SOLUBILITY AND MIXING IN FLUIDS

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INTRODUCTION

The standard definition (Mc-Graw Hill Dictionary (1984)) of solubility is as follows: It is the ability of the substance to form a solution with another substance. The solution is a single homogeneous liquid, solid or gas phase that is a mixture in which the components (liquid, gas, solid or the combination thereof) are uniformly distributed throughout the mixture. Finally, miscibility denotes the tendency or capacity of two or more liquids to form a uniform blend, that is to dissolve in each other. For historical reasons the substance less abundant in the mixture is called a solute, while the most abundant one a solvent. Here we shall concentrate on nonelectrolytes i.e. solutions in which none of the components is in the form of free ions.

Traditionally, solubility and mixing belong to the realm of chemistry and material sciences and many standard textbooks on physical chemistry (Nernst (1904), Atkins (1993)) or chemistry (Grant and Higuchi (1990), James (1986)) treat this problem, usually within the scope of thermodynamics. Here apart from thermodynamics we shall discuss other issues such as: the statistical mechanical theories of mixtures, relation between intermolecular interactions and demixing, coupling between ordering and demixing, and kinetics of demixing which includes spinodal decomposition in binary liquid mixtures. The following special examples will be discussed: polymer blends, diblock copolymers, liquid crystals, and ternary mixtures including surfactants (amphiphiles). Within the scope of physics of solubility and mixing one can study such diverse phenomena as: mixing of two simple liquids, collapse of the polymer chain in the solvent, flocculation of colloidal particle upon the addition of the polymer chains, mixing of two polymer components in a liquid state, ordering of copolymers and ternary mixtures of oil, water and surfactant or formation of micelles in aqueous solutions. In reality, very rarely we have completely
pure substances, thus the properties of mixtures and the phenomenon of mixing and demixing are of prime importance for science and technology.

An old alchemist maxim, “similia similibus solvuntur” (“like dissolves like”), is the oldest rule of solubility. This rule can be a very good guide in the study of mixing and solubility providing one can precisely define what in a given case is the degree of likeness. For example two simple liquids of low molecular mass can easily mix, say, at room temperature, while after polimerization they demix well above the room temperature.

1. THERMODYNAMICS

Solubility also means the maximum amount of the solute that can be solubilized in the solvent at the given thermodynamic conditions. Within thermodynamics one formulates simple rules for solubility of gases and solids in liquids (Hildebrand and Scott (1950)):

1. The solubility of a gas is proportional to its partial vapor pressure (Henry law).
2. The gas with the higher critical temperature, and boiling point, is more soluble than one with a lower critical temperature.
3. The solubility of a gas diminishes with increasing temperature.
4. The solubility of a solid increases with increasing temperature.
5. A solid having a higher melting point is less soluble at a given temperature than the one having a lower melting point, providing that the enthalpies of melting are comparable.
6. A solid with large enthalpy of melting is less soluble at a given temperature than the one with small enthalpy of melting, providing that the melting temperatures are comparable.
7. If the rule 1. is satisfied for a solute in two immiscible solvents in contact, then the ratio of its concentration in these solvents is, for a given pressure and
temperature, a constant (Nerst distribution law).

These rules are not always satisfied, sometimes only for very dilute solutions. Nonetheless, in many cases they provide very valuable informations about solubilities of different substances in different solvents based on few thermodynamic properties of pure substances. All these rules can be expressed in simple mathematical forms (Atkins (1993), Hildebrant and Scott (1950)) e.g. the rules 4., 5., 6. can be expressed as follows:

\[
\ln x = -\frac{\Delta H^s_{solute}}{R} \left( \frac{1}{T} - \frac{1}{T_m} \right),
\]

where \(x\) is the mole fraction of the solute in the saturated solution (solution in equilibrium with the solute solid), \(\Delta H^s_{solute}\) is the enthalpy of melting for the solute and \(T_m\) is its melting temperature. \(R\) is the gas constant and \(T\) the temperature.

1.1 Colligative properties

The elevation of the boiling point, the depression of the freezing point in a solution and the osmosis are properties which in the first approximation do not depend on the specific nature of the solute, but only on its amount in the solvent. Such properties are called colligative properties. For a dilute solution we find that the addition of the solute into the pure solvent rises its boiling temperature by:

\[
\Delta T = \left( \frac{RT_b^2}{\Delta H^v_{solvent}} \right) x,
\]

where \(T_b\) is the boiling temperature of the pure solvent and \(\Delta H^v_{solvent}\) is the enthalpy of vaporization for the pure solvent. Similarly the addition of small amount of solute into the solvent lowers its freezing temperature by

\[
\Delta T = -\left( \frac{RT_m^2}{\Delta H^s_{solvent}} \right) x,
\]

where \(T_m\) is the freezing temperature of the pure solvent.
The phenomenon of osmosis takes place when the solution is separated from
the pure solvent by a semipermeable membrane, which allows the flow of a solvent
from the pure phase to the solution. The pressure that has to be applied to stop
this flow is called the osmotic pressure, \( \Pi \). For a dilute solution one gets van’t Hoff
equation relating this pressure, the volume of the solution, \( V \), and the number of
moles of the solute in the solution \( n \):

\[
\Pi V = nRT. \tag{4}
\]

Since \( n/V \) is given by the total mass of the solute divided by the molar mass \( M \)
and the volume, combination of the measurements of the osmotic pressure and
van’t Hoff formula allows to determine the molar mass of the solute. This method
is particularly useful for determining the mass of macromolecules, however, in this
case it is often necessary to include in Eq(4) the next term in the virial expansion
of the osmotic pressure.

1.2 Binary mixtures: liquid-vapor coexistence

In the ideal mixture the components mix in all proportions without any change
of volume or enthalpy. The partial vapor pressure in the ideal binary mixture of A
(or B) component coexisting with the ideal liquid mixture is given by \( P_A = x_A(g)P \)
\( (P_B = x_B(g)P) \). The total pressure \( P \) is related to the (Raoult law) vapor pressures
above pure A \( (P_A^*) \) and pure B \( (P_B^*) \) liquids:

\[
P = P_A + P_B = x_A(l)P_A^* + x_B(l)P_B^*, \tag{5}
\]

These two equations define the vapor \( (x_A(g) = 1 - x_B(g)) \) and the liquid \( (x_A(l) =
1 - x_B(l)) \) composition at coexistence. In Fig.1 the composition pressure diagram
is shown; the region between the two curves (given by the above equations) is the
two phase region, where the relative amounts of vapor and liquid are given by the
lever rule (Atkins (1993)).
This type of diagram (now temperature and composition, Fig. 2) is the basis of fractional distillation. We start with the A,B mixture at point 1 on the diagram and evaporate it (1-2 dashed line). Next we condense it again until we reach point 3. The resulting liquid mixture is now richer in component B. Repeating these steps (evaporate it along the 3-4 dashed line etc) we can obtain almost pure B phase. Analogous process is used to purify solids and is called the zone refining. In many mixtures the process of distillation is stopped at a certain point where the composition of the vapor is the same as the composition of the coexisting liquid (Fig.3,4). This point is called the azeotrope. Since at this point the liquid boils without changing its composition, thus the fractional distillation proceeds only until positive azeotrope is met (Fig.4). On the example shown in Fig.3 we reach a negative azeotrope by straight distillation, i.e. by continuously removing the vapor from the vessel of the boiling liquid mixture. For example, the mixture of ethanol and water has the azeotrope at \( T = 78^\circ C \) and at 4% of water (by mass); water and nitric acid has the azeotrope at \( T = 122.4^\circ C \) and 60\% of HNO\(_3\) (mole fraction) (at 1 atm.); hydrogen chloride and water has the azeotrope at \( T = 108^\circ C \) and 20\% (by mass) of HCl (at 1 atm). Of course, the location of the azeotrope changes with pressure. The following rules can help us in deciding when we can expect an azeotrope in the liquid mixture (Rowlinson and Swinton (1982)):

1. The closer the vapor pressures of the pure components of the mixture the more likely is azeotropy. It is inevitable at any temperature at which they are the same. It also means that when the vapor pressures are very close then even small departures from ideality of the mixture can produce an azeotrope.

