

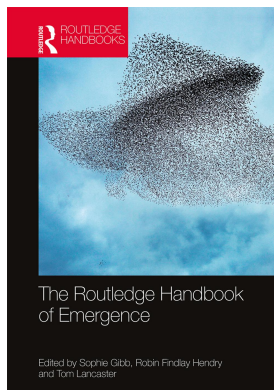
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### Soft Matter – an Emergent Interdisciplinary Science of Emergent Entities

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# SOFT MATTER – AN EMERGENT INTERDISCIPLINARY SCIENCE OF EMERGENT ENTITIES

*Tom McLeish*

From the decade of the 1990s, terms such as ‘soft matter’ and ‘soft matter physics’ began to appear with increasing regularity in conference announcements, review articles and books. Previously a much more fragmented disciplinary landscape had been evidenced by repeated reference to the individual research topics that ‘soft matter’ later subsumed: colloid physics, polymer physics and chemistry, liquid crystal science and more.<sup>1</sup> The language strongly indicates not simply a summation of research programmes, but the recognised emergence of a new field of science. The coherence of soft matter principally draws on both conceptual and experimental foundations, as we shall see, but the superficial consequence is that materials falling under the labels of colloids (Lekkerkerker and Tuinier 2011), polymers (Doi and Edwards 1986), liquid crystals (de Gennes and Prost 1995), self-assembly (Witten 2004), membranes (Safran 2003), foams (Weare and Hutzler 1999), granular materials (Duran 2000), biological materials (Nelson 2004), glasses (Jones 2002) and gels (Rubinstein and Colby 2003) now find a common scientific home within soft matter (Jones 2002). A more recent extension into biological science benefits from the ubiquity of soft matter material structures at the nanoscale level within biological cells (McLeish 2011). Conversations between these subfields, as well as within them are, as a consequence, now commonplace.

Furthermore, the nature of experimental and theoretical methodologies, epistemology and ontology in soft matter means that the field furnishes a rich conceptual hunting ground of emergence, top-down causation (Ellis 2012) and potential anomalies in supervenience (Batterman 2002) and multiple realisability (Aizawa and Gillett 2009) for the philosopher of emergent phenomena. This is not surprising given that one of the sources of the new subfield was the wider field of ‘condensed matter physics’ employed by Anderson (1972) in a landmark articulation of (weak) emergence as *More Is Different*. Soft matter provides many illustrations of Anderson’s claim that the notion of the ‘fundamental’ in physics should not be tied to any one scale of length or energy.

The scientific history of soft matter science was propelled by a combination of communication within the scientific community (through conferences, research departments and journals that attracted scientists from more than one subfield), intrinsic conceptual overlap and commonality and visionary leadership from a small number of pioneering scientists. Pre-eminent among those were two theoretical physicists, Pierre-Gilles de Gennes in France (and later Nobel Laureate in physics for 1993) and Sam Edwards in the UK. Both of these leaders realised that

broad conceptual frameworks and powerful theoretical techniques from other areas in physics could be applied to soft matter systems and that, as a result, simple and deep structure appeared beneath what had previously appeared as a disparate collection of very complicated materials. The conceptual leaps were considerable: ideas from fields dominated by the structures of quantum mechanics and many-body physics required translation into systems dominated by thermal physics, and even from those traditionally thought of as branches of chemistry (polymers, liquid crystals). In the case of de Gennes (a former student of Friedel), this background was superconductivity; for Edwards (a former student of Schwinger), quantum field theory. We examine the deep mathematical structures that generate this surprising connectivity in the next section, but first identify the physical characteristics of soft condensed matter systems. This chapter continues with a discussion of two relevant examples of philosophical interest and closes with an assessment of the application of soft matter physics to biological systems.

### Characteristics of soft matter

First, the energy scale of internal interactions in soft matter is comparable to the quantum of thermal energy,  $k_B T$ . So in contrast to systems whose physics are dominated by quantum mechanics, thermal transitions between microscopic energy levels are frequent, and quantum coherence is (usually) negligible. Classical statistical mechanics furnishes, as a consequence, the appropriate set of tools to model and calculate with. Fluctuations in structure are large, and local equilibrium the dominant paradigm.

Second, mesoscopic structure or order at the length scale of several nanometers is almost ubiquitous in soft matter systems. For example, colloids are suspensions of particles at this scale suspended in a solvent – stabilised because the thermal energy is large compared to their typical gravitational potential energy in the bulk fluid. To give some other examples: polymers are long-chain molecules of very high molecular weight whose internal flexibility results in configurations in solutions or in melts such that the random macromolecular coils are typically several tens of nanometers in scale. Liquid crystals are solutions of molecules with strong directional order that support lamellar and defect structures dominated by this length scale (much larger in this case than the scale of the molecules themselves). The dominance of this structural, ‘mesoscopic’ length-scale (neither macroscopic – mm to m, nor truly microscopic at the atomic dimension of sub-nanometer) is also responsible for the epithet ‘soft’. The existence of a typical structural length  $l$ , together with the condition of strong thermal dominance, leads to a natural estimate of the elastic modulus  $G \sim (k_B T/l^3) \sim 10^6$  Pa, a thousand times smaller than the modulus of metals or ceramics, and in the region of that of rubbers (of course another soft matter exemplar – a class of gels) (McLeish, Cates, Higgins and Olmsted 2003).

Third, the dynamics of soft matter systems are often very rich and contain one or more ‘slow variables’ – coordinates that due to constraints or internal energy barriers, return to equilibrium on much longer relaxation timescales than the typical intermolecular ballistic trajectory time (at 300 K) of  $\sim 10$  ps (Larson 1999). An example is the set of very slow viscoelastic relaxations in solutions and melts of polymers (Doi and Edwards 1986). These are generated from the multiple topological interactions between polymer chains, which typically (for chemically formed polymers) cannot cross each other. Another example is given by the long, and sometimes extremely long, structural rearrangement times in foams and glassy materials in the approach to the glass transition. In these cases dynamic arrest can arise from the requirement that any dynamical move implies the simultaneous rearrangement of increasingly large coherent volumes of the material. This in turn demands a large energy fluctuation  $\Delta E$ , suppressed by the Boltzmann weight  $e^{-\Delta E/kT}$ .

