Colloids—Novel condensed matter systems

A. K. SOOD
Department of Physics, Indian Institute of Science, Bangalore 560 012; and
Jawaharlal Nehru Centre for Advanced Scientific Research, IISc Campus, Bangalore 560 012, India.

Abstract

This paper will highlight the physics aspects of colloidal suspensions to show that these are novel systems to explore cooperative behaviour in condensed matter under equilibrium and non-equilibrium conditions

Key words: Colloids, condensed matter, cooperative behaviour.

1. Introduction

Colloids form one example of the newly emerging area of soft condensed matter, also referred to as complex or structured fluids. The main features of these systems are that their constituents are made of polyatomic structures whose sizes are much larger than the conventional molecules like water. They exhibit numerous forms of self-organization and have significant structure and dynamics on length scales ranging from ~10 to 1000 nm. Typically, these systems show strong response to modest external perturbations. Colloids are ubiquitous in nature and their examples are numerous. These include suspensions of polymeric and metal particles, ferrofluids, electrorheologicl fluids, emulsions, paints, ink, blood, gels, rubbers, bitumen, and surfactant-based systems like micelles and their organized structures (lyotropic liquid crystalline phases). Needless to emphasise, these systems not only have enormous technological importance but also offer a rich variety of phenomena to enhance the scope of conventional condensed matter physics[1-6]. The aim of this paper is to bring out some of the fascinating physics aspects of the colloidal systems.

2. Systems of interest

The multicomponent nature of the colloidal suspensions in terms of size and shape of the particles make their study almost intractable from physics point of view.

Fortunately, over the last three decades, it has become possible to synthesise monodisperse, spherical polymeric particles with a narrow size distribution. These model colloids are described below.

2.1. *Charge-stabilized suspensions—Latex spheres or polyballs*

The most popular system that has been investigated is the aqueous suspension of charge-stabilized polystyrene spheres. Each of these colloidal particles (nicknamed 'polyballs') consists of a large number of styrene polymeric chains entangled in a coil. Each of these chains starts and ends with an acidic group, like $-KSO_4$. In a solvent like water with high dielectric constant $\epsilon(\sim 80)$, the end surface groups dissociate and provide a large electrostatic negative charge per particle ($\sim 1000\,e$ for a particle diameter of 1000 Å, where e is the magnitude of the electron charge). The counter-ions (cations like K^+) liberated from the polyballs and additional ions present in the solvent form a cloud around each polyball and hence screen the Coulomb interaction between them. In simplest picture, the interaction between the polyballs over the relevant range of particle separation is predominantly screened Coulomb repulsion of the form.

$$U_R(r) \sim \frac{Z_p^2 e^2}{\epsilon} \left(\frac{\exp(ka_p)}{1+ka_p} \right)^2 \frac{e^{-kr}}{r} \tag{1}$$

where k^{-1} is the screening length given by

$$k^2 = \frac{4\pi}{\epsilon k_B T} \left[(n_p Z_p)e^2 + \sum_{\alpha} n_{\alpha}(z_{\alpha}e)^2 \right]. \tag{2}$$

Here n_p is the number density of the polyballs, each having a surface charge $Z_p e$ and radius a_p. The effect of the solvent is taken into account through its dielectric constant ϵ. T is the temperature and k_B, the Boltzmann constant. The additional ions of type α with number density n_{α} and charge z_{α} contribute to the screening in addition to the monovalent counterions whose number density is $n_p Z_p$. The potential given by eqn (2) is called the Derjaguin–Landau–Verwey–Overbeek (DLVO) potential. In addition to the repulsive potential, there is a short range (~ 20 Å) attractive potential U_A due to London–van der Waals interaction. The sum of U_A and U_R results in a Coulomb barrier of the order of a few $k_B T$ which is responsible for the stability of polyball suspension against flocculation. It is clear from eqns (1) and (2) that the strength and range of the repulsive interaction can be easily controlled by many experimental parameters, the most convenient of them being polyball number density n_p and excess ion concentration n_{α}. The former is typically measured in terms of volume fraction ϕ defined as $\phi = \pi \sigma_p^3 n_p/6$ where the polyball diameter is $\sigma_p = 2a_p$. When the screening length $k^{-1} \ll a_s$ (the average interparticle distance), the interactions between the polyballs are negligible and particles perform free Brownian motion as in the gas phase of atomic systems. As interactions build up, the particles exhibit spatial correlations over two or three interparticle spacings (liquid-like short-range order) and for sufficiently strong interactions, the colloidal particles freeze into a

body-centered cubic (bcc) or face-centered cubic (fcc) lattice with the lattice constants of a few particle diameters (order of optical wavelength). When the suspension crystallizes, beautiful iridescence is observed due to Bragg diffraction of visible light.

