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How soft matter correlates: three examples

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Abstract
This essay proposes a generalization of the notion of soft matter beyond the structured fluids such as polymer solutions extensively developed by Professor Schäfer.

1. Introduction

This Festschrift volume is focused on polymers and other complex systems. Its honoree, Lothar Schäfer, has played a major role in deducing properties of polymer liquids using many-body field theory [1]. They are complex systems in the sense that they show subtle spatial correlations requiring the cooperation of many degrees of freedom. These liquids also became an archetype of a new field now known as soft condensed matter. The term 'soft' emphasized the contrast between, for example, polymer liquids and the hard objects that traditionally occupied the interest of condensed matter physics. Hard condensed matter systems are often complex for their own reasons, arising from their quantum nature. In this essay I want to highlight a few recent examples of complex soft condensed matter. These examples are meant to show how soft condensed matter can extend our conceptions of complex, co-operative behaviour. I want to argue that the fundamental reason these are interesting is common between hard and soft condensed matter.

Softness means deformability. A gentle external influence has a big effect. We see this softness in a polymer system such as a rubber immediately when we stretch or bend it. A more microscopic look at the rubber reveals why its deformability is interesting. Each random-walk chain making up the rubber is very deformable, because it can readily take on many distinct configurations. The molecules are complex; much information is required to specify their state. The softness arises from the ability of the constituents (the bond orientations of the polymer molecules) to hold information. These systems are interesting because their information is connected to controllable physical properties. By manipulating the polymer architecture, one may control how the system responds to mechanical forces or the admixture of small molecules. Because the response is a collective result of many configurational variables, it is robust and predictable.

Soft matter often has a second feature that gives it unique capabilities. Its constituents *interpenetrate*. Thus, in a rubber, each polymer chain passes through and around many other chains. Interpenetration can produce rich behaviour, because the system cannot be described

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using a small set of variables at each point coupled to these same variables at adjacent points. That is, it has features not amenable to description by the simple partial differential equations of a classical field. If many polymers are attached to a surface to form a polymer brush, their mutual interpenetration gives rise to a distinctive profile of pressure that changes in striking ways when the chains are made immiscible or when the surface is curved [2]. Interpenetration and its resulting nonlocality play a strong role in the examples below.

In the last decade the field of soft matter has grown beyond its initial domain of polymers, colloids, surfactant solutions and liquid crystals. The three examples below illustrate these new directions. They are taken from work of my colleagues at the University of Chicago. The first is a simple sheet of elastic material, deformed to create a spontaneous singular structure called a d-cone [3]. The second is also a two-dimensional structure, a liquid-like bilayer of lipid surfactants. Sometimes when these bilayers are strongly concentrated, they avoid the flat multilayer equilibrium morphology and instead grow multilayer tubes called myelins. The third example comes from a static granular pack of beads. Here the structure of interest is the network of forces required to maintain static equilibrium.

2. Spontaneous structure in a deformed elastic sheet

An elastic sheet is a very simple physical system. It is a manifold that has a preferred distance between any pair of points: that is, a metric. It has an energy cost for displacing points from their preferred distance. This cost is local and quadratic in the displacements; this requirement essentially fixes its form. Finally, it has a spatial extent that is much smaller in one direction than in the others. The small dimension is the thickness h; the large dimensions are a much larger length L. The interesting spontaneous structure occurs for even the simple case of a flat sheet, where the metric is Euclidean. The ratio h/L is the only important physical parameter characterizing the system. It is in this sense that the system is simple.

The complex behaviour of an elastic sheet comes when external forces are exerted on it. For example, we may confine it within a sphere that is too small to accommodate the sheet in its resting state. The system must deform into the state of lowest energy compatible with the constraints. Remarkably the system chooses to deform in a singular way, with structures much smaller than its resting size L or the size R of the confining container. The deformation energy becomes focused into a small region rather than being distributed uniformly through the sheet (see figure 1). This focusing phenomenon is familiar to anyone who crumples a sheet of paper. What is less obvious is that many features of the singular structures are simple laws that are independent of the material.

Remarkably, *two* distinct singular structures called vertices and ridges play complementary roles in determining the structure. If our confining sphere contracts more and more, an initial flat state gives way to a sheet with a single vertex in it. Further contraction leads to more and more vertices. The ridge structures are a consequence of two or more vertices. Remarkably, these ridges turn out to be more important than the vertices that create them.

