Interdiffusion and polymer dissolution

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Guidelines for de Gennes Symposium talks

1. Introduction - state of the field before de Gennes' work (experimental + theoretical)
2. New ideas introduced by de Gennes
3. Development of the field after de Gennes' paper(s)
4. Current status of the field
5. Future directions
1. Introduction - state of the field before de Gennes' work (experimental + theoretical)

Prior to the 1970’s the ideas of polymer interdiffusion were not well developed at the molecular level (only small molecules in polymers, e.g. Crank 1968, Meares 1963)

Interdiffusion for condensed small molecules, however, was reasonably well understood

e.g. metals: Kirkendall (1942), Darken (1948) - first treated case of interdiffusion of metals of different mobilities
or
Simple liquids: e.g. Rowlinson (book 1964, 1969) - reviewed liquid mixing
But the case of highly entangled chains was intrinsically very different: no lattice hopping as in metals, and strong entanglement constraints, unlike liquids.

One difficulty was, that there was no adequate model for dynamics of entangled chains.

De Gennes reptation model (1971) was one of several proposed mechanisms.

Early experiments on the mechanism of entangled chain diffusion set out to discriminate between the different predictions.
Evidence for reptation in an entangled polymer melt

Entanglements, their nature and their role in the dynamic properties of concentrated polymer solutions and melts are not well understood\(^1\)\(^2\). The classical molecular view of entanglements has been one of rope-like intermolecular couplings at a number of points along the length of a molecule; molecules in motion would drag past these couplings the essential

\[ D \sim M^{-2 \pm 0.1} \]

This experimental result supported the reptation model
Following the 1978 experiments and the accompanying ‘News & Views’ in Nature, de Gennes’ reptation model took strong hold, providing finally a framework for understanding also of polymer interdiffusion.
In this talk we trace the development of an interdiffusion process intrinsic to polymers: how bulk polymers composed of chemically identical chains of **different lengths** interdiffuse.

Generally one expects two generic cases:

a) Chemically different, driven by mobility and $\chi$ (segmental interaction)

b) Only physically different (i.e. in length): driven by mobility alone ($\chi = 0$)
In 1980 de Gennes presented a good starting point for interdiffusion:

**Dynamics of fluctuations and spinodal decomposition in polymer blends**

P. G. de Gennes

Collège de France, 75231 Paris Cedex 05, France
(Received 3 December 1979; accepted 11 January 1980)


Treated chemically different chains of same mobility (i.e. N equal, monomer friction coefficients equal), basic equation for chemical potential $\mu$

$$\frac{\mu}{kT} = N^{-1} \ln \frac{\phi}{1 - \phi} + \chi(1 - 2\phi) - \frac{a^2}{36\phi(1 - \phi)} \nabla^2 \phi$$

(where $\phi$ is the volume fraction)

We are interested more in the other generic limit: chains of same chemistry but different lengths and hence different mobilities
This was first extended by Brochard and co-workers in 1983 to interdiffusion of short vs. long chains:

The issue is:

\[ D_s, N_s \quad \text{versus} \quad D_L, N_L \]

the constraint of constant density - i.e. equal monomer fluxes in both directions - led to strong coupling of the motion of short and long, and to mutual diffusion

**The BJL prediction:**

\[ D \sim (D_s D_L)^{1/2} \] - dominated by slower species since \( D \sim N^{-2} \)
What of interdiffusion experiments?
Pioneering experiments by Kramer, Green and Palmstrom (Cornell) showed that the fast mode apparently dominated, in contrast to the BJL prediction.

 Movements in polymer–polymer diffusion couples: E. J.

 POLYMER, 1984, Vol 25, April 473

 **Figure 2** Configuration of Rutherford backscattering experiment to determine gold marker movements.
They found that marker movement obeyed $x^2 \sim D_s t$

i.e. dominated by faster moving chains!

This was explained in terms of vacancy flux which allowed a decoupling of the short and long chain motion

(Sillescu (1984) used a different convection type explanation to account for the ‘fast mode’ interdiffusion)
Polymer-Polymer Interdiffusion.

F. Brochard and P. G. de Gennes
Colège de France - 75321 Paris Cedex 05

Europhysics Letters, 1986

In response, Brochard & de Gennes suggested that the Kramer et al. vacancy flux argument might lead to unacceptable density anomalies.

Rather, they accounted for the ‘fast mode’ observed thus: at the short length scales ($O(1 \mu m)$) involved in the gold marker experiments, the longer chains were merely being swollen - like a gel - by the shorter ones, and that at longer length scales than $L$,

$$L \approx (D_s \tau_L)^{1/2}, \quad (\text{cf. polymer/solvent dissolution}) \sim 1 - 10 \mu m$$

(\text{where } \tau_L \text{ is the reptation time of the longer chains) the ‘slow mode’ interdiffusion should prevail, as predicted.}
However, experiments were then carried out at much longer length scales (mm) to check this fast vs. slow mode controversy.

