Why should we pursue soft condensed matter?

Ajay K. Sood
Department of Physics, Indian Institute of Science, Bangalore 560 012, India and Jawaharalal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Jakkur P.O., Bangalore 560 064, India

This review highlights the physics aspects of soft condensed matter to show that these are novel systems to explore cooperative behaviour in condensed matter under equilibrium and non-equilibrium conditions. A case is made for focusing research in this area in our country.

The term soft condensed matter (SCM) or complex fluids encompasses systems whose constituents are supramolecular species of sizes much larger than conventional molecules. They exhibit numerous forms of self-organization and have significant structure and dynamics on mesoscopic length scales (~10 to 1000 nm). The organized state can range from a simple spatial or temporal ordering to the intricate interaction between order and function in biological systems. Notable examples include colloidal suspensions, ferrofluids, emulsions, surfactant assemblies, thermotropic and lyotropic liquid crystals, bio-membranes, polymer solutions, gels and foams. As pointed out by de Gennes[1] in his Nobel Lecture the expression 'complex fluids' incorporates two major features, viz. the *complexity* of the structure and *flexibility*. The latter results in a strong response to modest external perturbations.

There is a renewed interest in SCM not only because of their technological importance in industries dealing with detergency, biotechnology, enhanced oil recovery and catalysts, but also due to the realization that these systems are fertile grounds for new science[2–4]. The aim of this paper is to bring out some of the fascinating physics aspects of the soft matter (strongly biased by my own perceptions) to make a case for a serious thrust in this inter-disciplinary area in our country. The bibliography in this review is for some limited guidance and does not purport to be complete and exhaustive. The papers in this issue by Sriram Ramaswamy, C. Manohar and N. V. Madhusudana are somewhat complementary and should be read along with this review.

Systems of interest

Colloidal suspensions

Colloids are ubiquitous in nature and their examples are paints, ink, blood, bitumen, ferrofluids, grease, emulsions, suspensions of polymeric colloidal particles, etc. The multicomponent nature of the colloidal suspensions in terms of size and shape of the particles makes their study almost intractable from basic physics point of view. Fortunately, over the last four decades, it has become possible to synthesize monodisperse particles with a narrow size distribution. Examples of these model colloidal dispersions with spherical particles are as follows:

a) Charge stabilized suspensions of polystyrene particles or silica particles are termed as soft spheres because the interaction between the colloidal particles is long-ranged and is predominantly screened Coulomb repulsion. The screening length can be easily controlled either by tuning the particle density or by changing the charged impurity concentration. In addition to the repulsive potential, there is a short range attractive potential due to London–van der Waals interaction which, together with the repulsive interaction, results in a Coulomb barrier of a few K_BT providing the stability against flocculation.
b) Sterically stabilized suspensions of polymethylmethacrylate (PMMA) or silica particles with grafted polymeric chains, termed as nearly hard sphere suspensions.
c) Ferrofluids of magnetic particles[5], electrorheological fluids[6], etc.

Some examples of cylindrical shaped colloidal particles are naturally occurring γ-AlOOH, γ-FeOOH, clays like immogolite SiO_2-$Al_2O_3.2H_2O$, tobacco mosaic virus (TMV) (length L ~ 300 nm and diameter d ~ 18 nm) and fd virus (L ~ 880 nm and d ~ 6 nm)[7]. There are colloidal suspensions of worm-like chains like poly-γ-benzyl-L-glutamate (contour length L = 30–300 nm, persistence length P ~ 80 nm and diameter d ~ 1.6 nm), poly-*n*-hexylisocyanate (L = 15–330 nm, P ~ 40 nm, d ~ 1.3 nm) and DNA (L = 10–10^5 nm, P ~ 50 nm and d ~ 2.5 nm).