The reason for these singularities is based on simple geometric facts. First, the energy of a thin sheet can be divided into two distinct forms. One form is from bending of the surface; the other is stretching within the surface. A very thin sheet is arbitrarily easier to bend than to stretch; it may be viewed as virtually unstretchable. Second, an unstretchable sheet may not be bent in an arbitrary way. At every point in the surface, one of the two principal curvatures must vanish. That is, there is some line in the surface radiating from the point that is straight in space. If our surface has a vertex, the surrounding surface must be like a cone. At each point, the line pointing towards the vertex within the surface must be straight.

This constraint of vanishing curvature becomes surprisingly strong when a second vertex is present. We consider a generic point P on the surface that is in the vicinity of two vertices.

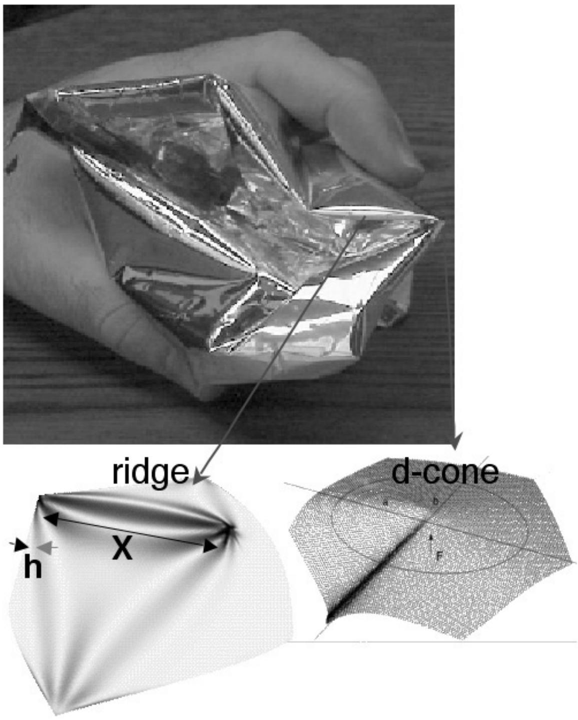

Figure 1. Top picture: a sheet of plastic film crumpled in the hand. The right arrow points to a numerical representation of a pointlike d-cone. The simulated sheet is a lattice of nodes and springs. The d-cone shape is made by exerting an upward force at the midpoint and constraining the sheet with the elliptical ring shown [6]. The left arrow points to a ridge singularity made numerically by cutting a sector out of two places on a sheet and then joining the cut edges together as described in [4].

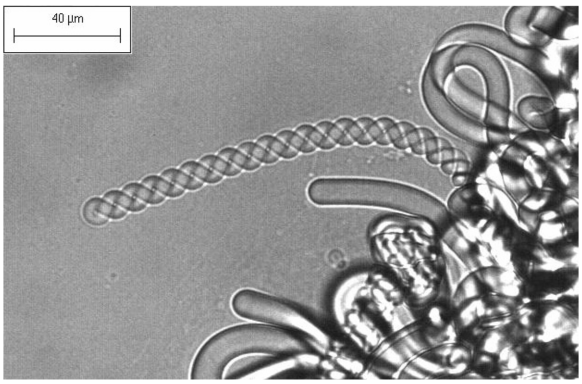

Figure 2. Light micrograph of myelin figures emerging from a drop of concentrated $C_{12}E_5$ surfactant in water, from [10].

If the sheet is unstretchable, there can be no curvature in the direction of the first vertex or the second. In general, these two directions are not the same; thus the curvature must vanish in two independent directions. That is, the surface must be completely flat at P. Since P is arbitrary, the entire surface must be flat except along the line joining the two vertices. Thus, in an unstretchable sheet, all the bending deformation would have to be concentrated on this joining line. The cost in bending energy would be infinite.

This fiction of unstretchable sheets shows why the deformation and energy must be concentrated along the line between two adjacent vertices. To deduce how great this concentration is, we must consider the competition between bending and stretching energy. Bending energy favours gentle bending at the ridge; stretching energy favours sharp bending. Once it is realized that this competition is responsible for the ridge structure, it is not difficult to find a simple geometry where the amount of bending and stretching energy can be estimated quantitatively [4, 5]. What emerges from this reasoning is an asymptotic description of the width w of the ridge in the limit $h/L \to 0$. Two consequences are notable. First, the width is asymptotically much smaller than L but much larger than the thickness h: $w \sim L(h/L)^{-1/3}$. Second, the ratio of bending to stretching energy is fixed as $h \to 0$; moreover, the asymptotic ratio is universal: bending energy is five times the stretching energy [5].

