

experimental measurements of structure, dynamics, rheology and phase transitions together with an in-depth theoretical understanding. This has been achieved in many laboratories in France, UK, US and Japan. Time is ripe to do so in India. One possible way is to nucleate centres, say three in number around the persons/groups which are already active in this field and have some infrastructure. This may involve, to start with a nominal funding of about rupees twenty million or less per group. It is sincerely hoped that the outcome will be very rewarding in terms of exciting science and possible technological applications.

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# Soft condensed matter: A survey and a proposal

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**In this perspective on the increasingly important field of soft condensed matter science, I make the case for a concentrated multidisciplinary effort to develop the area in India. I base my arguments on its demonstrated potential for new 'emergent' phenomena, interesting table-top experiments, and applications.**

The terms 'soft condensed matter'<sup>1</sup> and 'complex fluids'<sup>2</sup> are applied to materials which are highly deformable,

with characteristic length scales much larger than those of their constituent molecules. Examples include colloids (natural and synthetic)<sup>3</sup>, liquid crystals<sup>4</sup>, surfactant solutions<sup>2</sup>, polymeric materials (especially 'living polymers'<sup>5</sup>), membranes, gels, emulsions, foams<sup>6</sup>, even<sup>7</sup> greases, pastes, and powders. Most biological materials are also naturally included in this list, and much of the recent interest in the field has arisen from attempts to understand the mechanical properties of biomembranes<sup>8</sup>.

The condensed matter and materials science communities worldwide recognize this subject as a separate, exciting and growing field, as can be seen from the conferences (Gordon, Aspen, Institute for Theoretical Physics, Materials Research Society, European Physical Society...), summer schools such as Les Houches, research centres like those of Exxon and Unilever, and departments dedicated to the subject, such as the colloids and polymer groups at the Cavendish Laboratory and the substantial Complex Fluids group in the Materials Department at Santa Barbara. In France, the field is a mature one, and considered an integral part of condensed matter physics, with several large research groups across the country focused on various aspects of the subject. A new Max-Planck-Institut for Complex Fluids has opened in Germany. This *Physical Review E* has a section devoted entirely to the subject, and *Europhysics Letters* as well as the *Journal de Physique* always feature a large number of articles in the area. This is apart from the enormous traditional interest in colloid, surfactant, and polymer science on the part of chemists and chemical engineers. It should be noted that the physics of these systems is completely classical, and hence, in a reductionist sense, completely understood. The tremendous interest in the field is thus a kind of neo-classical revival!

In many of the systems I have mentioned, the large-scale structure is best thought of as an arrangement not of molecules but rather of spontaneously 'self-assembled' mesoscale aggregates, whose interactions then determine the macroscopic physical properties. The whole area is thus a marvellous hunting ground for *emergent*<sup>9</sup> collective phenomena, and is a great argument against the sort of naïve reductionism that would have us believe that 'fundamental' physics must involve only the smallest constituents of the universe! Moreover, the natural timescales in soft matter are generally large (microseconds to seconds). In addition, the length-scales involved are large when compared to those of their molecular constituents, and yet small enough (100 Å to several μm) for fluctuations to be important. This makes such materials a fertile area for novel, nontrivial applications of ideas in statistical mechanics, especially of *extended* objects *far* from equilibrium. The field, moreover, is conducive to table-top experiments in which the Indian *can* afford to compete. It is naturally multidisciplinary, providing an ideal meeting-place for physicists, chemical engineers, chemists, biologists, fluid mechanics, and mathematicians. The potential it holds for industrial application is obviously great—although this should not forcibly be made the *sole* basis for supporting research in the area.

I submit that the time is right—indeed it has been so for some years now—for an organized effort in this field, at several centres across the country. I present

below my arguments in favour of this position. I shall say nothing detailed about the relevance of complex fluids to biology or materials science. I shall restrict my remarks to some examples of *new physics* that have emerged from this field, and then offer a plan of action. Since my aim is persuasion, not pedagogy, references will not be complete and will tend to mention (disproportionately often) work with which my IISc colleagues or I were associated, and explanations will be rather brief.

