

6.60 — zagadnienia ogólne i varia

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7/1986

P. 269



WARSZAWA 1986

<http://rcin.org.pl>

ISSN 0208-5658

Praca wpłynęła do Redakcji dnia 27 września 1985 r.



56874



Na prawach rękopisu

Instytut Podstawowych Problemów Techniki PAN

Nakład 140 egz. Ark.wyd. 1,12 Ark.druk. 2

Oddano do drukarni w lutym 1986 r.

Nr zamówienia 189/86

Warszawska Drukarnia Naukowa, Warszawa,
ul. Śniadeckich 8

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THE MOLECULAR THEORY OF THE LIQUID-CRYSTAL PHASE TRANSITIONS

Abstract

An integral equation is formulated for the distribution function of the average density $\rho(\mathbf{r})$ for a system of uniaxial molecules, following the Kirkwood-Monroe approach. The coupling parameters introduced into the potential of the intermolecular force are used to derive the hierarchy of the integrodifferential equations. To close the hierarchy and to obtain the integral equation for $\rho(\mathbf{r})$, the superposition approximation for the correlation function is used. The nonlinearity of the problem and its association with phase transitions is outlined. The application of the derived equation to the liquid-solid phase transition is shown.

A brief description of various liquid crystal phases is given. The molecular anisotropic potential is introduced and the extension of the Kirkwood-Monroe theory to the case of anisotropic molecules is made. The translational and orientational order parameters describing the liquid crystal in isotropic-nematic-smectic A phase transitions within Kobayashi and McMillan theories are defined and discussed. The resulting phase diagrams are discussed. The approximations used in both models are discussed, regarding the kinetic integral equation for $\rho(\mathbf{r})$.

1. Introduction

Many organic materials, when undergoing the transition from solid to liquid, exhibit the existence of one or more intermediate phases, known as " mesophases ". The molecular ordering in these mesophases lies between that of a solid and that of an isotropic liquid. The partial ordering of the molecules in such a mesophase can be either translational or rotational or both. Ordered fluid mesophases are known as liquid crystals. They are composed of elongated molecules, which show some degree of rotational and translational order, even though the crystal lattice is destroyed. Friedel [1] proposed the classification of liquid crystals, depending upon their symmetry. They are divided into three major classes: the nematics, the smectics and the cholesterics. In this paper we will discuss only the nematics and the smectics A.

The three phases of matter are represented in Fig. 1 : isotropic, nematic and smectic A. The rod-like molecules are here represented as lines, each line showing the position of the long axis of the molecule.

i/ at high temperature the liquid is isotropic, the positions of the centers of mass are randomly placed, the long axes point in various directions. The isotropic liquid is completely disordered, it is optically isotropic.

ii/ at lower temperature some materials exhibit a nematic phase, in which there is no long range correlation of the centers of mass, they are randomly placed, but the long axes line up parallel to a preferred axis in the space. The nematic phase is

optically uniaxial.

iii/ at still lower temperatures some materials show the existence of the more highly ordered phase, known as smectic A, in which the long axes line up parallel to a preferred axis in the space and the centers of mass sit on planes perpendicular to that axis. The molecules are organized in layers. The layer thickness is approximately of a molecular length. The centers of mass may move randomly in the planes. The planes can move over one another, the viscosity is low in the planar directions. The smectics A phase is optically uniaxial.

We assume, that the molecules can rotate freely about the long axis and that they have no average dipole moment.

As an example of this simple model let consider a homologous series of 4-ethoxybenzal-4-amino-n-alkyl- α -methylcinnamate, studied by Arnold [15], Fig. 2. This compound consists of elongated molecules, which rigid central part defines the long axis, the alkyl endchains being presumably flexible. Each member of the series shows the existence of the isotropic nematic and smectic A phases.

The recent enhancement of interest in liquid crystals is caused by their wide scope of applications in science and modern technology. The numerous experimental investigations were performed, however from the theoretical point of view there is no satisfactory microscopic description of the ordered fluids and their phase transitions. The most widely known theory of Maier and Saupe [2] presented a microscopic statistical theory of orientational melting based on an interaction between the molecules, having the orientational order only.

They described the first order nematics - isotropic liquid phase transition in a molecular field approximation. In order to describe the isotropic-nematic-smectic phase transition one needs to introduce at least two order parameters : a translational and orientational order parameters.

