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LECTURES ON COLLOID PHYSICS – SCATTERING, CLOUDING PHENOMENA & ISOTROPIC TO NEMATIC TRANSITION [1]

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TABLE OF CONTENTS

LECTURES ON COLLOID PHYSICS –
SCATTERING< CLOUDING PHENOMENA & NEMATIC TRANSION

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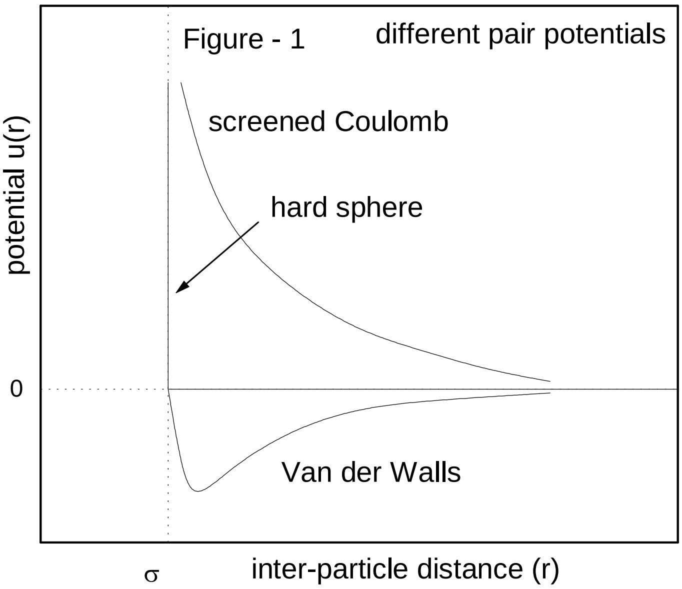
Three topics of current interest in the field of colloidal solutions form the subject discussed below: I) equilibrium structure of colloids, II) clouding phenomena and III) isotropic to nematic phase transition. While the first is concerned with the theory of structure of colloidal dispersions, the second one is about a phase transition of gas-liquid type observed on heating nonionic micellar solutions. The third topic illustrates Onsagar's theory of isotropic to nematic transition on increasing the number density of suspensions of long cylindrical particles.

1 Equilibrium Structure of Colloids

Colloids are suspensions of particulate matter in a fluid medium: milk, inks, blood, paints, etc. are a few common examples. Milk is a suspension of fats and proteins in water, various types of inks are suspensions of carbon particles in a suitable medium. Particle sizes in colloidal solutions are typically in the range of 10 A^o to 1 μm. Their number densities - depending on the specific situations - are in the range of 10^{12} cm^{-3} to 10^{17} cm^{-3}. All the physical properties of a suspension crucially depend on the inter-particle interactions. The interaction energy (or potential) between macroscopic bodies in a solvent medium has very many contributions [1]: a steric potential which describes the identity of the particles - it is usually modeled as a hard sphere potential, a repulsive Coulomb interaction between charged particles, an attractive van der Waals interaction - that arise due to different polarisibility of the particle and the solvent (Fig. 1). Two more important contributions arise in aqueous solutions: hydration repulsion between hydrophilic particle surfaces and hydrophobic interaction between water repelling particles. A simple way to model colloidal solution is to consider the particles as 'atoms' of a fluid with the solvent medium treated as a homogeneous background. In this approach all the intricate aspects of the solvent are incorporated in the inter-particle potential. Since colloidal phenomena occur at length scales of particle sizes (~ 100 A^o), it is appropriate to separate it from details of solvent structure at molecular sizes (~1 A^o). Once this aspect is realized, a wealth of concepts and techniques can be borrowed from the theory of atomic fluids [2]. Some of these from the theory of simple fluids or colloids are discussed in this section.



a) Statistical distributions:

Assume that there are N particles in a volume V, and let the total inter-particle potential is U($\mathbf{r}_1, \mathbf{r}_2, .. ,\mathbf{r}_N$). Hereafter, the notation {$\mathbf{r}_i$} will denote the set of co-ordinates of the N particles. The principal quantity used in describing equilibrium structure of fluids (at temperature T) is the Boltzmann - Gibbs distribution for the particle positions {$\mathbf{r}_i$}:

$$P(\{\mathbf{r}_i\}) = \frac{1}{Z} \exp[- \frac{U}{KT}]$$

where Z is the partition function and K is Boltzmann constant. All the physical quantities can be computed as averages (denoted with angular brackets <···>) with P:

$$\begin{aligned}\langle E\rangle &= \langle U\rangle + \frac{3}{2}\,\mathrm{N\,K\,T}\,,\\ \mathrm{F} &= -\,\mathrm{K\,T}\ln(\mathrm{Z}),\\ \mathrm{S} &= \frac{1}{\mathrm{K\,T}}\big(\langle E\rangle - \mathrm{F}\big)\,,\end{aligned}$$

where <E>, F and S are, respectively, the total average energy, free energy and entropy. If the potential energy is broken up into that between pairs (pair wise additivity), two reduced distributions are adequate to characterize all the thermodynamic quantities. The first is the probability distribution $p(\mathbf{r}_1)$ that a particle is in a volume element $d\mathbf{r}_1$ around the point $\mathbf{r}_1$. In a homogeneous fluid $p(\mathbf{r}_1)\,d\mathbf{r}_1 = (d\mathbf{r}_1/V)$. The second is the joint distribution $p(\mathbf{r}_1, \mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2$, which is the probability that one particle is in $d\mathbf{r}_1$ around $\mathbf{r}_1$ and another in $d\mathbf{r}_2$ around $\mathbf{r}_2$ (irrespective of others). It has the property: $p(\mathbf{r}_1, \mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2 \rightarrow p(\mathbf{r}_1)\,d\mathbf{r}_1 \times p(\mathbf{r}_2)\,d\mathbf{r}_2$ when $|\mathbf{r}_1\text{-}\mathbf{r}_2|$ is large compared to inter-particle separation. This is because a particle can induce a correlation only over a few inter-particle distances. Therefore, it is appropriate to introduce a function $g(|\mathbf{r}_1\text{-}\mathbf{r}_2|)$ defined as

$$p(\mathbf{r}_1,\ \mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2 \ = \ g(|\mathbf{r}_1 - \mathbf{r}_2|)\,\frac{d\mathbf{r}_1}{V}\,\frac{d\mathbf{r}_2}{V}.$$