Self-organizing systems from amphiphiles

Amphiphiles such as surfactants and lipids can associate themselves in aqueous solutions into a variety of supramolecular assemblies such as spherical, cylindrical or disc-shaped micelles, microemulsions, mono- and

bilayers, vesicles (liposomes), etc.[8-11]. These supramolecular assemblies can organize themselves on a larger scale with either long-range order (lyotropic liquid crystalline phases) or only short range order liquid isotropic phases. Examples of lyotropic liquid crystalline phases are nematic order in micellar disks or rods, ordering of bilayers in one-dimension (or lamellar L_α) smectic A phase, infinite cylinders packed as a two-dimensional hexagonal lattice, spherical micelles packed on a three-dimensional cubic lattice. A cubic phase is also formed from a continuous bilayer in the form of a periodic, saddle-shaped minimal energy surface[10]. In isotropic phases, long and semiflexible micelles give rise to polymer-like behaviour (called worm-like polymers) where the micelles constantly form and break. A dilute system of bilayer-forming surfactant can result in a continuous web of connected bilayer in a sponge-like structure[11]. This exotic 'sponge phase' is different from the random bicontinuous microemulsion formed by two intertwined labyrinthic networks of oil and water channels separated by a dense monolayer of surfactant, in the sense that the former is composed of only one type of solvent water or oil instead of water and oil. Recently, it has been shown that some lipids with chiral head groups can self-assemble to form submicrometer diameter tubules consisting of helically wrapped bilayers where the edges of the bilayers are packed together[12]. These tubules are a paradigm for molecularly engineered structures.

Some of the issues to be addressed

Equilibrium phase transitions

The phase diagram of polyball suspensions shows fluid, bcc and fcc phases[2]. Theories based on the self-consistent harmonic approximations have not been successful. Recently[13], density functional theory has been successfully applied wherein the inclusion of three-body along with the usual two-body direct correlation functions of the liquid is necessary to get the correct phase diagram. It is interesting to ask if the colloids can exhibit gas to liquid type transition as well. This can arise if the interparticle potential has both attractive as well as repulsive parts (like Lennard–Jones potential for atomic systems). The existence of attractive interaction between the polyballs in addition to the DLVO potential is controversial and is being debated extensively[14]. Fluid–fluid together with fluid–solid equilibria have recently been shown in colloid–polymer mixtures[15]. Here the attractive interaction between the colloidal particles arises due to the depletion forces. In such binary systems where the range of attractive and repulsive interactions can be controlled, statistical mechanics of equilibrium phase diagrams is very interesting.

The surfactants and lipids-based structures can transform from one to another by changing the solution conditions such as the electrolyte or amphiphile concentration, pH, temperatures or pressures[8-12]. A number of experimental studies have been carried out to investigate the molecular alignment within a bilayer. Theoretical developments have sought to elucidate the role of molecular geometry, topological concepts and theory of minimal surfaces in determining the structures. The questions of order of the transition (first vs continuous), symmetry breaking (e.g. in sponge phase) and phase separation are worth answering, both experimentally and theoretically. The concepts of differential geometry are needed to explain the shape fluctuations etc. of vesicles. In the case of vesicles with genus two (i.e. with two holes or two handles), it is predicted that the shape fluctuations are due to a new type of diffusive motion, termed conformal diffusion[16].

Matter under nonequilibrium conditions – effect of shear etc.

Elastic constants of colloidal solids are about 10 dynes/cm^2 (and hence the name soft matter). This can be qualitatively understood by noting that the elastic constants $G \sim Un_p$, where U is the interaction energy between the particles (~ 1 to 10 eV, same as in atomic systems) and $n_p \sim 10^{12}$ cm^{-3}. Interesting flow behaviour under shear can be observed where $\dot{\gamma}\tau \sim 1$, where $\dot{\gamma}$ is the applied shear rate and τ is the typical structural relaxation time. For conventional solids, $\tau \sim 10^{-12}$ s and hence one requires unachievable $\dot{\gamma}$ to satisfy the above condition. On the other hand, for colloids, $\tau \sim D_o/a_s^2 \sim 10^{-3}$ s, where $a_s = n_p^{-1/3}$ is the average interparticle distance and $D_o = K_B T/6\,\pi\eta\, a_p$ (η being the viscosity of the solvent) is the self-diffusion coefficient in the non-interacting limit. As a consequence, it is possible by readily available means to apply shear rates in the laboratory which are comparable to τ^{-1}. An extremely low value of G results in many interesting nonlinear flow behaviour as a function of applied shear[17].

Colloidal crystal can be melted by shear stress. The phenomenon of shear-induced melting is still poorly understood. Computer-simulation studies have shown that at high shear rates, there is a reentrant phase transition from fluid to the crystalline phase. The phenomena of shear-induced melting and the reentrant phase have to be quantitatively understood[18]. Brownian dynamics simulation[19] shows that in the steady shear limit, the enhancement of the self-diffusion coefficients in direction transverse to the flow shows a cross-over from a $\dot{\gamma}^2$ dependence to a $\dot{\gamma}^{+1/2}$ dependence as $\dot{\gamma}$ increases. There is a possibility of chain or layer formation in colloidal liquid at high shear rates.