## Systems and phenomena

The first class of systems I consider are surfactant solutions<sup>2,10</sup>, many aspects of which Ajay Sood and C. Manohar have already discussed at this meeting. I will concentrate on two remarkable thermodynamic phases formed in such solutions. Recall that one way of satisfying the double nature (hydrophilic head, hydrophobic tail) of a surfactant, and indeed a classic example of self-assembly, is to form bilayer sheets, with heads on the outside. These sheets can be organized in many ways to form macroscopic phases: two of these are the lamellar<sup>11</sup> phase, in which the sheets are stacked periodically, and the 'sponge'<sup>13</sup> phase, in which they form a random-surface structure.

### *The lamellar or $L_\alpha$ phase*

The particularly remarkable feature here is that it occurs at almost arbitrarily large layer spacing  $d$ , ranging from 20 to many thousands of Ångströms. Now this is extraordinary: given that the microscopic *repulsive* interactions that might stabilize the structure against collapse under the long-ranged van der Waals attraction are *short-ranged* (electrostatics can be effectively screened out by ionic impurities, or eliminated by using non-ionic surfactants), one would expect, as in crystals or conventional thermotropic liquid crystals, ordering at molecular length scales. The explanation<sup>11</sup> lies in a beautiful example of an *emergent interaction*. Each sheet, although on average flat, fluctuates thermally about its mean configuration, paying only a small bending energy cost. This thermal wandering of the sheet results in collisions with adjacent sheets, and the typical distance between contacts can be shown to be proportional to the layer spacing  $d$  itself. Thus, no matter how swollen the system, each sheet feels the presence of its neighbours on large enough lateral length scales. The result of this indirect thermally induced interaction is a *long-ranged* ( $1/d^2$ ) repulsive potential which can stabilize the periodic structure at almost unboundedly large length scales! Some surprises in the dynamics of lamellar phases have been studied recently as well<sup>12</sup>.

### *The 'sponge' or $L_3$ phase*

Light-scattering, conductivity, and other measurements have been used to show<sup>13</sup> that this optically isotropic but strongly flow-birefringent phase, which occurs in narrow regions of the phase diagrams of several surfactant solutions, consists of two bicontinuous regions (the 'inside' and the 'outside') of water separated by an intricate, multiply-connected random surface with practically no seams or boundary. This is not in itself so remarkable: it occurs in microemulsions as well, except that there the two sides (oil and water) are distinct. The important fact here is that there are *two* thermodynamically distinct sponge phases, the 'symmetric sponge', which has the same volume 'inside' as 'outside', and the 'asymmetric sponge', with an imbalance between the two subspaces, and that these are separated by a thermodynamic phase transition and the transition between the two is the breaking of a *hidden symmetry*!

### *Crystals made of surfaces*

There is also a rich variety of two- and three-dimensionally ordered phases in surfactant systems, in which the basic building block is best thought of as a piece of bilayer or monolayer. The modelling of such systems requires the understanding of interactions between geometrical elements, the theory of minimal surfaces, and so forth. I will not go into these here but it should be clear that even the crystallography and structural transitions of these systems involve geometrical and topological concepts in a nontrivial manner.

### *Membranes out of equilibrium*

These examples, although intriguing, are comparatively simple because they arise at thermal equilibrium. The physics of membranes and other deformable objects in *nonequilibrium* conditions contain remarkable new physics, and also bears on phenomena of importance to biology such as cell locomotion and transport across membranes. I will not discuss these here but simply offer some references for the interested reader<sup>14</sup>.

Let me turn next to colloids. The problem of colloid stability and dynamics is one of enduring interest, for obvious practical reasons<sup>15,16</sup>. Model suspensions of synthetic colloids, e.g. polystyrene spheres in water, stabilized either by surface charge or 'sterically' by the grafting of polymer chains onto their surfaces are still the subject of intense interest<sup>3</sup>, partly as scale models of classical liquids, and partly as elegant laboratories for the study of nonequilibrium phenomena (see, e.g. ref. 21 and references therein). I will mention

only two effects: (i) the depletion force<sup>17-20</sup> and (ii) shear-induced melting<sup>21</sup>.