2. The closer the vapor pressures of pure components the more rapidly does the azeotropic composition change with temperature.

3. An increase of temperature and of vapor pressure in a positive azeotrope (max-
imum on the p-x diagram and minimum on the T-x diagram (Fig.4)) increases the mole fraction of the component whose vapor pressure increases the more rapidly with temperature. The converse holds for a negative azeotrope (Fig.3). These rules are not without exceptions, but usually can be a very useful guide.

1.3 Partially miscible liquids

Mixtures are often far from being ideal and consequently at suitable conditions we can expect demixing in the liquid state. In some systems demixing can take place as we lower the temperature (Fig.5) or as we rise the temperature (Fig.6). More complicated cases are shown in Figs.7-10. (Atkins 1993, Landau and Lifshitz (1980)). The maximum (minimum) of the curve in Fig.5 (Fig.6) is called the upper (lower) critical (or consolute) point. Gases usually mix very well at normal pressures, however, at very high pressures they can demix; then sometimes the phrase gas-gas immiscibility is used (Rowlinson and Swinton (1982)). The densities of these fluid phases at high pressures are comparable to the density of the liquid phases at ‘ordinary’ low pressures critical points.

Fig.10 is very similar to the liquid-solid phase diagram for the binary mixture (instead of vapor we have liquid and instead of liquid we have solid). The lowest temperature of the liquid mixture at freezing in this case is obtained for the eutectic composition (point E on the diagram).

For ternary mixtures the phase diagram is often represented in the form of the Gibbs triangle. The Gibbs phase rule states that in a system of $r$ components and $M$ coexistent phases it is possible arbitrarily to preassign $r - M + 2$ variables from the set $T, P, x_j^i, i = 1 \cdots M, j = 1 \cdots r - 1$ (Callen (1960)). In particular, it means that the maximum number of coexistent phases in the system is $r + 2$. One should note here that if the system spontaneously orders in the arbitrarily small external field (magnetic or electric) then the number of coexistent phases can be larger if we
include in the set of thermodynamic variables these fields.

So far we have considered the liquid mixtures in the bulk system. The confinement of the fluid in a capillary also affects mixing and solubility. The detailed discussion of thermodynamics of confined mixtures can be found in Evans and Marconi (1987). However, the theoretical problem of whether confinement increases or decreases solubility and mixing is still not resolved. The problem is especially important for narrow pores of the size of few molecular diameters.

STATISTICAL MECHANICS THEORIES OF MIXTURES

The modern statistical mechanical approach to inhomogeneous and/or homogeneous fluids and fluid mixtures is based on density functional theory (DFT) (Evans (1979)). The central quantity of interest in DFT is the Helmholtz free energy \( F[\rho_1 \cdots \rho_m] \) which is a unique functional of the local densities \( \rho_i(r) \) \((i = 1 \cdots m)\) in the \( m \) component simple atomic mixture. In the homogeneous system \( \rho_i = N_i/V \) where \( N_i \) is the number of molecules of type \( i \) and \( V \) is the volume. The Helmholtz free energy as a functional of the densities completely specifies its statistical and thermodynamical properties. The equilibrium state of the system corresponds to the global minimum of the grand thermodynamic potential, obtained from \( F \) by a Legendre transform.

In the case of anisotropic liquids (e.g. liquid crystals) consisting of elongated rigid molecules one particle distribution function, \( \rho(r, \omega) \), which depends on the position of the center of mass \( r \) of the molecule and its orientation in space \( \omega \), represented by the three Euler angles, describes the structure of the system. Consequently the free energy of liquid crystals is a functional of \( \rho(r, \omega) \). More complicated cases are also possible, depending on the structure and flexibility of molecules.

For simplicity we confine further discussion to simple atomic fluids. The free
energy can be split into the ideal part and the excess part as follows:

\[ F[\rho_1 \cdots \rho_m] = F_{id}[\rho_1 \cdots \rho_m] + F_{ex}[\rho_1 \cdots \rho_m]. \quad (6) \]

For the non-interacting system the excess part is zero and the ideal part can be easily calculated from the partition function:

\[ F_{id} = k_B T \sum_{i=1}^{m} \int d\mathbf{r} \rho_i(\mathbf{r}) \left\{ \ln(\rho_i(\mathbf{r})\lambda_i^3) - 1 \right\}, \quad (7) \]

where \( \lambda_i \) is the thermal de Broglie wavelength of the \( i \)-th component in the mixture. The integrals are performed over the whole volume of the system. The excess part, arising from the interactions, can be written in the following general form:

\[ F_{ex}[\rho_1 \cdots \rho_m] = \sum_{i,j=1}^{m} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \int_0^1 dl (l - 1) c_{ij}(\mathbf{r}_1, \mathbf{r}_2; [l\rho_1, \cdots, l\rho_m]). \quad (8) \]

The functions \( c_{ij} \) are the Ornstein Zernicke direct correlation functions (Hansen and McDonald (1986)). Although this relation is formally exact, the form of the direct correlation functions is in general unknown for inhomogeneous and even for homogeneous liquids. Various approximations to the exact DFT functional has been proposed: weighted density approximation (WDA) (Tarazona(1985)) (Curtin and Ashcroft (1985)) and modified weighted density approximation MWDA (Denton and Ashcroft (1989)) for pure systems, later applied to binary mixtures of hard spheres (Denton and Ashcroft (1990) (1991)) (for different approach to mixtures see Xu and Baus (1987), (1992)). (for review Baus (1990)). Density Functional Theories have been also applied to the description of structural phase transitions in liquid crystals (Poniewierski and Holyst (1988), (1990), Allen et al (1993))). A recent review on this subject is given by Löwen (1994) and Allen et al (1993). In general, the theory has been aimed at explaining the properties of inhomogeneous systems from the known properties of homogeneous systems. Usually the form of
the direct correlation functions for homogeneous system are required as the input for the theory. For the homogeneous mixture these functions are defined via the Ornstein Zernicke (OZ) equation:

\[ h_{ij}(|\mathbf{r}_1 - \mathbf{r}_2|) = c_{ij}(|\mathbf{r}_1 - \mathbf{r}_2|) + \sum_{k=1}^{m} x_k \rho \int d\mathbf{r}_3 c_{ik}(|\mathbf{r}_1 - \mathbf{r}_3|) h_{kj}(|\mathbf{r}_3 - \mathbf{r}_2|) \] (9)

where \( \rho = \sum_{i=1}^{m} N_i / V \) is the total density and \( h_{ij} \) is the two point correlation function. This set of equations with suitable closure (e.g. Percus Yevick (PY) for hard spheres (Henderson and Leonard (1971))) can be solved and the functions \( c_{ij} \) can be calculated. Now combining these results together with MWDA completely specifies the properties of the inhomogeneous and/or homogeneous mixture.

In general, solving the OZ equation for mixtures interacting with complicated potential is very difficult. One can then resort to some old methods known in the theory of mixtures as a one fluid approximation in the more general scheme known as conformal theories of mixtures (section 2.3) (Rowlinson and Swinton (1982), Hansen and McDonald (1986)).

2.1 Homogeneous system and ideal mixtures

In homogeneous mixtures one defines mixing functions i.e. for any thermodynamic functions \( A(N_i) \) the mixing function is defined as

\[ A^{mix} = A(N_1 \cdots N_m) - \sum_{i=1}^{m} A_i(N) \] (10)

where \( N = \sum_{i=1}^{m} N_i \) is the total number of particles and \( A_i \) is the thermodynamic function of interest for the pure system of \( i \)-th component. The mixing function vanishes for the pure system. If the interactions between particles are the same then the form of the thermodynamic potentials is very simple. The Helmholtz free energy (same for Gibbs free energy) is then (Eqs.(6-8)):

\[ F^{mix} = N k_B T \sum_{i=1}^{m} x_i \ln x_i \] (11)
Strictly speaking real mixtures are non-ideal except in very special cases when we have mixtures of isotopes of low molecular mass and when quantum effects are negligible. However, often the ideal solution is a very good starting point in the description of many properties of mixtures e.g. gas-liquid coexistence.