Its argument is $|\mathbf{r}_1\text{-}\mathbf{r}_2|$, rather than $\mathbf{r}_1$ and $\mathbf{r}_2$, for a homogeneous fluid. Thus $g(|\mathbf{r}_1\text{-}\mathbf{r}_2|) \rightarrow 1$ for large values of $|\mathbf{r}_1\text{-}\mathbf{r}_2|$. This limiting form arises from the lack of interdependence between particles when they are separated by large distances. This function, $g(|\mathbf{r}_1\text{-}\mathbf{r}_2|)$, is called the pair distribution function; $g(|\mathbf{r}_1\text{-}\mathbf{r}_2|)\,d\mathbf{r}_2/V$ is the conditional probability that there is a particle in $d\mathbf{r}_2$ around $\mathbf{r}_2$ when there is one at $\mathbf{r}_1$. If g(r) is multiplied by the mean particle density N/V, one gets the density distribution n(r) around the particle at the origin: $n(r)\,d\mathbf{r} = (N/V)\,g(r)\,d\mathbf{r}$. The two reduced distributions, referred to earlier, are $p(\mathbf{r}_1)$ and g(r). For systems where interactions are pair wise pair wise additive, the total potential energy is that of all pairs:

$$U(\{\mathbf{r}_i\}) \ = \ \frac{1}{2}\sum_{i,\,j} u(\,|\,\mathbf{r}_i - \mathbf{r}_j\,|)\,,$$

where u(r) is the pair potential that depends only on $r = |\mathbf{r}|$ for spherical particles. The average of U is then given by

$$\langle U\rangle = \frac{N\,(N-1)}{2}\int u(r)\ g(r)\,\frac{d\mathbf{r}}{V}$$

The integral gives the interaction energy of a pair; one particle at the origin and another at a distance r, and the factor N(N-1)/2 is the number of distinct pairs.

Similarly, a formula for pressure can be derived. The total time derivative of the quantity $\sum_i \mathbf{r}_i\, \mathbf{p}_i$, where $\mathbf{p}_i$ is the momentum of the i^{th} particle, is

$$\frac{d}{dt}\sum_i \mathbf{r}_i \cdot \mathbf{p}_i = \sum_i \frac{d}{dt}\mathbf{r}_i \cdot \mathbf{p}_i + \sum_i \mathbf{r}_i \cdot \frac{d}{dt}\mathbf{p}_i$$

The time average of the left hand side over a (sufficiently) large time interval is zero if particles are confined to a finite volume V and velocities are not unbounded. The average of the first term on the right hand side is twice the kinetic energy which is 3 N K T. The average of the second term, which is the sum of terms like $\mathbf{r}_i\bullet\mathbf{F}_i$, $\mathbf{F}_i$ being the force on i^{th} particle, can be expressed as

$$\langle\, \mathbf{r}_i \cdot \frac{d}{dt}\mathbf{p}_i \,\rangle = -\int_{\text{surface}} P\ \ \mathbf{r}\cdot d\mathbf{s} - \frac{N(N-1)}{2}\langle\, \mathbf{r}\cdot\nabla u \,\rangle.$$

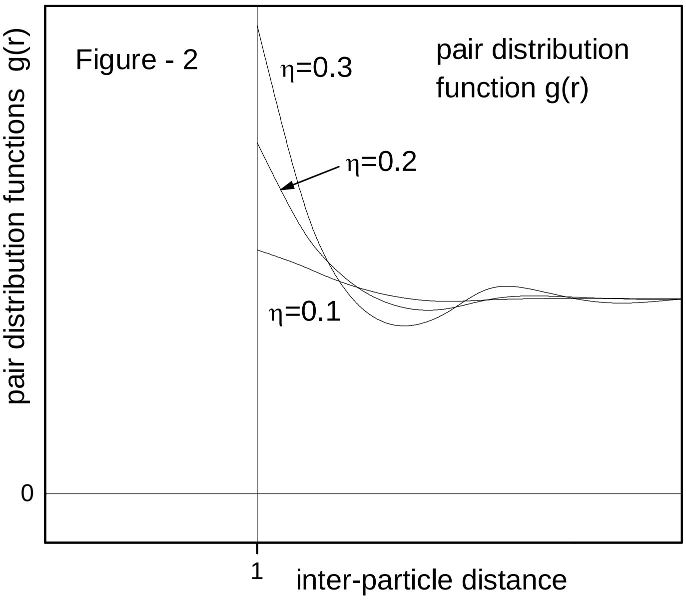
While the first integral term arises from the average pressure P acting on the surface of volume V, the second part accounts for the contribution from inter-particle forces of all distinct pairs; the force between any pair being replaced by the negative gradient of the potential. Then, using the result 3V for the surface integral of **r**, one gets the expression

$$P = \frac{N}{V}KT - \frac{N(N-1)}{2V}\int \mathbf{r}\cdot\nabla u\ \ g(r)\frac{d\mathbf{r}}{V}.$$

In this, the averaging is expressed in terms of the pair distribution function. This is known as the virial pressure as it is derived from the term $\sum_i \mathbf{r}_i\, \mathbf{p}_i$, called 'virial' in classical mechanics. Once pressure P is known, it can be related to free energy: $P = -(\partial F/\partial V)_T$, and thereafter all other thermodynamic quantities can be derived. Thus the pair distribution function g(r) contains all the information about the fluid. For an ideal gas g(r) = 1 for all r as the particles are uncorrelated. In the case of a low density hard sphere gas, g(r) = 0 for $r < \sigma$, the particle diameter, and g(r) = 1 for $r > \sigma$. The first condition shows that the shortest inter-particle separation is σ. For a general potential, an approximation to g(r) for low number density is $g(r) \approx \exp(-u / KT)$ which follows directly from Boltzmann distribution. It has the correct asymptotic behavior for large r. For denser systems, g(r) depends also on number density n = N/V. This dependence is shown in Fig. 2 for a hard sphere system. The position of the first peak in g(r) is always the mean inter-particle separation $\sim n^{-1/3}$.