The large-scale interior structure in complex fluids can be significantly distorted by shear flow due to their large τ. This distortion results in a breakdown of Newtonian hydrodynamics. This non-Newtonian flow behaviour plays a crucial role in many technological applications like lubricating films and processing of polymers. In addition, it is of basic scientific importance to correlate the bulk macroscopic response of the material to the underlying distorted structure. X-ray and light scattering studies are worthwhile to probe the nonequilibrium structures of the colloids, lamellar and sponge phase, etc., as a function of shear rates[20].

Physics of glassy state

Glassy state has been seen in dense monodisperse, binary mixtures and charge polydisperse colloids using small angle X-ray scattering, light scattering, optical microscopy and computer simulations[2]. A quantitative understanding of the glass transition is still not complete and hence the predictions of theories like mode-coupling theories can be compared with the experiments on these colloidal glasses[21].

Magnetic and electric field-induced ordering and instabilities in ferrofluids and electrorheological fluids

Ferrofluids are stable dispersions of subdomain magnetic particles and show magnetic field-induced ordering and instabilities[22]. Electrorheological fluids consisting of dielectric spheres in a medium solidify in the presence of electric field[6]. These together with hybrid systems like ferrosmectic[23] (magnetic particles in a lamellar phase) offer a vast range of phenomena to be explored in the realm of instabilities.

Optical matter

Optical matter refers to new ordered structures which can be created by manipulating the dielectric colloidal particles with the properly tailored electromagnetic fields[24]. The organization can be achieved either by directly transporting the dielectric matter by externally applied standing wave optical fields or by external field induced interaction between the particles. This manipulation of matter has applications in many diverse areas ranging from modern biology to microelectronics and optics. One of the important motivations in this field has been to create structures with bandgap for photons, similar to the well-known bandgaps for electronic states.

Chowdhry *et al.*[25] have demonstrated the freezing of 2D suspensions of strongly interacting colloidal particles by subjecting the suspensions to a 1D modulating potential V_e induced by a standing wave pattern of interfering fields. Recently, density functional theory of this phenomenon has been carried out to predict that the initial first order freezing transition (at small V_e) changes to a continuous one (at large V_e) via a tricritical point provided the modulation wavevectors are suitably chosen[26].

The recent advances in optical tweezers using focused laser beams open up possibilities of manipulating parts of membranes and vesicles to quantitatively estimate their elastic constants, stability, etc.

Physics in two-dimensions

The physics of low-dimensional systems is, in principle, very rich, but it is not always practicable to realize a true two-dimensional crystal in conventional solids, except the adsorbed atomic monolayers on substrates like graphite.

The macroscopic size of polyballs makes it relatively easy to confine them between two solid surfaces, thereby achieving two-dimensional colloidal crystals[2]. Solid surfaces such as glass plates appear perfectly smooth on the colloidal length scale. Two-dimensional colloidal monolayers can also be formed at water–air and water–solid interfaces. Monolayers and Langmuir–Blodgett films also offer themselves for interesting physics.

Direct measurements of the forces between surfaces in complex fluids

Experimental techniques like surface force apparatus (SFA) of Israelachvilli can determine the full force law[27] involving both attractive and repulsive forces. These forces have been extensively studied between silica (or mica) surfaces and between soft surfactant (e.g. bilayer) surfaces. The contributions of liquid structuring to the forces between the soft surfaces can be studied both experimentally and theoretically. The entropic or steric forces expected from the thermal fluctuations of the surfactant molecules and the thermal motions of flexible groups can be studied.

Colloid stabilization and flocculation

When the repulsive Coulomb potential between the colloidal particles is greatly reduced (by increasing the ionic strength or reducing the surface charge), the attractive van der Waals forces come into play and the particles form aggregates. Understanding the stability of colloidal dispersions has been one of the central aims in the field of colloidal physics. Needless to emphasize

its commercial importance, aggregation is a prototype example of the complicated random process which can reveal such aspects as self-similarity, scaling and universality. The concept of fractal dimension has been introduced in recent years to describe geometry of the colloidal aggregates[28]. The characterization of aggregates in terms of fractals and their role in rheology of complex fluids is very interesting and of technological importance.

