

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

A. Kumar

Department of Physics, Indian Institute of Science, Bangalore 560 012, India

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

better estimate of very weak critical exponents (like ϕ for shear viscosity and η , the Green-Fisher exponent) is feasible. The most significant impact of the tunability of critical exponents is the incredible increase in correlation length (ξ) near a multicritical point compared to that near a normal, single critical point³ (SCP). For instance, ξ is nearly 100 times larger near a DCP (for a loopsize, ΔT , of 250 mK and 1 mK below the lower consolute point, T_L) for the same distance away from a SCP. Even for 35 mK away from a QCP, ξ could be as large as 1 meter! (in an infinitely large experimental system). The influence on the slowing down of the local fluctuations of the order parameter is even more dramatic. In the wake of an exceptional enhancement in ξ , in the close vicinity of a multicritical point, the following fundamental problems of condensed matter physics can be addressed readily: (a) Critical adsorption profile between a critical and non-critical phase⁴ (b) Finite size scaling⁵ (crossover from 3D to 2D) due to the suppression of growth of bulk ξ in one direction (c) Morphology⁶ of critical fluctuations to deduce their fractal dimensionality etc.

In essence, any process that is linked to criticality should be manifested in a more spectacular fashion near a DCP, CDP, CIP and QCP.

(ii) Anomalous behaviour is expected^{1,2,7} even in the *absence* of a bulk phase separation (e.g. for $X < X_D$ in Figure 1). This idea has been invoked in aqueous alcohol solutions and supercooled water (which show anomalous behaviour without actually phase separating) in terms of the influence of *hidden* critical points. These critical points could be in the pure system or in the system

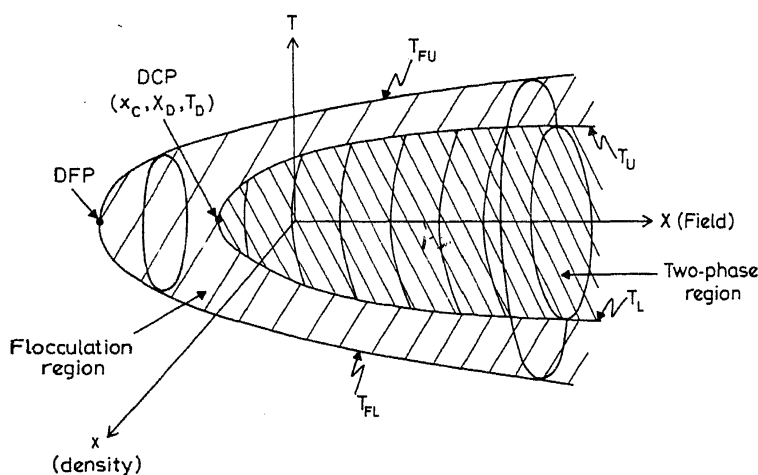


Figure 1. Schematic (not to scale) of the bulk coexistence surface² versus the dome of flocculation temperatures⁸ (T_F) of silica colloids in reentrant ternary liquid mixtures [3-methylpyridine (MP) + water (W) + heavy water (HW)] at a constant pressure. In this case x denotes MP weight fraction and $X = HW/(W + HW)$ by weight. The double flocculation point (DFP) could be a surface analogue of the double critical point (DCP). The two surfaces bear similarity but exhibit different⁸ exponents and amplitudes in each case. T_U and T_L are the upper and lower consolute points respectively. T_{FU} and T_{FL} are the upper and lower flocculation temperatures respectively. For $X < X_D$, there is no bulk phase separation.

perturbed in some way (salting, pressure, isomeric substitution, H_2O/D_2O exchange etc.). This thought is relevant in numerous other situations in complex fluids (e.g. multicomponent microemulsion solutions).

(iii) The status of theory to quantify the multicritical points is not as advanced as that for a single critical point^{2,3}.

(iv) An illustration of the rich physics that can be uncovered by using multicritical points is the recent observation of the flocculation (or aggregation) of silica colloids^{7,8} in a reentrant ternary mixture [3-methylpyridine (MP) + water (W) + heavy water (HW)] which exhibits a closed-loop phase diagram and thus has a DCP (Figure 1). This flocculation of dilute suspensions of charge stabilized colloids is reversible with temperature in the sense that the suspension becomes stable again if the system is taken away from the bulk phase separation. The colloids act as a nonflat substrate for the wetting/adsorption process. It is emphasized that this phenomenon is distinctly different from the regular and irreversible flocculation which occurs for salt concentrations $> c_c$ as described by Derjaguin, Landau, Verwey and Overbeek (DLVO) theory.