A fourth characteristic of soft matter is the thermodynamic (and emergent – Ellis 2012) property of multiple realisations at lower levels than the operative structure. For example, even when states of a colloidal or polymeric system are characterised by a specific configuration of colloidal particles, or entire polymer chains (at suitable small-scale resolution), there are many configurations of solvent molecules and/or of subchain states that correspond to the same ‘meso-state’. For many purposes (e.g. the analysis of scattering experiments, or the measurement of osmotic pressure) even coarser variables, such as local mean density averaged over a mesoscopic volume, are sufficient and hyper-exponentially more multiply realised in microstates. The techniques of statistical mechanics can therefore be applied even to these mesoscopic structural volumes.

Fifth, and consequent on the other four, the variety of soft materials and their phases exhibits a high degree of ‘universality’. Essentially the same emergent material arises from different underlying chemistries. With a rescaling of a few coarse-grained parameters, the mapping may be essentially exact. So, for example, the linear elastic modulus of a polymeric gel is dependent on the density and distribution of the cross-links between its constituent polymer chains, not on the chemistry of the chains themselves. The similarity may persist into even non-linear response.

The interdisciplinary nature of the (multiple) sub-discipline of soft matter is remarkably broad. The nature of the materials required in each of the exemplars listed earlier frequently implies just as significant challenges to synthetic chemistry in their fabrication as it does to theoretical and experimental physics in explanation and characterisation. In nearly every case soft matter has also found application in structural and functional materials (personal care products, plastic materials, displays and more) so engineering disciplines are frequently involved, often at a fundamental level, while the scientific community conversation over soft matter spans industry and academia. The more recent application of soft matter science to the analysis of biological and bio-inspired phenomena (Nelson 2004) increases the interdisciplinary palette even further. The consequences are as yet hard to predict, but already two promising directions for research have been generated by the confluence of biology and the statistical physics of soft matter. The first sheds new light on the physical basis biological phenomena; the second draws inspiration from biology to define new research programmes in physics. An example is the rapidly growing field of ‘active matter’. The pickings for historians and philosophers of science interested in the social functioning of scientific communities will, I suspect, prove very rich when a little more dust (some of it ‘active’) has settled (McLeish 2011).

### **Theoretical and experimental provenance of soft matter**

The selection of de Gennes and Edwards as the two leading pioneers of soft matter as a recognised sub-discipline is not a controversial one. But in each case their contribution illustrates the power of theoretical and explanatory concepts to unify and propel research programmes, especially when accompanied by ready-made mathematical machinery. In this case, the techniques of path (and functional) integration from quantum field theory and symmetry breaking (especially within the Landau-Ginzburg theory of superconductivity) proved particularly powerful tools to the new field, witnessing at the same time the deep commonality enjoyed by the underlying structures of physics.

#### ***Polymer physics and path integrals***

The concept of a polymer within the mathematical physics of statistical mechanics illustrates the point. Feynman’s early work on quantum theory provided a third mathematical representation of quantum mechanics, in addition to the two previous instantiations arising from the wave

mechanics of Schrödinger and the matrix mechanics of Heisenberg. Feynman's contribution was the framework of *path integrals*. In particular, he found a new way of conceiving of the propagator  $G(\mathbf{r}, t)$  for the wave function of a quantum particle. This central and generative object is the ('Greens-') function that gives the amplitude that the particle is at position  $\mathbf{r}$  at time  $t$  given that it was at the origin  $\mathbf{r} = \mathbf{0}$  at time  $t = 0$ . After some formal care in definitions, this function can be calculated as a formal sum over all possible classical trajectories from  $(\mathbf{0}, 0)$  to  $(\mathbf{r}, t)$ , weighted by a phase  $S$ , itself a functional of the path, denoted as follows:

$$G(\mathbf{r}, t) = \int D[\mathbf{r}(t)] e^{\frac{i}{\hbar} S[\mathbf{r}(t)]} \quad (1)$$

Here, the physical contribution to the phase from each path  $S([\mathbf{r}(t)])$  is the classical action for the single path  $[\mathbf{r}(t)]$ , and the integral is the *functional* or *path* integral – summing not over the measure of a single variable, but over all possible functions (in this case paths) connecting the origin to the space-time point  $(\mathbf{r}, t)$ . This extension of the notion of an integral to a functional integral is denoted by the special measure  $D[\mathbf{r}(t)]$ . The action is, in turn, the (standard) time integral of the classical Lagrangian for that path, so that, for a single spinless particle of mass  $m$  moving in a potential  $V(\mathbf{r})$ , the expression for the propagator becomes (Feynman and Hibbs 1965):

$$G(\mathbf{r}, t) = \int D[\mathbf{r}(t)] e^{\frac{i}{\hbar} \int_0^t \left[ \frac{m(\partial \mathbf{r}}{\partial t})^2 - V(\mathbf{r}(t)) \right] dt} \quad (2)$$

The path-integral formulation illustrates very powerfully the connection between classical and quantum physics – the former provides phases for the state-addition of the latter. It can also be shown that, in the classical limit, where these phases change very sensitively in response to perturbations of the paths, that the propagator is dominated by a quantum mechanical superposition of paths that lie very (exponentially) close to the classical trajectory. Far from the classical path, phase contributions from close trajectories cancel each other. Techniques for the computation of such path integrals in various potentials, and under perturbation theory, were developed in the 1950s and 1960s.