This example of ridges in elastic sheets shows how new and nontrivial forms of energy focusing can happen in these simple physical systems. It appears that this structure is only one of many forms of structure in these sheets [3, 6]. One very recent example discovered by University of Chicago student Tao Liang is especially intriguing. It arose from our studies of the d-cone structure, resulting from exerting forces at specific sites on the surface. The simplest d-cone arises from pushing a disc of paper into a coffee cup with a pencil point (figure 1, lower right).

The structure near the point has been much studied [3, 6]. Our interest was in the little-studied deformation at the constraining cup rim. We were interested in the bending caused by the rim. The principal directions of the bending are clear from symmetry: one principal curvature is in the radial direction towards the vertex, the other is in the tangential direction along the rim. Moreover, the tangential bending is constrained by the rim. This leaves only the radial bending undetermined. Inside or outside of the rim, this radial bending is negligible compared to the transverse bending. This straightness is a consequence of the near unstretchability of the sheet, as discussed above. However, when Tao measured this radial curvature at the rim numerically, he found something striking. The radial curvature was equal and opposite to the tangential curvature, so that the mean curvature vanished to the accuracy of our measurements [7].

This vanishing mean curvature is a robust phenomenon. It happens everywhere that the sheet contacts the rim. It happens for all the thicknesses we studied; the zone of radial curvature near the contact point changes with thickness, but the amount of curvature at the contact point does not. What sort of constraint can account for this surprising cancellation in the mean curvature? It cannot be a local constraint involving only the region near the contact point. If one isolates such a region and uses external forces to press the region against the rim, one can obtain a range of radial curvatures from zero to values larger than the tangential curvature. The cancellation cannot be a consequence of unstretchability. An unstretchable sheet must have vanishing radial curvature. Though stretching energy must play an important role in creating the cancellation, the phenomenon itself is not energetic but geometric.

This cancellation of mean curvature shows an apparent new law of behaviour in elastic sheets emerging from a surprising new direction. We do not understand it at present. But this phenomenon shows that major aspects of elastic-sheet singularities are awaiting discovery. These new properties are possible because thin elastic sheets are soft. There are particular modes of deformation that require arbitrarily small energy. This deformation ultimately leads to the re-entrant, interpenetrating structure of a crumpled sheet, with its nonlocal relationship between manifold points and spatial points.

3. Multilamellar tubes in fluid membranes

A second domain of new soft matter phenomena occurs in another two-dimensional structure called a fluid membrane. Many kinds of surfactant molecules, such as lipids, spontaneously form these membranes when mixed with water. As their name suggests, they differ qualitatively from the solid elastic sheets of the previous section. Any local bending requires energy as with an elastic sheets. But stretching in the form of shear strain within the surface carries no energetic cost. The behaviour of these membranes in solution is a rich and long-studied subject [8]. Our focus here is on one aspect of these solutions that has resisted understanding: the so-called myelin tubes.

A hundred and fifty years ago, a physician named Rudolf Virchow noticed a remarkable phenomenon when he diluted a concentrated extract of lipids [9]. Microscopic tubes grew from the concentrated region into the surrounding water (see figure 2). We now know that these tubes, called myelin figures, consist of concentric cylindrical fluid membranes [11]. Each membrane is a bilayer of lipid or other surfactant molecules. These bilayers are symmetric and thus their preferred state of curvature is zero curvature. The equilibrium state of a concentrated solution of lipids is a stack of flat, parallel bilayers. Yet under the right conditions, a structure quite different from this lamellar structure spontaneously develops, namely the tubular myelin figures. This growth is evidently some sort of non-equilibrium growth process. But the understanding of the conditions for creating the tube morphology and reason why this morphology is selected have eluded researchers, despite several insightful investigations [11, 12].

Recently a University of Chicago student named Ling-nan Zou found a way [13] to make myelins grow with a new level of control and precision. He showed that individual tubes could be grown from large disc-like lamellar stacks. His experiment shows the paradox of these tubes in an acute form. The mysterious structure grows directly from a disc structure that is expected to be more stable. In this experiment, as in other myelin-growing experiments, the tubes grow from regions in which the surfactants are very concentrated and water-starved.

