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Dynamics of polymers in solution and melts

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Simple models of polymer dynamics are available in dilute solution, moderate concentrations and melts, since it is possible to make models of the motion in these cases. A series of power laws result which fit well with computer simulation. It is more difficult to derive these models directly from sensible equations of motion, but progress in this direction is reported in the paper.

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INTRODUCTION

Polymer dynamics involve different time scales according to the part of the polymer involved and the environment that it finds itself in. In smaller molecule dynamics one can identify three obvious regimes, the molecule alone, usually meaning in the gaseous phase where one has an n body problem if there are n atoms, an n body problem with external noise and friction which, roughly speaking, is what one expects in a liquid, and to some extent a glass, and finally part of an Nn body problem in a crystal. Notoriously the middle problem is the worst since the first has non stochastic equations, and the crystal is at least quite explicit, and there is a well defined band theory. The liquid case is the most difficult since the molecule has a structure comparable to its surroundings, it could for example be in the liquid phase of its own species, and there is no easy way to simplify the environment as there is with a large Brownian particle in a small molecule fluid.

If one studies a polymer which is a string of smaller monomers then only those aspects of its behaviour which have to do with the polymerized nature have any hope of being easier to understand than the corresponding monomeric liquid, and the solid state of polymers will always be more difficult than the crystalline phase of the monomer, although again they may have some features which are simpler than the monomeric glass.

One can consider the behaviour of polymers characterized by relaxation times or typical frequencies, and the discussion above amounts to saying that when one studies high frequencies, a polymer melt is only marginally different from a monomeric melt, and indeed this is borne out experimentally. But the polymerized nature of the material totally alters melt and solution behaviour at low frequencies, the long chain nature being reflected in the spectacular increases in viscosity which are so characteristic of polymers. There will of course be effects in the solid state also, but they are not so spectacular since the fall of temperature means that Van der Waals or hydrogen bonds are now real bonds and all glasses are polymer networks in some sense; a glass made of polymer is much the same as any other glass once one is well past the glass temperature.

So if one wants to study stimulating theoretical ideas it is natural to aim at effects which are characterized by long

time scales, and an obvious pitfall ensues. To graft that kind of theory onto monomeric structure is a hard problem, because it is no good solving by methods which are fine on long time scales and extrapolating to short time scales. This is a general caution to be noted. Current polymer dynamics initiated in the famous Rouse paper is at the level of elastic wave theory of solids, the Born Von-Karman theory, or equivalently the Rayleigh, Jeans and Wien formulae of black body theory. The Born Von-Karman theory does not produce the multiplicity of branches in the vibrational spectrum, nor the way that faults affect the spectrum. But there is an enormous richness in polymer theory at the Rouse level since a whole host of new problems, still entirely confined to long time scales, appear in polymer problems, and they pose problems which are very deep mathematically but intuitively obvious, for example: how long will it take for a knot to untie if the string is subjected to Brownian motion? (If the string is in a melt, the melt encloses it like a tube, and one question is asking how long it takes for the chain to wriggle out of this knotted configuration into a new configuration. This is clearly a shorter time than wriggling right out of the initial tube into an entirely new tube, and that time can be calculated by reptation theory and is proportional to L^{-2} . So unless the new tube is the same class of knot one has the solution to the query at a crude level).

I shall put forward a chain of developments of dynamics in recent years which amount to a reasonable intuitive solution for long time scales, and point out the basic problem of improving these theories to the level of mathematical proof.

THE SINGLE CHAIN

Forces between monomers, and also forces between the polymer and its surroundings have the effect of expanding or contracting the chains. This paper is concerned with dynamics, so it will omit all discussions of swelling or precipitation. This is a topic 'under control' and can be built into the analysis without too much difficulty; it is not worth while muddying the equation with complexity which will not be used. There is a dynamical equivalent to this simplification in that every motion involves crossing

potential barriers in quite complex ways, and these ways are affected by the environment just as a single particle can have complex jump behaviour but still in the end will have its long time motion governed by a simple diffusion equation:

$$\left(\frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2}\right) P(x,t) = 0 \quad (1)$$

one can hope for a similar equation for the polymer.