In statistical mechanics, the generative object within a theory for any physical system is the *partition function*,  $Z(\{X_i\}, T)$ , where the  $\{X_i\}$  are the external constraints on the system and  $T$  the temperature.  $Z$  is calculated as a sum over all accessible microstates of the system, weighted by a 'Boltzmann Factor':

$$Z(\{X_i\}, T) = \sum_{states\ i} e^{-E_i/kT} \quad (3)$$

All thermodynamic properties can be calculated from this object – for example, the free energy  $F = kT \ln Z$ . In the case of a polymer, a single microstate is just one of the spatial paths accessible to it. Providing that the molecular chain is long enough, even the single steps of the path can be large compared to the scale of atoms, so that an appropriate mathematical coarse-graining becomes a trajectory  $[\mathbf{r}(s)]$  in terms of a contour variable  $s$  that runs from  $0$  at one end of the chain to the total number of steps ('monomers')  $N$  at the other end. A small subchain of  $\Delta s$  steps of mean length  $b$  is a small random walk and so has a Gaussian distribution of end-to-end displacements  $\Delta \mathbf{r}$ ,  $\exp(-3(\Delta \mathbf{r})^2/2b^2\Delta s)$ . Adding in this local weight for each small section of the polymer and allowing the chain to pass through a general potential energy for its monomers  $V(\mathbf{r})$  generates an expression for the partition function of a polymer chain that takes the form of a

path integral, since the sum over states is simply a sum over paths constrained to the same end-to-end displacement  $\mathbf{R}$ :

$$Z(\mathbf{R}, T) = \int D[\mathbf{r}(s)] e^{\frac{1}{kT} \int_0^N \left[ \frac{-3}{2b^2} \left( \frac{\partial \mathbf{r}}{\partial s} \right)^2 - V(\mathbf{r}(s)) \right] ds} \quad (4)$$

Comparing the expressions (4) and (2) demonstrates the remarkable analogy between the quantum mechanics of single particles and the statistical mechanics of polymers. Both ‘sum over paths’ follow the visual recipe of Figure 20.1.

The contour length  $s$  takes the form of an imaginary time variable in the Feynman propagator. The (square) step length maps onto an (inverse) particle mass, and the temperature (suitably converted to the units of energy) plays the role of Planck’s constant. Varying the temperature of the polymer system is the correspondence of varying the scale of dimensionless action of the quantum system between quantum and classical limits. So, for example, extreme tension applied to a polymer chain stretches it so that all fluctuations in its typical path lie close to a ‘classical’ trajectory of a straight line between its endpoints. Such a situation is equivalent to the large-mass limit in the quantum case, where this is the dominant classical trajectory of the particle.

For all that these considerations might appear arcane, they provide the physical insight, as well as computational strategies, into phenomena such as rubber elasticity and nanoscale structuring of reinforced plastics. When a rubber band is stretched, the force with which it responds comes not from any physics at the atomistic level, such as the stretching of molecular bonds. Rather, it is an emergent effect arising from the increased restriction on the multiplicity of realisations of all the polymer chains belonging to the rubber network into which they are chemically linked. Similarly, the local separation of nanoscale volumes of rubbery polymer within a glassy matrix of more brittle polymer – an example is the self-composite styrene-butadiene (SBS) – can be conceived of as the interplay between the two terms in the ‘action’ of the polymer partition function (4). A repulsive effective potential  $V(s)$  between the two different chemistries of polymer chain, which would on its own drive them into two bulk phases, is moderated by the ‘kinetic energy’ term penalising polymer chain stretch. Together the two effects create the local length scale and structure of the all-important separated structure. This in turn leads to the remarkable emergent property of toughness.

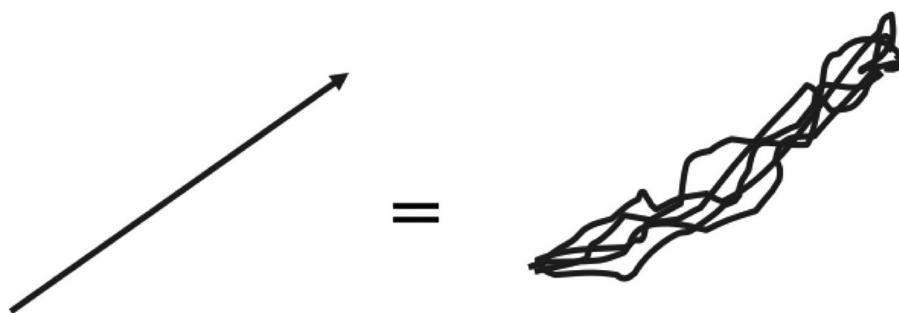


Figure 20.1 The propagator (arrow on left) can be calculated as a weighted sum over all possible paths from starting to finishing points. A situation close to the classical limit (for the quantum particle) or high-tension limit (for the polymer) is illustrated, where the highly weighted paths cluster around a single trajectory.

### Liquid crystals and symmetry breaking

A similar deep structure from condensed matter physics (superconductivity) and field theory (the so-called ‘Higgs mechanism’) provided a conceptual framework for the physics of liquid crystals. For all these systems exhibit ‘phase transitions’, as a function of temperature, that change the emergent symmetry at the bulk material level. As we saw, liquid crystals possess molecules with a high degree of anisotropy – one can think of them as molecular ‘rods’ or ‘needles’. At high temperatures, the thermal fluctuations at the molecular level are large enough to maintain complete randomness in the distribution of orientations of the molecular rods. At the macroscopic level the material is a fluid – with no translational structure or preferred orientation, even though there is very local orientation (‘short-range order’) in the immediate vicinity of a single molecule, since near neighbours tend to be correlated in their orientation. However, as the temperature is lowered, the thermal fluctuations become weaker, and the local interactions between rods that tend to align them are able to drive a transition of the entire system. In the resultant ‘nematic’ phase of the liquid crystal, a preferred orientation appears at the bulk level. Although there is no spatial order so that the system is still a fluid in its propensity to flow, there is orientational order (experimentally apparent, for example, in the optically polarising properties of the fluid).

When the liquid crystal system is described in terms of the emergent field of orientational order, a mathematical similarity to phase transitions in superconducting materials becomes apparent. The general structure of the formalism invokes a field of coarse-grained local ‘order parameter’  $S(\mathbf{r})$ . In the case of a liquid crystal,  $S$  describes the degree of local orientational molecular order; in the case of a superconductor, it measures the strength of the superconducting wave function. The free energy becomes a functional of the field  $S(\mathbf{r})$ :

$$F(S(\mathbf{r}), T) = \int \left\{ a_0(T) + a_2(T)[S(\mathbf{r})]^2 + a_3(T)[S(\mathbf{r})]^3 + a_4(T)[S(\mathbf{r})]^4 + K(\nabla S)^2 \right\} dV \quad (5)$$

Symmetry considerations can eliminate some of the orders of expansion of the field in this expression – for example, in two dimensions the nematic liquid crystal order parameter must satisfy the symmetry  $S \rightarrow -S$ , so  $a_3$  can be set to zero. The ‘Landau–Ginzburg’ form of (5) was first written down as an ansatz for a coarse-grained free energy in terms of averaged quantities. Later a formal procedure enabled the coarse-graining to be computed from a fine-grained Hamiltonian.

