Ordered Fluids

The Orientational and Spatial Distribution of Solutes in Thermotropic Liquid Crystals

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Measurement of the deuterium NMR spectra of suitably deuteriated solutes provides a powerful technique for studying solute alignment in liquid crystals. We have used this approach to investigate the orientational order of perdeuterio-n-octane and perdeuterio-benzene dissolved in the nematic and smectic A phases of 4,4′-di-n-heptylazoxybenzene (T_{CS_A} 34 °C, T_{S_AN} 54 °C, T_{NI} 71 °C).

The order parameter for each segment in n-octane is found to increase with decreasing temperature in the nematic phase. However, within the smectic A phase the four order parameters show a small but definite decrease with decreasing temperature. Thus unusual behaviour contrasts with that exhibited by benzene where the orientational order parameter increases with decreasing temperature throughout the nematic and smectic A phases.

We believe that these results can be understood by considering the heterogeneous nature of the smectic layers and the non-uniform spatial distribution of the solute. The solvent molecule is composed of a rigid aromatic core which is highly ordered in a smectic layer and two flexible alkyl chains which are poorly ordered. The solute will be distributed between these two regions and its order parameter is then an average of the values in these regions. For both energetic and entropic reasons the n-octane solute prefers to be associated with the alkyl chain; a tendency which increases with decreasing temperature. Since the order parameter of the solute is smaller in the alkyl chain region that in the aromatic region the orientational order parameter for n-octane decreases with decreasing temperature even though the order of the alkyl chain increases.

The behaviour of the orientational order for benzene can be understood in similar terms although now the solute prefers to be associated with the aromatic core. This region is highly ordered and the order increases with decreasing temperature; in addition the association of benzene with the aromatic core also increases with decreasing temperature. As a consequence the order parameter of benzene increases with decreasing temperature in the smectic A phase.

Statistical Mechanical Studies of Intermolecular Interactions in Mesogenic Solutions

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Statistical mechanical models have been used to study the roles of solvent–solvent, solvent–solute, and solute–solute interactions in two types of systems which exhibit mesomorphism.

(*1*) Nematogenic solutions have been studied using a van der Waals approach, in which very short-range intermolecular repulsions are approximated by hard-particle exclusions and somewhat longer-range intermolecular attractions are subject to a self-consistent mean field treatment. The general theory, applicable to mixtures of any number of rodlike or effectively spherical components, has been applied to (*i*) binary solutions with rodlike solvent molecules and effectively spherical solute molecules (here, predicted temperature–mole fraction phase diagrams are in rather good agreement with available experimental data) and (*ii*) binary mixtures of nematogens. In the latter case, some very interesting effects are predicted when the two components differ considerably in their molecular dimensions.

(*2*) The formation of lipid bilayers has been studied in amphiphile–water systems which do not form globular/cylindrical micelles (*e.g.*, lecithin–water mixtures), using a model system of water molecules and straight, inflexible amphiphilic 'r-*mers*' (*i.e.*, rodlike molecules with length-to-width ratio r), constrained to lie on a simple cubic lattice. The 'r-*mers*' and water molecules are hard in that multiple occupancy of any lattice site is forbidden; in addition, molecules interact *via* nearest-neighbor segmental interaction energies ϵ_{AA}, ϵ_{AB}, ϵ_{BB}, ϵ_{AS}, ϵ_{BS}, and ϵ_{SS}, where S, A, and B represent, respectively, a water molecule, a polar head segment, and a lipid tail segment. Using the Bragg–Williams approximation, temperature–mole fraction phase diagrams have been calculated for model systems with various values of the amphiphile length-to-width ratio r and the interaction energies ϵ_{AA}, ϵ_{AB}, *etc.* in an effort to elucidate more fully the molecular factors which govern the formation and stability of lipid bilayers. This basic model has been modified by allowing the amphiphilic 'r-*mers*' to form bilayer vesicles which can be packed on the lattice together with water molecules and individual amphiphile molecules. It is hoped that this modified model will be useful for studying the phase transition between the bilayer smectic phase and a solution of bilayer vesicles.

Unusual Mesogenic Compounds; Molecular Geometry and Stability of Ordered Fluid Mixtures

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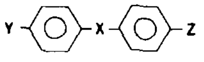
The most known mesogenic molecules have the following structure



(calamitic molecules) conducting to nematic and smectic mesophases.

With this general scheme and particular terminal groups pure compounds exhibiting stable nematic or smectic mesophases and particular physical properties can be obtained. For example with stable free radicals we obtain mesomorphic spin labels for the structural studies by ESR technique. With a side group incorporating an appropriate heavy metal atom we obtain derivatives suitable for Mössbauer measurements.

Other mesophases can be obtained with non extended molecules: plastic crystals with globular molecules and discotic mesophases with disk-like molecules.

A simple way to study the respective stabilities of the mesomorphic and isotropic binary mixtures *versus* temperature and concentration is the selting of isobaric phase diagrams.

Generally two mesogenic molecules having a similar geometrical form are totally miscible in the mesomorphic states. Contrarily, two mesogenic molecules exhibiting dissimilar forms (calamitic and globular, calamitic and disk-like, globular and discotic) are totally miscible in the liquid phase, but the common miscibilities in the partially ordered states are very small.

Relaxation Effects and Molecular Interactions

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The molecular rotational motion is one of the most important mechanisms determining relaxation of macroscopic physical properties and spectral profiles in liquid crystals. Under these circumstances, the relaxation effects are interpreted in terms of a conditional probability $P(\Omega_0;\ \Omega,\ t)$ for the change of orientation from Ω_0 to Ω. When this is assumed to occur through small angular steps, $P(\Omega_0;\ \Omega,\ t)$ is the solution of a generalized diffusion equation in which the anisotropic pseudo-potential $V(\Omega)$ responsible for the liquid crystalline ordering is introduced [1]:

$$(\partial/\partial t)P(\Omega_0;\Omega,t) =$$
$$-L\cdot D\cdot[L + (LV)/kT]P(\Omega_0;\Omega,t)$$

where L is the operator generating infinitesimal rotations and D the diffusion tensor.

In this way, information on the long-range interactions which give rise to the orientational ordering can be obtained from relaxation experiments. As an example, it is examined the effect of a 'diffuse cone' or 'tilted' rotation [2, 3] in smectic-A mesophases on a variety of spectroscopical techniques, including NMR relaxation, ESR lineshapes, dielectric dispersion and neutron scattering. To describe the tilted rotation, the orientational potential is written as a sum of second and fourth-rank legendre polynormals:

$$V(\beta) = \alpha[P_2(\cos\beta) + \lambda P_4(\cos\beta)]$$

the parameters α and λ being adjusted to give selected order parameters $\bar{P}_2$ and tilt angle. With this choice $V(\beta) = V(\pi - \beta)$, as it is the case for uniaxial, non-polar mesophases. The orientational distribution function generated from this potential can give negative values for $\bar{P}_4$.

The validity of the diffusional model is theoretically supported by a general memory-function approach, which also provides additional information on the short-range frictional forces. The method