In the presence of a potential $V(x)$ a particle in equilibrium will have $P_0 = (e^{(F-V(x))/\kappa T})$ where $e^{F/\kappa T}$ is the normalization. This modifies equation (1) to

$$\left(\frac{\partial}{\partial t} - D \frac{\partial}{\partial x} \left(\frac{\partial}{\partial x} + \frac{1}{\kappa T} \frac{\partial V}{\partial x}\right)\right) P = 0 \quad (2)$$

a simple but rather unfamiliar form since one generally does not find Brownian particles in central fields of force. The mathematical form is familiar in the Fokker-Planck equation for the case of particles with inertia and soft forces which has the form:

$$\left(\frac{\partial}{\partial t} + v \cdot \frac{\partial}{\partial \mathbf{r}} - \frac{\partial}{\partial v_\mu} D_{\mu\nu} \left(\frac{\partial}{\partial v_\nu} + \frac{m v_\nu}{\kappa T}\right)\right) P = 0 \quad (3)$$

$D_{\mu\nu}(v)$ being the velocity dependent tensor diffusivity required in say plasma physics.

What is P_0 for a polymer? In equilibrium it is a random walk. Suppose it were freely hinged rods whose ends were at $\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_n$ and each rod is of length l :

$$P_0 = \prod_i \delta(|\mathbf{r}_i - \mathbf{r}_{i+1}| - l) \quad (4)$$

It is well known that the end-to-end statistics or indeed the statistics of any points distant from one another long the chain is independent of the precise neighbour configuration, and the analogue of the variable which described elastic waves in a solid, or the macroscopic density or velocity in a liquid, are the Fourier components

$$\mathbf{R}_q = \sum \mathbf{r}_n e^{2\pi i n q / L} \quad (5)$$

which gives (by a well known straightforward derivation not reproduced here)

$$P_0 = N \exp\left(-\frac{3}{2l} \frac{1}{2\pi} \sum_q q^2 |\mathbf{R}_q|^2\right) \quad (6)$$

(N the normalization)

(I have used the complex form for simplicity, but it contains the real form if required by relations between the real and imagining parts of \mathbf{R}_q) The q in the sum cannot exceed the number of links (recall the Born theory) but in fact if ever we need to restrict the sum the theory will be wrong since high q brings us into a region outside the present validity. Note that there is no κT in P_0 , the random walk has entropy but no internal energy. The analogue of equation (2) is now

$$\left(\frac{\partial}{\partial t} - \sum_q \frac{\partial}{\partial \mathbf{R}_{-q}} D \left(\frac{\partial}{\partial \mathbf{R}_q} + \frac{3q^2}{2\pi l} \mathbf{R}_q\right)\right) P = 0 \quad (7)$$

Provided one realises that only the q variables have meaning, one can also back Fourier transform

$$P_0 = N e^{\frac{3}{2l} \int_0^L \left(\frac{\partial \mathbf{R}}{\partial s}\right)^2 ds}$$

$$\left(\frac{\partial}{\partial t} - \int ds \frac{\partial}{\partial \mathbf{R}(s)} D \left(\frac{\partial}{\partial \mathbf{R}(s)} - \frac{3\mathbf{R}''(s)}{l}\right)\right) P = 0 \quad (8)$$

where the continuous arc lengths have replaced the discrete nl , but for those who find functional differential equations hard to swallow one may emphasize that equation (7) is exactly the same as an equation for highly damped phonons in a solid, or radiation in a highly emitting and absorbing material.

Equation (7) is the Rouse equation and the q 's label Rouse modes. It can be solved exactly, for if one writes

$$P = \tilde{P} e^{-\frac{1}{2} \left(\frac{3}{2\pi} \sum_q q^2 |\mathbf{R}_q|^2\right)} \quad (9)$$

one has

$$\left(\frac{\partial}{\partial t} - \sum_q D \left(\frac{\partial^2}{\partial \mathbf{R}_q \partial \mathbf{R}_{-q}} - \frac{q^4}{4} |\mathbf{R}_q|^2 \left(\frac{3}{4\pi l}\right)^2 + \frac{3}{2i} \frac{1}{2\pi} \frac{q^2}{2}\right)\right) P = 0 \quad (10)$$

which is Hermite's equation and is in all the books under the quantum theory of the harmonic oscillator, give or take a few constants and i .