The phenomenology of (5) is very rich, identifying similar phenomena in magnetism, liquid crystals and particle theory. To take one example, when the symmetry  $S \rightarrow -S$  applies, a ‘second-order phase transition’ appears at the temperature for which  $a_2 = 0$ . When  $a_2 > 0$  the equilibrium value for the field  $S$  is zero everywhere, but when  $a_2 < 0$ , the free energy is minimised at  $S = \sqrt{-a_2/2a_4}$ . Below the transition point (which might be the onset of a finite magnetisation or a finite orientation of a liquid crystal field), the field grows continuously in strength. The form of  $F$  at temperatures above and below the transition is shown in Figure 20.2.

When spatial structure is added to the theory (for example, the last term in (5) penalises spatial gradients in the order parameter), the appearance of ‘textures’ and ‘defects’ can be understood. The underlying symmetry of the system, expressed by zero field at high temperature, is at low temperature recovered by an unbiased choice of direction in which the symmetry is broken locally. This naturally gives rise to spatial structures in which the direction of the liquid crystalline order is different at different spatial locations. To accommodate such spatial variation of local orientations, very localised ‘topological defects’ arise – points at which the orientation field is mathematically singular and cannot be defined. Figure 20.3 illustrates four possible such topological defects in terms of the local behaviour of the orientation field around them and an experimental micrograph of a nematic liquid crystal that contains instantiations of these objects.

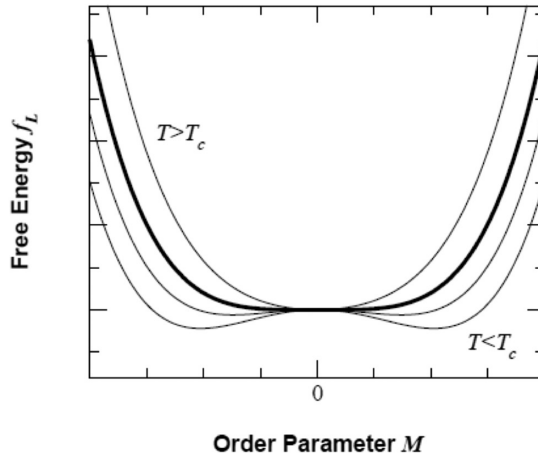


Figure 20.2 The Landau free energy (5) for a field undergoing a continuous phase transition

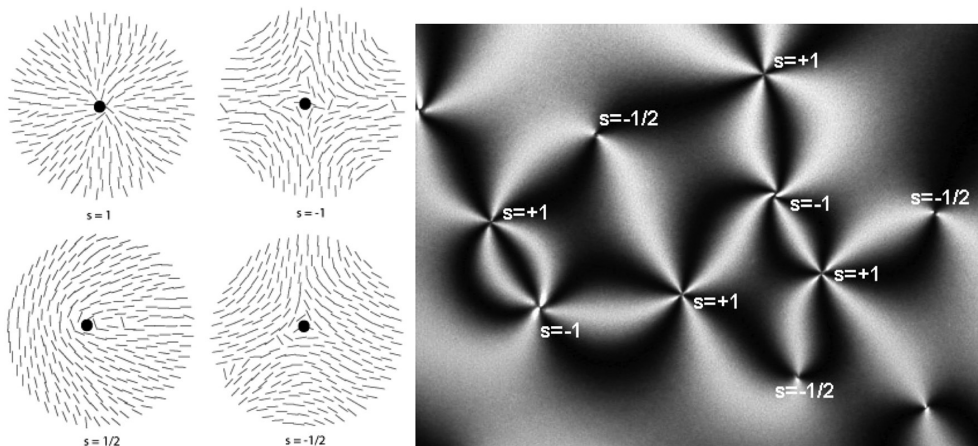


Figure 20.3 (a) Nematic liquid crystal defects of four different orders; (b) a spatial defect structure containing the examples in (a) under polarised light microscopy

[Courtesy of B. Senyuk, University of Colorado]

The nematic liquid crystal, in which the only order parameter is the mean molecular orientation, is the simplest of a very complex family of materials. ‘Smectic’ liquid crystals introduce one-dimensional (layered) order in addition to the orientational order (so breaking spatial symmetry), and ‘cholesteric’ liquid crystals introduce the characteristic of twist and a breaking of mirror symmetry. The defect structures of these higher-order liquid crystals are correspondingly richer. They also possess similarity mappings with completely different physical systems. So, for example, an analogue of a vortex phase in a (Type II) superconductor that supports a lattice of magnetic field lines was predicted in smectic cholesteric liquid crystals and later found experimentally as their ‘twisted grain boundary’ phase.



### Experimental commonalities

It would be wrong to suggest that the coherence of soft matter as an emergent discipline is generated entirely by its underpinning theoretical ideas, although such conceptual cross-ties are essential. There is also a strong family of experimental tools that reflect the universality within the materials themselves, and especially their meso-structural properties. Characterising the nano-scale structures within polymeric, colloidal or membrane-dominated materials relies on both electron and optical microscopies (see Figure 20.3). However, material opacity and complexity mean that spatial information is often acquired more effectively by scattering techniques. Rather than probe spatial structures directly, recording the variation of density at different *positions*, scattering of light or, more often, x-rays, responds to the averages of density waves of different *wavelengths* within the materials (one might speak loosely and say that scattering is the Fourier transform of microscopy).