Now we shall present the more general treatment, based on the Kirkwood-Monroe theory of fusion, in which the translational and orientational order parameters are taken into account. We shall be concerned with the nematic and smectic A liquid crystals.

2. Distribution function theories

The Kirkwood-Monroe theory of fusion, being the distribution function theory, is based upon the very principles of statistical mechanics. Consider a classical system of N molecules in a volume V at a temperature T . The probability density $f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, t)$ fulfills the Liouville equation.

$f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, t)$ is the function, which describes the distribution of the phase points corresponding to an ensemble of systems in phase space at time t . The time evolution of the density $f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, t)$ is governed by the Liouville equation, which can be treated as an $6N$ - dimensional analogue of the 3-dimensional equation of continuity for an incompressible fluid.

The Liouville equation has the form [3,4]:

$$(2.1) \quad \frac{\partial f^{(N)}}{\partial t} = \{ \mathcal{H}, f^{(N)} \}$$

where $\{ , \}$ is the Poisson bracket

$$(2.2) \quad \{ \mathcal{H}, f^{(n)} \} = \sum_{i=1}^N \left(\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i} \frac{\partial f}{\partial \mathbf{p}_i} - \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \frac{\partial f}{\partial \mathbf{r}_i} \right)$$

The description of the system, given by the probability density $f^{(N)}$ is rather too detailed to have any practical use. Thus we introduce the set of lower order probability densities $f^{(n)}$, defined as:

$$(2.3) \quad f^{(n)}(\mathbf{r}^n, \mathbf{p}^n, t) = \frac{N!}{(N-n)!} \int \dots \int f^{(N)}(\mathbf{r}^N, \mathbf{p}^N, t) d\mathbf{r}_{n+1} \dots d\mathbf{r}_N d\mathbf{p}_{n+1} \dots d\mathbf{p}_N$$

Then, integrating both sides of (2.1) over $3(N-n)$ coordinates and momenta, we get:

$$(2.4) \quad \left\{ \frac{\partial}{\partial t} + \sum_{i=1}^n \left[\frac{1}{m} \mathbf{p}_i \frac{\partial}{\partial \mathbf{r}_i} + \left(\mathbf{X}_i + \sum_{j \neq i} \mathbf{F}_{ij} \right) \frac{\partial}{\partial \mathbf{p}_i} \right] \right\} f^{(n)}(\mathbf{r}^n, \mathbf{p}^n, t) = - \sum_{i=1}^n \iint \mathbf{F}_{i, n+1} \frac{\partial}{\partial \mathbf{p}_i} f^{(n+1)}(\mathbf{r}^{(n+1)}, \mathbf{p}^{(n+1)}, t) d\mathbf{r}_{n+1} d\mathbf{p}_{n+1}$$

where \mathbf{X}_i is an external force acting on the particle i and \mathbf{F}_{ij} is the intermolecular force. This is an exact integro-differential equation, which relates the time-dependent n -body probability density $f^{(n)}$ to the $(n+1)$ body density $f^{(n+1)}$. The set of equations for $n=1 \dots N-1$ was first derived by Yvon (1935). The same problem was treated by Kirkwood (1935), Bogolyubov (1946), Born and Green (1949) and the hierarchy of equations (2.4) is called the BBGKY hierarchy. In eq. (2.4), the unknown function $f^{(n)}$ is expressed by another unknown function $f^{(n+1)}$. To solve the problem, one has to make certain approximations, which can close the hierarchy.

This important step, the closure of the hierarchy, can be made in various ways, depending on the approximations used. In many works different approximations were postulated and resulting closures of the hierarchy were done. These various approaches gave rise to numerous kinetic equations, such as Kirkwood-Salsburg [4,9] eq., Yvon-Born/Green [4] eq., Kirkwood-Monroe /or Kirkwood coupling-parameter eq. [5,9] /eq., and others.