2.2 Homogeneous systems and excess mixing functions

The difference between the actual value of the thermodynamic mixing function and its ideal value (Eq.(11)), for the same temperature, composition and volume (or pressure), is called the excess function (the same name is used in DFT (Eq.(8)), but its meaning there is different). The simplest form of the mixing function for a binary mixture is given by the Guggenheim quadratic form (Henderson and Leonard (1971), Rowlinson and Swinton (1982),

\[ F^E = N\chi x_1 x_2 \]  

obtained in the simplest lattice approximation. In the lattice approximation both the excess Gibbs free energy and the excess Helmholtz free energy are the same and \( \chi/k_BT \) is the interaction parameter independent of temperature and pressure (volume). Lattice models are often used for the description of certain properties of mixtures (Furman et al (1977), Walker and Vause (1983), Carneiro and Schick (1988)). By comparing Eq(10-12) and Eq(6-8) it follows that in general \( \chi \) is a complicated integral of the direct correlation function. Only in the limit of low density \( \chi \) is independent of \( x_i \). In this limit \( c_{ij} = f_{ij} = \exp (-v_{ij}/k_BT) - 1 \), where \( v_{ij}(|r|) \) is the two body interaction potential between molecules of components \( i \) and \( j \). In this approximation \( \chi \) can be explicitly calculated from Eq(8).

Usually in thermodynamics one defines by Eq(12) the Gibbs free energy, \( G^E \), assuming that \( \chi \) is the function of temperature and pressure. Then the heat of
mixing (enthalpy)

\[ H^E = N \left( \chi - T \frac{\partial \chi}{\partial T} \right) x_1 x_2 \]  

(13)

and the change of volume in the system upon mixing is

\[ V^E = N x_1 x_2 \frac{\partial \chi}{\partial P} \]  

(14)

Most mixtures of simple liquids (e.g. argon, krypton) have positive heat of mixing i.e. heat is absorbed, but the excess volume \( V^E \) can be of either sign. The excess quantities are usually small, e.g. \( V^E \) per mole in the 50% solution (in mole fraction) of tetrachloroethene in cyclopentane at 25°C is -8 mm\(^3\) (the mixture contracts) (total volume is \( \sim 10\)cm\(^3\)) and the excess heat of mixing \( H^E \) is 800J per mole.

### 2.3 Conformal fluid theories and one fluid approximation

One of the oldest approaches to the theory of homogeneous mixtures dates back to van der Waals and it is known as the one fluid approximation. In this approach the excess properties of the mixture are expressed in terms of the quantities of a hypothetical pure fluid. It applies to mixture in which the interaction potential \( v_{ij}(r) \) satisfies the scaling relation

\[ v_{ij}(r) = \epsilon_{ij} v(r/\sigma_{ij}) \]  

(15)

for all \( i, j \). Often \( \sigma_{ij} \) and \( \epsilon_{ij} \) (for \( i \neq j \)) are related to pure components. The most frequently used combination rules are as follows: \( \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \) and \( \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \) known as the Lorentz and Berthelot rule, respectively. The hypothetical fluid is characterized by the potential given by Eq(15) with some energy parameter \( \epsilon \) and length parameter \( \sigma \). In order to specify these parameters one makes the following approximation:

\[ h_{ij}(r) = h(r/\sigma) \]  

(16)
and sets
\[ \sigma^3 = \sum_{i,j=1}^{m} x_i x_j \sigma_{ij}^3 \]  

(17)

The interaction parameter for this hypothetical one component fluid reads
\[ \epsilon = \sum_{i,j=1}^{m} x_i x_j \epsilon_{ij} \sigma_{ij}^3 \sigma_{ij}^3 \]  

(18)

and the interaction potential is \( \epsilon v(r/\sigma) \). Now the excess mixing properties of the mixture are related to the excess properties of this fluid. This approximation is known as the van der Waals one-fluid approximation (Henderson and Leonard (1971)). The comparison with computer simulations for the model binary mixture of Lenard-Jones fluids shows a very good agreement with the theory (Hansen and McDonald (1986)). The approximation breaks down when the molecules of different components are very disparate in sizes and have very different energy parameters. Another of its drawbacks is that it always leads to a negative volume change, \( V^E \), upon mixing. More complicated approximations are also possible but usually lead to worse agreement with computer simulations. For real systems the simple Lenard Jones mixture constitutes a rather poor approximation (Hansen and McDonald (1986)).

One has to remember that excess mixing quantities are rather small and that small deviations of the model interaction potential from the real potential between the molecules can change even the sign of the excess quantity (e.g. \( V^E \)).

3. INTERACTION POTENTIAL AND MIXING

The intermolecular forces have their origin in quantum mechanics and classical electrostatics. According to the Hellman-Feynmann theorem the interactions between the molecules can be calculated according to the laws of electrostatics, once the distribution of electrons has been determined from the Schrödinger equation.
From the simple Coulomb potential originates various important interactions at the molecular level. The dispersion van der Waals attractive interactions are responsible for boiling (gas liquid transition). It is now known that the reduction of the range of attraction in the system results in the complete disappearance of the liquid phase even if the attraction is strong at short distances (Tejero et al (1994)). It implies for example that \( C_{60} \), where interactions are of the short range, is a substance which should not have a liquid phase (Hagen et al (1993)). Molecules, when brought together, strongly repel each other, preventing the overlap of electronic orbitals. This interaction gives the molecule its size and shape and is known as hard core repulsion or steric interaction. Steric interactions are responsible for freezing transition (Alder and Wainwright (1957)) structure of liquids (Hansen and McDonald (1986)), and structural transitions in liquid crystals (Onsager (1949), Frenkel (1990)). Van der Waals attraction and steric repulsion are very important since they are present in every molecular system. Apart from them there are many specific interactions. One interesting example considered here is hydrogen bonding occurring between e.g. water molecules. This interaction is responsible for the fact that ice has lower density than liquid water; and that the highest density of water occurs at 4\(^\circ\)C. The extremely high boiling and freezing point of water is also due to this interaction and the tetrahedral structure formed by water molecules. Here we shall try to partially answer the question how these various interactions affect mixing.

3.1 Van der Waals interactions

If we apply the Berthelot rule, which holds resonably well for van der Waals forces (Israelachvili (1985)), in the Guggenheim model (Eq(12)) for the binary mixture we find:

\[
\chi \sim (\sqrt{\epsilon_{11}} - \sqrt{\epsilon_{22}})^2 > 0. \tag{19}
\]
Since \( \chi \) is always greater than zero, we may conclude that van der Waals interactions promote demixing. At sufficiently low temperatures the excess part of the Gibbs free energy outweights the ideal part (Eq.(11)) and demixing occurs. With this simple model we obtain the type of phase diagram shown in Fig.5. In the first approximation the square root of the energies \( \epsilon_{ii} \) are proportional to the polarizability of the molecules of \( i \)-th component.

The van der Waals interactions for any two bodies in vacuum are always attractive. Also they are attractive for identical bodies in a solvent. However, one may have repulsive van der Waals interactions between two different solute molecules in a solvent. This happens whenever the index of refraction (related to polarizabilities) of the solvent is intermediate between two different solute molecules (Israelachvili (1985)). It happens in many mixtures of organic solvents and different organic polymers (Van Oss et al (1980)).

3.2 Steric interactions

It has been believed until recently that steric interactions alone cannot induce demixing. This belief has been based on the fact that the ideal entropy of mixing decreases if the demixing transition takes place. This decrease of the entropy, \( S \), can be compensated by the decrease of the energy, \( U \), so that the free energy, \( F = U - TS \) decrease upon mixing. Since in the hard core system the interaction energy is zero, one has not expected the demixing transition in such a system. This conclusion is supported also by the explicit calculation of \( \chi \) parameter (Eq.(12)) for the binary fluid mixture of hard spheres in the low density approximation. One finds \( \chi < 0 \) in this limit and concludes that mixing is favored in the system.