From this equation one can work out the probability of the polymer getting from any given shape to any other. By taking the first moment of equation (7) we see that it is derivable from a Langevin equation:

$$v \dot{\mathbf{R}}_q + \frac{3\kappa T}{2\pi l} q^2 \mathbf{R}_q = \mathbf{f}_q \quad (11)$$

where v is a friction

$$\frac{\kappa T}{v} = D \quad (12)$$

and

$$\frac{3\kappa T}{4\pi l} q^2 |\mathbf{R}_q|^2 \quad (13)$$

is the free energy per mode, \mathbf{f}_q being a random force. This friction $v\mathbf{R}$ is just like the ' $6\pi\eta a$ ' of a Brownian sphere in Stokes formula, which amounts to saying that the chain suffers a Stokes drag along its length and this drag shows no coupling along the chain.

In fact it must show coupling since the flow around any point will affect neighbouring parts of the chain, unlike Stokes' problem where each Brownian sphere is considered remote from each other one. The hydrodynamic effects have been put in by Zimm and modify the diffusion equation in a way most easily written in the form of equation (8).

$$\left(\frac{\partial}{\partial t} - \sum_{\alpha\beta} \iint ds_\alpha ds_\beta \frac{\partial}{\partial \mathbf{R}_{\mu(s_\alpha)}} D_{\mu\nu}(\mathbf{R}_{(s_\alpha)}, \mathbf{R}_{(s_\beta)}) \left(\frac{\partial}{\partial \mathbf{R}_{(s_\beta)}} - \frac{3\mathbf{R}''(s_\beta)}{l}\right)\right) P = 0 \quad (14)$$

where α, β label a pair of polymers, μ, ν are Cartesian indices and $\mathcal{D}_{\mu\nu}$ is known in the hydrodynamical literature as the Oseen tensor. It is most easily written in Fourier transform

$$\mathcal{D}_{\mu\nu}(k) = \left(\frac{\delta_{\mu\nu} - k_\mu k_\nu / k^2}{\eta k^2} \right) \kappa T \quad (15)$$

(The speed of propagation of the signal through the liquid is ignored here).

Equation (10) is frequently simplified by replacing D by its average for a random walk:

$$\langle e^{ik \cdot (R^{(\alpha)}(s) - R^{(\beta)}(s'))} \rangle = \delta^{\alpha\beta} e^{-k^2 l |s - s'|/6} \quad (16)$$

so that

$$\sum_{\alpha\beta} \iint ds_\alpha ds_\beta \frac{\partial}{\partial R_\mu^{(\alpha)}(s_\alpha)} \mathcal{D}_{\mu\nu}(R^{(\alpha)}(s_\alpha) R^{(\beta)}(s_\beta)) \frac{\partial}{\partial R_\nu^{(\beta)}(s_\beta)}$$

which, on averaging \mathcal{D} , becomes

$$\sum_\alpha \frac{\partial}{\partial R_q^{(\alpha)}} \frac{\kappa T}{\eta q^{1/2}} \left(\frac{\partial}{\partial R_q^{(\alpha)}} + \frac{3q^2 R_q^{(\alpha)}}{2\pi l} \right) \quad (17)$$

From these forms, or directly from the Langevin equation one can derive the correlation functions

$$\langle e^{ik(R^{(\alpha)}(s_\alpha, t) - R^{(\beta)}(s_\beta, 0))} \rangle = e^{-k^2 \langle (R^{(\alpha)}(s_\alpha, t) - R^{(\beta)}(s_\beta, 0))^2 \rangle} \quad (18)$$

$$\begin{aligned} & \langle (R^{(\alpha)}(s_\alpha, t) - R^{(\beta)}(\delta_\beta, 0))^2 \rangle \\ &= \delta^{\alpha\beta} \int dq d\omega \frac{(1 - e^{i\omega t + iqs}) D \kappa T}{\omega^2 + (Dq^2 \kappa T)^2} \end{aligned} \quad (19)$$

for the Rouse case and

$$\frac{\int dq d\omega (1 - e^{i\omega t + iqs})}{\omega^2 + \left(\frac{3\kappa T q^{3/2}}{y} \right)^2} \left(\frac{3\kappa T q^{1/2}}{y} \right)^2 \quad (20)$$

for the Zimm case. The Zimm result is more realistic since it is derived from possibly realistic model, that of a polymer embedded in a fluid with normal hydrodynamics. The weakness of the model lies in the neglect of the entanglements. The Rouse model on the other hand is not realistic as it stands since there is no justification for assuming a drag coefficient in the form of a simple constant, which certainly will not result from the equations of hydrodynamics. Experimentally the viscosity of a dilute polymer solution verifies the Zimm result, for the viscosity in this case is proportional to $L^{1/2}$, i.e. $M^{1/2}$ where M is the molecular weight.