With the clues provided by Zou's experiment, another student named Jung-ren Huang has made a promising hypothesis [14] of how the tubes form. The near-impermeability of the bilayers suggests that water cannot enter them except via some defect in the structure. Such defects are present in the experiment, but they occur at the edge of the disc opposite from where the tubes grow. Other features of the experiment suggest that the disc–tube complex does not rely on continuing growth for its stability. Growth can be stopped, yet the tube and disc retain their form over long periods.

What possible energetics or constraints could lead to an equilibrium structure like this disc–tube complex? After many unsuccessful attempts, Huang found an answer. First, he hypothesized that lipid and water enter the complex in such a way that the lipids remain starved for water. This hypothesis appears in good accord with observations. In such conditions, the lipid bilayers repel each other strongly: they seek a state in which their separation is as large as possible. They cannot just spontaneously separate, since water cannot enter. Instead, they seek that structure that maximizes their separation with a given quantity of lipid and water.

One can readily compare the spacing in the original disc morphology with the spacing that would result if the disc were converted to a myelin tube. The spacing is larger for the tube. The reason is connected to a familiar geometric fact. A circle encloses a given area of space with smaller perimeter than a rectangle does. When this fact is applied to a disc made of N concentric discs at spacing D_{d}, one finds a slightly increased spacing D_{t} when the disc is converted to a tube given by $D_{\mathrm{t}} = D_{\mathrm{d}}(1 + 1/(2N - 1))$. This increased spacing diminishes the repulsive energy. Under conditions like those observed experimentally, the decreased repulsion is sufficient to compensate for the bending-energy cost of making the tubes.

Here again the deformability of soft matter leads to new forms of spontaneously generated structure. The crucial qualities in this case were the easy bendability and shearability of a lipid bilayer combined with its strongly favoured incompressible two-dimensional morphology. The distinctive myelin structure itself depends on the possibility that the bilayers may interpenetrate. They are able to deform sufficiently to form the necessary concentric cylinder structure.

4. Forces and vibrations in a solid bead pack

Granular materials have recently aroused the interest of soft matter physicists [15, 16]. At first sight, these assemblies of hard grains appear to be the antithesis of a soft material. But on reflection these have much in common with other soft materials. Certain types of deformation are very strongly constrained; others have little or no constraint. A few beads floating in a large box may move freely with virtually no constraints. As the number of beads increases the motions are more and more hindered; there comes a point when the assembly of grains is solid and many of the grains cannot move. Then the system transmits shear stress. The point where this immobilization occurs is called the jamming threshold [17]. As this threshold is approached, an arbitrarily small increase in the volume fraction makes the difference between liquid-like motion and the jammed, solid state. To explain this discontinuous change of behaviour as the conditions change continuously is a big challenge. Such behaviour occurs in percolation phenomena, yet jamming appears different from percolation. In percolation, there is a clear criterion for when two sites are connected or not. In jamming, no corresponding criterion is apparent.

One urgent question in understanding jamming is to see how a marginally jammed solid reveals its closeness to an unjammed state. Although the particles cannot move without violating constraints, we want to know what motions are the easiest or least restrictive. For this purpose it is sufficient to take the simplest system that exhibits jamming. The studies described below use frictionless spheres as the grains. Deformation is either forbidden or expressed as a stiff, harmonic interaction between contacting grains. Using such models, several University of Chicago researchers have gained an understanding of how marginally jammed solids are distinctive.

The basic criterion of jamming in an N-particle system in d dimensions is that the particles are too constrained to move. That is, the Nd degrees of freedom are all fixed by the contact constraints. Denoting the number of contacts by N_c, this means there must be at least as many contact constraints as degrees of freedom: $N_c \geqslant Nd$. At the threshold of jamming, this inequality becomes an equality. The system is then said to be *isostatic*.

