Screening concepts in polymer solution dynamics

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When the concentration of polymers in solution reaches a level where the polymers begin to interpenetrate each other, screening phenomena come into existence. There are two screening lengths, one relating to the size of the molecule, an equilibrium effect, and a dynamic screening length. These effects are compared by the use of extrapolation formulae which express these lengths in terms of the physical parameters of the system.

Keywords Polymer; screening; solution; parameters; dynamics

INTRODUCTION

The various viscoelastic properties of solutions of long polymer chains are dependent on the degree of polymerization, n, the polymer monomer concentration, ρ, and the nature of the solvent. These properties can be understood in terms of the excluded volume interaction, the hydrodynamic interaction and the entanglement constraints. When many chains are present in the solution, the bare excluded volume and hydrodynamic interactions are screened. Let ξ and ξ_H be the screening lengths for the excluded volume and hydrodynamic interactions, respectively. Although ξ and ξ_H are assumed to be the same in the semidilute case in the literature[1], the physical reason for this identity is not obvious since the excluded volume effect is static and the hydrodynamic interaction is purely dynamic. It is also important to know the ratio of these quantities even in the case where it is a pure number. We present here explicit formulae for the relation between ξ and ξ_H in terms of monomer concentration and the strength of the excluded volume interaction both varying from very low to very high and verify various scaling results, where applicable, by explicit calculation. In this brief communication we focus on the important results obtained and an outline of the mathematical methods used. The algebraic details are presented elsewhere.

Screening of excluded volume effect

The excluded volume interaction[1-4] between polymer segments is modelled by a delta function pseudopotential of strength w so that the interaction between two polymer segments at a distance $\underline{r}$ apart is given by $wl^2\delta(\underline{r})$, where l is the Kuhn step length. The parameter w includes the net result of polymer–solvent effects and varies with temperature, T, as $\frac{T-\theta}{T}$ ($\theta=$ the Flory temperature). For a semidilute solution, where the chains strongly overlap, the density fluctuations are significantly correlated. It is this correlation which leads to the screening of the excluded volume interaction. We consider the correlation of density fluctuations using a combination of path integral and field theoretic techniques. Our treatment leads to the renormalizations of the bare excluded volume interaction and the step length of a labelled chain. The details are presented in ref 5. The bare interaction $w\delta(r)$ becomes, upon renormalization, an effective screened interaction, $\Delta(r)$,

$$\Delta(r)=wl^2[\delta(r)-(4\pi\xi^2r)^{-1}\exp(-r/\xi)] \tag{1}$$

where ξ is the screening length which depends on polymer monomer concentration, ρ, and the nature of the solvent through w.

The renormalization of the step length, l, arising from the correlated density fluctuations, leads to a new effective step length, l_1, such that the mean-square end-to-end distance of the labelled chain is given by

$$\langle R^2\rangle=Ll_1 \tag{2}$$

where $L=nl$ is the contour length of the chain. l_1 depends on w and ρ through ξ. In general l_1 and ξ are coupled by integral equations. Both of these depend on L, w, ρ, q and k, where q is the chain mode label and k is the Fourier conjugate variable to the position variable. In the limit of ξ and l_1 being independent of wave vectors and for infinitely long chains, the coupled integral equations reduce to algebraic equations:

$$\xi^{-2}=6w\rho l/l_1(1+27w\xi/8\pi l_1^2) \tag{3}$$

$$l_1^3-l_1^2l=\alpha w\xi l \tag{4}$$

where α is an unknown numerical prefactor of order unity. This unknown factor arises from the statistics of a single chain in an infinitely dilute solution. Although α can be given a theoretical estimate[6], there are difficulties in reconciling the theoretical, computer simulated and

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experimentally found values. So we suggest it to be taken as an experimental quantity for it can be obtained from experimental measurement of the mean-square end-to-end distance of a chain in an infinitely dilute solution from

$$\langle R^2\rangle = Ll_1$$
$$\alpha=\frac{2\sqrt{6\pi}}{wlL^{1/2}}(l_1^{5/2}-l_1^{3/2}l) \tag{5}$$