The dome of flocculation temperatures (T_F 's) were determined⁸ in the complete vicinity of the bulk coexistence surface (paraboloid), as sketched in Figure 1. The two surfaces appear similar, but display different exponents and amplitudes in each case. It is tempting to conjecture if the double flocculation point (DFP) signifies a surface analogue of a DCP.

This flocculation occurs as a result of the preferential adsorption^{7,8} of one of the liquid species (MP in our case) on to the surface of colloids. The presence of the adsorbed layer on spheres introduces attractive (London–van der Waals type) interactions between them, which at one stage overcome the Coulombic repulsions stabilizing the dispersion. The exact mechanism beneath this flocculation phenomenon still remains unclear and these ideas have been debated: prewetting^{7,9} transition on the surface of each sphere, capillary condensation^{10–12} between two spheres (phase separation in the restricted geometry), adsorption-driven modification of the interparticle potential and the appearance of a secondary minima¹³ in DLVO potential, the effect of reduced dimensionality⁵ when the gap between spheres becomes comparable with the bulk correlation length (ξ), etc.

The novelty of probing the above aggregation phenomenon near a DCP is brought out by these considerations^{2,8} (as is also illustrated in Figure 1): (a) the flocculation process can be observed *without* the interference from the bulk phase separation ($X < X_D$, Figure 1), thus one can examine the dynamics of both aggregation and its reverse process, fragmentation, by varying temperature (T) in the *same* direction, (b) the

thickness of the adsorbed layer on the colloids can be deduced from turbidity by a set of experiments for different X 's near and around DFP (Figure 1, $X < X_{DFP}$)—the goal here is to avoid the aggregation altogether because earlier experiments had failed to distinguish between the divergence in the layer thickness and the early stages of aggregation.

It is pointed out that unlike the conventional colloidal aggregates (which have normally fractal geometry), the aggregates in the present case are formed by a flexible binding between the particles and hence have compact¹⁴ structure. Besides, the aggregated phase is a dense¹⁵ phase (with spheres well separated from one another) and the process is thus not coagulation.

(v) Finally, a fundamental problem of the dynamics of phase separation in liquids still remains poorly understood and many new facets are unearthed from time to time. Recently, it was shown¹⁶ that the coalescences in an iso-density binary liquid mixture reveal dimple and nose features, the former underlining the role of deformable surfaces or interfaces. The dimple coalescence corresponds to the linear growth of domains and nose coalescence relates to the slower growth regime. The whole phenomenon reflects the interplay between the 'lubrication' and the capillary forces. The similar behaviour has been seen in macromolecules and in microemulsions.

Similarly, the study of the ordering process in polymer-poor solvents merits attention as the nucleation of a dilute phase in a viscoelastic matrix should yield anomalies^{17,18} in growth. Secondly, spinodal decomposition of the interconnected phases, which should generate a large density of interfaces in the medium, is adequate to examine the interface motion in semidilute polymer solution, a subject which is still under debate¹⁹. In particular, the motion close to a wall would be worth comparing with more usual¹⁸ cases.

The long range Coulombic forces can significantly influence the dynamics of phase separation in ionic fluids and in neutral fluids with dissolved electrolytes. An intermediate ordered single phase might appear²⁰ as a transient phase during the phase separation. In the presence of a strong solvent-solute interaction, a charge density wave state could develop²¹ near the critical point of a high dielectric constant solvent.

These interesting scenarios deserve immediate scrutiny.

Outlook

The problems outlined above reflect an overlap of the areas of physics, chemical physics, metallurgical and chemical engineering. The multicomponent liquids (and the associated critical points) only facilitate the *quan-*

titative probe of the intriguing phenomena that occur in diverse systems in nature. For instance, the newly observed phenomenon of reversible flocculation appears to be ubiquitous^{7,8,15,22} among different liquid mixtures and colloids. It should be investigated in simple host liquids (pure fluids) and more complex liquids (aqueous surfactant solutions). In view of its possible biological applications, it is envisaged to examine the reversible aggregation phenomenon with largest polystyrene latex particles in order to mimic living cells (latex have sulphonate groups identical to the cell heparin) and in more complex liquid mixtures with critical points $\sim 35^\circ\text{C}$ and $\text{pH} \approx 7$.

To provide the quantitative thrust to the pursuit of the above problems, a sustained support to develop these techniques is needed: ellipsometry, Brillouin scattering, optical imaging and image analysis and high pressure in liquids. A few laboratories in India have the personnel and the infrastructure to undertake and accomplish the above task.

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