Recent computer simulations have shown that this is not the case and that in a binary mixture of model system of hard core molecules differing in size only the demixing transition driven by the increase of entropy occurs. Although the
ideal entropy is the largest in a homogeneous mixture, the entropy associated with the free volume is larger in the demixed fluid (Biben and Hansen (1991) Frenkel and Louis (1992), Van Duijneveldt and Lekkerkerker (1993), Dijkstra and Frenkel (1994), Dijkstra et al (1994)). At certain concentration of solute molecules the latter outweights the former and demixing occurs. The role of steric interactions in real mixtures has not been resolved yet. Clearly it is a many body effect.

### 3.3 Hydrogen bonding

The unique properties of water follow from its ability to form the tetrahedral structure in the liquid, induced by hydrogen bonding (Israelachvili (1985)). The interaction is electrostatic, but its strength (10-40 kJ/mol) is one order of magnitude larger than the strength of the van der Waals energy ($\sim 1$kJ/mol). This interaction depends on the orientation of molecules and in general is not pair-wise additive.

The solubilization of molecules which do not form hydrogen bonds (e.g. alkanes and other hydrocarbons) in a hydrogen bonding solvent (methane, water, acetic acid) involves forming a clathrate cage around the solute molecule (Fig.11). The solvent molecules adapt such orientation close to the non bonding solute as to saturate its hydrogen bonds with other solvent molecules. It means that solvent molecules around the solute molecules are more ordered than the molecules in the bulk solvent. It leads to the decrease of entropy in the process of solubilization, which for this reason becomes unfavorable. For n-butane in water the heat of mixing is $\Delta H = -4.2$kJ/mol, while the change of the entropy $-T\Delta S$ (at $T = 25^\circ C$) is 28.7kJ/mol. Thus, the change of entropy contributes 85% to the change of the Gibbs free energy $\Delta G = \Delta H - T\Delta S$. For longer hydrocarbons the contribution of entropy to the total change of the Gibbs free energy is even larger (Israelachvili (1985)). Low solubility of non hydrogen bonding molecules in water is entropic in nature and is known as a hydrophobic effect. The solubility of hydrocarbons in hydrogen
bonding solvent (e.g. methane) decreases with the length of the hydrocarbon, e.g. the critical temperature for n-pentane is $T_c = 287^\circ C$, while for n-hexane becomes $T_c = 307^\circ C$ (at normal pressure) (Rowlinson and Swinton (1982)).

Methane and water mix very well in all proportions at room temperature and this is due to the fact that both form hydrogen bonds. We expect that molecules of right geometry, containing electronegative atoms (oxygen atoms in alcohols, nitrogen atoms in amines) are capable of forming hydrogen bonds. At low temperatures the hydrogen bonds forming between the solute and solvent molecules enhance mixing ($\chi < 0$). If we raise the temperature the bonds are broken and liquids demix above the lower critical temperature due to van der Waals forces ($\chi > 0$). Thus, hydrogen bonds are responsible for enhanced mixing at low temperatures and consequently for the existence of the lower critical point (Fig.6) (Walker and Vause (1983)). We expect that this phenomenon should strongly depend on the molecule geometry.

4. POLYMER BLENDS AND POLYMERS IN SOLUTIONS

The simple lattice model presented in section 2 (Eq.(12)) has been applied to polymer blends and polymers in solutions by Flory and Huggins. (Flory (1953)). The free energy for the binary mixture of two homopolymers A and B consisting of $N_A$ and $N_B$ monomers respectively is given by the Flory-Huggins expression:

$$F_{mix}/(Mk_BT) = \frac{x_A}{N_A} \ln x_A + \frac{x_B}{N_B} \ln x_B + \frac{\chi}{k_BT}x_A x_B.$$  \hspace{1cm} (20)

Here $x_A = n_A N_A / (n_A N_A + n_B N_B)$ is the mole fraction of A monomers in the mixture, $n_i$ is the number of polymer molecules of $i$ (A or B) component, $M = n_A N_A + n_B N_B$ is the total number of monomers in the system and $\chi$, in the polymer physics and chemistry, is called the Flory-Huggins interaction parameter. In the Flory-Huggins theory incompressibility is assumed, same as in the Guggenheim
model of simple mixtures. The critical temperature is

\[ T_c = \frac{2N_AN_B}{k_B\chi(\sqrt{N_A} + \sqrt{N_B})^2} \]  \hspace{1cm} (21)

and at the critical composition

\[ x_A^c = \frac{\sqrt{N_B}}{\sqrt{N_A} + \sqrt{N_B}}. \]  \hspace{1cm} (22)

The ideal mixing entropy is reduced by a factor \( N_A \) and/or \( N_B \) and thus, the critical temperature is very large for the polymer mixtures \( (N_A, N_B \gg 1) \). Indeed polymers separate very easily. Even small differences in the interaction potential get magnified by a factor of \( N_A, N_B \) and thus the critical temperatures are often much higher then the temperature at which the polymer molecule breaks due to the breakage of chemical bonds linking the monomers. Even a binary mixture of isotope polymers (one deuterated) can undergo a demixing transition at room temperature if \( N_A, N_B \) are sufficiently large (Gehlsen et al (1992)).

A mesoscopic theory of polymer chains has been formulated by Edwards (1966) and applied to polymer blends, polymers in solutions, membranes in solutions etc.

### 4.1 Polymer blends

Despite the fact that the Flory-Huggins theory has been used for more than four decades, only recently it has been carefully checked experimentally (Bates et al (1988), Gehlsen et al (1992)) and in computer simulations (Deutsch and Binder (1992)). It follows, from computer simulations that \( \chi \) parameter has the following form

\[ \frac{\chi}{k_BT} = \frac{\alpha}{T} + \beta, \]  \hspace{1cm} (23)

where \( \alpha \) and \( \beta \) are constants independent of temperature or composition. In the first approximation \( \alpha \) is related to the attractive van der Waals forces while \( \beta \) to steric interactions (called sometimes excluded volume interactions). Sometimes, in
experimental works, it is assumed that \( \alpha \) depends linearly on the concentration \( x \) (Roe and Zin (1984)). Typically we find \( \alpha \sim 1 \) and \( \beta \sim 10^{-3} - 10^{-4} \). From the previous section we know that the effective interaction \( \chi \) is related to the integrals of the direct correlation functions (Schweizer and Curro (1988)) and thus \( \chi \) can be, in principle, a complicated function of temperature, density and concentrations. In general, \( \chi \) should not depend on the global architecture of the polymer chain.

In polymer systems the quantity of interest is the radius of gyration, i.e. the linear size of the region occupied by a single polymer molecule, consisting of \( N \) monomers of length \( l \). It is defined as follows (Doi and Edwards (1986)):

\[
R^2 = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle (r_i - r_j)^2 \rangle. \tag{24}
\]

Here \( r_i \) gives the location of the \( i \)-th monomer in the polymer chain and \( \langle \cdots \rangle \) denotes the statistical average. For the polymer blend the dependence of \( R \) on \( N \) is (the leading term in \( N \)) as follows:

\[
R = \sqrt{\frac{N l^2}{6}} \tag{25}
\]

characteristic for the non-interacting chain. It means that interactions between monomers in the same polymer chain are screened by the presence of other chains (Doi and Edwards (1986), de Gennes (1979)) or a solvent (Edwards (1975)). As the temperature is lowered the scaling of \( R \) with \( N \) does not change. However, the chains shrink progressively (\( R \) decreases) as the critical temperature is approached (Holyst and Vilgis (1994)).

One can deduce the structure of a polymer blend from the scattering experiments. The scattering intensity \( S(q) \) has the following form (de Gennes (1979)):

\[
S^{-1}(q) = \frac{1}{x_A g(N_A, q)} + \frac{1}{x_B g(N_B, q)} - 2 \frac{\chi}{k_B T}, \tag{26}
\]
where \( g(N, q) = 2N(y + \exp(-y) - 1)/y^2 \) and \( y = Nq^2l^2/6 \). The contrast for the neutron scattering is achieved by the deuteration of one of the components. This approximation is known as the random phase approximation (RPA). The characteristic length in the problem is given by the radius of gyration \( R \) (Eq(25)).