Equations (3) and (4) give the dependences of ξ and l_1 on w and ρ which can vary from zero to infinity. In the region of criticality, limit $w\to\infty$ or $\rho\to 0$, equations (3) and (4) reduce to the familiar scaling results

$$l_1=\left(\frac{9\alpha}{16\pi}\right)^{1/4} w^{1/4}\rho^{-1/4} \tag{6}$$

$$\xi=(9/16\pi\alpha^{1/3})^{3/4}w^{-1/4}l^{-1}\rho^{-3/4}. \tag{7}$$

Thus for low polymer concentrations, the excluded volume screening length depends on ρ with $-3/4$ power law for very good solutions. Also note that $\langle R^2\rangle$ in good solvent varies like $\rho^{-1/4}$.

In the other limit of $\rho\to\infty$, or $w\to 0$, l_1 and ξ become from equations (3) and (4)

$$l_1=l+\frac{\alpha}{6^{1/2}}\frac{w^{1/2}}{l\rho^{1/2}}+\ldots \tag{8}$$

$$\xi=(6w\rho)^{-1/2}. \tag{9}$$

Thus for very high polymer concentrations, ξ depends on ρ with $-1/2$ power law, a result obtained earlier by Edwards[4]. Therefore equations (3) and (4) are the extrapolation formulae valid from very low to very high concentrations for any strength of the excluded volume interaction. Note that for a mathematical theta solution (all the virial coefficients except the first are zero), ξ diverges to ∞ because $w\to 0$. These results are presented in *Table 1* for a comparison with ξ_H.

The various thermodynamic properties like the osmotic pressure of the polymer solution, and the average size of a labelled chain can be obtained from l_1 and ξ.

Table 1 Comparison of the screening length, ξ, for the excluded volume effect and the screening length, ξ_H, for the hydrodynamic interaction as functions of polymer monomer concentration, ρ

Concentration regime	ξ	ξ_H
Concentrated solution	$\rho^{-1/2}$	ρ^{-1}
Semidilute solution poor solvent	∞	ρ^{-1}
Semidilute solution good solvent	$\rho^{-3/4}$	$\rho^{-3/4}$ $\xi_H=\frac{32}{9}\xi$
Extrapolation formulae connecting different regimes	$\xi^{-2}=\frac{6w\rho l}{l_1(1+27w\xi/8\pi l_1^2)}$ $l_1^3-l_1^2l=\alpha w\xi l$	$\xi_H^{-1}=\frac{\pi}{2}\rho l l_1$ $l_1^3-l_1^2l=\alpha w\xi l$

Screening of hydrodynamic interaction

In the absence of polymer chains the solvent alone is assumed to satisfy the linearized Navier–Stokes equation

$$\rho_0\frac{\partial\mathbf{v}(\mathbf{r},t)}{\partial t}-\eta_0\nabla^2\mathbf{v}(\mathbf{r},t)+\nabla P(\mathbf{r},t)=\mathbf{F}_{\mathrm{ext}}(\mathbf{r},t) \tag{10}$$

Here $\mathbf{v}(\mathbf{r},t)$ is the velocity field at any space point $\mathbf{r}$ and time t, P is the pressure, η_0 is the shear viscosity of the solvent, ρ_0 is the mass density of the solvent and $\mathbf{F}_{\mathrm{ext}}$ is the external force driving the solvent flow. The velocity field at $(\mathbf{r},t)$ due to a disturbance at $(\mathbf{r}',t')$ is obtained from the Green function of equation (10),