In addition to the gas, liquid and crystalline states, the glassy state can also be formed in the colloids. This has been demonstrated recently in monodisperse colloids at high particle density[7,8] ($\phi > 0.2$) and in dilute binary mixtures containing two different particle diameters[9]. As in atomic systems, the glassy state is characterized by the absence of Bragg diffraction, distortion in the static structure factor, finite rigidity to low-frequency shear and much slower diffusion than in the liquid state.

Charge-stabilized monodisperse colloids can also be formed from silica spheres prepared by hydrolysis and subsequent polymerization of tetraethoxysilane (TEOS), and order–disorder transitions have been studied in these systems as well.

2.2. Nearly hard colloidal spheres

In addition to the charged colloids which have long-range interaction (soft spheres), there are two other model colloidal systems in which a number of interesting studies have been carried out. These systems interact through a steep repulsive potential and are good examples of nearly hard sphere systems, a few examples of which are: (i) polymethylmethacrylate particles stabilized sterically by poly-1,2-hydroxystearic acid, and (ii) colloidal silica spheres sterically stabilized by stearyl chains grafted on to the surface. The control parameter as a function of which one observes changes in structural ordering in nearly hard colloidal sphere systems is the volume fraction ϕ. The disorder–order transition occurs[7] close to $\phi \sim 0.5$, in agreement, with computer simulations.

2.3. Colloids of rod-shaped particles

Examples are: (a) Tobacco mosaic virus (TMV) of length $L=300$ nm and diameter $D=18$ nm, (b) fd virus ($L=880$ nm, $D=6$ nm), (c) inorganic rod-like particles, *e.g.*, V_2O_5, γ-AlOOH and clays (Immogolite SiO_2–$Al_2O_3 \cdot 2H_2O$). All these particles are charged.

3. Issues to be addressed

3.1. Equilibrium phase transitions

The phase diagram of polyball suspensions shows fluid, bcc and fcc phases. Theoretical understanding of this phase diagram has been a major challenge. Theories based on the self-consistent harmonic approximations have not been successful. Recently, 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[10].

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 debated extensively[11]. Recently, it has been reported that there is a gas–liquid-type transition in polyball suspensions[12].

Fluid–fluid plus fluid–solid equilibria have recently been shown in colloid-polymer mixtures[13]. Here, the attractive interaction between the colloidal particles arise due to the depletion forces[14]. In such binary systems where the range of attractive and repulsive interactions can be controlled, statistical mechanics of equilibrium phase diagrams is very interesting.

3.2. Physics of glassy state

Glassy state has been seen in dense monodisperse[7,8], binary mixtures[9,15] and charge-polydisperse colloids using small-angle x-ray scattering, optical microscopy and computer simulations[17].

3.3. Matter under non-equilibrium conditions—effect of shear

Elastic constants of colloidal solids are about 10 dyne/cm^2 (and hence the name soft matter). This can be qualitatively understood[18] by noting that the elastic constant is $G \sim U n_p$ where U is the interaction energy between the particles ($\sim$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 when $\dot{\gamma}\tau \sim 1$, where $\dot{\gamma}$ is the applied shear rate and τ is the typical structural relaxation times. For conventional solids, $\tau \sim 10^{-12}$s and hence one requires un-achievable $\dot{\gamma}$ to satisfy the above condition. On the other hand, for colloids, $\tau \sim D_0/a_s^2 \sim 10^{-3}$s, where $a_s = n_p^{-1/3}$ is the average interparticle distance and $D_0 = k_B T / 6\pi \eta a_p$ (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 behaviours as a function of applied shear[19].

Colloidal crystal can be melted by shear stress[18]. The phenomena of shear-induced melting is still poorly understood. Computer simulation studies have shown that at high $\dot{\gamma}$ values, there is a re-entrant phase transition from fluid to the crystalline phase[20]. The phenomena of shear-induced melting and the re-entrant phase have to be understood[21]. Brownian dynamics simulation shows that in the steady shear limit, the enhancement of the self-diffusion coefficients in direction transverse to the flow shows a crossover from a $\dot{\gamma}^2$ dependence to a $\sqrt{\dot{\gamma}}$ dependence as $\dot{\gamma}$ increases[22].