For the stationary problem we have:

$$(2.5) \quad f_0^{(n)}(\mathbf{r}^n, \mathbf{p}^n) = \mathcal{P}^{(n)}(\mathbf{p}^n) \mathcal{G}^{(n)}(\mathbf{r}^n)$$

where $\mathcal{P}^{(n)}(\mathbf{p}^n)$ is the Maxwellian distribution for momenta \underline{p}_i and $\mathcal{G}^{(n)}(\mathbf{r}^n)$ is the n-particle density. The stationary conditions reduce the set of eqs. (2.4) to the form

$$(2.6) \quad \sum_{i=1}^n \left[\frac{1}{m} \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} + \left(X_i + \sum_{j \neq i}^n F_{ij} \right) \frac{\partial}{\partial \mathbf{p}_i} \right] f_0^{(n)}(\mathbf{r}^n, \mathbf{p}^n) =$$

$$= - \sum_{i=1}^n \iint F_{i, n+1} \frac{\partial}{\partial \mathbf{p}_i} f_0^{(n+1)}(\mathbf{r}^{n+1}, \mathbf{p}^{n+1}) d\mathbf{r}_{n+1} d\mathbf{p}_{n+1}$$

Using the properties of (2.5), from (2.6) we can derive the general expression for the Yvon-Born-Green hierarchy in the presence of an external field and with the pair interaction potential \mathcal{V} giving the internal forces:

$$(2.7) \quad F_{1j} = -\nabla_1 \mathcal{V}(\mathbf{r}_{1j}) \quad 2 \leq j \leq n+1$$

These systems of equations are linear in the n-body functions and inhomogeneous.

From the hierarchy of eqs. (2.6), stems also the Kirkwood-Monroe set of kinetic equations:

$$\frac{1}{\beta} \frac{\partial \rho^{(n)}}{\partial \xi} = - \rho^{(n)} \sum_{i=2}^n u(r_{i1}) + \frac{\rho^{(n)}}{N} \iint_V u(r_{12}) \rho^{(2)}(r_1, r_2, \xi) dr_1 dr_2$$

$$(2.8) \quad - \int u(r_{1, n+1}) \rho^{(n+1)}(r_1, \dots, r_{n+1}, \xi) dr_{n+1}$$

ξ - coupling parameter

As we said before, the proper closure of such hierarchy is essential and the results and applications apparently depend on the approximations used.

3. Kirkwood - Monroe equation

In order to obtain the hierarchy of equations for $\rho^{(n)}$ Kirkwood introduced so called coupling parameters ξ_1, \dots, ξ_N each of which ranges from zero to unity. They describe the coupling of the N molecules in the system. $\xi_i = 0$ denotes a completely uncoupled system and $\xi_i = 1$ denotes the full coupling of the intermolecular forces. In this definition U is the sum of potentials due to molecular pairs:

$$(3.1) \quad U(r_1, \dots, r_N, \xi) = \sum_{1 \leq i < j \leq N} \xi_i \xi_j u(r_{ij}) ; 0 \leq \xi \leq 1$$

Then $\rho^{(n)}$, the n -particle density, is given by the following expression, in the canonical ensemble :

$$(3.2) \quad \rho^{(n)}(r_1, r_n, \xi) = \frac{1}{Z(\xi)} \frac{N!}{(N-n)!} \int \dots \int_V \exp[-\beta U(\xi)] dr_{n+1} \dots dr_N$$

and $Z(\underline{\xi})$ is the configurational partition function:

$$(3.3) \quad Z(\underline{\xi}) = \int \dots \int \exp[-\beta U(\underline{\xi})] d\mathbf{r}_1 \dots d\mathbf{r}_N$$

Now if we differentiate (3.2) with respect to one of ξ , say ξ_1 and take the rest of them equal to 1; $\xi_2 = \xi_3 = \dots = \xi_N = 1$ we get the hierarchy of integrodifferential equations (2.8), valid for a fluid or a crystal; eq. (2.8) provides us with a set of $N-1$ interdependent integrodifferential equations. For $n=1$, $\xi = 1$, when we integrate over ξ , we get the integral form of Kirkwood- Monroe equation:

$$\frac{1}{\beta} \ln \rho^{(1)}(\mathbf{r}_1) = \frac{1}{\beta} \ln \rho + \frac{1}{N} \int \int \int U(\mathbf{r}_{12}) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \xi) d\mathbf{r}_1 d\mathbf{r}_2 d\xi$$

$$(3.4) \quad - \int \int \int U(\mathbf{r}_{12}) \rho^{(1)}(\mathbf{r}_2) g^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \xi) d\mathbf{r}_2 d\xi \quad \rho = \frac{N}{V}$$

where the correlation function $g^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \xi)$ is defined as

$$(3.5) \quad \rho^{(n)}(\mathbf{r}_1 \dots \mathbf{r}_n, \xi) = \rho^{(1)}(\mathbf{r}_n, \xi) g^{(n)}(\mathbf{r}_1 \dots \mathbf{r}_n, \xi)$$

Note, that in eq. (3.4) the effect of the partial coupling of the molecule in \mathbf{r}_1 on the $\rho^{(1)}(\mathbf{r}_2, \xi)$ is neglected. That means, that the system size is supposed to be large and the effect of the partial coupling is small.