From the theoretical point of view it is interesting to note that although the critical point in a binary mixture of polymers belongs to the universality class of the Ising model, in the limit \( N \to \infty \) the mean field theory becomes exact. In particular the critical exponents measured for the system have the mean field values for \( |T - T_c|/T_c \geq 1/N \) (de Gennes (1977), Holyst and Vilgis (1993)). This behavior has been confirmed in experiments (Schwahm et al (1987)).

Polymer blends are compressible mixtures (Floudas et al (1993)), but the role of this factor in the Flory-Huggins theory is still under theoretical study (Lifschitz et al (1994)).

4.2 Polymers in solutions

In the theory and experiment one often discusses three types of solvents: good, bad and theta solvents. Since for \( N_A \gg N_B = 1 \) the critical concentration is very low \( (x_A^c \sim \sqrt{1/N_A}) \) we can expand \( F^{mix} \) in \( x_A \) and find for this dilute solution:

\[
F^{mix}/(Mk_BT) = \frac{x_A}{N_A} \ln x_A + Bx_A^2 + \frac{1}{6}x_A^3 \cdots,
\]

(27)

where \( B = (1/2 - \chi/(k_B T)) \) is the osmotic virial coefficient (Atkins (1993), de Gennes (1979)). For \( B > 0 \) the solution is classified as bad, for \( B < 0 \) it is classified as good and for \( B = 0 \) it is classified as theta or Flory solvent. The nature of the solvent depends on temperature. For each solvent there is a unique temperature (called the theta temperature) when \( B = 0 \) and the solution becomes nearly ideal. In a theta solvent the chains behave, in the first approximation, according to Eq.(25).
In a good solvent the polymer molecule swells and

\[ R \sim N_A^{\nu} \]  

(28)

with the Flory exponent \( \nu \approx 3/5 \), which should be compared with \( \nu = 1/2 \) (Eq(22)) for the polymer chain in a blend and polymer chain in a theta solution. In a bad solvent the chains shrink and \( \nu \leq 1/2 \). In fact, close enough to the critical temperature each solvent becomes a bad solvent. The Flory-Huggins theory predicts correctly the location of the critical point (de Gennes (1979), Holyst and Vilgis (1993)) but not the shape of the coexistence curve close to the critical point. More informations on polymers in solutions can be obtained in a recent monograph (des Cloizeaux and Jannik (1990)).

It is often assumed that the theta temperature must reflect the competition between the attractive van der Waals forces and the short range steric interactions. However, it does not have to be the case. As shown explicitly by Frenkel and Louis (1992) in a simple lattice model of a polymer chain consisting of monomers interacting with steric interactions only and solvent consisting of small molecules interacting with the the same steric interaction the Flory-Huggins parameter is

\[ \frac{\chi}{k_BT} = \frac{1}{2}c \ln (1 + z_s) > 0. \]

(29)

Here \( c \) is a coordination number of the lattice and \( z_s \) is the fugacity of the solvent molecules. Thus, in this system with purely steric interactions we may have a bad, good and theta solvent by changing the chemical potential of the solvent (Dijkstra et al (1994)). The mechanism of demixing in such a mixture is clear. The fraction of the volume accessible to small solvent particles increases when the large particles cluster. Of course, in this model system, demixing is a purely entropic effect. Also the coagulation (clustering) of colloidal particles in a polymer solution is an entropic
effect (Meijer and Frenkel (1994)). The clustering of colloidal particles increases the total number of accessible polymer configurations. The effective attraction between the colloidal particles, responsible for coagulation, is not pair-wise additive (Shaw and Thirumalai (1991)) and that is why its quantitative theoretical description is so difficult. The role of steric interactions in polymer solutions is not fully understood.

We note that in the process of preparation of the polymer blend, one first prepares a solution of A and B polymers in a solvent and then evaporates the solvent. The comparison of the theory and experiment is often plagued by the inevitable polydispersity of the polymer masses. And finally, we point out that often instead of using mole fraction one uses either volume fraction or simply the density of monomers in the description of the free energy of mixing in polymer solutions (Atkins (1993), De Gennes (1979)).

As we see, polymers are not easily mixed even at high temperatures. Usually chemical means are used to induce mixing. One of them is a chemical modification of one of the components in such a way as to induce hydrogen bonds between the different components. For example PSD (deuterated polystyrene) and PBMA poly (butyl methacrylate) are not miscible. However, modifying PSD by attaching at random OH groups along the chain makes PSD(OH)/ PBMA blend miscible. It is due to the fact that OH groups from PSD(OH) form hydrogen bonds with CO groups on any segment of PBMA (Hobbie et al (1994)). Another way to induce miscibility is even more direct. One can simply join one polymer chain with the other by chemical methods. In this way diblock and multi block copolymers are formed.

5. ORDERING AND DEMIXING

There are many examples of demixing induced by ordering and vice versa. These effects occur in complex fluids such as diblock copolymers (Bates (1991),
Bates and Fredrickson (1990)), amphiphilic systems (Gompper and Schick (1994), Laughlin (1994)), and mixtures of liquid crystals (De Gennes and Prost (1993)).

5.1 Mixtures of liquid crystals

For commercial applications in the display industry only mixtures of liquid crystals are used. By mixing two nematic liquid crystals one can lower its freezing point (eutectic composition Sec 1. on Thermodynamics) without strongly affecting its isotropic-nematic phase transition point. Such mixture exhibits anisotropic properties in the liquid state in a much wider temperature range than the pure substances. Usually the point at which the nematic-isotropic transition occurs is called the clearing point.

Miscibility is used as a first test for new phases in liquid crystals. If the two materials give the same texture and are miscible in all proportions maintaining this texture they must have the same symmetry. However, we have learned that demixing does not have to reflect differences in the symmetry of phases. Differences in the shape and size of molecules are sufficient to induce demixing. Nonetheless, the miscibility test is still very useful, since it is quick and simple.

NMR allows to measure internuclear distances of solute molecules if the solvent is nematic. Elongated isomers are more readily to be solubilized by nematic solvents and this effect is used in chromatography.

Doping the nematic solvent with chiral solute induces a cholesteric (twisted) ordering in the system with a very large pitch (the wavelength of the twist). Changing the composition of this mixture allows to vary the pitch continuously. The pitch, in a dilute solution, is inversely proportional to the concentration of the solute molecules. In chiral, ferroelectric smectic C* one can increase the pitch by dissolving in the system non chiral solute.

In the homogeneous solution of the small monomeric units and nematic solvent
the fast polymerization reaction between the monomers results in the demixing and leads to the formation of the polymer dispersed liquid crystals (PDLC), which are used as switchable windows, light shutters, displays. Demixing is induced here since the length of the polymeric component of the mixture grows in the polymerization reaction and according to Eq.(21) the critical temperature gets higher for longer chains. If the reaction is fast, the droplets of the nematic solvent, which forms in the process of demixing, are homogeneously distributed in the solid polymeric matrix. Usually the reactions require more components such as curing agents, catalysts etc (Doane (1990)).

The extremely rich phase behavior of liquid crystals and liquid crystalline polymers has been described theoretically in several models: lattice spin model (Sivardière (1980)), Onsager model for elongated molecules (Deblieck and Lekkerkerker (1980), Van Roij and Mulder (1994)), combination of the Flory-Huggins model for mixtures and Maier-Saupe model for liquid crystals (Brochard et al (1984)), Maïssa and Sixou (1989), Holyst and Schick (1992)). The following results follow from these theoretical studies. Nematic-isotropic phase transition in mixtures is always accompanied by partial demixing. Nematic phase is always richer in the component which orders easier. Azeotrope at the nematic-isotropic phase transition is found in binary mixtures where both components have very similar isotropic-nematic transition temperatures in pure systems. The azeotrope concentration is very close to the critical concentration for demixing inside the nematic phase. All the diagrams shown in (Figs.(1-10)) are found in binary mixtures of liquid crystals if instead of vapor we have the isotropic phase and instead of liquid the nematic phase. The topology of many diagrams is even more complicated (Brochard et al (1984)). Nematic order parameter (De Gennes and Prost (1993)) always couples to the concentration. The demixing at the isotropic nematic phase transition is driven
by ordering, however, inside the nematic phase we can also observe the isotropic demixing (Fig.5,9) which changes the nematic order parameter. The demixing inside the ordered nematic mixture has the same origin (isotropic van der Waals or steric interactions) as the demixing shown in Fig.5 for simple isotropic liquid mixture. The roles of the anisotropic steric (shape) interactions and attractive interactions in the process are not fully understood. The demixing in the ordered nematic liquid mixture (Casagrande et al (1982), Dorgan and Soane (1990)) and ordered smectic liquid mixture (Siaud et al (1990)) has been observed in experiments, confirming many of the above stated predictions.