3.4. 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 a two-dimensional colloidal crystal[23]. 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 interfaces and water–solid interfaces. Trapping of polyballs at the water–air interface occurs because of a finite contact angle between water and polystyrene.

3.5. Optical matter

Optical matter refers to new ordered structures that 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 application in many diverse areas ranging from modern biology to microelectronics and optics. One of the important motivations has been to create structures with band gap for photons, similar to the well-known bandgap for electronic states.

Chowdhry et al[25] have demonstrated the freezing of 2-d suspensions of strongly interacting colloidal particles by subjecting the suspension to a 1-d modulating potential V_e induced by a standing wave pattern of interfering fields. Recently, density functional theory of this phenomenon has been carried out[26] 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.

3.6. 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[27]. Electrorheological fluids consisting of dielectric spheres in a medium solidify in the presence of electric field[28]. These systems offer a vast range of phenomenon to be explored in the realm of instabilities, etc.

3.7. 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 force comes 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[29]. In the recent computer simulation experiments, it has been shown that two-point density–density correlation function $g(r)$ is of power-law form $g(r) \sim r^{D^f - d}$ for values of r intermediate between the monomer (particle) size a and the average aggregate size R_g. Here, D^f is called the Hausdorff–Besicovitch volume or mass fractal dimension and relates mass of the aggregate M to R_g: $M \sim R_g^{D^f}$. The value of D^f is less than or equal to the Eucledian dimension d.

3.8. 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 medium. Interference effects
in multiple elastic scattering of optical waves can lead to photon weak localization,
analogous to 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 λ, the elastic
transport mean free path, geometric size of the system and the inelastic mean free
path[30,31].

Multiple light scattering has recently been used to probe the dynamics of the col-
loid. This technique, called diffusive wave spectroscopy[32], is very promising[33], and
needs to be understood quantitatively.

4. Conclusions

The mesoscopic structures observed in colloidal suspensions mimic the phases seen
in atomic systems. The collective behaviour in colloids is varied and conceptually rich
and hence colloids are novel condensed matter systems to study cooperative be-
haviour as well as many to explore unique features like shear-induced melting inacces-
sible in conventional solids.

Acknowledgement

References

1. SOOD, A. K.   Structural ordering in colloidal suspensions. In *Solid state physics*,
                                  Vol 45 (H. Ehrenreich and D. Turnbull, eds), 1991, pp 1–73,
                                  Academic Press.

2. DE GENNES, P. G.   Soft matter (Nobel Lecture), *Angew. Chem.*, 1992, **31**, 842–845.

3 PROST, J. AND   Structures in colloidal physical chemistry, *Nature*, 1991, **350** (sup-
   RONDELEZ, F   plement), 11–23.

4. LUBENSKY, T.C. AND   Superpolymers, ultraweak solids and aggregates, *Phys. Today*,
   PINCUS, P.A.   1984, 44–50.

5. WITTEN, T.A   Structural fluids, *Phys. Today*, 1990, 21–28.

6. RINGSDORF, H., SCHILARB, B   Molecular architecture and functions of polymeric oriented systems,
   AND VENZMER, J.   *Angew. Chem.*, 1988, **27**, 113–158.

7. PUSEY, P.N. AND   Observations of a glass transition in suspensions of spherical
   VAN MEGEN, W.   colloidal particles, *Phys. Rev Lett.*, 1987, **59**, 2083–2086.

8. SIROTA, E.B., OUYANG, H.D ,   Complete phase diagram of a changed colloidal system. A
   SINHA, S.K., CHAIKIN, P.M.   synchrotron x-ray study, *Phys. Rev. Lett.*, 1989, **62**, 1524–1527.
   AND AXE, J.D.

9. KESAVAMOORTHY, R.,   Split second peak in structure factor of binary colloids—glass-like
   SOOD, A.K., TATA, B.V.R.   order, *J. Phys. C*, 1988, **21**, 4737–4748.
   AND ARORA, A.K.

10. SENGUPTA, S. AND   Theory of liquid–bcc–fcc coexistence in charge-stabilised colloidal
    SOOD, A.K.   systems, *Phys. Rev. A*, 1991, **44**, 1233–1236.

11. SOGAMI, I. AND ISE, N.   On the electrostatic interaction macroionic solutions, *J. Chem. Phys.*, 1984, **81**, 6320–6329.

12. TATA, B.V R , RAJALAKSHMI, M. AND ARORA, A.K.   Vapour–liquid condensation in charge colloidal suspensions, *Phys. Rev Lett.*, 1992, **69**, 3778–3781.

