

in having another centre for liquid crystal research which Prof. Chandrasekhar has started and as it is associated with Bharat Electronics, hopefully R & D on applications will get a boost from this new centre. Yashwant Singh of BHU has systematically developed the density functional theory of nematics³⁰ and Saha and others at the Calcutta University have been active in developing molecular theories of different types of liquid crystals. Synthetic work on liquid crystals is being carried out both in our Institute and the M.S. University of Baroda.

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Chemistry and physics of dispersions

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Here we consider the importance of dispersions in industry and academics to make an attempt to evolve a frontline research programme which would be relevant but yet challenging. Examples are given to point out the emergence of new disciplines which combine rheology, phase transitions and chemical reactions which include some biological systems too. These developments are likely to lead to important industrial consequences.

We discuss here some of the fascinating areas in the field of dispersions with the main stress on solid/liquid and liquid/liquid dispersions¹. Dispersions have recently been considered as a branch of Condensed Matter Science – the ‘Soft Matter’ or ‘Complex Fluids’. Uni-

queness of this branch of science is that it is close to a number of industrial systems and is therefore of great relevance in applications. This character offers an opportunity to discuss science starting from applications – *down to earth, but yet challenging science*. This is the strategy used here.

Solid-liquid dispersions are of great interest in paints, pharmaceuticals, pesticides, waste treatment, etc. These basically consist of solid particles dispersed in water or hydrocarbon medium. One of the main characteristics of these systems is the large interfacial area. Any small change in the interfacial structure makes dramatic macroscopic changes in the structure and properties of the system. For example, the viscosity of dispersions with say about 40% solids would be extremely high ($> 10^4$ cP)

without adsorption of suitable molecules on the surface of the particles and the viscosity drops to only a few cP with adsorption. This drastic reduction of viscosity is of great importance because it dramatically facilitates the handling of these dispersions like pumping of the slurry, grinding the pigments, improving the paintability, etc. Other 'cleaner' examples of the dramatic macroscopic changes occurring due to small changes in interface are, for example, the systems which result from precipitation of colloidal sulphur which seem to be extremely sensitive to the nature of the salt present. Presence of sodium salts in water used for precipitation seems to result in jelly-like precipitate, while the presence of potassium salts produces low viscous slurries easy to handle. Similarly it has been observed that use of H₂O or D₂O seems to matter in the colloidal systems – temperature of phase transitions shift and drastic changes occur in viscosities. Similar effects in the difference in behaviour of Cl⁻ ion or Br⁻ ion in some of the colloidal dispersions exist. These problems are extremely interesting needing highly interdisciplinary approach in research. The structural changes which result in view of these small modifications in the interfacial are extremely interesting and have not been probed by structural techniques because the *conventional scattering techniques are affected by multiple scattering and even after obtaining the results there are no suitable theories which can be used to interpret the data.* Unconventional techniques like CATSCAN and other imaging techniques can be applied but there have not been many studies (theoretical and experimental) for understanding these systems of relevance. While the science of dilute solid liquid dispersions is fairly well understood, the laws governing the concentrated dispersions (even of spherical particles) is not known and these systems become more complex when the shape of the particles deviates from a sphere. The whole science of such systems has not attracted sufficient curiosity matching their potential and remains uninvestigated.

Other aspect of these systems is the classification of these systems. The conventional solids have been defined as 'substances which hurt our toe when we kick it'. The interesting aspect is that even water hurts our hand if we hit it sufficiently 'fast'. Once the rate of shear is large and does not give time for water molecules to adjust to new positions to follow the changing shear, the water resists any change in shape on these time scales and thus behaves as a solid! The dispersions are systems where this time scale can be varied from few seconds to microseconds and thus offer very interesting liquid–solid like transitions on various time scales. *Coupling flow to structural investigations is a new trend and there have not been many studies¹* and different types of systems can be thought of, which are examples from the real world of industry. *Common day experience*

of preparing the flour–water mixtures for preparations of bread offer a beautiful set of rheological transitions which need to be looked at from a structural point of view by modelling the systems scientifically.