5.2 Diblock copolymers

Polymers are usually not miscible (section 3.), but at the same time for practical applications we need homogeneous mixtures. One way to prevent demixing transition is the chemical bonding of A polymer to the B polymer. In this way diblock and multiblock copolymers are formed (Bates and Fredrickson (1990)). Although the phase separation is now prohibited at the macroscopic scale, the system can undergo the so called microphase separation. The ‘demixing’ in the AB diblock copolymer system takes place at the scale given by the size of the radius of gyration and at much lower temperatures than the demixing in the polymer AB blend. The system forms many ordered phases in a liquid state: lamellar, gyroid (Matsen and Schick (1994)), diamond, cubic and hexagonal. The microscopic interactions responsible for the formation of these phases are the same as those responsible for the demixing transition in the AB polymer blend (Leibler (1980)) and the same Flory-Huggins parameter $\chi$ is used in the description of both systems. The AB diblock copolymer molecules form A rich and B rich domains and chemical bonds joining A and B molecules reside at the interface between the domains (Fig.12). The molecules are stretched in the ordered phase at low temperature and the char-
acteristic period of the ordered structures scales with the number of monomers in a molecule, $N$, as $N^{2/3}$. The mixing of the A and B homopolymers can be enhanced by the addition of the AB diblock copolymer. The latter has similar effect on the AB polymer blend as an amphiphilic molecule on the mixture of oil and water, although amphiphiles can be more effective in enhancing mixing between immiscible liquids (Holyst and Schick (1992)).

5.3 Amphiphilic systems

The amphiphilic molecules consist of two parts: a polar head which can form hydrogen bonds and a hydrocarbon tail. Such molecules are not easily solubilized in water because of their long tails. At a certain, usually low, concentration called critical micelle concentrations the amphiphilic molecules aggregate and form closed structures called micelles. The interior of the micelle consists of the hydrocarbon tails and has the structure and density of the hydrocarbon liquid. The polar heads reside on the surface of the micelle, shielding solvent molecules (water) from the interior hydrocarbon liquid. The geometrical shape of the micelles depends on the maximum length of the hydrocarbon chain, $l_c$, cross section area occupied by the polar head, $a_0$, and hydrocarbon volume, $v$ (Israelashvili (1985), Proceedings (1985)). For example, spherical micelles can form for $v/(a_0 l_c) < 1/3$, nonspherical micelles (in particular cylindrical) for $1/3 < v/(a_0 l_c) < 1/2$ and flat bilayers or vesicles for $1/2 < v/(a_0 l_c) < 1$. They are usually polydisperse in size. As we see, the hydrogen bonding and hydrophobic effect are responsible for the formation of these structures. When the concentration of amphiphilic molecules becomes comparable to the concentration of the water solvent, certain ordered, bincontinuous phases are formed such as: simple cubic (Fig.13), diamond (Fig.14), and gyroid structures (Fig.15). The internal surfaces of these structures are formed by the polar heads. The structures are periodic in three dimensions and the internal surfaces may
assume the configuration of minimal surfaces. The minimal surface is characterized by zero mean curvature at every point; each point on this surface is a saddle point.

Amphiphilic molecules strongly reduce the surface tension between hydrocarbon liquid and water and enhance mixing between these two immiscible liquids. One characteristic structure formed in the ternary mixture of oil, amphiphiles and water is the microemulsion. This homogeneous phase is characterized experimentally by the enhanced scattering at a certain nonzero $q$ vector. The form of the water-water scattering intensity

$$S(q) = (a + gq^2 + cq^4)^{-1}$$

with negative $g$ fits the data from scattering experiments very well (Teubner and Strey (1987)). It reveals the internal structure of the microemulsion with a characteristic length of order of 400 Å (size of the amphiphile molecule is about 30 Å). Inside the microemulsion water rich regions of the size of the characteristic length are separated by the amphiphiles from the oil rich regions of a similar size. On the macroscopic scale the system can be characterized by the large amount of these internal water-oil interfaces. Various surface and bulk properties of microemulsions are described by Ciach (1992) and Gompper and Schick (1994). The simplest Landau model which can be used for the description of bulk and surface properties of microemulsion is given by the following functional:

$$F[x(r)] = \int d\mathbf{r}((\triangle x)^2 + g(x)(\nabla x)^2 + f(x)),$$

where, $\triangle$ denotes the laplacian, $\nabla$ the gradient,

$$g(x) = g_2 x^2 - g_0$$

and

$$f(x) = x^2(x - 1)^2(x + 1)^2.$$
Here $x$ is the local concentration difference between oil and water, $f(x)$ is the simplest Landau bulk free energy for the three phases (pure water, pure oil and microemulsion) at coexistence and $g_2$ and $g_0$ are constants. Interestingly the bicontinuous phases shown in Figs. 13, 14, 15. correspond to the local minima of this functional.

6. KINETICS OF DEMIXING

When the homogeneous binary AB mixture above its critical point is suddenly cooled (quenched) below its critical temperature it ceases to be in the thermodynamical equilibrium (for review on kinetics see Langer (1992)). The homogeneous state can be now either a metastable or unstable state. In the case of metastable state the process of demixing requires, in the first place, nucleation of droplets of the minority phase, say A rich phase. Then the droplets starts to grow. At first they grow independently and their radius, $L(t)$ changes with time, $t$, according to the formula:

$$L(t) \sim \sqrt{t}$$

(34)

This behavior has been observed in binary polymer blends (Cumming et al (1990)). At the later stage significant fraction of A molecules disappear from the homogeneous mixture (most of them form droplets) and competitive growth starts. Small droplets decrease in size and the A atoms diffuse towards large droplets which grow. This mechanism is known as ‘evaporation-condensation’ mechanism and is described by the Lifshitz-Slyozov-Wagner (LSW) law for the growth rate of large droplets:

$$L(t) \sim t^{1/3}$$

(35)

When the system is quenched into the thermodynamically unstable region the demixing proceeds via the spinodal decomposition mechanism. Early stages of this process are described by the Cahn-Hilliard theory. According to the theory the
The system becomes unstable with respect to small fluctuations of wavevector \( q \) smaller than some value \( q_0 \). The key prediction of the theory is the exponential growth of the scattering intensity \( S(q, t) \) in time with a well defined maximum at \( q_{\text{max}} = q_0/\sqrt{2} \). Interpenetrating A rich and B rich domains of the size of \( L \sim 1/q_{\text{max}} \) are formed. The mixtures, of low viscosity, undergoing spinodal decomposition do not remain for a long time in their unstable early configuration, contrary to the high molecular weights polymer blends. The latter are very viscous liquids and the whole kinetics of phase separation is very slow allowing a detailed experimental observation of the process (Bates and Wiltzius (1989)). In the late stages of spinodal decomposition the scattering intensity can be represented by the following scaling form:

\[
S(q, t) \approx L^d(t)Y(qL(t)) \times \text{Const}
\]

where \( Y \) is a scaling function, \( d \) is the dimension of space and \( L(t) \) is the time dependent length characterizing the size of the interpenetrating A-rich and B-rich regions when the volume fractions are equal. \( L(t) \) grows in time, the pattern coarsens and the interfacial area, whose energy drives the coarsening, decreases. In the case of the unequal volume fractions \( L(t) \) is the size of A (minority phase) droplets (Eq.(35)). The late stage configuration depends on the initial volume fractions, but not on the early stage mechanism of demixing. In the late stage we have either a dilute gas of droplets of the minority phase in the sea of the majority phase, dense system of the droplets of one of the phase in the sea of another or the interpenetrating network of A-rich and B-rich domains which coarsen in time. The growth rate and the growth mechanism for the first case is described by the LSW law (Eq.(35)). In the second case a Binder-Stauffer mechanism of collisions and coalescence of droplets is valid. It gives \( L(t) \sim t^{1/3} \), similarly as in the first case. Finally, in the last case if the coarsening proceeds via the flow induced by the surface tension of interfaces,
the scaling law \( L(t) \sim t \) holds. The scaling function \( Y \) and the late stage of spinodal decomposition have been studied in computer simulations (Koga and Kawasaki (1993)). Although the field of kinetics of demixing or, in general, of first order phase transitions is rather old, new experimental results suggest that the problem is far from being understood. First of all, a new mechanism of coarsening called ‘collision induced collision’ has been observed (Tanaka (1994)). It has been also shown that surface effects and confinement play an important role in spinodal decomposition (Tanaka (1993), Jones et al (1991), Wiltzius and Cumming (1991)). Finally, the problem of heat release during demixing has been addressed in experimental studies (Bailey and Cannell (1993)). Concluding: the kinetics of demixing is still an active field of research.