These showed conclusively that interdiffusion between long and short chains (but both $N_s, N_L >> N_e$) was dominated by the faster $N_s$ chains.
Reconciliation of the theory and experiment resulted when analysis by Brochard (1988) showed that correct picture involved reptation of chains in ‘tubes’ that were themselves in motion: recovered ‘vacancy flux’ and ‘convection’ predictions.

In a review of polymer-polymer interdiffusion, *Science* **260**, 640 (1990), it was finally concluded that:

"
So where is this area going now?

Answer: in many directions, often application-driven - welding, adhesion, advanced composites, nanosystems and nano-confinement, lubrication

But one of the main threads that runs through PGG work: a toolbox containing a few powerful concepts that turn up again and again

e.g. ‘Blobs’ (in solution); reptation; entropy of stretching; simple modelling and free energy minimization; …

Using this toolbox it is often possible to understand situations (in interdiffusion) not previously envisaged
One example which we discuss in more detail: interdiffusion between surface-attached polymer layers, such as brushes, which affect their friction and lubrication properties.

Moderate compressions

High compressions

This was examined experimentally by compressing and shearing polymer brushes at different compressions and shear-rates.
Probing of dynamics in shearing chains using Polystyrene chains: failed due to onset of glassy concentration \( (T_g \approx 100^0C) \) (e.g. Klein et al., *Nature* 1994).

So use low \( T_g \) polymer brushes: poly(ethylene propylene)*, PEP, -[CH\(_2\)-CH\(_2\)-CH(CH\(_3\))CH\(_2\)]\(_N\)-, terminated with zwitterion (PEP-X), for which \( T_g = -60^0C \).

*Rafael Tadmor, Joanna Janik, Lew Fetters, JK (PRL 2003)
Detailed analysis of the stress relaxation region c - d revealed the extent of interdiffusion and disentanglement of the opposing brushes.
Varying the ‘rest time’ during which interdiffusion occurred enabled a delicate probe of the growth of the interpenetrated region via the shear stress on sliding.

Longer rest time
From arm-retraction mechanism (as for star-branched chains)

\[ t(l_r) = \tau_1 \exp(\alpha l_r / l_e), \]

where \( \alpha \approx 0.6, l_e \) is (concentration-dependent) entanglement length, \( \tau_1 \) varies weakly with \( l_r \).

This gives tension in unrelaxed portion of chain

\[ f_s(t) \propto [L_0 - l_r(t)], \]

and finally, for overall shear force \( F_S(t) \)

\[
\frac{F_S(0) - F_S(t)}{F_S(0)} \cong \frac{l_r(t)}{L_0} = \frac{l_e}{\alpha L_0} \ln \left( \frac{t}{\tau_1} \right)
\]

(Note \( \frac{l_e}{\alpha L_0} \approx 0.04 \) for \( D = 7\text{nm} \))
Variation of shear force following cessation of applied lateral motion (predicted slope for PEP-X brushes in toluene (at D = 7nm) ≈ 0.04)

This prediction was quantitatively confirmed for PEP-X brushes
Move to melt-brushes

\[ s = \sqrt{A} \approx 13 \text{ Å} \]
Repeat experiments using PI-X melt brushes.
A similar analysis applies to the PI-X melt brush relaxation, but with a predicted logarithmic argument an order of magnitude larger than for PEP-X!

\[
\frac{F_S(0) - F_S(t)}{F_S(0)} \approx \frac{l_r(t)}{L_0} = \frac{l_e}{\alpha L_0} \ln \left( \frac{t}{\tau} \right)
\]

Earlier PEP-X brushes in toluene, predicted slope \( \frac{l_e}{\alpha L_0} \approx 0.04 \) (for \( \phi \) corresponding to \( D = 7\text{nm} \))
measured slope = 0.038

Expt. 0.038

For PI-X melt brushes, predicted slope \( \frac{l_e}{\alpha L_0} \approx 0.3 \) (independent of \( \phi \))

(nearly order of magnitude difference due to larger \( l_e \), smaller \( L_0 \))
Experiments show close quantitative agreement with new predicted logarithmic argument of stress relaxation, confirming the brush interdiffusion and relaxation picture.

Tsarkova, JK et al., *Macromolecules* 2007
So using simple tools of reptation under constraint and arm-retraction, can account for new forms of interdiffusion, disentanglement and relaxation - for surface-attached polymers - not envisaged at time these tools were formulated.

Open questions include interdiffusion of charged polymers - crucial for understanding biological lubrication, and dominated by effects very different to neutral chains such as counterions and salt concentration, as well as hydration effects.

Interdiffusion in nanometrically confined systems - competition of different length scales
Summary

The reptation model and the 1980 PG paper set the field for molecular understanding of interdiffusion processes (both $\chi$ and mobility-dominated), and introduced the tools to treat more complex cases.

Extension to interdiffusion of entangled chains - chemically identical but of different lengths (with Brochard) - reconciled with experiments showing fast-mode interdiffusion.

With auxiliary tools (e.g. arm-retraction) can understand interdiffusion/relaxation processes in new and unanticipated configurations.