Propagation of electromagnetic waves in random media

Colloidal suspension is an ideal medium to study statistical and interference phenomena in propagation of optical waves in random media. Interference effects in multiple elastic scattering of optical waves can lead to photon weak localization, analogous of electron localization in a random medium. These optical and electron effects arise from a common origin of both being wave phenomena and depend on the relative magnitudes of four different length scales: the wavelength, the elastic transport mean-free path, geometric size of the system and the inelastic mean-free path[29]. Interesting effects arising from the interplay of randomness and order on the propagation of light can be studied in interacting colloidal suspensions.

Multiple light scattering has recently been used to probe dynamics of the colloids. This technique, called diffusive wave spectroscopy[30] is very promising[31] and needs to be understood quantitatively.

Complex fluids in constrained geometries

The flow behaviour and phase transitions in the colloids, polymers, micelles and lamellar phases in porous media can be different than those without geometrical contraints and hence need careful studies.

Physics of biological systems

The physics of structure and functioning of biological systems—cell, biomembranes, membrane proteins, etc., is challenging in terms of complexity and novelty. Their organization and functions are intricately interelated and will be pursued (also by physicists) in the near future[32].

Experimental studies

Structures of the complex fluids in equilibrium and non-equilibrium conditions have been studied by X-ray, neutron diffraction and static light scattering techniques. A judicious choice of these techniques which include small-angle X-ray and neutron scattering, high resolution X-ray diffraction using two-dimensional detectors is essential to probe the structure at different length scales. Structures with length scales ~ 1000 Å can be investigated in real space and real-time by optical microscopy (phase contrast, fluorescence and confocal) where the use of CCD cameras, video-recording and image digitization has made this technique very powerful. The structures of vesicles, membranes and lamellar phases are studied by relatively recent techniques of cryo-transmission electron microscopy and freeze fracture.

Dynamics is best studied by dynamic light scattering wherein the fluctuations of the scattered intensity are analysed in real-time in terms of intensity auto-correlation function. This technique based on single scattering of photons has been extended to multiply scattered radiation called diffusing wave spectroscopy from optically turbid media like foam, concentrated colloids, etc.[30]. Another technique for studying dynamics is neutron spin echo.

Rheological behaviour of complex fluids is of great importance. The response of the complex fluids to shear excitation, i.e. dynamic mechanical susceptibility is a fundamental property to be measured. The main difference between a solid and a fluid lies in their contrasting response to an applied shear strain: solids store mechanical energy and are elastic whereas fluids dissipate mechanical energy and are viscous. Some materials are viscoelastic. This behaviour is frequency-dependent and is parametrized by the complex shear modulus.

Some other experimental studies to be pursued are: (i) direct measurement of forces using surface force apparatus, (ii) dielectric and conductivity measurements, (iii) microcalorimetry, and (iv) nuclear magnetic resonance. Like in many branches of science and engineering, computer simulations have been shown to be very useful in understanding the equilibrium and non-equilibrium properties of soft matter. The latter has not been so extensively studied and will be a point of focus in the near future.

Indian scene

Over the last few years, there have been a few groups in India working in the area of soft condensed matter. Some of these are at the Indian Institute of Science (Bangalore), Bhabha Atomic Research Centre (Bombay), Indira Gandhi Centre for Atomic Research (Kalpakkam), Raman Research Institute (Bangalore), National Chemical Laboratory (Pune), Bhavnagar University, UDCT (Bombay University), Indian Institute of Technology, Bombay and Hindustan Lever Research Laboratory (Bombay). In my opinion, most of us are 'windowing' the problems to the experimental techniques available to us. This approach has indeed achieved some limited success. The most effective and desirable way is to have an integrated approach involving synthesis of new and novel systems,

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.