Neutron scattering is especially associated with soft matter for a number of reasons. Neutrons possess a wavelike nature by virtue of quantum mechanics, and as neutral particles, are not affected by the charged electrons of atomic and molecular orbitals. They can therefore penetrate into the bulk of any matter whose nuclei scatter them weakly enough. The existence of different isotopes of elements gifts another precious tool to the neutron scatterer from soft matter: careful synthetic chemistry may incorporate different isotopes into selected parts of the molecular components of a material. Although such ‘isotopic labelling’ does not change the chemical behaviour of the molecules, thus leaving the structure unchanged, the strength with which different isotopes scatter neutrons can differ markedly. The most common secondary isotope of hydrogen – deuterium – scatters neutrons, but with the opposite phase. So with careful quantitative matching, hydrogen-containing molecules can be made to ‘disappear’ from a neutron-scattering experiment. In this way, the spatial structuring of components of a soft matter system may be visualised. For example, polymers composed of blocks, themselves comprising segments of different chemistry (we recalled a commercial example in the two-phase material SBS earlier) may self-assemble into periodic structures so that sub-chains of the same chemistry are in mutual contact. Scattering from labelled polymers can pick out the spatial patterns of just one component and by repeated application can provide very rich and selective spatial information on self-organised structures in soft matter.

There is an appealing and direct link between scattering experiments and common theoretical framings of soft matter systems. In the absence of crystalline order, the expressions for the density of free energy (in terms of density, or concentration of one or more components) of polymers, liquid crystals or colloids at the coarse-grained level must obey translational symmetry. They are also typically short range and so contain powers of the density and its spatial gradients and higher derivatives; equation (5) is an example, with the field  $S(\mathbf{r})$  now interpreted as a density. If this local variable is also the density of relevant *scatterers* within the experimental framework, then the scattering function (the Fourier transform of the scattering density) can be calculated as a thermal average directly, where the spatial gradient terms become simply algebraic in the scattering function. The simplest example is the very common Ornstein-Zernicke function for a field whose free-energy density is quadratic in density and its gradient:

$$F(\rho(\mathbf{r}), T) = \frac{1}{2} \int \left\{ a_2(T) [\rho(\mathbf{r})]^2 + K (\nabla \rho)^2 \right\} dV \quad (6)$$

In terms of the scattering intensity  $I(\mathbf{k}) = \langle \widetilde{\rho(\mathbf{k})} \widetilde{\rho(-\mathbf{k})} \rangle$  predicted experimentally ( $\mathbf{k}$  is both the experimental ‘scattering vector’ and the Fourier transform conjugate variable for  $\mathbf{r}$ ) from

this density field, the form is simply ‘read off’ from (6) once the ‘recipe’ Gaussian integrals are applied:

$$I(\mathbf{k}) = \frac{1}{2\pi} \frac{V\rho^2}{(a_2(T) + Kk^2)} \quad (7)$$

Scattering experiments possess a pleasingly direct access onto the coarse-grained, mesoscopic Hamiltonians of soft matter. The presence of thermal disorder, spatial symmetry and local structure of interactions means that the natural language for theory is in the scattering function of the density variables, not in their spatial correlation functions. Spatial structures are better thought of as consequences of, rather than fundamental to, the physics. So to complete our example, the density correlation function corresponding to the general quadratic and local expression for the free energy of a scalar field in (6) that has the scattering function of (7) takes the ‘Yukawa’ form, of a screened Coulomb field:

$$I(\mathbf{r}) \equiv \rho(0)\rho(\mathbf{r}) = \rho^2 \frac{e^{-r/\zeta}}{(r/\zeta)} \quad (8)$$

where the screening length  $\zeta = \sqrt{(K/a_2)}$  reflects the interplay of energies from density and its gradient, manifest in the Hamiltonian (6) in terms of the Fourier variables. Near a critical point where two mixed polymers of different chemical character begin to demix, large and long-range fluctuations in composition are modelled by this form of correlation.

The feature of slow dynamical structures within soft matter motivates a further set of techniques to identify and characterise, common to soft matter, and which focus on the mechanical properties of the material. Furthermore, there are complex connections between the structural changes at the nanoscale and the resultant dynamical properties of the bulk material. When these appear in macroscopic flow or deformation, the corresponding techniques fall under the banner of ‘rheology’. Careful application of different geometries of material deformation – shear (equivalent to ‘lubrication flow’) and uniaxial extension (equivalent to ‘fibre spinning flow’) and at different rates – can identify processes of structural reorganisation at a range of timescales. The mechanical stress on the material surface is typically measured at the same time through sensitive transducers. Since stress has many components, corresponding to forces on the material surfaces in both parallel and normal directions, the rheology of soft matter is often especially rich. There is a historical and conceptual resonance with scattering experiments here: Weissenberg, who invented one of the first rheometers for soft matter, called it a ‘rhegoniometer’, deliberately alluding to the detector device used in scattering experiments. He conceived of rheology as a sort of scattering experiment – samples ‘received’ a range of geometries of strain and ‘scattered’ a range of geometries of stress (McLeish 2008).

Examples will serve to illustrate the point. The uncross-linked melt of polymers, which flows as a liquid at long timescales, mimics a cross-linked gel when mechanical oscillation is performed on it at high enough frequencies. This is because the polymer chains are subject to *topological* constraints – they are unable to pass through each other, even if they are not chemically linked. So in the melt form, the dynamical reconfigurations that a single chain would rapidly adopt through random thermal motion are strongly suppressed. Since these are precisely the reconfigurations that would be responsible for the relaxation of mechanical tension created by extending or deforming the chains through flow, they will retain these strained configurations for extended periods until much slower, topologically allowed modes of motion are able to re-equilibrate the ensemble. In this case, de Gennes and Edwards together contributed insights that identified the predominant

slow mode of structural relaxation in dense, entangled polymer systems. Each individual polymer chain is constrained by topological constraints from its neighbours to a tube-like path that follows its own contour. It renews its (random-walk) configuration via the only non-constrained mode of Brownian motion – the one that carries its centre of mass in diffusive dynamics along this path. This is the motion de Gennes termed ‘reptation’ (Doi and Edwards 1986) and is described in more detail later. When the flow rate is increased, the topological constraints between chains are removed by convection as well as by the diffusional reptation, thus endowing the material with a ‘shear-thinning’ property (the apparent viscosity reduces with flow rate).

A range of colloidal fluids with very dense packing exhibit an opposite effect: while fluids at low flow rates, they may suffer a strong increase in the effective viscosity as the imposed flow rate increases, leading in some cases to a liquid-to-solid like transition. As in the dense polymer case, this solidification is a macroscopic consequence of microstructural processes. But here, rather than a moderation due to flow, as in the (topological) interactions of polymer chains, attractive colloidal particles suffer an increased rate of collision in a shear flow and can build up temporary chains of particles under compressive load that can no longer disassemble through diffusion. Such ‘jamming transitions’ constitute a highly cooperative non-equilibrium change of state and give rise to remarkable bulk phenomena. An example is the extreme, but temporary, thickening of cornflour paste made with very little water or milk.