**GLOSSARY**

**Solubility**: is the ability of the substance to form a solution with another substance. It also denotes the maximum amount of the solute that can be solubilized in the solvent at the given thermodynamic conditions.

**Solution**: is a single homogeneous liquid, solid or gas phase that is a mixture in which the components (liquid, gas, solid or the combination thereof) are uniformly distributed throughout the mixture.

**Miscibility**: denotes the tendency or capacity of two or more liquids to form a uniform blend, that is to dissolve in each other.

**Solute**: the substance less abundant in the mixture.

**Solvent**: the substance most abundant in a mixture.

**Upper (Lower) Consolute (Or Critical) Temperature For The Liquid Mixture**: temperature, for the the binary mixture of A and B components, above (below) which A and B components mix in all proportions i.e. they exhibit full miscibility.
**Azeotrope**: the point on the phase diagram where two different phases of same composition coexist. Usually in simple liquids the two phases are: vapor and liquid.

**Eutectic Composition**: the liquid mixture composition with the lowest freezing point.

**Excess Thermodynamic Quantities**: the difference between actual mixing functions and ideal mixing functions.

**Mixing Functions**: the difference between the function defined for the mixture and the sum of these functions for pure systems. The mixing function vanishes for the pure system. (Eq(10)).

**Ideal Mixture**: mixture in which all the components mix in all proportions without the change of volume or enthalpy. Interactions between various components in the mixture are the same. See also Eq(11)).

**Spinodal Decomposition**: process of phase separation of the mixture in the region (of the phase diagram) of the thermodynamical instability of the mixture.

**Works Cited**

Alder, B.J. and Wainwright, T.E., (1957) *J.Chem.Phys.* **27**, 1208-1209.

Allen, M.P., Evans, G.T., Frenkel, D. and Mulder, B.M. (1933), *Advances in Chemical Physics*, Vol. XXXVI, ed. Prigogine, I. and Rice, S.A. John Wiley & Sons, Inc, 1-166.

Atkins, P.W., (1993) *Physical Chemistry*, Oxford University Press.

Bailey A.E. and Cannell, D.S. (1993), *Phys.Rev.Lett.*, **70**, 2110-2113.

Bates, F.S. (1991), *Science*, **251**, 898-905.

Bates, F.S. and Fredrickson, G.H. (1990), *Annu.Rev.Phys.Chem.* **41**, 525-557.

Bates, F.S. and Wiltzius, P. (1989), *J.Chem.Phys.*, **91** 3258-3274.
Bates, F.S., Muthukumar, M., Wignall, G.D. and Fetters, L.J. (1988), *J.Chem.Phys.* **89**, 535-544.

Baus, M. (1990) *J.Phys.Condens.Matter* **2**, 2111-2126.

Biben, T. and Hansen, J.P. (1991), *Phys.Rev.Lett.*, **66**, 2215-2218.

Brochard, F., Jouffroy, J. and Levinson, P. (1984), *J. de Physique*, **45**, 1125-1136.

Callen, H.B. (1960), *Thermodynamics*, John Wiley & Sons, Inc.

Carneiro, G.M. and Schick, M. (1988), *J.Chem.Phys.* **89**, 4368-4373.

Casagrande, C., Veyssié, M and Finkelmann, H. (1982), *J.Physique Letters*, **43**, L671-L675.

Ciach, A. (1992) *Polish Journal of Chemistry*, **66**, 1347-1381.

Cumming, A., Wiltzius, P. and Bates, F.S. (1990), *Phys.Rev.Lett.*, **65**, 863-866.

Curtin, A. and Ashcroft, N.W. (1985), *Phys.Rev.A* **32**, 2909-2919.

Deblieck, R. and Lekkerkerker, H.N.W. (1980), *J. de Physique Lett.* **41**, L351-L355.

De Gennes, P.G. (1977), *J. de Physique Lett.* **38**, L441-L443.

De Gennes, P.G. (1979), *Scaling Concept in Polymer Physics*, Cornell University Press.

De Gennes, P.G. and Prost, J. (1993), *The Physics of Liquid Crystals*, Clarendon Press- Oxford.

Denton, A.R. and Ashcroft, N.W. (1989), *Phys.Rev. A* **39**, 4701-4708.

Denton, A.R. and Ashcroft, N.W. (1990), *Phys.Rev. A* **42**, 7312-7329;

Denton, A.R. and Ashcroft, N.W. (1991), *Phys.Rev. A* **44**, 8242-8248.

Des Cloiseaux, J. and Jannik, G. (1990), *Polymers in solutions: their modelling and structure*, Oxford - Clarendon Press.

Deutsch, H.-P. and Binder, K., (1992), *Macromolecules* **25**, 6214-6230.
Dijkstra, M. and Frenkel, D. (1994), *Phys.Rev.Lett.* **72**, 298-300.

Dijkstra, M., Frenkel, D. and Hansen, J.P. (1994), *J.Chem.Phys*, **101**, 3179-3189.

Doane, J.W. (1990), in *Liquid Crystals: Applications and Uses*, ed. Bahadur, B. World Scientific 362-396.

Doi, M. and Edwards, S.F. (1986), *The Theory of Polymer Dynamics*, Clarendon, Oxford.

Dorgan, J.R. and Soane, D.S. (1990), *Mol.Cryst.Liq.Cryst*. **188**, 129-146.

Edwards, S.F. (1966), *Proc.Phys.Soc*. **88**, 265-280.

Edwards, S.F. (1975), *J.Phys. A*, **8**, 1670-1680.

Evans, R. (1979), *Adv.Phys*. **28**, 143-200.

Evans, R. and Marconi, M.B. (1987), *J.Chem.Phys*. **86**, 7138-7148.

Flory, P. (1953), *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY.

Floudas, G., Pakula, T., Stamm, M. and Fischer, E.W., (1993), *Macromolecules*, **26**, 1671-1675.

Frenkel, D. (1991), in *Liquids, Freezing and Glass Transition* ed by Hansen, J.P., Levesque, D., and Zinn-Justin, J. (Les Houches session LI) North Holland, 689-762.

Frenkel, D. (1994), *J.Phys.Condens. Matter* **6**, A71-A78.

Frenkel, D. and Louis, A.A. (1992) *Phys.Rev.Lett* **68**, 3363-3365.

Furman, D., Dattagupta, S., and Griffiths, R.B.(1977), *Phys.Rev. B* **15**, 441-464.

Gehlsen, M., Rosendale, J.H., Bates, F.S., Wignall, G.D., Lotte, H. and Almdal, K., (1992) *Phys.Rev.Lett.* **68**, 2452-2455.

Gompper, G. and Schick, M. (1994), *Self-Assembling Amphiphilic Systems*, vol
Grant, D.J.W., Higuchi, T., (1990), *Solubility Behavior of Organic Compounds*, John Wiley & Sons Inc.