b) Structure factor:

The pair distribution function is directly measurable by scattering experiments which are invariably used to probe the structure of solutions. In a scattering experiment, one measures the scattering intensity I(q) with respect to the scattering vector $\mathbf{q} = \mathbf{q}_i - \mathbf{q}_f$ where $\mathbf{q}_i$ and $\mathbf{q}_f$ are wave vectors of the incident and scattered radiation. If the scattering angle is θ, then for elastic scattering, $q = |\mathbf{q}| = (4\pi/\lambda)\ \sin(\theta/2)$; λ being the wavelength of the radiation. If a(q) is the scattering amplitude of a single particle - which is decided by the structure of the particle and its interaction with the radiation - the scattering intensity from a single particle is $I(q) = |a(q)|^2$. The radiation scattered by two particles separated by a distance r has a phase difference $\exp(i\,\mathbf{q}\cdot\mathbf{r})$. Therefore, for coherent elastic scattering, the total scattering amplitude from all the N particles which are at positions $\{\mathbf{r}_i\}$ is



$$A(q) = \sum_j a(q)\ \exp(i\,\mathbf{q}.\mathbf{r}_j)$$

The total scattered intensity is then given by $I(q) = \langle |A(q)|^2 \rangle$ where the angular brackets denote average over the (statistical) distribution of particle positions. Thus one gets

$$I(q) = \left| a(q) \right| \; N \left[1 + \frac{1}{N} \sum_{j \neq k} \left\langle \exp(i\, \mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k)) \right\rangle \right]$$

The average in this expression can be expressed in terms of the pair distribution function:

$$\left\langle \exp(\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k)) \right\rangle = \iint \exp(i\, \mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k)) \; g(|\mathbf{r}_j - \mathbf{r}_k|) \frac{d\mathbf{r}_k}{V} \frac{d\mathbf{r}_j}{V}$$

$$= \int \exp(i\, \mathbf{q} \cdot \mathbf{r}) \; [\, g(r) - 1] \frac{d\mathbf{r}}{V} + \int \exp(i\, \mathbf{q} \cdot \mathbf{r}) \frac{d\mathbf{r}}{V}$$

The double integral has been reduced to a single integral in the relative co-ordinate r. Further the last term - which is the delta function $\delta(\mathbf{q})$ - is separated out so that the Fourier transform is of [g(r) - 1], which goes to zero for large r. Since there are a total of $N(N\text{-}1) \cong N^2$ exponential terms in I(q), it can now be written as

$$I(q) = I_0(q) \; N \left[1 + \frac{N}{V} \int \exp(i\, \mathbf{q} \cdot \mathbf{r}) \, [g(r) - 1] \, d\mathbf{r} \right], \; \mathbf{q} \neq 0.$$

The terms inside the square bracket are called the structure factor S(q) - then, I(q) = N I(q) S(q) - since it contains information on the spatial distribution of particle positions. The first term N I(q) results from addition of intensity from N particles. The second term - proportional to N - denotes inter-particle interference effects. Thus the Fourier transform of [g(r) - 1] is directly measured by scattering experiments. The function h(r) = g(r) - 1 describes the correlation between two particles, and so it is called the pair correlation function.

If we take V as a sub-volume of the system, the number of particles, say N, in it will vary in time, and the mean single particle density is <N> / V. The average value of the number of pairs in V is <N(N-1)>. This can be expressed in terms of $g(|\mathbf{r}_1 - \mathbf{r}_2|)$:

$$\langle N(N-1) \rangle = \iint \langle N \rangle \frac{d\mathbf{r}_1}{V} \; g(|\mathbf{r}_1 - \mathbf{r}_2|) \, \langle N - 1 \rangle \frac{d\mathbf{r}_2}{V},$$

since the integrand gives the probability of finding one particle (out of N) at $\mathbf{r}_1$ and another (out of N-1) at $\mathbf{r}_2$. Note that <N> (d**r**/V) is the probability of finding any one of the particles in $d\mathbf{r}_1$. Using <N-1> ≅ <N> on the right hand side, one gets

$$\langle N^2 \rangle - \langle N \rangle = \left\langle \frac{N}{V} \right\rangle^2 V \int g(r) \, d\mathbf{r} = \langle N \rangle^2 + \left\langle \frac{N}{V} \right\rangle^2 V \int [g(r) - 1] \, d\mathbf{r}$$

which shows that the relative number fluctuation in V is given by

$$\left(\frac{\langle N^2 \rangle - \langle N \rangle^2}{N} \right) = 1 + \left\langle \frac{N}{V} \right\rangle \int [g(r) - 1]\, d\mathbf{r}$$

While the right hand side is simply the limit of S(q) as q → 0, the left hand side is the ratio of the isothermal compressibility to that of an ideal gas. Thus we arrive at an important relation:

$$S\,(q \to 0) = 1 + \frac{\langle N \rangle}{V} \int [g(r) - 1]\, d\mathbf{r} \equiv \frac{\langle N \rangle}{V^2} KT \times \left(-\frac{\partial V}{\partial P} \right)_T$$

which relates two measurable macroscopic quantities. Note that in the case of an ideal gas g = 1 and one gets the ideal gas law P = <N> KT/ V. Using the low density expression g = exp(-u/KT) in the above relation, it is also possible to derive the van der Waals equation. It is known that the isothermal compressibility diverges near the gas-liquid critical point. This means that h(r) = g(r) -1 becomes significant over the entire volume of the system which indicates the development of strong particle correlations near critical points.