### *The depletion force*

Let us consider a mixture of large and small hard spheres, with diameters  $D$  and  $d$ , and volume fractions  $F$  and  $f$ , respectively, at thermal equilibrium at temperature  $T$ . Let us assume that there is no interaction between the particles apart from excluded volume. Nonetheless, if the distance between the surfaces of two of the large spheres is less than  $d$ , the small spheres are excluded from the region between them. The pressure of the small spheres (regarded as a gas) acts only on the exposed portion of the large spheres, driving them together, with an effective attractive potential of depth  $TfD/d$  and width  $d$ . This idea was proposed a long time ago, in the context of colloid-polymer mixtures<sup>17</sup>, and exploited cleverly in the separation of emulsion droplets by size<sup>18</sup>. Recent experiments have given direct evidence for this force in mixtures of chemically identical large and small near-hard-sphere colloids<sup>19,20</sup>. The depletion force is yet another example of an emergent interaction, and the underlying general idea continues to find fruitful application in theories of the interactions of colloids, membranes, and polymers.

### *Shear-induced melting*

Colloidal crystals<sup>3</sup> are so weak (shear-moduli  $\sim 10^2$  dyn  $\text{cm}^{-2}$ ) that they can be made to flow like liquids. However, there are two distinct flowing states: one which retains (in a sense which I will not make precise here) the structural correlations of a crystal, and one which is truly like a liquid in shear flow. The shearing liquid and shearing crystal are separated by a well-defined 'shear-melting' transition, at a shear-rate which goes to zero as the parameters of the system approach the values at which the colloidal crystal would melt at equilibrium. This nonequilibrium phase transition poses several fundamental questions: What is the other parameter for a flowing crystal? Is there a nonequilibrium analogue of a free-energy whose minima are the stable and metastable states of the system? If not, what is the rule by which the system chooses its state? Although the issues are by no means settled, there has been some progress on these questions recently<sup>21</sup>. I close the discussion on colloids by mentioning that even colloidal liquids away from equilibrium e.g. diffusion of interacting colloids in a shear flow<sup>22</sup>, directional motion of brownian particles out of equilibrium in asymmetric potentials without macroscopic gradients<sup>24</sup> show remarkable behaviours with broad relevance to field such as chemical engineering and the study of motor proteins.

## Polymers

No discussion of soft condensed matter is complete without a mention of polymers<sup>24,25</sup>. Much recent interest in the field has centred on polymers in membranes or at interfaces, colloid-polymer interaction, and polymers in shear flows. The relevance of these topics to engineering and biology needs no explanation, but again let me mention just two topics of interest from the point of view of fundamental physics. 'Living polymers', which are long micelles which constantly form and break, have attracted attention recently as realizations of non-Brownian random walks<sup>26</sup>, of considerable interest to mathematicians. The phase diagram and dynamics of melts of semiflexible living polymers are subjects on which considerable recent progress has been made at IISc (ref. 5). Sheared concentrated polymer solutions are of obvious practical interest from the point of view of polymer processing. Their rather dramatic light-scattering properties have received attention recently, and are a striking example of how nonequilibrium conditions can give rise to unexpected long-range correlations<sup>27</sup>.

## What is to be done?

Having argued that there is wealth of interesting emergent phenomena in this class of materials, let me try to say what is needed for the field to take off in India. There are already many centres at which various aspects of soft condensed matter are being studied, but there is not a great deal of collaboration between these centres, nor, I believe, much of an attempt by one discipline to solve the problems of another. Worldwide, the phenomena in this field arise in engineering, or sometimes in biophysics. The role of the physicist or physical chemist has been to find in these phenomena a worthwhile problem to solve, or class of systems to investigate, with all the experimental and theoretical tools of his or her field. The result, as the examples above testify, can be exciting new science with a clear benefit to the applied disciplines in which the problems originally arose. If soft-matter science is to establish itself here in India, I believe the same approach is called for. In particular, neither the traditional, entirely phenomenological approach that the average engineering student is taught nor the typical theoretical physicist's reaction (these systems are too dirty) is appropriate. At least among academic chemical engineers in India there is a trend away from *ad hoc* modelling; it remains to be seen to what extent physicists are attracted to the field.

