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Heterogeneous polymers and self-organization

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Abstract. A striking number of new spatial structures or modes of self-organization in liquids have recently been discovered. Such a new structure can be expected to give rise to further new properties in the liquid, which are not apparent from the structure itself. To illustrate such 'hidden consequences', two instances of heterogeneous polymer systems are reviewed. The first is the associating polymers, whose heterogeneity causes them to stick together at specific points. This gives rise to unusual consequences in the solubility of the polymers and in the rheology of their solutions. The second instance is diblock copolymers, whose heterogeneity gives rise to extended periodic domains. The elastic free energy stored in the elongation of the polymers in these domains qualitatively alters the motion of these chains and the response of the liquid to applied stress.

1. Introduction

One concern that unites virtually all of us at this meeting is a fascination with structures in liquids. These structures range from the short-range solid-like order on the atomic scale to the largest vortices of turbulent flow. A major theme of this meeting concerns the ability of liquids to organize themselves in ways not previously recognized. Figure 1 illustrates one of these new modes of self-organization: the 'labyrinth phase' [1]. The figure shows a strongly paramagnetic fluid, a suspension of colloidal ferromagnetic particles. The labyrinth phase forms when a puddle of this fluid is sandwiched between glass plates. Then the sandwich is placed in a moderate magnetic field. The induced magnetic polarization of the fluid gives rise to a long-range self-repulsion. This opposes the fluid's normal tendency to form a compact disc shape. The result of this competition between the magnetic dipole force and the surface tension is a fascinating pattern of curving and branching stripes of fluid. The same principle of self-organization appears in surfactant monolayers at an air-water interface [2]. The surfactant molecules have an electric dipole moment; these dipoles have some net orientation perpendicular to the interface; the result is a repulsive dipole force between the molecules with the same long-range character as in the magnetic fluid [3]. As with the magnetic fluid, a labyrinthine pattern of stripes appears. These stripes have a width of order 10 microns. The reason for the two similar patterns is probably the same, despite the great difference in their molecular realization and spatial scale. The labyrinth phase is thus a model of self-organization of matter independent of its molecular realization. It is only recently discovered, and its statistical nature is not understood.

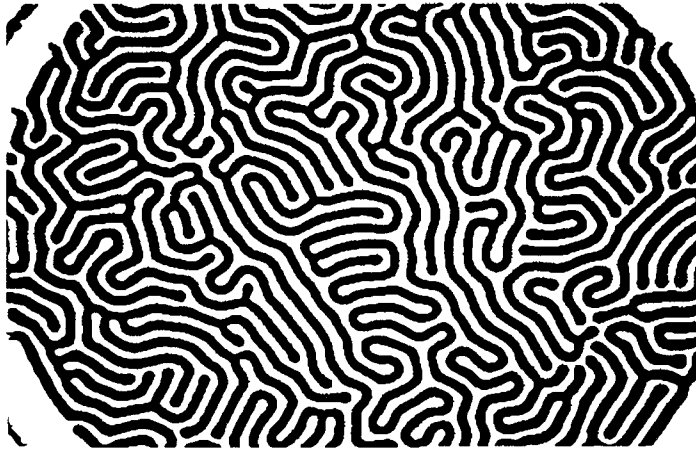


Figure 1. Ferrofluid drop in a gap between two glass plates in a magnetic field perpendicular to the plane of the picture, courtesy of R E Rosensweig. The gap is about 1mm thick; the field strength is a few hundred gauss; the stripes are about 1mm wide [1].

In the last few years a startling number of such large-scale modes of fluid self-organization have been reported. A few examples will serve to illustrate the rich variety of these discoveries. Under proper conditions, water, oil and surfactant form a microemulsion quite unlike the conventional droplet picture. Instead, the surfactant-coated oil-water interfaces form extended random surfaces which are essentially statistically invariant under the interchange of the oil and water regions. Graphic electron-microscopy evidence for this phase, showing oil and water regions a thousand Å across has recently been published [4]. Surfactants in the lamellar regime with (magnetic) colloidal particles, produce a square, quilt-like pattern reported at this conference [5]. The size of the squares is roughly 10 microns. Other new modes of self-organization are dynamic structures, such as the tree-like pattern seen when a surfactant solution spreads on a wet surface [6]. The branches range from tens of microns to millimetres in size. Another dynamic pattern is the chaotic square ripple pattern which appears on the surface of a sinusoidally shaken liquid [7].