The hydrodynamic interaction \mathcal{D} is screened once the density of the polymer is such that the chains overlap. If one takes equation (14) and averages away all polymers except one, one finds that simple screening does obtain, and just using mean densities the equation governing the effective hydrodynamics equation.

$$\frac{\partial u}{\partial t} + \eta(k) u_k + \frac{\nabla \rho}{\rho_{\text{fluid}}} = f_{\text{external}} \quad (21)$$

and the effective polymer dynamics

$$\dot{R}_q + \kappa T q^2 R_q J(q) = \int u(R(s)) e^{iqs} ds \quad (22)$$

where

$$\eta(k) = \eta_0 + c \sum_q \left(\frac{k^2 l/3}{k^4 l^2/36 + q^2} \right) \frac{3\kappa T q^2/l}{i\omega + 3\kappa T q^2 J(q)/l} \quad (23)$$

where c is the polymer concentration, and

$$J(q) = \frac{1}{3\pi^2 y_0} \int_0^\infty dj \frac{j^2}{j^2 \eta(j^2)} \frac{j^2 l/3}{(j^4 l^2/36) + q^2} \quad (24)$$

If an arbitrary friction term is still left in, it will appear as

$$(1 + \nu J(q)) \dot{R}_q + \kappa T q^2 J(q) R_q = u \quad (25)$$

At high enough densities one can expect a solution

$$\left. \begin{aligned} \eta(k) &= (\eta_0 + \delta\eta) k^2 & k^2 L l < 1 \\ &= \eta_0 (h^2 + \xi^{-2}) & h^2 L l > 1 \end{aligned} \right\} \quad (26)$$

where, by studying equations (23) and (24) one finds that

$$\xi^{-2} = \frac{\pi}{2} c \xi^{-1}$$

so that

$$\xi = \frac{2}{\pi c}$$

This is of course an asymptotic solution to have so simple a form and the full equations are quite complicated. A particular problem is that the entanglements must dominate at high enough density, and it is not clear if this screened regime is ever realistic; but experimentally one certainly has a regime of viscosity M before the melt behaviour characterized by M^{3+} sets in. This region will be considered below.

The conclusion of this section is then that the diffusion of a single point on a polymer in solution, or the two body correlation function, can be obtained provided that entanglements are ignored, from the formula

$$\begin{aligned} & \langle e^{ikR(st) - R(s', 0)} \rangle \\ &= \exp \left(-\frac{k^2}{3} \iint \frac{(1 - e^{i\omega t + iq(s-s')}) \kappa J J(q)}{(\omega^2 + (\kappa T q^2 J(q))^2)} d\omega dq \right) \end{aligned} \quad (28)$$

(one point function has $s = s'$, the two body correlation is integrated over $s - s'$) where J is given by equation (24) coupled with equation (23).

ENTANGLEMENTS

We have seen in the last section that the dynamics of chains which are transparent to themselves can be resolved when they are in Brownian motion with a simple drag friction, or surrounded by a viscous fluid, and when many chains are present some screening phenomenon intervenes. But in fact all chains are non-transparent, and this fact