c) Ornstein - Zernike equation:

Theories of pair correlation function h(r) invariably employ the Ornstein - Zernike equation (OZE). The principal idea in setting up this equation is to separate h(r) into a direct part c(r) and an indirect part. It is assumed that the direct part is short ranged just like the inter-particle potential. More explicitly, let c(| **r-r**' |) denote the direct correlation between a particle at **r** and another at **r**'. So h(r) - the total correlation between a particle at the origin and another at **r**'- can be expressed as

$$h(r) = c(r) + \int h(r')\, \langle N \rangle \, \frac{d\mathbf{r}'}{V} \; c(|\mathbf{r} - \mathbf{r}'|)$$

The first term on the right hand side is the direct part. Now, d**r**'/V is the probability of finding a particle in d**r**' and <N> d**r**'/V times c(| **r-r**' |) expresses the direct correlation between the particle at **r** and another at **r**'. This term multiplied by h(r'), then, yields the correlation between one particle at **r** and another at the origin. Since **r**' can be anywhere, it is integrated over the volume V. Seen in this way, the OZE expresses a consistency relation between the two parts of the correlation function. This is only one equation for two unknowns: c(r) and h(r). An approximation valid in the limit of small density, i.e. for <N>/V → 0, is c(r) = h(r) = exp(-u/KT) - 1.

Closure relations can now be introduced between the two correlation functions and the pair potential so as to get a closed system of equations. One of such relations is the mean spherical approximation which is specified by $c(r) = -u/KT$ for $r > \sigma$ (particle diameter) - this is obtained by assuming a weak potential (compared to KT) in the low density approximation - and the hard sphere condition $g(r) = 0$ for $r < \sigma$. A better approximation - called the Percus-Yevic closure (PYC) - is obtained as follows. In the low density approximation yields, $c \approx g-1 = \exp(-u/KT) - 1 = [1-\exp(u/KT)] \exp(-u/KT)$. Now we may replace the last term $\exp(-u/KT)$ by g itself - so as to correct for the low density approximation - and obtain the PYC:

$$c = \left[1 - \exp\left(\frac{u}{KT}\right)\right] g.$$

The mean spherical approximation (MSA) is obtained if the exponential is linearized and g is approximated to unity for values of r outside the hard core:

$$c\,(r) = -\frac{u}{KT}, \quad r \rangle \sigma; \qquad g(r) = 0, \quad r \langle \sigma$$

Note that the hard sphere condition must be imposed, as indicated above, when MSA is used To motivate yet another closure, note that the right hand side of OZE - which equals h – c - accounts for the correlation between two particles due to the presence of others. Now $h - c = 0$ in the low density limit. As a minor improvement, we may write

$$h - c \approx \left[\exp\left(\frac{-u_{eff}}{KT}\right) - 1\right] - \left[\exp\left(\frac{-u}{KT}\right) - 1\right] \approx \frac{u - u_{eff}}{KT}$$

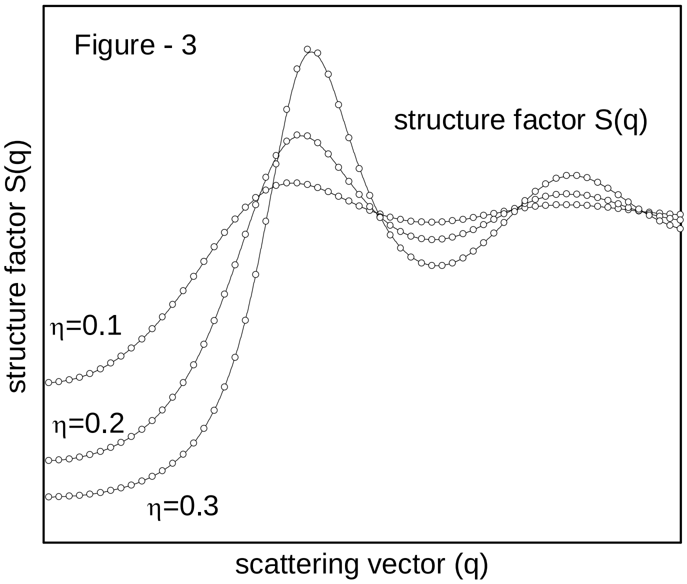
where u_{eff} is an effective potential which also includes effects of particle correlations. The last step is obtained by approximating the exponential functions. We may now write

$$g \approx \exp\left(-\frac{u_{eff}}{KT}\right) \equiv \exp\left[-\frac{u}{KT} + \frac{u - u_{eff}}{KT}\right]$$

Finally, $(u - u_{eff})/KT$ is eliminated in terms $(h - c)$ to obtain the hypernetted closure (HNC):

$$g = \exp\left[-\frac{u}{KT} + h - c\right]$$

Rigorous derivation of these relations are available in the literature [2]. However, it is clear that once the pair potential u(r) is known, the OZE can be solved together with an appropriate closure to obtain h(r), and then the structure factor. HNC for long range potentials and PYC for short range potentials are found to give good results. The pair distribution functions g(r) shown in Fig. 2 for hard sphere system are obtained using PYC. The corresponding S(q) are given in Fig. 3. Note that as the number density increases, i.e. as the mean separation between particles decreases, the peak position q_m in S(q) shifts to lower q values. It is possible to establish an approximate relation $2\pi q_m \langle r \rangle = 1$, analogous to Bragg's law, where $\langle r \rangle$ is the mean inter-particle separation.