## Centres

It is clear that progress in soft matter research requires

dedicated centres which, I feel strongly, should be in a university setting. The long-term aim should be to have two or three such groups in the country, each ideally with three experimenters and two theoreticians, although of course even one group would be a welcome start. It should be kept in mind that (as a result of retirements) there should be at least 50-100 positions opening up for physicists in the country, while by contrast the job market in the US is contracting. It is therefore a good time to get and keep people. With sufficiently imaginative and critical leadership, it would not be unrealistic to start *one* group or centre now. The cost would be a few per cent of a giant telescope or pelletron, and the payoff in terms of science would be substantial.

## Equipment

A soft-matter laboratory (although this will depend to some extent on the specialities of the persons actually hired) must have static and dynamic light scattering, Brillouin scattering, a rotating-anode X-ray setup, high-resolution viscometry, sound-attenuation, light microscopy (phase contrast, with video, frame-grabber and digitiser), conductimetry, and a triple-distillation setup, apart from access to cryo-electron-microscopy, NMR, and neutron scattering, including perhaps spin-echo, and a facility for organic synthesis. Much has been learned about the structure and dynamics of membrane and colloidal systems from neutron scattering; we should accordingly staff our neutron facilities more substantially, say 12 persons per beamline. I believe Ajay Sood is discussing equipment in more detail; all I wish to point out is that, perhaps even more than in other fields, it is important that an experimental group in working on soft condensed matter (indeed, even the individual experimenter) not be wedded to a single probe. For theoretical work, of course computing is essential. Many insights on random-surface, colloid, and polymer physics has come from direct simulation. If the group is in an institution with excellent central computing, then a state-of-the-art PC for each desk (all networked) is all that is called for. If existing facilities are poor, then I would suggest fast workstations instead, at about Rs 10 lakh each, updated every three years, or Internet connections (on desk) to existing or proposed supercomputing centres.

## Finding the people

This is obviously the most important part of the exercise. It is both practical and desirable to combine disciplines in the process of funding (or creating) people for the centre(s) proposed above. This calls for a serious search, both at home and abroad. Several PhDs are coming

out of the groups working in this area in India, and a somewhat larger number (of Indians), mainly engineers, abroad. We can only keep our eyes open: I am sure we can all think of examples of good people we could have got if an offer had been made at the right time. Clearly what we will have to work hard to get are experimenters. Any practitioner of statistical mechanics can undergo an adaptive mutation to become a soft-matter theorist, a course of action which I strongly recommend!

### Industry funding

This is an important component of support for complex fluids/soft matter research in Europe and the UK, and to an extent in the US as well. The colloids group (headed until recently by S. F. Edwards) at the Cavendish Laboratory is substantially funded by Unilever. Elf-Aquitaine, the French national petroleum firm, funds a lot of complex fluids research in France (see the special supplement<sup>7</sup> to *Nature* which they sponsored). The US petroleum corporation Exxon has a research lab of exceptional quality dedicated almost entirely to soft condensed matter. Even cosmetics firms fund post-doctoral positions and give research grants to CNRS laboratories in France. Such support is essential if the Indian effort in this area is to be a serious one. Moreover, this support will result in an increased improved interaction between basic and applied science, and root our research in reality.

### Conclusion

I believe my remarks have established a strong case for developing focused research groups in the exciting area of soft condensed matter science. The field holds promise for new science and new materials. Experiments in the area are affordable, and the beginnings of groups in this area already exist in the country. It is time to act.

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