The obvious structuring of these liquids indicates that the microscopic interactions are being made to co-operate in new ways. When this occurs, we have every reason to expect new properties—new ways of responding to perturbations. An example is the associating polymer solution sketched in figure 2. There is no self-organization apparent to the eye. Yet something in this liquid makes its flow response quite unusual. If its container is gently rocked, it flows like a viscous oil. But if the container is rapidly inverted, the fluid temporarily transforms into a gel. This strong shear thickening response is thought to be a consequence of self-organization on the scale of the individual polymer molecules. I wish to discuss this in more detail, to illustrate how subtle features of self-organization may lead to surprisingly strong effects on material properties.

2. Associating polymers

The fluid of figure 2 consists of a few volume per cent of flexible linear polymers like polystyrene in a small-molecule hydrocarbon solvent like xylene. Each polymer

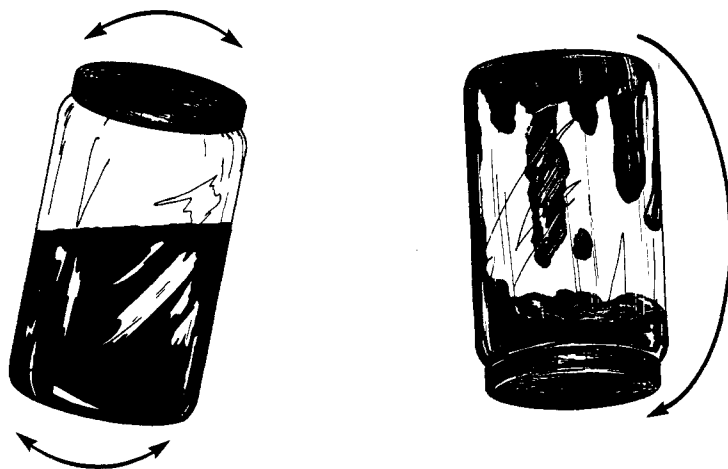


Figure 2. Shear-induced gelation as seen in associating polymer solutions [8]. Left: viscous flow behaviour when the container is gently rocked. Right: lumpy gel consistency when the container is rapidly inverted.

chain is a sequence of many chemical units connected by rotatable chemical bonds. The heterogeneity in the chain consists of ionic side groups like sodium sulfonate chemically attached at sparse intervals along the chain [8]. These ionic groups are strongly immiscible with the bulk of the polymer and with the solvent. Accordingly, they try to phase separate; they cluster together into micelles each containing a handful of associating groups [9]. The number of groups in a micelle appears to be controlled by the size of the ionic groups and the steric crowding of the polymer chains near them. Clearly the associating groups serve to stick the chains to themselves and to one another. This sticking may be treated as a topological constraint: each associating group or ‘sticker’ must (almost always) be found in a micelle containing a well defined number f of other stickers. The sticking is long-lived relative to the viscous relaxation time of the polymer chains fluctuations; the sticker lifetimes may easily exceed a tenth of a second [10]. Thus on short timescales the polymers act as though permanently cross linked. But unlike covalently cross linked polymers, these are free over longer times to sample the available cross linking topologies. Therefore the associations are labile enough to adjust readily to externally imposed conditions such as stress.

To decide how the sticker constraints affect the associating polymer solution we must answer a fundamental question: what is the typical distance along the chain between associated stickers? The two extreme answers to this question are illustrated in figure 3. For simplicity we have assumed that each micelle contains exactly two stickers. In the left-hand figure the sticking is *local*: two associated stickers are chemically nearby along the chain. No matter how long the chain is, the typical chemical distance between associated stickers remains essentially fixed. The right-hand side illustrates the opposite extreme: *global* sticking. Here the typical distance between associated stickers is of the order of the entire chain length.

Local sticking is a relatively minor modification of the overall state of the polymer coil. If one regards the chain at a scale larger than the typical sticking distance, it still retains its linear topology. We expect it to behave like a simple polymer in a good solvent: i.e. like a self-avoiding random walk. We expect a solution of these chains to



Figure 3. Local versus global sticking. The left-hand sketch shows the extreme of local sticking: only chemically adjacent stickers are associated. In the right-hand sketch stickers are associated independent of their position along the chain.

behave like simple polymers in a good solvent, as well. Global sticking, on the other hand, leads to a dense tightly-connected chain topology quite unlike a linear polymer. The polymer chain thus behaves as though it attracts itself. The various chains in a solution also behave as though they attract one another; the result is bad solvation or phase separation: the polymers refuse to disperse in the solvent.