The discovery that polymer and colloid chemists, theoreticians thinking about the same systems, and experimentalists exploring the simultaneous measurement of macroscopic and microscopic structure in complex fluids all faced common challenges and had developed similar tools proved a significant cohesive force in the constitution of the new field of soft matter. Ideas from one material-dependent subfield nourished others, and continue to do so.

### **Multiple realisation and top-down causation – examples from polymer physics**

From what has been said already, there is clearly a rich field of exemplars in soft matter physics that constitute relevant source material for current discussions within the philosophy of science. In particular, soft matter physics indicates why the level of physical structure, energy or coarse-graining to which is attributed the label ‘fundamental’, or assigned causal powers, is up for debate (Anderson 1972). In this section we re-examine two examples from the case of polymer physics that explore two important ideas for the philosophy of emergence: multiple realisation and top-down causation.

#### ***Multiple realisation***

A central theme in the discussion of the tension between emergence and reductionism has been the notion of multiple realisability (Bickle 2016). Originally adopted by Putnam and Fodor in the context of multiple realisability of mental states by physical ones, it has since been recognised as a pervasive yet contentious challenge to reductionism (Aizawa and Gillett 2009). The claim against reductionism is that the observation that all mental (or otherwise defined high-level or ‘special science’ states) are multiply realised renders implausible the reductionist requirement that all high-level states, including their causal relations, map onto physical (low level) states via bridge laws that preserve causal relations for every realised kind.

The idea is normally discussed in the context of the contested reduction of the mental to the physical, but examples from soft matter, underpinned as they are by statistical mechanics, provide rather cleaner examples of multiple realisation that are more straightforward to discuss (in that all

the science is understood at both levels) than the mental. We saw earlier (the path integral expression of equation 4) that the statistical physics of a polymer chain is expressed mathematically and explicitly as a sum over the multiple realisations of its end-to-end vector. One emergent quantity that can be derived from the integral is the effective force-displacement relationship  $f(\mathbf{R})$  of this vector between the chain endpoints. From standard statistical mechanics:

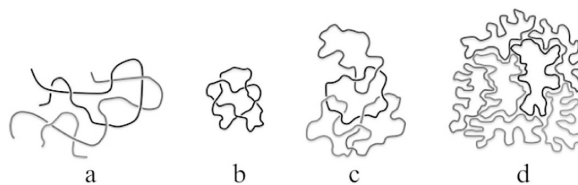
$$f(\mathbf{R}) = -kT \nabla_{\mathbf{R}} \ln Z(\mathbf{R}, T) = -\frac{3kT\mathbf{R}}{2b^2} \quad (9)$$

The Hookean linear spring behaviour of the polymer is an emergent property of the entire chain, predicated *on the multiple realisability of the microstates alone*. Here the emergent physics at the level of the polymer chain (its ‘rubber elasticity’) depends on the many realisations of the chain configuration and nothing else. Furthermore, causal powers of the chain itself (its role in sustaining elastic waves in a cross-linked polymer rubber, for example) depend upon this chain-level property, not the time-dependent microphysics of the chain segments. This is because, through the thermal coupling to the environment accounted for in the canonical ensemble within which the path integral is performed, the dynamics of the microstates are (explicitly) non-causal, while the dynamics at the level of the Hookean chains are.

### ***Top-down causation – long-range topological order in polymer rings***

The topological physics that constrains the snake-like ‘reptation’ diffusion of polymers in the melt phase, albeit for kinetic, not thermodynamic, behaviour, becomes much stronger in the case of polymer rings. This fascinating soft matter system has emerged both experimentally and theoretically to generate a rich and puzzling ensemble of materials from the liquid to the solid. In these cases the polymer chains have no ends at all, but are synthesised as connected rings. The richness in the multiple possibilities for the macroscopic behaviour of a system of many such rings arises from the multiplicity of topologies that the rings may enjoy with respect to each other.

Figure 20.4 demonstrates the variety of topologies of a single ring (4b) and multiple rings (4c and d) in contrast to the temporary interactions of non-cyclised chains (4a). The unlinked system of 4b has remarkable properties (Eveaers 2004) – the constraints on the chains generated by the trivial topology (all linking numbers are zero) becomes, via its large restriction on entropy in the partition function (multiple path integral) of the system, a huge ‘topological pressure’ on the chains. They collapse, as a consequence, into much smaller dimensions that would be the case for free rings. Furthermore, the emergent material is a fluid, with no memory of its initial configuration and with each polymer able to diffuse arbitrarily long distances. The linked melt (4c), by contrast, generates a solid at the macroscopic level, even though the polymer chains possess as



*Figure 20.4* Possible configurations of polymer chains in different topological states in a melt of other chains; (a) linear chains in Gaussian interpenetration; (b) a single ring-chain self-knotted (the trefoil knot); (c) a melt of Gaussian ring-chains with typically complex topological invariants leading to an emergent network; (d) melt of rings in trivial topology in crumpled globule states.

much local mobility as they do when unlinked. The long-range topological order between the linked rings both localises their mobility and creates an emergent elastic solid from the ensemble.

From the point of view of emergence and causation, this system bears strong structural similarities to the fractional quantum Hall effect (FQHE), discussed recently by Lancaster and Pexton (2016). High-level and causative degrees of freedom (those of the elastic solid) emerge because of the long-range topological constraints. Without knowing the linking numbers of the chains, constituting a set of variables to be specified in addition to the molecular-scale configurations, the trajectory of the system at the coarse-grained scale is not possible to compute. Furthermore, the causative macroscopic trajectory is explored through multiple realisations of the low-level molecular (chain-linked) variables, which are themselves not causal (they are coupled to an external heat bath which exchanges heat with them in the canonical way). The topological variables are not an epistemological convenience in this case – a charge that can be made of the coarse-grained Fourier variables of theories such as the Landau-Ginzburg Hamiltonian of equations (5) and (6). They appear as ontologically constitutive of the emergent material, be it the gel-like solid of the linked system, the viscoelastic fluid of the unlinked melt, or any one of the infinite family of anomalously viscoelastic fluids that lie between these two limits.