One can write the more concise form of eq. (3.4)

$$(3.6) \quad \ln \lambda \rho^{(1)}(\mathbf{r}_1) = \int \int \int K(\mathbf{r}_1, \mathbf{r}_2) \rho^{(1)}(\mathbf{r}_2) d\mathbf{r}_2$$

where

$$(3.7) \quad \ln \lambda = -\ln \varrho - \frac{\beta}{N} \int_0^1 \iint U(r_{12}) \varrho^{(2)}(r_1, r_2, \xi) dr_1 dr_2 d\xi$$

λ can be fixed by the normalization conditions

and

$$(3.8) \quad K = -\beta \int_0^1 U(r_{12}) \varrho^{(2)}(r_1, r_2, \xi) d\xi$$

We may also write the eq.(3.6) as:

$$(3.9) \quad \varrho^{(1)}(r_1) = \lambda^{-1} \exp \left[\int K(r_1, r_2) \varrho^{(1)}(r_2) dr_2 \right]$$

The eqs(2.8) can be derived both for closed and open thermodynamic systems and apply to any pure phase. They are the hierarchy of inhomogeneous, linear equations for n-particle densities.

4. Nonlinearity of the kinetic equations

We draw the attention to the fact, that although the full system of Kirkwood equations is linear in $\varrho^{(n)}$, consideration of a single equation in the hierarchy leads to a nonlinear equation. The system of integral eqs.(2.8) forms an inhomogeneous system, linear in the n-particle distribution functions. The first equation in this hierarchy can be written formally as a nonlinear equation with the nonlinearity of the exponential form :

$$(4.1) \quad \Psi(r_1) + \int \tilde{K}(r_1, r_2) \exp[\Psi(r_2)] dr_2 = 0$$

$$\Psi(r_1) = \ln [\varrho^{(1)}(r_1) \cdot \lambda] \quad \tilde{K} = -\lambda^{-1} \cdot K$$

The resultant nonlinear problem can be specified precisely only if certain assumptions are made regarding the n-body correlation function $g^{(n)}$, which appears in the kernel K. The whole importance of the n-body problem is now contained in the kernel K. The n-body correlation functions are not known. In other words, the equation is not closed. To close the equation one must introduce some assumptions regarding the correlation function. The approximation most commonly used, introduced by Kirkwood [4,5,9] and called the superposition approximation, concerns the 3-body correlation function

$$(4.2) \quad g^{(3)}(1,2,3) = g^{(2)}(1,2)g^{(2)}(2,3)g^{(2)}(1,3)$$

This approximation effectively decouples the infinite system of integral or integrodifferential equations and leaves us with a single, closed nonlinear equation for the distribution function. The approximation (4.2) is rather general and when treating the particular system, one must carefully check, whether the Kirkwood closure is suitable. The use of the superposition approximation gives exact results in certain cases only.

Even after a closure has been specified, we have to choose some particular correlation function appearing in the kernel, in other case the problem would be not defined precisely. Kirkwood [5,8] chose $g^{(2)}(1,2)$ as that of a radial correlation function $g^{(2)}(\tau)$ of the disordered fluid. The justification for that is following. The correlation function appears in the kernel K together with the intermolecular potential

$U(r_{12})$. The two-body intermolecular potential goes rapidly to zero with increasing particle distance. The most important difference among the gas, liquid and solid correlation functions is in the long-range behaviour of $g^{(2)}(r)$. Then considering the rapid truncation induced by the intermolecular potential function, we can assume that there will be no particular difference in the kernels constructed using $g_{\text{gas}}, g_{\text{liquid}}, g_{\text{solid}}$ when the long range behaviour is concerned. For short range behaviour, where $U(r_{12})$ is significantly different from zero, the fluid and solid correlation functions show similar shapes and the corresponding kernels are similar as well.

Those nonlinear problems, discussed above, can exhibit multiple solutions and as such can be connected with the phase transitions [9]. In this sense, a phase transition can be linked with the occurrence of multiple solutions to one of the nonlinear equations of BBGKY hierarchy. We may say that if in a given region of thermodynamic parameter space a unique, basic solution of the nonlinear problem is found, with the change of the thermodynamic parameters the equation admits other real solutions and the new distribution functions describe a new phase of the system.