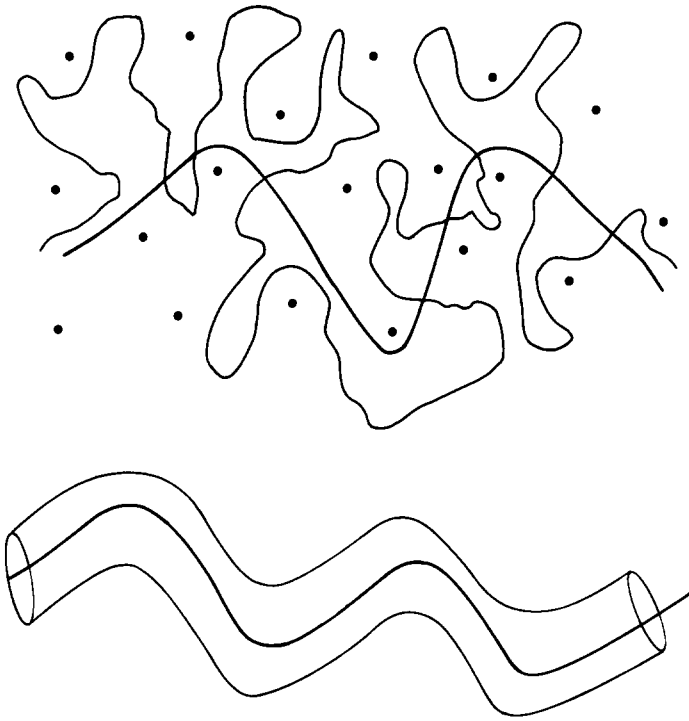


Figure 1 Schematic illustration of two dimensional lattice defining a tube

dominates motion in melts or concentrated solutions since almost all motions are blocked. A surviving motion will be the wriggling of the chain up and down the statistical tube which one can imagine surrounding it on average, and a plausible viscoelastic theory can be developed from the reptative motion. It is also possible that some kind of collective motion could exist, but no convincing theory of this exists at present. To illustrate the concept of reptation there is a simple computer experiment.

Suppose a lattice is made up in two or three dimensions which we illustrate by a two dimensional array of dots (Figure 1). The polymer is moved by Monte Carlo moves. It is well known that without the lattice this gives the Rouse equation. If one regards the lattice as defining a tube one can characterize this by pulling the polymer taut generating another walk with a larger steplength, called the primitive path. The steplength of this primitive path, a say, is also the thickness of the tube.

Suppose the distance along the tube is S and the absolute coordinate R

$$\langle (R(S_1) - R(S_2))^2 \rangle = a|S_1 - S_2| \quad (29)$$

Now consider a point on the polymer initially labelled S_2 and after a time labelled S_{21} . Then

$$\langle (S_1 - S_2)^2 \rangle$$

is given by the Rouse equation in one dimension and this as was shown above gives

$$\int \frac{dq \delta m^2 \omega t / 2}{\omega^2 + q^4} \sim \sqrt{t} \quad (30)$$

(Note the distinction between this and a Brownian point particle which gives t .) Hence

$$\langle (S(t) - S(0))^2 \rangle \propto \sqrt{t} \quad (31)$$

$$\langle (R(S,t) - R(S,0))^2 \rangle \propto t^{1/4} \quad (32)$$

Thus one might expect a time scale initially of $t^{1/2}$ for the polymer has yet to notice the tube. Then $t^{1/4}$, it is diffusing up and down the tube. The centre of mass is the special component $q=0$ and will have the usual t for S and hence $t^{1/2}$ for R , so after a longer time again the centre of mass will diffuse and take any point with it, giving $t^{1/2}$.

Finally the polymer gets right out of the tube and creates a new tube and the final t law must result. Thus one expects the hierarchy

$$t^{1/2}, t^{1/4}, t^{1/2}, t \quad (33)$$

The initial $t^{1/2}$ is a bit difficult to find with a computer which is moving the system very quickly indeed to get into the other ranges, but with the eye of faith one can see the other three ranges (Figure 2).

This is for a fixed lattice and a free polymer. When all the polymers move the time taken over the computation has to be immense both because one has to move many more polymers and the checking of the topological integrity is much more difficult and no longer can be incorporated into the program without the use of memory and because the system becomes 'soggy' and collective modes are clearly possible, but not easy to incorporate in a one point Monte Carlo system. Various authors give various results, but my belief is that the reptation picture has to be the starting point of any theory. The author's papers with Evans² illustrate a whole range of dynamical effects of the fixed lattice models, and these results have been extended by Needs to star molecules, verifying the