### Soft matter and biology – emergence from looped causation

The classical structures of soft matter – macromolecules, membranes, self-assembled nanoscopic systems – are all recruited by biology to serve the structural and functional substrate of life. In a surprising recent development in the history of science, these features, together with the experimental and theoretical developments discussed in this chapter, have furnished the scientific community with the latest example of a series of translations from the physical to the biological sciences of both people and ideas.

Inasmuch as the scientific structures apply, but with careful and specific modifications, then so do the philosophical applications. In particular, the self-replicating, evolving and functional aspects of biological organisms recruit, but also extend, soft matter materials. As a consequence, the illustrations of emergent variables, top-down causation and non-locality become even stronger in the biological than in the non-living context. There are several reasons for this, whose provenance is the special additional features that apply to biological soft matter. Principally these are:

- 1 The ubiquitous context of evolution, a context of both temporal and spatial non-locality which also provides a pressure towards optimisation of replication within niches at every level of an organism.
- 2 The ‘active’ properties of biological matter, in contrast to the ‘passive’ equilibrium or out-of-equilibrium behaviour of non-living soft matter, endow the colloidal, polymeric or self-assembled structures with the capability to metabolise (‘burn fuel’) and via entropy production globally to sustain highly non-equilibrium occupation of phase-space.
- 3 The duality of genotype and phenotype: so every biological structure is implicit in another biological structure (the DNA of the relevant sections of the genome) in an information-processing sense.

These three additional dimensions to the science of soft matter have generated in turn their own programmes of research, including non-living models of active matter (Ramaswamy 2010), computational coarse-graining of genotype–phenotype maps and both experimental and computational evaluations of evolution (Khatrı *et al.* 2009). These have now entered the graduate physics curriculum in many leading research institutions (Nelson 2004).

To exemplify the way that biological physics is linked to and emerges from soft matter physics, we briefly look at one example which draws heavily on the macromolecular topology of rings.

### ***Entangled DNA and topoisomerases***

A remarkable application of polymer physics came to light in the theoretical examination of bacterial cell division. Since the early work of de Gennes, Doi and Edwards (Doi and Edwards 1986) motivated by the phenomenon of viscoelasticity in concentrated polymer solutions and melts, we have understood that the principle underlying physics is that of the *topology* of strings in random, fluid configurations. Rather than attractive or repulsive interactions between molecules, as we saw earlier, it is the uncrossability of two 1-dimensional objects embedded in a 3-dimensional space that endows the system with very slow dynamics. For in order that the coarse-grained fluid composed of many overlapping polymer molecules may flow, the molecular chains must themselves repeatedly reconfigure themselves, adopting new neighbours and leaving old ones. This process cannot be achieved by simple convection with the flow, as the molecular chains cannot pass through each other.

In synthetic polymeric fluids, the dominant diffusive process is the only one not inhibited by these topological constraints: the diffusion and convection of chains along their own contours. It is the chain ends, not subject to the same topological constraints as the inner chain segments, which allow new configurations to be adopted. As described earlier, this one-dimensional contour diffusion was named *reptation* by De Gennes, who was reminded of a snake-like crawling (Figure 20.5). He showed, since confirmed by many experiments, that the timescale for reconfiguring a single polymer molecule by the reptation process scales as the third power of its molecular weight. Since macromolecular chains can reach very high molecular weights, these times can become (in molecular terms) extremely long, even seconds or minutes.

This topological slowing down of the dynamics of diffusion and flow appears in biological contexts as well. The most extreme example is the requirement of the separation of daughter strands of bacterial DNA into the two new daughter cells. In bacteria, DNA is not confined to the ordered structures of chromosomes, but is much more randomly distributed through the organism. So when it divides into two strands prior to cell division, the two macromolecules thus created are in a highly entangled state. If they were to disentangle by reptation, or even by forced

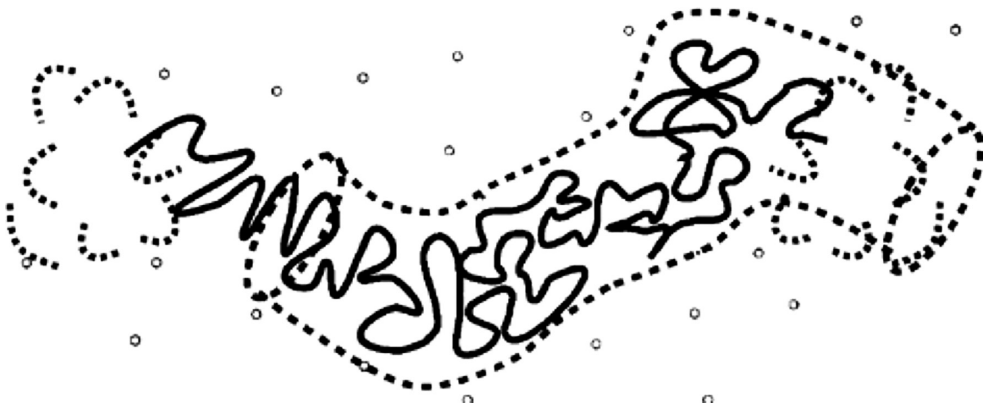


Figure 20.5 Schematic of the reptation of a polymer chain (solid curve) entangled with neighbours (dots intersecting the plane) and moving in an effective tube (dashed lines)

diffusion along the contour length determined by the topological uncrossability constraints, the timescale for cell division would be astronomically long. Instead, one of a family of enzymes known as topoisomerases (Roca 1995) performs local breaking and recombination of DNA strands at points at which two strands meet together with the enzyme. During the process, the unbroken strand is passed through the nick in the other strand before it is healed and the enzyme releases from the two strands. The action of the topoisomerase is to change the topological state of the two strands. Essentially, this is an *active* process – the information of the earlier state is erased, and as shown by Landauer (1961), this must be accompanied by the dissipation of heat from a fuel source or another source of free energy. The topoisomerase oxidises the common biochemical fuel of ATP into ADP for each information-processing event.