$$\mathbf{v}(\mathbf{r},t)=\int \mathrm{d}\mathbf{r}'\mathrm{d}t'\,\mathbf{G}(\mathbf{r}-\mathbf{r}';t-t')\cdot\mathbf{F}_{\mathrm{ext}}(\mathbf{r}',t')$$
$$\mathbf{G}(\mathbf{r}-\mathbf{r}';t-t')=\int\frac{\mathrm{d}^3k}{(2\pi)^3}\int\frac{\mathrm{d}\omega\,\mathrm{e}^{\mathrm{i}\mathbf{k}(\mathbf{r}-\mathbf{r}')-\mathrm{i}\;(t-t')}}{2\pi(\eta_0k^2+\mathrm{i}\omega\rho_0)}(\mathbf{1}-k^{-2}\mathbf{k}\mathbf{k}) \tag{11}$$

where k is $|\mathbf{k}|$. In the zero frequency limit, $\mathbf{G}$ becomes the familiar static hydrodynamic interaction tensor,

$$\mathbf{G}(\mathbf{r})=\frac{1}{8\pi\eta_0 r}\left(\mathbf{1}+\frac{\mathbf{r}\mathbf{r}}{r^2}\right) \tag{12}$$

The presence of polymer chains alters the hydrodynamic interaction between any two spatial positions so that equation (12) is significantly renormalized. Indeed this renormalization leads to hydrodynamic screening. The hydrodynamic screening can be obtained by deriving the equations of motion for the coupled polymer–solvent system, and is summarized by formulae (21), (22) and (25). Readers not wishing to study an outline derivation can go to these equations.

Consider a solution containing N chains ($\alpha=1,2,\ldots N$) each of contour length L. Let $\mathbf{R}_\alpha(s_\alpha)$ denote the position of αth chain at an arc length of s_α from its end. We assume that all these chains undergo excluded volume interaction given by $\Delta(r)$, equation (1). In addition, we employ the 'stick' (or Stokes) boundary condition,

$$\frac{\partial}{\partial t}\mathbf{R}_\alpha(s_\alpha,t)=\mathbf{v}[\mathbf{R}_\alpha(s_\alpha,t),t], \tag{13}$$

to couple the dynamics of the chains and the solvent. Since frictional forces are now present in the system, the Rayleighian of the system should be constructed first and its time integral should be varied (see refs 8–10 for details) to obtain the following coupled equations of motion,

$$\rho_0\frac{\partial\mathbf{v}(\mathbf{r},t)}{\partial t}-\eta_0\nabla^2\mathbf{v}(\mathbf{r},t)+\nabla P(\mathbf{r},t)$$
$$=\mathbf{F}_{\mathrm{ext}}(\mathbf{r},t)+\sum_{\alpha=1}^{N}\int_0^L \mathrm{d}s_\alpha\,\delta(\mathbf{r}-\mathbf{R}_\alpha(s_\alpha,t))\boldsymbol{\sigma}_{\mathrm{A}}(s_\alpha,t) \tag{14}$$

$$-\frac{3k_BT}{l}\frac{\partial^2\mathbf{R}_\alpha(s_\alpha,t)}{\partial s_\alpha^2}+\sum_{\beta=1}^{N}\int_0^L \mathrm{d}s_\beta\nabla\mathbf{R}_\alpha(s_\alpha,t)\Delta[\mathbf{R}_\alpha(s_\alpha,t)-\mathbf{R}_\beta(s_\beta,t)]$$
$$=-\boldsymbol{\sigma}_{\mathrm{A}}(s_\alpha,t)+\mathbf{f}_{\mathrm{random}}(s_\alpha nt). \tag{15}$$

These equations are obtained by ignoring inertial effects. Here $\boldsymbol{\sigma}_\alpha(s_\alpha,t)$ is a Lagrangian multiplier arising from the stick boundary condition and possesses a simple physical interpretation of the force exerted by s_αth position of αth chain on the surrounding solvent. $\mathbf{f}_{\text{random}}(s_\alpha,t)$ is the random force acting on the s_αth position of α originating from the various hydrodynamic fluctuations present in the solution. k_B is the Boltzmann constant.

Equation (15) differs from the corresponding equation of Freed and Edwards[9,10] in that the latter omits excluded volume effect altogether and that it includes an *'ad hoc'* term for the bead friction coefficient which is unnecessary to describe the viscous properties of polymer solutions. The earlier work[11] of Freed, Edwards and Warner to include the effect of excluded volume effect on the dynamics of polymer chains in solution attempts only in a perturbation sense of omitting terms of order w^2 and is not adequate.