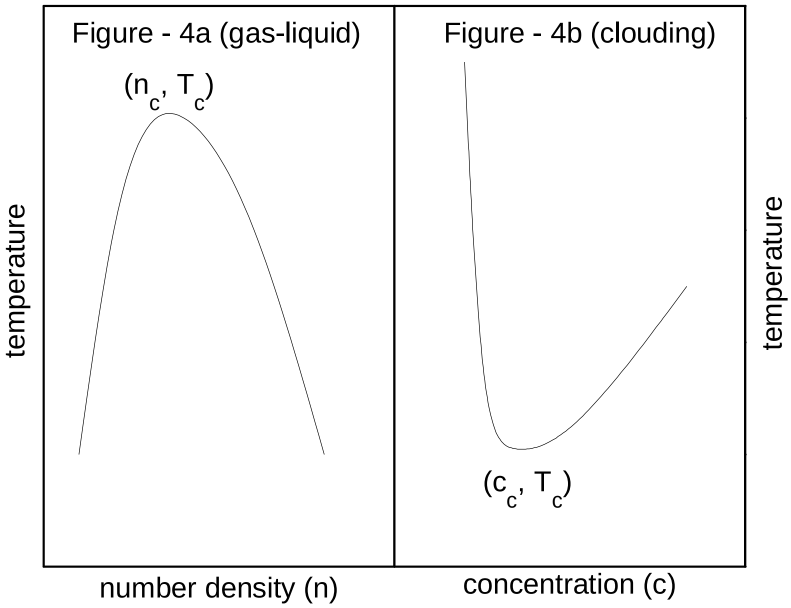


II. Clouding Phenomena in Nonionic Micellar Solutions

Equilibrium structure of matter - at a given temperature, T, and volume, V - is determined by the principle of minimum free energy: F = E - TS, where E is the average total energy and S is the entropy. The principles of minimum energy for mechanical equilibrium and maximum entropy for isolated thermodynamic equilibrium are combined together in terms of free energy when T and V are fixed externally. Phase changes occurring in various systems are understood in terms of this principle. A common example of such a phase transition is condensation of gases - see a schematic phase diagram in the temperature (T) number density (n) plane in Fig. 4a. The gaseous phase prevails above the critical temperature T_c. Below T_c, may have a gaseous phase, liquid phase or co-existence of both depending on number density. On approaching T_c (from above) in a system at critical density, n_c , one finds predominant scattering of light. This is modeled in terms of the Ornstein - Zernike formula for scattered intensity:

$$\frac{I(q)}{I_0} = \frac{S_0}{(1 + q^2 \xi^2)}$$

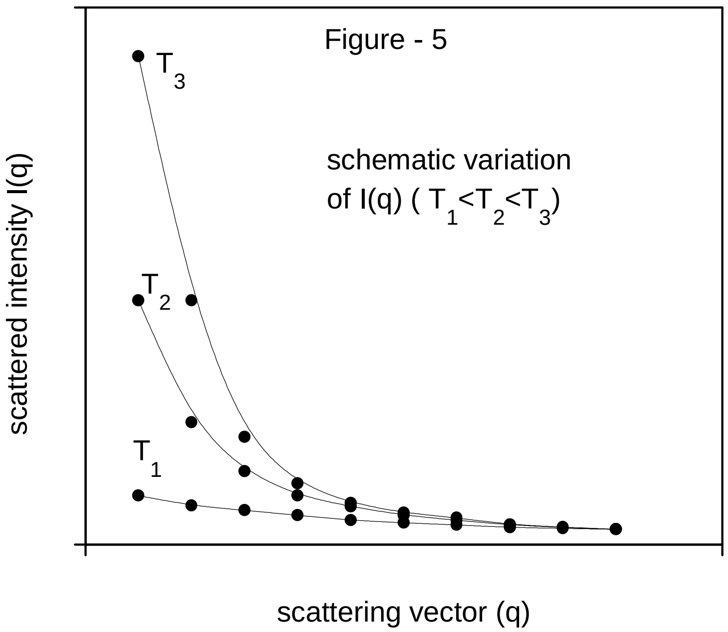
Here S_0 is the isothermal compressibility factor, explained earlier, and ξ is a characteristic length - called correlation length - over which strong correlations between particle positions persist in the system. These quantities diverge as power laws as $T \rightarrow T_c$: Thus $S_0 \sim t^{-\gamma}$ and $\xi \sim t^{-\nu}$ where $t = (T-T_c)/T_c$ is the reduced temperature; $\gamma \sim 1.23$ and $\nu \sim 0.63$ are two critical exponents.



a) Clouding Phenomena:

A phenomenon very similar to that just explained occurs in binary mixtures of water and certain organic compounds called surfactants. However, the phase transition occurs on heating the system: Fig. 4b shows a schematic clouding curve in the temperature (T) and surfactant concentration (c) plane. The solution that is found to be transparent below T_c becomes milky (or cloudy) as the phase boundary is approached. If the solution is heated and brought to a point inside the phase boundary, it separates into two phases - one rich and the other poor in surfactant concentration. Divergence of (osmotic) compressibility and correlation length are also observed.

Scattering experiments with slow neutrons (wavelength ~5 A^o) show the buildup of scattered intensity on approaching T_c (from below): see Fig. 5. The clouding phenomena, in surfactant-water mixtures, is like condensation of gases; but it occurs on heating the solution!



Surfactants are long organic molecules. Aqueous solutions of these molecules show many fascinating properties [1, 3]; they find applications in many industrial and biological processes. A common surfactant is Triton X-100 (isooctylphenoxy polyethoxy ethanol) which has the formula $(CH_3)_3$-C-CH_2-C-$(CH_3)_2$-C_2H_6-O-$(CH_2$-O-$CH_2)_{10}$-H. Its molecular weight is around 640. Another family of surfactants is polyoxyethelene glycol monoethers, $CH_3(CH_2)_{i-1}$ -O-$(CH_2$-O-$CH_2)_j$-H, denoted by C_iE_j (eg. C_8E_4, $C_{12}E_6$, etc.). These are called nonionic surfactants as they do not get ionized in aqueous solutions. There are also ionic surfactants, eg. cetyl trimethylammonium bromide (CTAB) with the formula $CH_3(CH_2)_{15}(CH_3)_3N^+Br^-$. Clouding phenomena is generally found in aqueous solutions of nonionic surfactants. For Triton X-100 solutions, T_c ~335 K and the critical concentration is ϕ_c ~ 6 Wt %. To understand the mechanism of clouding phenomena, we must first discuss the hydrophobic effect.