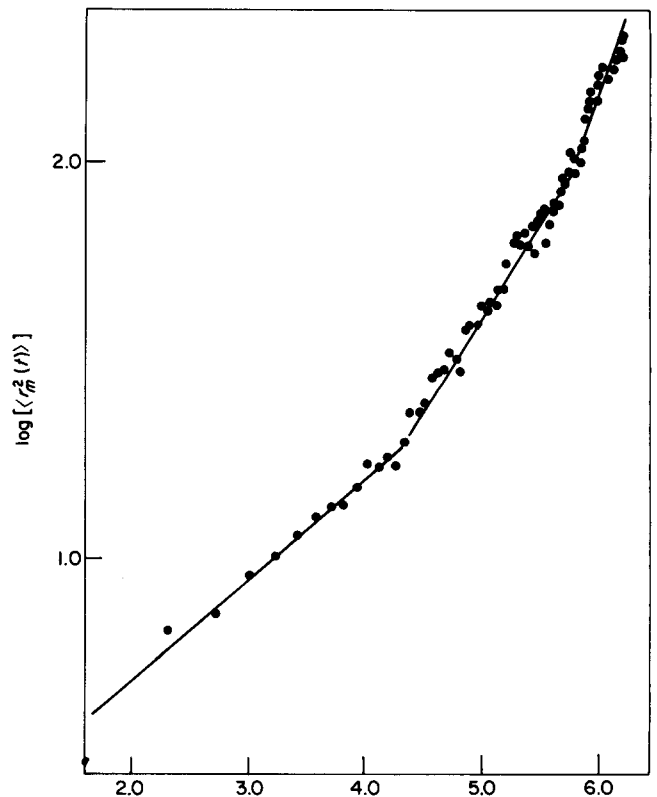


Figure 2 Time scale ranges for polymer chain movement in a statistical tube

results of the theories of de Gennes¹ and of Doi, and the experimental diffusion results of Klein.

Thus we can now argue that the diffusion law as a function of concentration will go as follows:

Low concentration (hydrodynamics Zimm)	$t^{2/3}$ finally t	
Higher concentration (screened to Rouse)	$t^{1/2}$ finally t	(34)

Melt (reptation: de Gennes) $t^{1/2}$, $t^{1/4}$, finally $t^{1/2}$ then t

The intermediate regions are difficult and a principal difficulty is that the fundamental problem of how to describe the motion of entanglements has to be resolved in the region between higher concentration and very high concentration. In the former (and in the Zimm regime) one just ignores it. In the very high density regime it becomes straightforward once it can be represented by a tube.

How can one give a representation of the tube in mathematics? One way is to consider the polymer at two times. Since this paper is being read at an n.m.r. conference I will not worry about very long time scales; alternatively we can consider rubbers where the tubes are permanent. Suppose the polymer is initially $R_2(S)$ or $R_2(q)$ and later at $R_1(q)$. Then over the time scale over which the polymer moves a tube step length it will not encounter the walls. (This whole argument is going to be 'average'). Let this time be called $(Dq_0^2)^{-1}$ where q_0 has the dimension of q and is related to a ,

$$q_0 \sim la^{-2} \quad (35)$$

The Rouse equation is a version of Hermite's equation and the joint probability of finding $\mathbf{R}_1(q)$ at $t=0$ at $t=t$ is given by

$$P([\mathbf{R}_1][\mathbf{R}_2]) = \prod_q \left\{ \exp \left\{ -\frac{3q^2}{22\pi} (|\mathbf{R}_{1q}|^2 + |\mathbf{R}_{2q}|^2) - \frac{3}{2\pi} q^2 \right. \right. \\ \left. \left. (|\mathbf{R}_{1q}|^2 + |\mathbf{R}_{2q}|^2) \coth Dq^2 t + \frac{3}{2\pi} q^2 (\mathbf{R}_{1q} \mathbf{R}_{2q} \right. \right. \\ \left. \left. + \mathbf{R}_{1-q} \mathbf{R}_{2q}) \operatorname{cosech} Dq^2 t \right\} \right. \\ \left. \times [(\sinh Dq^2 t) / Dq^2 t]^{-3/2} \right\} \quad (36)$$

Note that

$$\int P([\mathbf{R}_1], [\mathbf{R}_2], t) \Pi dR_{1q} = P_0([\mathbf{R}_2])$$

and

$$\int P([\mathbf{R}_1], [\mathbf{R}_2], t) \Pi dR_{2q} = P_0([\mathbf{R}_{1q}]) \quad (37)$$

where

$$P_0 = N \exp \left(-\frac{3}{2l} \frac{1}{2\pi} \sum_q |R_q|^2 \right) \quad (38)$$

This is for a *free* polymer.