By Fourier transforming with respect to s_α, equation (15) gives the equations of motion for the Rouse modes,

$$\frac{3k_BT}{l}q^2\mathbf{R}_\alpha(q,t)+\sum_{\beta=1}^{N}\int_0^L \mathrm{d}s_\alpha\int_0^L \mathrm{d}s_\beta\int\frac{\mathrm{d}^3k}{(2\pi)^3}\mathrm{l}\mathbf{k}\Delta(\mathbf{k})$$

$$\exp\{\mathrm{i}qs_\alpha+\mathrm{i}\mathbf{k}\cdot[\mathbf{R}_\alpha(s_\alpha,t)-\mathbf{R}_\beta(s_\beta,t)]\}=-\sigma_{\mathrm{A}}(q,t)+\underset{\text{random}}{\mathbf{f}}(q,t), \tag{16}$$

where q is the mode variable. This shows that every chain mode is coupled to all other modes due to excluded volume interaction. We have calculated the effective force on the qth mode due to excluded volume effect by averaging over all other modes using mode–mode coupling arguments. The details are presented elsewhere[5] and the result is that equation (16) reduces to

$$\frac{3k_BT}{l_1(q)}q^2\mathbf{R}_\alpha(q,t)=-\sigma_{\mathrm{A}}(q,t)+\underset{\text{random}}{\mathbf{f}}(q,t). \tag{17}$$

In the limit of $q\rightarrow 0$, l_1 is given in terms of the excluded volume screening length, ξ, by equations (3) and (4).

Utilizing the stick boundary condition, equation (13), $\underset{\sim}{\sigma}_\alpha$ from equations (14) and (17) can be eliminated and the microscopic velocity field $\mathbf{v}(\mathbf{r},t)$ can be expressed as a multiple scattering series involving various polymer chains in terms of l_1. Instead of these complicated microscopic quantities we are interested in the average properties like macroscopic velocity field, etc. Performing the average over the positions of the chains, an effective macroscopic equation of motion can be written for the whole polymer solution,

$$\rho_0\frac{\partial\mathbf{u}(\mathbf{r},t)}{\partial t}-\eta_0\nabla^2\mathbf{u}(\mathbf{r},t)+\nabla P(\mathbf{r},t)-\int\mathrm{d}\mathbf{r}'\mathrm{d}t'\,\underset{\approx}{\Sigma}(\mathbf{r}-\mathbf{r}';t-t')\cdot\mathbf{u}(r',t')$$
$$=\mathbf{F}_{\text{ext}}(\mathbf{r},t) \tag{18}$$

where $\mathbf{u}(=\langle\mathbf{v}\rangle_{\text{chains}})$ is the average velocity field after averaging over the positions of all chains and P is now the average pressure. The tensor $\underset{\approx}{\Sigma}$ accounts for the contribution of all the chains to the average divergence of stress tensor of the polymer solution. By Fourier transforming equation (18) with respect to $\mathbf{r}$ ($\mathbf{k}\sim$conjugate variable) and t ($\omega\sim$conjugate variable), and defining $-\Sigma(k)/\eta_0\equiv\xi_H^{-2}(k)$, we get

$$[\mathrm{i}\omega\rho_0+\eta_0(k^2\xi_H^{-2}(k))]\mathbf{u}(\mathbf{k},\omega)+\mathrm{i}\mathbf{k}P(k,\omega)=\mathbf{E}_{\text{ext}}(\mathbf{k},\omega). \tag{19}$$