b) Hydrophobic Effect:

It is known that H_2O molecules form hydrogen bonds in water. They also form hydrogen bonds with chemical groups containing electronegative atoms (O, N, F, S, etc.) and hydrogen atoms covalently bonded to such atoms. Compounds having such molecular groups are soluble in water (eg. alcohols). These groups generally have electric dipole moments. On the other hand, non-polar molecules such as hydrocarbons with which water molecules cannot form hydrogen bonds are insoluble in water. The immiscibility of the later type of molecules is mainly of entropic origin and is known as the hydrophobic effect. A molecule of hydrocarbon in water is in an (imaginary) cage devoid of water molecules. Water molecules just outside this cage are more ordered as they organize in such a way to form hydrogen bonds among themselves - and not with the hydrocarbon. This induced ordering leads to a reduction in the entropy of water molecules. Thus, as per second law of thermodynamics - which states that all spontaneous processes must lead to an increase of net entropy - hydrocarbons do not mix uniformly with water; rather they exist in a separate phase. The loss of entropy of water turns out to be more than the entropy gain in case of uniform mixing of hydrocarbon and water molecules. Measurements of the (rather poor) solubility of hydrocarbons yield two empirical relations: i) The change in energy (more correctly enthalpy) on taking a hydrocarbon - which has n_c carbon atoms - from its bulk phase to water is $h \sim [-3.04 + 1.05\ (n_c-1)]$ KT, where $T \sim 298$ K. ii) The associated change in entropy is $s \sim [-5.06 - 0.44\ (n_c-1)]$ K. Thus uniform mixing of hydrocarbons with water is not favored even energetically when $n_c > 4$. There is always a reduction in entropy and consequently an increase in free energy $f = h - T\ s$. Thus the hydrophobic effect is mainly of entropic origin.

c) Aggregation of surfactants:

Surfactants have a water soluble head group (hydrophilic part) and a water insoluble hydrocarbon tail (hydrophobic part). For example, in Triton X-100 molecule, the part containing the ethelene oxide units ($-O-(CH_2-O-CH_2)-H$) - which is about 17 A^o in size - is water soluble while the remaining (~ 10 A^o) is the hydrocarbon part. Surfactants in aqueous solutions are expelled to the air-water interface, and they form a monolayer with the hydrophobic part pointing out of water. When their concentration is increased above a critical value - the critical micellar concentration - they self assemble to form aggregates. The inner core of the aggregates contains the hydrocarbon parts, and hydrophilic parts remain on the aggregate surface in contact with water. Aggregates -

that are generally called micelles - can be of several types: spherical micelles, cylindrical micelles, bilayers etc. In the first two cases, the radius of the aggregates is about the size of the molecule. Bilayers have a thickness that is twice the molecular size. Cylindrical micelles can become very long (~ 1 μm); in which case, they become flexible and entangled as in semi-dilute polymer solutions. A bilayer can close on itself to form vesicles - which have water inside as well as outside. Association of bio-molecules in water to form cell membranes - which are very much like vesicles - tissues, etc., and many other biological processes arise out of their duel (hydrophobic and hydrophilic) character. *It is the second law behind all these phenomena, including even the origin of cell formation and hence life itself, is an exciting line of thought.*

d) Mechanism of Clouding Phenomena:

For the sake of simplicity, let us assume that there are only spherical micelles in a nonionic surfactant solution. If we consider Triton X-100 solutions, it has a molecular weight around 645. Experiments determining particle sizes show that about 140 molecules aggregate to form a micelle. Thus, there would be around 2×10^{17} micelles per cm^{-3} in a 4 Wt % solution. The free energy gained in the formation of micelles is, typically, of the order of 10 KT per surfactant, and so micelles can be considered as the basic units to characterize the solution structure. Thus, as a first approximation, the micellar solution can be modeled as a superamolecular fluid with micelles as the 'atoms' of the fluid. However it is necessary to have an inter-micellar potential to make use of the theories of fluid structure already discussed. As explained earlier, two competing reasons are responsible for the formation of micellar aggregates: the hydrophobic effect which forces the hydrocarbon tails to assemble together and the hydrophilic tendency of head groups to mix with water. As solution temperature increases, the latter contribution becomes weaker [1] due to alterations in the polar character of the head groups. The net effect is an increase in the effective attraction between the micelles. In addition, there is a reduction in the range of the repulsive interaction between the micelles due to decrease in hydration of the head groups on increasing temperature. Fig. 6 shows a schematic illustration of the temperature dependence of the inter-micellar interaction. The increase of attractive interaction with temperature is the primary mechanism behind clouding phenomena.

e) Baxter's Model:

To solve a simple statistical model for clouding phenomena, one may approximate the inter-micellar potential with a hard sphere part - describing the micelle - followed by a square well part with a temperature dependent depth $u_0(T)$. The range (or width Δ) of the potential is much smaller (~ 5 A^o) in comparison with the particle diameter (σ ~ 60 A^o). For this model, the OZE and PYC can be solved approximately by treating Δ/σ as a perturbation parameter [4]. The first order approximation, then, turns out to be the same as a model proposed by Baxter to demonstrate the gas-liquid phase transition in atomic fluids. The structure factor of the model - which also can be derived analytically - can be used to analyze neutron and light scattering data from nonionic micellar solutions. The clouding curve can also be mapped onto the theoretical phase diagram of the model [5]. These applications yield the temperature dependence of the potential depth $u_0(T)$ which is an important parameter for characterizing nonionic micellar solutions.