One way to address the question of local versus global sticking is to consider the net mutual interaction between two short segments of a chain. We shall consider a chain with alternating long and short intervals between stickers. We imagine dividing this chain at the middle of each long segment to produce identical pieces each containing two stickers. We wish to know whether the net interaction between two such pieces is attractive or repulsive. If the interaction between two pieces is repulsive, we expect the chain's interaction with itself to be repulsive as well. Self-repelling chains asymptotically show self-avoiding-walk behaviour and dispersion in solution [11]. Two effects act to cause an interaction between the two pieces. First, the constituent chains are assumed to be well solvated—their mutual interaction is repulsive. The range of the repulsion is the linear size R of each piece (e.g. their radii of gyration). The strength of the interaction is of order kT . If the two pieces approach sufficiently closely they may exchange stickers. The possibility of exchange roughly doubles the number of configurations. This increased number of configurations amounts to an entropic attraction of order kT , extending to distances of order R . Thus the attractive and repulsive effects are of the same order of magnitude.

Subtle alterations of the chain construction can alter the balance between attraction and repulsion. Thus, for example, if the segment between stickers is relatively short, the attraction is less important. More systematic estimates [12] confirm that the attractive and repulsive effects are balanced when the stickers are spaced at some universal finite fraction of the way along the pieces.

The delicate balance between self-attraction and self-repulsion shows up in another way when we consider the response of a solution to flow. Shear flow elongates polymers in solution. Accordingly, it increases the equilibrium size R of our chain pieces. It increases the incidence of sticker exchange between nearby pieces in the solution. If the concentration is high enough, a chain piece will often be adjacent to a piece from a separate chain. The cross-pairing thus links two chains. Stronger flow increases the cross linking and produces larger mechanically connected clusters of chains. In this way [8, 13] a moderate distortion of the chains may be easily imagined to produce gelation.

I have recalled these old ideas about associating polymers to illustrate how self-organization can have far-reaching consequences. To summarize, two free-energy scales are important in determining the solution properties of these chains. The state of interconnection of a chain within itself and with other chains is controlled by self-

avoiding-walk and exchange entropy corresponding to a small free energies of order kT per sticker. These energies are easy to alter substantially by mild changes in the chain architecture or in the state of flow. But once the interconnections are established, the strength of the resulting network is controlled by the much larger energy of dissociation of the stickers. This can easily reach tens of kT for the strong ionic dipoles used in many associating polymers. This interplay of two energy scales makes associating polymers at once an intriguing many-body problem and a candidate for further new fluid properties.

3. Block copolymers

I now turn to the other extreme in polymer heterogeneity: the extended heterogeneity exemplified by diblock copolymers. These are formed by joining two polymer chains end-to-end. When the two chains are sufficiently immiscible, diblock copolymers in the liquid state form extended domain structures. Symmetric ones, with roughly equal volumes of each immiscible species, produce well-ordered lamellar domains. By varying the proportion of the two blocks one discovers a well-defined sequence of different structures: these are ordered lattices of spheres, cylinders, lamellae and the fascinating double-diamond structure [14, 15] analogous to the bicontinuous Luzzati phases in surfactant solutions [16].

Again, the fact that these domains are formed from flexible mesoscopic polymers implies further structure than that apparent in the domains. One gets an inkling of this hidden structure if one considers the *size* of the domains [17]. The same driving force that creates the domains wants to make their size h as large as possible. In these strongly phase-separated domains, the tendency to phase separate is measured by the interfacial tension Γ times the total surface area. Each phase is essentially one pure species at its dense-liquid density. For chains displacing volume V in the liquid the interfacial energy per chain is of order $\Gamma V/h$. This energy acting alone would make the domains indefinitely large. But the polymer connectivity prevents this. Each chain must have its junction point *confined* at the interface. (Otherwise, if a junction point wandered into one domain or the other, this would necessarily drag one species into an immiscible region.) A given domain must be uniformly filled with monomers each attached to a chain ending at the interface. Thus the chains must have a typical spatial extent of order h or more. If the domains are large, the chains must stretch: the energy required is a classic result of the theory of random walks or of rubber elasticity. It is of order $kT a h^2/V$, where the elasticity constant a is typically about 10 Å: polymers behave like Hookian springs. This energy added to the interfacial energy has a minimum for $h \sim V^{2/3}$. Evidently the elastic energy in each chain grows as $v^{1/3}$ and thus becomes indefinitely larger than kT : the chains are strongly perturbed from their normal random-walk state.

This stretch of each polymer means that the domains are full of stress. A cube the size of a domain may easily have 100 kT of interfacial and stretching energy. This large energy makes it clear why the domains are ordered in periodic spatial arrangements. It also raises the question of how to describe the forces responsible for stretching each chain. Evidently, a given chain stretches because of some non-uniform pressure in the surround fluid. This pressure profile arises in turn from the stretching of the surrounding chains, since if these were not stretched the liquid would be an ordinary polymer melt with a uniform pressure. The problem of self-consistently determining

the pressure and chain stretching has been recognized by polymer scientists for a number of years, and numerical means of achieving self-consistency have been devised [18–20].