13 CALDERSON, F.L., BIBETTE, J. AND BIAS, J.   Experimental phase diagram of polymer and colloid mixtures, *Europhys. Lett.*, 1993, **23**, 653–659.

14. SANYAL, S., EASWAR, N., RAMASWAMY, S. AND SOOD, A.K.   Phase separation in binary nearly hard sphere colloidal Evidence for depletion force, *Europhys Lett.*, 1992, **18**, 107–110.

15. MELLAR, A. AND STAVANS, J.   Glass transition and phase diagrams of strongly interacting binary colloidal mixtures, *Phys. Rev. Lett.*, 1992, **68**, 3646–3649.

16. LOWEN, H., HARSEN, J.P. AND ROUX, J.N.   Brownian dynamics and kinetic glass transition in colloidal suspensions, *Phys. Rev. A*, 1991, **44**, 1169–1181.

17. SUBRATA, S AND SOOD, A.K.   To be published

18. CHAIKIN, P.M., MEGLIO, J M. DOZIER, W.D., LINDSAY, H.M. AND WEITZ, D.   Colloidal crystals. In *Physics of complex and supermolecular fluids*, (S.A. Safran and N A. Clark, eds), 1987, pp. 65–81, Wiley.

19. WEITZ, D.A., DOZIER, W.D. AND CHAIKIN, P.M.   Periodic structures in driven colloidal crystals, *J Phys. C*, 1985, **3**, 257–268.

20 STEVENS, M.J., ROBBINS, M.O. AND BELAK, J.F.   Shear melting of colloids: A nonequilibrium phase diagram, *Phys. Rev. Lett.*, 1991, **66**, 3004–3007.

21. LAHIRI, R. AND RAMASWAMY, S   Shear-induced melting and reentrance—a model, *Phys. Rev. Lett.*, 1994, **73**, 1043–1046.

22. CHAKRABORTY, J., SOOD, A.K. AND KRISHNAMOORTHY, H.R.   Brownian dynamics simulation studies of a charge-stabilised colloid under shear flow, *Phys Rev. E*, 1994 (in print).

23. TANG, Y., ARMSTRONG, A.J., MOCKLER, R.C. AND O'SULLIVAN, W.J.   Free expansion melting of a colloidal monolayer, *Phys. Rev. Lett.*, 1989, **62**, 2401–2404.

24. BURNS, M.M., FOURNIER, J.M. AND GOLOVCHENKO, J.A.   Optical matter: Crystallization and binding in intense optical fields, *Science*, 1990, **249**, 749–754.

25. CHOWDHRY, A., ACKERSON, B.J. AND CLARK, N.A.   Laser-induced freezing, *Phys Rev. Lett.*, 1985, **60**, 833–836.

26. CHAKRABORTY, J., KRISHNAMOORTHY, H.R. AND SOOD, A.K.   Density functional theory of laser-induced freezing in colloidal suspensions, *Phys. Rev. Lett.*, 1994 (in print).

27. WANG, H., ZHU, Y., BOYD, C., LUO, W., CEBERS, A. AND ROSENWIG, R.E.   Periodic branched structures in a phase-separated magnetic colloid, *Phys. Rev. Lett.*, 1994, **72**, 1929–1932.

28. HALSEY, T.C. AND MARTIN, J.E.   Electrorheological fluids, *Sci. Am.*, 1993, 42–48.

29. MEAKING, P.   Formation of fractal clusters and networks by irreversible DLA, *Phys. Rev. Lett.*, 1983, **51**, 1119–1122.

30. KAVEH, M.   Electron and optical wave phenomena, *Physica B*, 1991, **175**, 1–8.

31. WOLF, P.E., MARET, G., AKKERMANS, P. AND MAYNARD, R.   Optical coherent backscattering by random media, *J. Phys. (Fr.)*, 1988, **49**, 63–75.

32. PINE, D.J., WEITZ, D.A. MARET, G., WOLF, P.E., HERBOLZHEIMER, E. AND CHAIKIN, P.M.   Dynamical correlations of multiply scattered light. In *Scattering and localization of classical waves in random media*, (P. Sheng, ed.) 1990, pp. 312–372, World Scientific.

33. SANYAL, S., SOOD, A.K., RAMAKUMAR, S., RAMASWAMY, S. AND KUMAR, N.   Novel polarization dependence in diffusing wave spectroscopy of crystallizing colloids, *Phys Rev. Lett.*, 1994, **72**, 2963–2966.