Hagen, M.H.J., Meijer, E.J., Mooij, G.C.A.M., Frenkel, D., Lekkerkerker, H.N.W., (1993), *Nature*, 365, 425-426.

Hansen, J.P. and McDonald, I.R. (1986), *Theory of Simple Liquids*, Academic Press.

Henderson, D. and Leonard, P.J. (1971) in *Physical Chemistry (an advanced treatise)* Vol. VIIIB ed. Henderson, D., Academic Press, 414-510.

Hildebrand, J.H., Scott, R.L. (1950), *Solubility of Nonelectrolytes* 3rd ed., Reinhold Publishing Corp.

Hobbie, E.K., Bauer, B.J. and Han, C.C. (1994), *Phys.Rev.Lett*, 72, 1830-1833.

Holyst, R. and Vilgis, T.A. (1994), *Phys.Rev.E* 50, 2087-2092.

Holyst, R. and Vilgis, T.A. (1993), *J.Chem.Phys*. 99, 4835-4844.

Holyst, R. and Schick, M. (1992), *J.Chem.Phys.*, 96, 721-729.

Holyst, R. and Schick, M. (1992), *J.Chem.Phys.*, 96, 7728-7737.

Israelachvili, J.N., (1985), *Intermolecular Interactions And Surface Forces*, Academic Press.

James, K.C. (1986), *Solubility and related properties*, Dekker, New York.

Jones, R.A.L., Norton, L.J., Kramer, E.J., Bates, F.S., Wiltzius, P. (1991), *Phys.Rev.Lett*, 66, 1326-1329.

Koga, T. and Kawasaki, K. (1993), *Physica A*, 196, 389-415.

Landau, L.D. and Lifshitz, E.M. (1980), *Statistical Physics* 3rd Edition part 1, Pergamon Press.

Langer, J.S. (1992) in *Solids far from Equilibrium* ed. C.Godrèche, Cambridge
University Press, 298-362.

Laughlin, R.G. (1994), The Aqueous Phase Behavior of Surfactants, Academic Press.

Leibler, L. (1980) Macromolecules, 13, 1602-1617.

Lifschitz, M., Dudowicz, J. and Freed, K.F. (1994), J. Chem. Phys. 3957-3978.

Löwen, H. (1994) Phys. Rep. 237, 251-324.

Maïssa, P. and Sixou, P. (1989), Liquid Crystals, 5, 1861-1873.

Matsen, M.W. and Schick, M. (1994), Phys. Rev. Lett., 72, 2660-2663.

Mc-Graw Hill Dictionary of Chemical Terms (1984) 3rd ed.

Meijer, E.J. and Frenkel, D. (1994), J. Chem. Phys. 100, 6873-6887.

Nernst, W. (1904) Theoretical Chemistry, MacMillan and Co., Ltd.

Onsager, L. (1949) Proc. NY Acad. Sci., 51, 627-655.

Poniewierski, A. and Holyst, R. (1988), Phys. Rev. Lett., 61, 2461-2464.

Poniewierski, A. and Holyst, R. (1990), Phys. Rev. A 41, 6871-6880.

Proceedings of the Int. School. of Physics, (1985) Course XC Physics of Amphiphiles: Micelles, Vesicles and Microemulsions ed. Degiorgio, V., North Holland.

Roe, R-J. and Zin, W-C. (1984), Macromolecules 17, 189-194.

Rowlinson, J.S. and Swinton, F.L. (1982), Liquids and Liquid Mixtures, Butterworth Scientific.

Schwalm, D., Mortensen, K. and Yee-Madeira, H. (1987), Phys. Rev. Lett., 58, 1544-1546.

Schweizer, K.S. and Curro, J.G. (1988), Phys. Rev. Lett. 60, 809-812.

Shaw, M.R. and Thirumalai, D. (1991), Phys. Rev. A, 44, R4797-R4800.

Sigaud, G., Nguyen, H.T., Achard, M.F. and Twieg, R.J. (1990), Phys. Rev. Lett., 65, 2796-2799.
Sivardière, J. (1980), *J. de Physique* **41**, 1081-1089.

Tanaka, H. (1994), *Phys.Rev.Lett.*, **72**, 1702-1705.

Tanaka, H. (1993), *Phys.Rev.Lett.*, **70**, 2770-2773, 3524.

Tarazona, P. (1985) *Phys.Rev.A* **31**, 2672-2679.

Tejero, C.F., Daanoum, A., Lekkerkerker, H.N.W. and Baus, M. (1994) *Phys.Rev.Lett.* **73**, 752-755.

Teubner, M and Strey, R. (1987), *J.Chem.Phys.*, **87**, 3195-3200.

Van Duijneveldt, J.S. and Lekkerkerker, H.N.W. (1993), *Phys.Rev.Lett.* **71**, 4264-4266.

Van Oss, C.J., Absolom, D.R. and Neumann, A.W. (1980), *Colloids Surf.* **1**, 45-56.

Van Roij, R. and Mulder, B. (1994), *J.Phys. II France*, **4**, 1763-1769.

Walker, J.S. and Vause, C.A. (1983), *J.Chem.Phys.* **79**, 2660-2676.

Wiltzius, P. and Cumming, A. (1991), *Phys.Rev.Lett.*, **66**, 3000-3003.

Xu, H. and Baus, M. (1987), *J.Phys.C* **20**, L373-L380.

Xu, H. and Baus, M. (1992), *J.Phys.Condens.Matter* **4**, L663-L668.

**Figure Caption**

Fig.1 The pressure composition phase diagram for the ideal binary mixture (A,B components) (see Eq.(5)). The region between the solid lines is the two-phase region where vapor and liquid coexist. Along the upper curve evaporation of the liquid starts and along the lower curve the condensation of the vapor starts.

Fig.2 The temperature composition phase diagram for the binary mixture. The dashed line shows how the process of fractional distillation proceeds. In this way we can obtain almost pure (B rich) liquid.

Fig.3 A phase diagram with a high boiling or negative azeotrope (maximum on the temperature-composition diagram). At this point liquid boils without changing
its composition. This type of diagram occurs for example for water/nitric acid, chloroform/acetone and hydrochloric acid/water.

Fig.4 A phase diagram with a low-boiling or positive azeotrope (minimum on the temperature-composition diagram). This type of diagram can occur for water/ethanol, dioxane/water.

Fig.5 Typical phase diagram for the partially miscible liquids with the upper critical point (maximum on the coexistence curve) (e.g. methanol and hydrocarbon liquids).

Fig.6 Typical phase diagram for the partially miscible liquids with a lower critical point (minimum on the coexistence curve) (e.g. water and diethylamine or triethylamine).

Fig.7 The phase diagram with the upper and lower critical points (e.g. nicotine and water).

Fig.8 The phase diagram with a lower and upper critical point and the miscibility gap between these point (e.g. acetone and polystyrene).

Fig.9 The phase diagram for the mixture, where the upper critical point is below the boiling curve.

Fig.10 The phase diagram for the mixture, not fully miscible (i.e. in all proportions) in the liquid state (e.g. water/diethyl ether, water/chloroform and high hydrocarbons and methanol).

Fig.11 The clathrate cage around the non hydrogen bonding solute molecule. The lines indicate the hydrogen bonds between the solvent molecules.

Fig.12 Lamellar phase (periodic in one direction) of the AB diblock copolymer. The dots denote the position of the points where A block (dashed line) is chemically joined to the B block (solid line).

Fig.13 The cubic bicontinuous phase in the amphiphilic system. Symmetry Pm3m.
Known as the Schwartz P triply periodic minimal surface. Here only the unit cell is shown. The internal interfaces are shown only. In the binary mixture of water and amphiphiles, water is on both sides of the surface. In the ternary mixture of oil, water and amphiphile we have oil on one side of the surface and water on the other. The interface is formed by the amphiphilic molecules. Water (oil) form interconnected channels which span the whole volume.

Fig.14 The cubic bicontinuous phase in the amphiphilic system. Symmetry F43m.

Known as the Schwartz D triply periodic minimal surface. Legend as in Fig.13.

Fig.15 The gyroid structure., Known as the Schoen G surface. Symmetry Ia3d. Legend as in Fig.13.