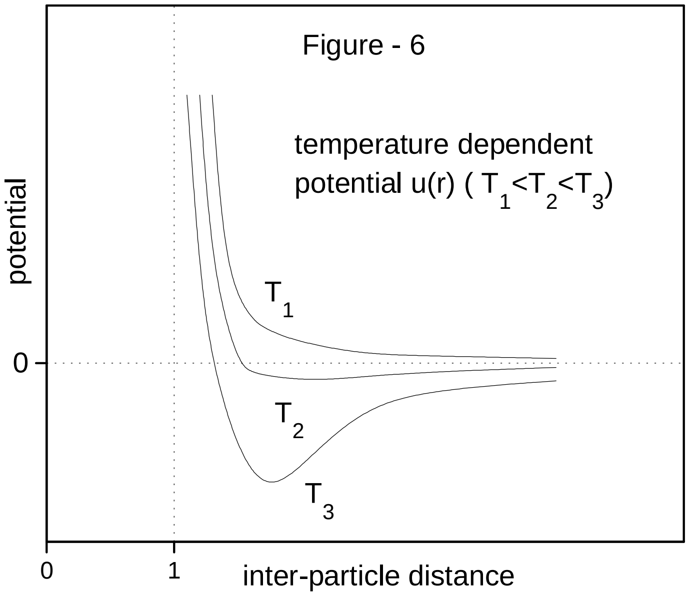


Figure - 6

III Isotropic to Nematic Phase Transition

Atomic systems show three main phases of matter: gas, liquid and crystalline phases. The gaseous phase has a random distribution of atoms because the large inter-particle distances do not give rise to any correlation between particle positions. There are short ranged correlations - described by the pair distribution function g(r) - in the liquid phase. Crystalline phase has long range order. Liquid crystal consists of highly anisotropic rod-like molecules (eg. p-azoxy-anozole PAA) which have orientational degrees of freedom as well as translational degrees of freedom. In liquid crystals, correlations as in liquids as well as in crystals co-exist, and there are many possible phases: nematic, smetic and cholesteric are the main types. In the nematic phase, the centers of mass of molecules are distributed as in liquids, but there is a long range order in the orientation of the molecules. The smetic phase is a stack of slabs of molecules; most of the molecules in a slab are oriented at a specific direction with respect to the plane. In the cholesteric phase, molecules in a slab are oriented along a direction in the plane of the slab, but the direction changes in a continuous way between successive slabs and repeats after a few number of slabs.

The aim of this section is to discuss a simple theory - due to Onsagar [6] - which predicts a phase transition from the isotropic to nematic phase in a fluid of rod-like particles. Consider an assembly of N hard rods in a volume V. In the hard rod model - just as in the hard sphere model - the only interaction among the rods is that arising out of the excluded volume effect. For anisotropic particles, there are two contributions to entropy: translational and orientational. Particles are quite far apart at very low density, (N/V), and both entropic contributions are maximized for random positions and orientations, the resulting structure is that of an isotropic fluid. On increasing the density, the volume available per particle reduces. Translational entropy is then maximized if this volume is maximized. This is achieved if most of particles align along a particular direction. Alignment certainly reduces the orientational entropy, however, the total entropy gets maximized as there are 3 translational degrees of freedom in comparison to 2 orientational degrees of freedom for a particle. Thus, on increase of density, one would expect a transition from an isotropic fluid to a nematic liquid crystal. Now, an orientational distribution function $f(\omega)$ can be introduced such that $f(\omega)\, d\omega$ is the fraction of particles oriented within the solid angle $d\omega$ around the direction ω. Then, $f(\omega)$ must be a constant in the isotropic phase, and the normalization condition $\int f(\omega)\, d\omega = 1$ shows that $f(\omega) = (1/4\pi)$ in that phase. As density increases, $f(\omega)$ deviates from this isotropic value. If the length to diameter ratio of particles is large (~20), the transition would occur at relatively lower density. So a simple theory - using the virial expansion for

Hemholtz free energy - can be developed to estimate the thermodynamic variables at the transition.

a) Virial Theory:

Free energy has the virial expansion:

$$\frac{F}{N\,KT} = \ln(\lambda^3 \rho) - 1 - \rho B_2 + \cdots$$

In this equation, $\rho = N/V$ is the particle number density, λ is the thermal wavelength and B_2 is the second virial coefficient. For anisotropic particles, the inter-particle potential $u(\mathbf{r}_1, \mathbf{r}_2, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$ depends on the relative orientations of the particles as well. So the usual expression for B_2 must be averaged over the orientationl distribution function:

$$B_2 = -\frac{1}{2\,V} \iint f(\boldsymbol{\omega})\, f(\boldsymbol{\omega}')\, d\boldsymbol{\omega}\, d\boldsymbol{\omega}' \iint \left[\exp(-u/KT) - 1\right] d\mathbf{r}_1\, d\mathbf{r}_2 \,.$$

For hard bodies, $u = \propto$ when particles overlap and $u = 0$ otherwise. Therefore the integral over $\mathbf{r}_1$ and $\mathbf{r}_2$ yields V times the excluded volume, $V_{ex}(\boldsymbol{\omega}, \boldsymbol{\omega}')$, for two particles oriented along directions $\boldsymbol{\omega}$ and $\boldsymbol{\omega}'$. Thus B_2 can be simplified as

$$B_2 = \frac{1}{2} \iint f(\omega)\, f(\omega')\, d\omega\, d\omega'\, V_{ex}(\omega, \omega').$$

Note that $V_{ex}(\boldsymbol{\omega}, \boldsymbol{\omega}')$ reduces to 8 times the particle volume if particles are spherical. It is also necessary to add the orientational entropy

$$S_{or} = -N\,K \int f(\boldsymbol{\omega})\, \ln(4\pi f(\boldsymbol{\omega}))\, d\boldsymbol{\omega}.$$

to the free energy. This expression, which is simply the definition of entropy in canonical ensemble, vanishes in the isotropic phase since $f(\boldsymbol{\omega}) = (1/4\pi)$. Thus the free energy (accurate to B_2) for an anisotropic fluid is

$$\frac{F}{N\,KT} = \ln(\lambda^3 \rho) - 1 - \rho B_2 + N\,K \int f(\boldsymbol{\omega})\, \ln(4\pi f(\boldsymbol{\omega}))\, d\boldsymbol{\omega}$$

