α where $\alpha \sim 0 \cdot 1$.

References

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