Nonlinearity suggests the multiple solutions and then it may be connected with the phase transitions. That was the basic idea of Kirkwood, when he tried to construct a nonlinear equation for the n -particle density function, an equation admitting two different solutions, describing two various phases. With varying the temperature one could be able to obtain the uniform

density solution, characteristic for a fluid or a periodic density solution, characteristic for a solid.

5. Liquid - solid phase transition

The equation (3.4) Kirkwood used for the discussion of liquid - solid phase transition. He was interested in the solutions of this equation with the period of a specified space lattice. Among the possible lattice and distribution functions the one corresponding to a minimum value of the free energy for given temperature and volume was selected. The periodic distribution function and its logarithm was then expanded in the Fourier series [7, 8] :

$$(5.1) \quad \rho^{(1)}(\underline{r}) = \sum_{\substack{h_1, h_2, h_3 \\ = -\infty \\ +\infty}} s(\underline{h}) \exp(2\pi i \underline{h} \cdot \underline{r})$$

$$\ln \lambda \rho^{(1)}(\underline{r}) = \sum_{\substack{h_1, h_2, h_3 \\ = -\infty \\ +\infty}} q(\underline{h}) \exp(2\pi i \underline{h} \cdot \underline{r})$$

$$\underline{h} = h_1 \underline{b}_1 + h_2 \underline{b}_2 + h_3 \underline{b}_3$$

where h_1, h_2, h_3 are integers and $\underline{b}_1, \underline{b}_2, \underline{b}_3$ are the basic vectors of the reciprocal lattice of the assumed structure. Substituting it to (3.6 - 3.7) we obtain :

$$(5.2) \quad q(\underline{h}) = \alpha(\underline{h}) \cdot s(\underline{h}) \quad h = |\underline{h}|$$

$$\alpha(\underline{h}) = \left(\frac{2}{h}\right) \int_0^{\infty} r K(r) \sin(2\pi \underline{h} r) dr$$

Thus the determination of real periodic solutions of the inte-

gral equation (3.6) is equivalent to determining the solutions of the set of eqs. (5.2) as functions of the transforms $\alpha(h)$ of the kernel $K(r)$.

One finds that eqs (5.2) always have the solutions $q_h = 0$ for $h > 0$, according to which $g^{(1)}(r)$ has the constant value unity everywhere, corresponding to a disordered phase. Eq (5.2) forms the infinite set of equations. However when the transforms $\alpha(h)$ vanish for h greater than some finite h_0 , the equations reduce to a finite set of eqs. It may be shown that for specified lattices, non-trivial periodic solutions $g^{(1)}(r)$ with non-vanishing Fourier coefficient $S(h)$ for $h > 0$ exist for sufficiently large value of $\alpha(h)$ and correspond to lower free energy than the solution $g^{(1)}(r) = 1$. $\alpha(h)$ are functions of temperature and volume.

Using the condition of a minimum value of the free energy for given temperature and volume and the conditions for heterogeneous equilibrium between the liquid phase /disordered/ and crystalline /ordered/ phase, Kirkwood calculated the excess free energy, Gibbs energy and internal energy for a system.

For instance the entropy of fusion was found as :

$$\frac{\Delta S}{R} = \frac{1}{2} \sum_{h \neq 0} \alpha(h) |S(h)|^2 + \frac{\Delta S_0}{R}$$

$$(5.3) \quad \frac{\Delta S_0}{R} = \frac{\delta_0 \Delta V}{\kappa_0} + \frac{V_{solid}}{\kappa_0 RT} \left\{ \ln \left(\frac{V_{liq}}{V_{solid}} \right) - \frac{\Delta V}{V_{solid}} \right\}$$

where κ_0 - the compressibility, δ_0 - the thermal expansion coefficient, V - volume.

The calculations were made for the face-centered cubic lattice with the unit cell volume $\Delta = 4\sqrt{V}/N$.

The reciprocal lattice vectors $\underline{b}_1, \underline{b}_2, \underline{b}_3$ are orthogonal and of magnitude $1/a$, a - the lattice vector length.