Among many remarkable aspects of this near-miraculous example of evolved molecular engineering is that a small fleet of topoisomerase II molecules are able to resolve the topological constraints that would otherwise inhibit DNA segregation on cell division. This is all the more surprising since the crossing-over events are local but need to respond to a direction of topological complexity (the strands need to move from higher degrees of entanglement to lower in order to separate) which is defined only globally. It is not, for example, possible to decide whether two loops of string are knotted by examining them locally, but only from their global configurations. The current hypothesis for the mechanism of communication from the global topology to the local activity of the enzyme draws on statistical mechanics. There small biases in thermal fluctuations will tend to explore less constrained states slightly more frequently than more. So if the complex of topoisomerase and the two strands of DNA is sensitive to the bias in these fluctuations, represented as an attempt frequency to cross or to escape, after many such encounters, there will be a drift in the very high dimensional space of DNA topologies toward simpler entangled states.

The ‘top-down’ causative role of long-range topology in the physics of string-like structures is directly connected to and analogous with the synthetic case of ring polymers. Here, as we saw, the two extreme states in which no ring molecule is linked with any other and in which they all are constitute an emergent liquid and solid, respectively. This is true in spite of the fact that all local physics is identical in the two cases. Intermediate topological states tune continuously between the liquid and solid states via an unusual type of percolation transition. Usually for any liquid-to-solid transition, this is second order, not first order, in the control parameter (the mean linking number of the ring molecules).

Topology is defined in all these systems only globally and in terms of the coarse-grained variables of the complete molecular paths. Furthermore, it furnishes an additional set of state variables themselves undefined at the atomistic level, yet which are highly determinative of the future evolution and macroscopic properties of the systems. In the biological case, the long-range topology is not only causatively operative on the macromolecular chains themselves and the microstates to which they are restricted, but onto the function of the smaller, topoisomerase molecules as well. Their enzymatic function is controlled, through biases in dynamic fluctuations locally, from the long-range topological relationships between crossing DNA strands, and is therefore another example of a physical instantiation of multiple realisability.

The role of evolution is evident from the highly specific function of the topoisomerase, which depends delicately on its internal fluctuations, hydrophobic and charged interactions, and a delicately tuned affinity for DNA that is enhanced when strands cross. The selection of protein structures over very long periods of evolutionary time has found solutions to the entanglement problem of extraordinary sophistication. We might note here that a different strategy seems to have been adopted by eukaryotes, in which DNA packing in the chromosome is affected in such a way that entanglements are highly suppressed (Mirny 2011).

### ***Biological lessons***

The potential for strongly emergent physics within soft matter seems to be recruited by biological systems ubiquitously. Perhaps this is not surprising, given our prior experience of candidates for top-down causation within living organisms. What may be more surprising is the relatively low level at which examples are already multiply far removed from considerations of mind and cognition.

The example earlier has allowed us to follow in detail the way that long-range (e.g. topological) physics is differentiated from the merely coarse-grained and leads to a strong, rather than weak, notion of emergence. Similarly the phenomenon of multiple realisability serves to ground a strongly emergent ontology for realised material form and function in addition to the weak coarse-graining of low-level descriptions.

The approach of taking a physical perspective onto biological matter additionally illustrates the unboundedness of physics from any special scale of length or energy. Rather, it locates the ‘physical’ at the set of fundamentally causal variables, which themselves may simultaneously occupy multiple length scales (and in biology unvaryingly do).

Finally, the biological context seems to provide a unique theatre for the emergence of loops of causality between different levels of coarse-graining. To follow our example, the top-down causation generated by the long-range entanglement topologies are in this case implemented through protein structures themselves coded for by the DNA polymers themselves. The direct physical, contextual emergence of biological mesostructures, such as the entanglements of prokaryotic DNA, is a consequence of local molecular structures in the gene. These in turn are consequences of the large-scale assembled structures that they code for. Another example is furnished by the structure of cell membranes, themselves active in bringing membrane-resident proteins together for enzymatic or signalling activity, while the membranes themselves are coded for at a lower level.

The development of ‘biological physics’ in the sense of a truly new sub-discipline at the same level as ‘chemical physics’ shows every sign of being at a very early stage (McLeish 2011 and other articles in the same issue). Beyond the mere application of theoretical and experimental ideas from physics to biological systems, the maturation of the field would fill out with more examples of new physics motivated by the interdisciplinary encounter. The original work on active matter and a possible field of the physics of evolution seem promising in this regard.

### **Conclusions**

Soft matter science constitutes a rich exemplar for both historians and philosophers of science. Although this chapter has focussed on the philosophical material relevant for the debate around emergence, the historical context is relevant as well, as it traces an inherently interdisciplinary encounter of physics, chemistry, materials science and, latterly, biology. To take one example, there are deep mathematical relationships, through the structure of field theory, between the statistical mechanics of soft matter and quantum field theory which have been historically operational in the development of the field.

Soft matter physics has clarified the salient difference between coarse-graining and non-locality and has identified examples of causal variables which, while ‘fundamental’ in at least the same sense by which atoms are ‘fundamental’, are non-reducible, have mathematical description and have causal power. The field also illustrates how the philosophical notion of ‘multiple realisation’ carries essential physical concomitant structures, strongly exemplified by the statistical mechanics of polymers. Material properties such as polymer elasticity and membrane curvature emerge from (thermally generated) multiple realisability.



Biological matter is amenable to a perspective from soft matter science and suggests additional components (evolutionary context, active matter, self-coding) that create new possibilities for causal connection between variables at different length scales that form self-sustaining loops. Not present in non-living soft matter, these long-range/short-range connected causal structures may provide another route to define what we mean by ‘living’.

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I would like to thank Robin Findlay Hendry, Alex Carruth, Mark Pexton, Tom Lancaster and others in the Durham Emergence project and the John Templeton Foundation for support. Helpful conversations are also acknowledged with George Ellis, Jennifer Wilson, Carl Gillett and Robert Bishop.

## Note

- 1 The long-running Gordon Conferences on ‘Polymer Physics’ and ‘Condensed Matter Physics’, for example, still continue, but spawned a new biennial series on ‘Soft Condensed Matter Physics’ from 2009, see [www.grc.org/conferences.asp?id=0000050](http://www.grc.org/conferences.asp?id=0000050)

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