Since we are discussing here the Navier–Stokes fluid flow, equation (19) should satisfy the invariance symmetry of $\Sigma(k=0)=0$. For low k, $\Sigma(k)$, i.e., ξ_H^{-2} indeed behaves like k^2 as shown below. The coefficient of k^2 of $\Sigma(k)$ for small k, gives the change in viscosity, $\eta-\eta_0$, due to the polymer chains,

$$(\eta-\eta_0)/\eta_0=\lim_{k\rightarrow 0}\xi_H^{-2}(k)/k^2 \tag{20}$$

The average velocity field, $\mathbf{u}(\mathbf{r},t)$, in addition to being given by equation (19), is also given by $\langle\mathbf{v}(\mathbf{r},t)\rangle_{\text{chains}}$ where $\mathbf{v}$ is a multiple scattering series in terms of l_1, as mentioned earlier. By averaging the various terms in the multiple scattering series of $\langle\mathbf{v}\rangle$ and summing up and then combining with equation (19), ξ_H is given, in the zero frequency limit, by the coupled integral equations,

$$\xi_H^{-2}(k)=\frac{\rho l}{\pi\eta_0}\int_{2\pi/L}^{\infty}\mathrm{d}q\frac{(k^2l_1/3)J(q)}{[(k^2l_1/6)^2+q^2]} \qquad (21$$

$$J^{-1}(q)=\frac{1}{3\pi^2\eta_0}\int_0^{\infty}\mathrm{d}j\frac{j^2}{[j^2+\xi_H^{-2}(j)]}\frac{(j^2l_1/3)}{[(j^2l_1/6)^2+q^2]} \tag{22}$$

The preaveraging approximation and the averaging over chain statistics have been employed in deriving equations (21) and (22).

Note that, in the limit of $k\rightarrow 0$, ξ_H^{-2} is proportional to k^2, thus satisfying the Navier–Stokes fluid flow symmetry. In addition, for infinitely dilute solutions where $\xi_H^{-2}(j)$ can be ignored in equation (22), $J^{-1}(q)$ is proportional to $(\eta_0^2 l_1 q)^{-1/2}$. Substitution of this result in equation (21) yields

$$\xi_H^{-2}(k)=\alpha\rho l l_1^{3/2}L^{1/2}k^2 \tag{23}$$

Therefore the intrinsic viscosity, $[\eta]=(\eta-\eta_0)/\eta_0\rho$, is given by

$$[\eta]=\alpha l l_1^{3/2}L^{1/2}$$
$$\alpha\begin{cases}L^{1/2} & \theta\ \text{solvent}\\ L^{4/5} & \text{good solvent}\end{cases} \tag{24}$$

for infinitely dilute solutions. The results of equation (24) for θ and good solvents are obtained by using the expression for l_1 from equation (5).

Now the average velocity field at $\mathbf{r}$, $\mathbf{u}(\mathbf{r})$, due to an external disturbance at $\mathbf{r}'$ is given by the Green function of equation (19), in $\omega\rightarrow 0$ limit,

$$\mathbf{u}(\mathbf{r})=\int\mathrm{d}\mathbf{r}'\,\hat{\underset{\approx}{G}}(\mathbf{r}'\mathbf{r}')\mathbf{E}_{\text{ext}}(\mathbf{r}')$$
$$\hat{\underset{\approx}{G}}(\mathbf{r})=\frac{1}{\eta_0}\int\frac{\mathrm{d}^3k}{(2\pi)^3}\frac{(1-k^{-2}\mathbf{k}\mathbf{k}}{[k^2+\xi_H^{-2}(k)]}\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r}) \tag{25}$$

This is analogous to equation (11) except that the effect of all chains on the dynamics of the whole polymer solution appears through $\xi_H^{-2}(k)$ of the Green function, $\hat{\underset{\approx}{G}}$. It is obvious from the structure of $\hat{\underset{\approx}{G}}$ that the bare hydrodynamic interaction $\underset{\approx}{G}$ is screened when $\xi_H(k)$

becomes independent of k. Therefore we shall look for a solution of ξ_H from equations (21) and (22) such that $\xi_H(k)$ is independent of k to entail hydrodynamic screening. Clearly for small k, i.e., for large characteristic distances, $\xi_H^{-1}(k)$ is proportional to k ensuring that for such large distances as the size of the container the fluid flow dominates and that there is no hydrodynamic screening. However, for large k, $\xi_H(k)$ becomes independent of k provided $J(q)$ in equation (21) is independent of q. Satisfying these conditions self-consistently in equations (21) and (22), the solution is