So the free energy is a functional of $f(\boldsymbol{\omega})$. Minimizing this functional, under the constraint $\int f(\boldsymbol{\omega})\, d\boldsymbol{\omega} = 1$, yields the equation:

$$\ln(4\pi\, f(\boldsymbol{\omega})) = 1 + \mu + \rho \int f(\boldsymbol{\omega}')\, V_{ex}(\boldsymbol{\omega}, \boldsymbol{\omega}')\, d\boldsymbol{\omega}'$$

which determines f(ω). The Lagrange multiplier μ, which was introduced to incorporate the normalization condition, can be determined using the same condition once f(ω) is known. Thereafter, F and other thermodynamic quantities like pressure, chemical potential, etc. can be computed.

b) Simple calculations:

To give a simple illustration of this theory, consider hard rods of diameter D and length L with $D << L$. If two rods are perpendicular, the excluded volume is $L^2 (2D)$. In the general case, when the angle between the rods is γ, one finds that

$$V_{ex}(\omega,\omega') = 2\ L^2\ D \left| \sin(\gamma) \right|$$

This expression is the leading term - neglecting all end effects - valid when $D << L$ [6]. If (θ,φ) are the polar angles (denoting **ω**) for one rod, and similarly (θ′,φ′) for the other, then γ satisfies the equation

$$\cos(\gamma)\ =\ \cos(\theta)\cos(\theta')\ +\ \sin(\theta)\sin(\theta')\ \cos(\varphi-\varphi')\ .$$

Assuming that the rods are more or less aligned along the z-direction - when θ and θ′ are nearly zero - we can use a trial function

$$f(\theta)\ = \frac{\alpha}{4\pi}\ \exp(\ -\ \alpha^2\,\theta^2 / 4\ ),\quad 0 \le \theta \le \pi / 2\ ,$$

to describe the orientation distribution function. The parameter α is assumed to be much larger than unity since f(θ) is highly peaked around θ = 0. Again, assuming reflection symmetry about the x-y plane, we have f(θ) = f(π-θ). The normalization constant (α/4π) is only approximate since it is calculated by extending the range of θ to (0, ∝) which is acceptable as $\alpha >> 1$. Now, α is to be determined by minimizing the free energy. The orientation entropy is calculated as

$$S_{or} \cong\ -N\,K\left[-\ln(\alpha)+1\right].$$

This is obtained by using two approximations: extending the limit of θ and using 2 π θ dθ for the angular element 2 π sin(θ) dθ. These approximations are reasonable since our interest is to estimate the free energy in the well ordered nematic phase. In a similar way [8], the virial coefficient is calculated as

$$B_2 = \frac{L^2\,D\,\pi}{4}\ \frac{4}{\sqrt{\pi\,\alpha}}\ \ \equiv\ b\ \frac{4}{\sqrt{\pi\,\alpha}}$$

The parameter $b = L^2 D\, \pi/4$ has been introduced because - as can be easily verified - $B_2 = b$ in the isotropic phase. Then the free energy, expressed in terms of KT, is

$$\frac{F}{N\,KT} = \ln(\rho) + \rho b \frac{4}{\sqrt{\pi\alpha}} - \ln(\alpha) - 1 + C_0 .$$

where $C_0 = \ln(\lambda^3) - 1$. Minimizing with respect to α yields its optimum value: $\alpha_0 = 4\, b^2 \rho^2 / \pi$. On putting it back into F, the free energy of the nematic phase (subscript- *n*) is obtained as

$$\frac{F_n}{N\,KT} \cong \ln(\rho) + 2\ln(\rho b) + 1\ln(4/\pi) + C_0 .$$

For the isotropic phase (subscript- *i*) the orientation entropy S_{or} is zero, and since $B_2 = b$, the free energy is given by

$$\frac{F_i}{N\,KT} \cong \ln(\rho) + \rho b + C_0 .$$

The standard thermodynamic relations:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,\,T} , \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,\,T} ,$$

can now be used to calculate the osmotic pressure and chemical potential of particles. It is easy to verify the resulting expressions in the two phases:

$$P_n = 3KT , \quad \mu_n = KT\left[\ln(\rho_n) + 2\ln(\rho_n b) + 1\ln(4/\pi) + C_0\right] .$$

for the nematic phase, and

$$P_i = KT\rho_i\,(1 + b\,\rho_i) , \quad \mu_i = KT\,[\,\ln(\rho_i) + 2b\rho_i + 1 + C_0\,]$$

for the isotropic phase. The region of density, over which the two phases co-exist, is determined by the equilibrium conditions: $P_i = P_n$ and $\mu_i = \mu_n$, which yield the equations

$$3\phi_n = \phi_i\,(1 + \phi_i) , \quad 3\ln(\phi_n) + 3 + \ln(4/\pi) = \ln(\phi_i) + 2\phi_i .$$

Here, we have introduced the dimensionless variables: $\phi_i = b\,\rho_i$ and $\phi_n = b\,\rho_n$. Note that $\phi = \eta\, L/D$, where η is the volume fraction of the rods. These equations yield the solutions $\phi_i \cong 3{\cdot}45$ and $\phi_n \cong 5{\cdot}12$. The corresponding value of the variational parameter is $\alpha = 33{\cdot}4$, which is much larger than unity as expected. Thus the assembly of rods is isotropic for $\phi < \phi_i$; it is nematic for $\phi > \phi_n$, and both phases co-exist for intermediate values ϕ. So this simple theory predicts a first order phase transition; the volume fraction of the rods at the transition can be very small for large values of L/D. There is another set of solutions which satisfy the equilibrium conditions, however, the value of α is small (~ 0·5) and hence does not represent a nematic phase. Two review articles [8,9] discuss several extensions and applications of this theory.

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