We now argue that for a polymer in a pipe the joint probability is the expression above with

$$Dq^2 t = q^2 / q_0^2$$

giving

$$P_{00} = P \left([\mathbf{R}_1], [\mathbf{R}_2], \frac{1}{Dq_0^2} \right)$$

Note the complexity of the joint form. It would have been quite wrong to solve the problem of a single polymer constrained to one dimension. The dynamics of a polymer \mathbf{R} tied by a tube constraint represented by a locus \mathbf{R}_2 can be developed by noting that $P_{00}([\mathbf{R}], [\mathbf{R}_2])$ is the equilibrium distribution of \mathbf{R} hence the equation:

$$\left(\frac{\partial}{\partial t} - \iint D \frac{\partial}{\partial \mathbf{R}} \left(\frac{\partial}{\partial \mathbf{R}} - \frac{1}{P_{00}} \frac{\partial P_{00}}{\partial \mathbf{R}} \right) \right) P_{\text{tube}}([\mathbf{R}], t) = 0 \quad (39)$$

It will be seen from the structure of P_{00} that \mathbf{R} and \mathbf{R}_2 are strongly correlated over $q < q_0$, i.e. $S > a$, but weakly correlated for $q > q_0$, i.e. $S < a$, which is precisely the primitive path picture.

It will be seen that $\frac{1}{P_{00}} \frac{\partial P_{00}}{\partial \mathbf{R}}$ is a linear expression in \mathbf{R} and \mathbf{R}_2 , so that equation (39) is *still* a version of Hermite's equation and can still be written down in closed solution so that one can now derive a form

$$P([\mathbf{R}], [\tilde{\mathbf{R}}], [[\mathbf{R}_2]]) t$$

for the probability that a chain constrained by a tube to \mathbf{R}_2 starts at $\tilde{\mathbf{R}}$ and is at \mathbf{R} at t .

But the answer is sufficiently algebraically tedious that I will not write it down (it possesses the property of being tedious even though trivial!).

A phenomenology is now complete, but what of the mathematics of entanglement?

A RIGOROUS THEORY

This can be derived from the full hydrodynamic form equation (14), because this equation comes from the Stokes boundary condition

$$\dot{\mathbf{R}} = \mathbf{u}(\mathbf{R})$$

where \mathbf{u} is the fluid velocity. Hence if $\mathbf{R}_1 = \mathbf{R}_2$

$$\dot{\mathbf{R}}_1 = \dot{\mathbf{R}}_2$$

It is now possible to argue that this condition is sufficient to stop the polymers crossing. Hence the entanglements are *already* in equation (14). A particularly simple version of this is to freeze all the polymers except one. Then one can show that the last polymer $R^{(1)}$, satisfies

$$\left(\frac{\partial}{\partial t} - \iint ds ds' \frac{\partial}{\partial R^{(1)}(s)} D(R^{(1)}(s) [R^{(2)}] [R^{(3)}] \dots \right) \\ \left(\frac{\partial}{\partial R^{(1)}(s')} - \frac{3}{2l} R^{(1)} \right) = 0 \quad (40)$$

where D vanishes if any point of $R^{(1)}$ touches any point of $R^{(2)}, R^{(3)} \dots$

So at a rigorous level we have equation (40) which must be equivalent to equation (39) which expresses the primitive path structure explicitly, i.e. if one could average away $R^{(2)}R^{(3)} \dots$ it would have to be in terms of *one* of the primitive paths defined by these loci. The point is that the solutions of equation (40) (as shown in ref. 3) break up into a set of probabilities each associated with one of the primitive paths of the network.

This is all quite straightforward for melts for in spite of the apparent complexity it is merely showing a pathway from basic equations to the results of the 'Entanglements' section, and to a much more accurate form of correlation functions. I have hope that having got these basic

equations one can explore the transition region, but have a horrible suspicion that computer simulation will get there first.

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