Isostaticity is a global constraint. It can be shown that removing even one contact from the set of N_c constraints gives rise to one mode of (infinitesimal) free motion [18]. Thus one way to probe the proximity of the jammed state to a mobile state is to investigate these modes of free motion. It is evident that these modes should involve many particles. The addition of a new contact constraint anywhere in the system is in general sufficient to suppress the free mode. That means the free mode must involve motion that would be suppressed by such a contact. Beyond this qualitative observation it is difficult to anticipate the nature of the free modes. Our numerical study from a few years ago [19] shows their fascinating character, as illustrated in figure 3. Each contact removed gives rise to a free mode that threads through the whole system. The motion is very heterogeneous, affecting some particles greatly, and others hardly at all. Often the greatest motions occur far from the removed constraint. The many modes corresponding to the various contacts comprise a rich interpenetrating network.

A second way to probe the easiest motions of a marginally jammed system is to weaken the contact constraints on all the contacts. For example, the hard contact constraints can be

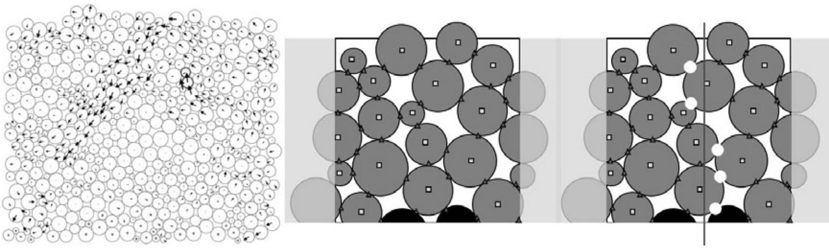

Figure 3. Left: a free mode [19] in a simulated stable granular assembly in two dimensions using the method of [18]. When the contact constraint for the two heavily drawn particles is removed, this free mode is liberated. Arrows indicate the direction and relative magnitude of the free motion. Centre: an isostatic packing with 18 particles and 36 contacts. The system is periodically continued in the horizontal direction. Right: contact constraints indicated by white erasures are removed along a boundary indicated by the central vertical line. Five contacts are removed, thus liberating five free modes. From these modes [21] deduces five variational trial modes that account for the anomalous low-frequency vibrational modes in the granular assemblies of [20].

replaced by stiff springs. Then the particles may be displaced at some cost in spring energy. Different displacement fields cost different amounts of energy. The energy is a quadratic functional of the Nd-component displacement vector. It is thus defined by a symmetric matrix in this vector space, known as the dynamical matrix. The easiest modes of motion in the jammed system are thus the eigenvectors of the dynamical matrix having the smallest energy eigenvalues—that is, the lowest-lying normal modes. Any differences between a marginally jammed system and an ordinary solid should show up in the form of these normal modes.

Recently Sidney Nagel, Leo Silbert and their collaborators [20] studied this matrix. They showed numerically that the distribution of modes is indeed much different from those of an ordinary solid. It is customary to express this distribution as the density of vibrational frequencies. Each frequency is the square root of the corresponding energy of the dynamical matrix. An ordinary solid in three dimensions has a density of states that grows from zero at zero frequency, increasing quadratically with frequency. The corresponding density of states for their simulated jammed solid indeed shows qualitatively greater deformability. The density of states does not diminish to zero as the frequency goes to zero; instead, it remains constant. This constant is independent of the system size. However, the reason for this behaviour and the nature of the many low-lying modes was a mystery.

Very recently an explanation for the low-frequency modes was proposed by a visiting student named Matthieu Wyart [21]. He was able to relate the free modes arising from removed constraints to the low-frequency normal modes, using an insightful variational ansatz. From the set of free modes arising from breaking boundary constraints, one can impose a gentle distortion that allows these constraints to be restored (figure 3). The frequencies of such modes are comparable to the lowest acoustic frequency in a well-connected solid with a large excess of contacts. In such a solid, the number of such modes is of order unity. However, in the marginally jammed solid the number of such modes is proportional to the number of boundary particles—a number indefinitely greater than unity. Given this new picture of the modes, one can predict quantitatively how the lowest modes of the marginal system give way to ordinary acoustic modes as the system is progressively compressed [21].

5. Conclusion

The subtle structures I have discussed above represent new forms of spatial correlation in matter. The language of correlation invites comparison with the intriguing forms of correlation emerging in hard condensed matter. Examples include high-temperature superconductivity [22], quantum Hall liquids [23] and quantum-condensed phases of trapped atoms [24]. These new quantum collective behaviours are subtle and fundamental. But one need not seek out such exotic quantum systems in order to find fundamental new collective behaviours, correlations, and structures. The simple world of soft matter is providing such new structures in abundance.

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