1. deGennes, P. G., *Angew, Chem.*, 1992, **31**, 842–845.
2. For a review, see Sood, A. K., *Solid State Physics* (ed. Ehrenreich, H. and Turnbull, D.), Academic Press, New York, 1991, vol. 45, pp. 1–73.
3. Prost, J. and Rondelez, F., *Nature (Supplement)*, 1941, **350**, 11–23.
4. A number of papers have been compiled in *Physics of Complex and Supermolecular fluids* (eds Safran, S. A. and Clark, N. A.), John Wiley, New York, 1987.
5. Rosensweig, R. E., *Ferrohydrodynamics*, Cambridge University Press, Cambridge, 1985.
6. Halsey, T. C. and Martin, J. E., *Sci. Am.*, 1993, **269**, 42–48.
7. See, for example, Lowen, H., *Phys. Rev. Lett.*, 1994, **72**, 424–427.
8. Degiorgio, V. and Corti, M., *Physics of Amphiphiles: Micelles, Vesicles, Microemulsions*, North Holland, Amsterdam, 1985.
9. Ringsdorf, H., Schlarb, B. and Venzmer, J., *Angew. Chem.*, 1988, **27**, 113–158; Kunitake, T., *Angew. Chem.*, 1992, **31**, 709–726.
10. Nelson, D., Piran, T. and Weinberg, S. (eds.), *Statistical Mechanics of Membranes and Surfaces*, World Scientific, Singapore, 1989.
11. Roux, D., Coulon, C. and Cates, M. E., *J. Phys. Chem.*, 1992, **96**, 4174–4187.
12. Schnur, J. M., *Science*, 1993, **262**, 1669–1676.
13. Sengupta, S. and Sood, A. K., *Phys. Rev.*, 1991, **A44**, 1233–1236.
14. Sogami, I. and Ise, N., *J. Chem. Phys.*, 1984, **81**, 6320–6329.
15. Calderon, F. L., Bibette, J. and Bias, J., *Europhys. Lett.*, 1993, **23**, 653–659.
16. Julicher, F., Seifert, U. and Lipowsky, R., *Phys. Rev. Lett.*, 1993, **71**, 452–455; Michalet, X., Bensimon, D. and Fourcade, B., *Phys. Rev. Lett.*, 1994, **72**, 168–171.
17. Weitz, D. A., Dozier, W. D. and Chaikin, P. M., *J. Phys.*, 1985, **C3**, 257–268.
18. Lahiri, R. and Ramaswamy, S., *Phys. Rev. Lett.*, 1994, **73**, 1043–1046.
19. Chakraborti, J., Sood, A. K. and Krishnamoorthy, H. K., *Phys. Rev. E.*, 1994, (Rapid Commun.) (in print).
20. For examples, see Safinya, C. R., Sirota, E. B., Bruinsma, R. F., Jeppesen, C., Plano, R. J. and Winzel, L. J., *Science*, 1993, **261**, 588–591.
21. van Megen, W. and Underwood, S. M., *Phys. Rev. Lett.*, 1993, **70**, 2766–2769.
22. See, for example, Wang, H., Zhu, Y., Boyd, C., Luo. W., Cebers, A. and Rosensweig., R. E., *Phys. Rev. Lett.*, 1994, **72**, 1929–1932.
23. Fabre, P., Casagrande, C., Veyssie, M., Cabuil, V. and Massart, R., *Phys. Rev. Lett.*, 1990, **64**, 539–542.
24. Burns, M. M., Fournier, J. M. and Golovchenko, J. A., *Science*, 1990, **249**, 749–754.
25. Chowdhry, A., Ackerson, B. J. and Clark, N. A., *Phys. Rev. Lett.*, 1985, **60**, 833–836.
26. Chakraborty, J., Krishnamoorthy, H. R. and Sood, A. K., *Phys. Rev. Lett.*, 1994, **73**, 2923–2926.
27. Israelachvilli, J. N., *Intermolecular and Surface Forces*, Academic Press, San Diego, 1992.
28. See, for example, Thorn, M. and Seeselberg, M., *Phys. Rev. Lett.*, 1994, **72**, 3622–3625; Earnshaw, J. C., and Robinson, D. J., *Phys. Rev. Lett.*, 1994, **72**, 3682–3685.
29. Kaveh, M., *Physica*, 1991, **B175**, 1–8.
30. Pine, D. J., Weitz, D. A., Maret, G., Wolf, P. E., Herbolzheimer, E. and Chaikin, P. M., in *Scattering and Localization of Classical Waves in Random Media* (ed. Sheng, P.), World Scientific, Singapore, pp. 312–372.
31. Sanyal, S., Sood, A. K., Ramakumar, S., Ramaswamy, S. and Kumar, N., *Phys. Rev. Lett.*, 1994, **72**, 2963–2966.
32. See, for example, a special issue of *Physics Today*, February 1994, devoted to physics and biology.