$$J^{-1}(q)=2\xi_H/\pi\eta_0 l_1 \qquad (26)$$

$$\xi_H^{-1}=(\pi/2)\rho l l_1. \qquad (27)$$

Thus the hydrodynamic screening length, ξ_H, is given in terms of l_1 which in turn depends on the excluded volume screening length, ξ, through equations (3) and (4).

Use of equation (26) in equations (20) and (21) yields in small k limit

$$(\eta-\eta_0)/\eta_0=\rho l l_1^2 L/12\pi\xi_H=(1/24)\rho^2 l^2 l_1^3 L \qquad (28)$$

thus reporducing the Rouse result of $(\eta-\eta_0)\propto L$ when the hydrodynamic interaction is screened. Since l_1 depends, in general, on ρ as given by equations (3) and (4), the polymer solution viscosity, in the hydrodynamically screened regime, depends on ρ as ρ^y where y varies from 5/4 to 2 depending on the strength of the excluded volume interaction.

As mentioned earlier, $\xi\propto\rho^{-\chi}$, with χ varying continuously from 3/4 to 1/2 as ρ increases. Also χ decreases from 3/4 as the strength of the excluded volume interaction, w, decreases. In the limit of $w\rightarrow 0$, ξ diverges to infinity as explained earlier. On the other hand, equations (3), (4) and (27) show that $\xi_H\propto\rho^{-\chi_H}$ with χ_H varying continuously from 3/4 to 1 as ρ increases or w decreases. Thus ξ and ξ_H possess distinctly different ρ dependences. However, in the region of criticality, $w\rightarrow\infty$ or $\rho\rightarrow 0$, both ξ and ξ_H behave as $\rho^{-3/4}$ in agreement with de Gennes' result[12]. In spite of the same concentration dependence, they are not identical since their ratio is

$$\xi/\xi_H=9/32 \qquad (29)$$

This result is obtained from equations (6), (7) and (27). The inequality $\xi<\xi_H$ for a semidilute solution of phantom chains in the critical limit of $w\rightarrow\infty$ suggests that the excluded volume interaction is screened out faster than the hydrodynamic interaction as a function of the spatial distance. This casts doubt on the validity of extending the scaling arguments over a wider range of variables as is often done in the literature[13,14] utilizint $\langle R^2\rangle\propto\rho^{-1/4}$ and Rouse behaviour for the chain mobility in describing the chain dynamics in semidilute solutions. If these arguments were valid then the viscosity should vary with ρ as $\rho^{5/4}$ [see equation (28)]. However, the experimental data of Pearson and coworkers[14] show a dependence of $\rho^{3/2}$. Another important difference between ξ and ξ_H is that while ξ is determined by the wave-vector independent limit (i.e., large distances characteristic of the size of the system), ξ_H is determined by large wave-vector limit of characteristic distances within the size of a single chain. In conclusion, ξ and ξ_H are two different screening lengths arising from widely different physical origins, and are compared in *Table 1*.

The results presented so far are obtained by assuming that all the chains are penetrable phantom chains without any entanglement constraints roughly speaking corresponding to physical conditions where there is little viscoelastic behaviour. The problem of the entanglement effects on the dynamics of chains in semidilute solutions and a derivation of the radius of the tube, if and when it exists, through which a chain reptates, remain still formidable. Therefore the *Table 1* needs to be appended with another column for the radius of the tube in a polymer solution. It is of interest to also find out the effect of entanglements on the ratio ξ/ξ_H of equation (29) for semidilute solutions. Although ξ should be independent of entanglement effects, it is not obvious how ξ_H is affected by the entanglement effects. The question of whether the entanglement constraints change the ratio ξ/ξ_H only merely by a constant or by a functional dependence on ρ remains open.

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