The second class of systems we shall consider are liquid/liquid dispersions – say, oil–water mixtures. The ability to make stable oil–water mixtures is of great importance in a variety of fields like pharmaceuticals, agricultural sprays, lubricants, fuels, oil recovery, etc. Let us consider one class of systems called microemulsions, other examples being lyotropic liquid crystals, gels and vesicles. These microemulsions are thermodynamically stable, transparent mixtures of oil and water stabilized by suitable mixtures of surfactants. Recently these structured fluids have given birth to a number of emerging technologies. The fluids by themselves are of great interest from the point of view of structural studies to observe the curvature induced transitions – strongly linked to liquid crystals, gels and other structures. However in view of the fact that these are neither aqueous nor non-aqueous systems, the chemistry is interesting. Even simple precipitation reactions in these systems have given rise to a way of preparing nanophase materials. One of the beautiful results of these approaches has produced CdS particles of about 40 Å coated with a layer of ZnS of about 19 Å (ref. 2)! The other one is the preparation of Pt, Pd, Rh catalysts with a size control of 30 ± 5 Å (ref. 3). It is of interest to investigate, since the band structure of these particles is different from those of bulk, the catalytic properties and to check if one can prepare novel alloys which cannot be prepared by 'bulk' methods. The other aspect is the use of the microemulsions to encapsulate enzymes. The enzymes do not lose their activity if they are enclosed in the water pools present in the microemulsions. In exploiting these systems in biotechnology, it has been possible to prepare unconventional gels. The structure of these systems is extremely interesting. While macroscopically the viscosities are of the order of 10⁶ cP or more – the oil and water molecules seem to be oblivious to these changes and continue to move just as they are present in pure form. The microemulsions used as fuels are again fun. The burning of these microemulsions is of great interest in defence. These systems have self-extinguishing properties yet they operate in engines without much problem. The science of 'burning' in these systems is of great challenge yet is of great value in applications. While the chemistry and physics of these systems is interesting as they are, there are indications that there are interesting phase transitions and chemistry under shearing. Examples, from work done in our country, indicating the coming trend could be given. Agarwal and Khakhar⁴ have shown that the polymerization rates of *p*-phenylene diamine and terephthaloyl chloride could be enhanced by shearing

the solution and this is a result of the alignment of molecules by the shear. This is one indication that the rheology couples to structural changes which in turn modify the reactions occurring in the medium. There are several examples in the literature which indicate that there is a close connection between structure and chemical reactivity, e.g. critical effects slowing or enhancing the reactions. The structures of complex fluids like gels, liquid crystals, etc. can be modified by shear and thus one should anticipate chemistry in these systems would be altered by shear. So one of the emerging areas in condensed matter science is to *combine rheology + phase transitions + chemistry* and evolve new systems, new science which are close to technologies relevant to our country.

In summary the following are the emerging areas in the science of dispersions where we should direct our research in the coming few years:

Development of model systems

Preparation of particles with controlled

- shape (spherical and non-spherical)
- size polydispersity
- flexibility
- interface.

Development of methods of investigating structure and interpreting the results

- Scattering techniques based on multiple scattering

(theory + experiments)

- Use of unconventional methods (CATSCAN, magnetic resonance imaging, etc.)
- Theories of concentrated systems.

Investigating the coupling between rheology and phase transitions

- Development of new instruments (e.g. flow + scattering)
- Study of flow induced phase transitions
- Transfer the instruments to industry.

Exploitation of reactions in these systems

- Enzymatic reactions
- Nanophase materials
- Conversion of two phase reactions to one phase
- Separation techniques.

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Role of multicritical points in addressing some key problems concerning condensed matter science

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We illustrate the potential of using higher order critical points in the deeper understanding of several interesting problems of condensed matter science, e.g. critical adsorption, finite size effects, morphology of critical fluctuations, reversible aggregation of colloids, dynamics of the ordering process, etc.

The quantitative understanding of a double critical point¹ (DCP) in ternary liquid mixtures has led to the search

for other multicritical points. This quest concerns the critical double point (CDP), critical inflection point (CIP), quadruple critical point (QCP), etc. in ternary or quaternary liquid mixtures². The interest in comprehending the nature of these critical points stems from the following factors²:

- (i) It is possible to tune the critical exponents, e.g. they double near a DCP and are anticipated to triple and quadruple near a CIP and QCP respectively. Thus, a