Recently there has been heightened interest in the deformed state of the chains in copolymer domains, and in the material properties they produce. A key realization in this new work is that in the asymptotic state of strong stretching the statistical description of the chains becomes simple [21,22]. Each chain, with its free end at some given point in the layer, must be arranged so that its other end is at the phase interface. Since the distance is typically large relative to the chain's random-walk size, the chain is stretched like a rubber band along a path connecting the free and the confined end. This imagined rubber band is stretched not by an external tension holding the free end out, but rather by forces all along its length. The force on a given small segment of the chain at position r is the gradient of the pressure $p(r)$ there times the volume ΔV displaced by the segment.

We may readily find the conformation of this stretched chain by considering the equilibrium position of a segment i . The force on this segment consists of the external force in $\nabla p(r)$ plus the elastic tensions from the predecessor and successor of the segment i . Like all random-walk polymers, these segments have a mean tension proportional to their elongation. Thus the balance of the three forces implies

$$(r_{i+1} - r_i) - (r_i - r_{i-1}) \propto \nabla p(r_i).$$

Taking a continuum limit of the second difference on the left, this force equilibrium equation takes the form $d^2r/di^2 \propto \nabla p$. This is the same as Newton's law of motion for a fictitious particle moving from the assumed free end to the interface under the action of a potential $-p(r)$. In finding the path of least energy of our stretched rubber band, we are implicitly finding the path of least action of a classical particle.

The classical-mechanics description has recently been used to infer a number of properties of block copolymer domains. Many of these apply also to chains in solution grafted at one end to a surface [23,24]. A remarkable property common to all these systems is a strong constraint on the potential-energy profile. (For the copolymer domains this is $p(r)$ as noted above.) Seen as a Newtonian particle, each chain must travel from its arbitrary starting point to the grafting interface in some transit time that depends on the potential profile. As noted above, this 'transit time' is simply the number of monomers in the chain. Thus the known transit time puts a restriction on $p(r)$ for every point r where chain ends are to be found. For instance, if all the chains have length N and the layer has some ends everywhere, then $p(r)$ must be such that the transit time is the same from all starting points: it must be a parabola [21,22], whose curvature is set by the chain length. Remarkably, $p(r)$ is fixed, except for an additive constant, by this 'equal-time' requirement, which is independent of how the chains interact. The parabolic form arises from the requirement of mechanical equilibrium within each chain, plus the requirement that all chains are stretched by a common potential.

Given the potential profile and an elastic energy parameter for the chains one may explicitly calculate further important properties. The work required to compress the domains may be found explicitly in terms of handbook properties of the constituent homopolymers. For the case of grafted chains in a solvent, the prediction agrees quantitatively with surface-forces experiments [25]. The bending moduli for mean and for Gaussian curvature may also be found explicitly [26]. These moduli are of the

order of the energy stored in a cube whose size is the domain size h . Bent lamellar layers are predicted to be qualitatively different in their pressure profile, depending on the direction of bending. If the interface is bent towards the chains, the potential profile remains parabolic, but if it is bent away from the chains, the potential takes on a new functional form, with two distinct sublayers [21]. In the sublayer nearest the interface, chain ends are excluded. The thickness of this exclusion zone increases with curvature to a fraction $2/\pi$ of the total layer thickness [27].

The stretching of end-confined polymers gives rise to striking dynamical effects. One which was recently studied [28] is the kinetics of formation of a grafted layer in a solvent. The end-attachment of chains is progressively inhibited by the pressure profile of the already attached chains. This gives rise to a predicted logarithmic time dependence [29], which appears to be consistent with observations. A further important question is the dynamics of chain disentanglement in copolymer domains. Disentanglement is the primary process controlling stress relaxation in polymer liquids. In some aspects these copolymer chains should be less entangled than those of a simple homopolymer melt. The chains from opposite layers in a lamella, for instance, should be entangled over a vanishingly small fraction of their length, because the pressure $p(r)$ inhibits the interpenetration of two grafted layers. The result is a predicted stretched exponential dependence of the relaxation time on chain length, in contrast to the cubic power-law dependence for simple melt, or a simple exponential dependence for star polymers [30].

In this paper I have discussed a particularly simple mode of self-organization: that which arises in polymers containing mutually immiscible parts. Because flexible chain polymers have simple statistical properties, it is possible to infer many subtle consequences of the immediately apparent domain-forming behaviour. These consequences show that self-organization gives rise to materials with qualitatively new behaviour. The other modes of self-organization I mentioned at the beginning are less well understood. As with the polymer examples, these too should have further behaviour beyond the apparent self-organization, which distinguishes them in their own ways from simple liquids. As these are discovered, our appreciation for the possibilities inherent in liquid matter can only grow.

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