The approximation was made for $\alpha(h)$

$$(5.4) \quad \alpha(h) = 0 \quad \text{for } h \geq \frac{2}{a}$$

and

$$(5.5) \quad q(h) \quad \text{for } h \geq \frac{\sqrt{3}}{a}$$

The liquid - solid transition in argon were investigated as a testing case [7,8]. The two-body potential energy of argon and the radial distribution function $g(r)$ has to be known for the calculation of the fusion parameters of argon. In this case the potential energy of argon was chosen of the Lennard-Jones form and the radial distribution function was determined from the experiment / Eisenstein and Gingrich data, for liquid argon at 90 K under a pressure of .5 atmos [7].

Some of the calculated values of the fusion parameters for argon are [7,8] :

$$T = 83.9 \text{ K}, p = 1 \text{ KG/cm}^2$$

$$S/R = 1.74 \quad \text{/calculated/}$$

$$S/R = 1.63 \quad \text{/observed/}$$

$$\Delta V = 3.25 \text{ cc/mole} \quad \text{/calculated/}$$

$$\Delta V = 3.53 \text{ cc/mole} \quad \text{/observed/}$$

Apparently, the calculated fusion parameters agree remarkably well with the observed experimentally values, considering all

approximations involved into the theory.

6. Liquid crystals phase transitions

If we try to develop a microscopic theory of liquid crystals, we have to know the nature of the intermolecular force, acting on the constituent molecules. Due to a highly complicated structure of liquid crystals, the precise mathematical expression for the interaction potential between pairs of the molecules is not known. One has to assume a rather general form of the pair potential and introduce it into the theory.

It is obvious, that the pair potential for liquid crystals would have the attractive and repulsive contributions, like in normal liquids. But for the rod-like molecules, which form the liquid crystal, the interactions are anisotropic. There must be both orientational and distance dependence in the intermolecular pair potential. There must exist forces, due to which the molecules align parallel to each other and form layers perpendicular to the director. A simple form of the potential of interaction, but containing the minimum necessary features, can be assumed in the mean field approximation.

Let each molecule be described by the coordinates $\underline{r} = (ax, ay, az)$ of its center of mass and by the angular coordinates (θ, ϕ) , which describe the orientation of the molecule. We assume, that the molecule is elongated and rod-like. The interaction energy between two such molecules can be expressed as [1,2]:

$$(6.1) \quad U(\underline{r}_1, \Theta_1, \Phi_1; \underline{r}_2, \Theta_2, \Phi_2) = V(\underline{r}_1 - \underline{r}_2) + W(\underline{r}_1 - \underline{r}_2) P_2(\cos \gamma)$$

Here $V(\underline{r}_1 - \underline{r}_2)$ describes the usual short-range central forces and the second term represents orientational forces / anisotropic part of the dispersion force and a quadrupole-quadrupole interactions / , γ is the angle between the molecular axes and P_2 is the Legendre polynomial of the second order. $P_2(\cos x) = \frac{1}{2}(3 \cos^2 x - 1)$

Kobayashi [10 - 12], following Kirkwood and Monroe treatment proposed a theory of melting for anisotropic molecules, where both the translational and orientational order parameters are considered.

He expanded a one-particle distribution function $g(\underline{r}, \Theta, \Phi)$ now dependent also on angular coordinates Θ and Φ in the Fourier series in the reciprocal lattice vectors. He considered a simple cubic lattice with the lattice constant a :

$$(6.2) \quad g(\underline{r}, \Theta, \Phi) = \sum_{l_1, l_2, l_3 = -\infty}^{+\infty} S_{l_1, l_2, l_3}(\Theta, \Phi) \exp[2\pi i(l_1 x + l_2 y + l_3 z)]$$

The equation for $g(\underline{r}, \Theta, \Phi)$ was found from the minimalization condition for the free energy with respect to g ,

$$(6.3) \quad \ln \lambda g(\underline{r}, \Theta, \Phi) = -\frac{\beta}{4\pi V} \int d^3 r' \int d\Omega' \{V(|\underline{r} - \underline{r}'|) + W(|\underline{r} - \underline{r}'|) \times P_2(\cos \gamma)\} g(\underline{r}', \Theta', \Phi') g^{(2)}(|\underline{r} - \underline{r}'|, \cos \gamma)$$

ν is the volume of the unit cell, $d\Omega$ denotes the element of the solid angle, λ is the normalization constant for ξ

$$(6.4) \quad \frac{1}{4\pi\nu} \int d^3r \int d\Omega \cdot g(\underline{r}, \Theta, \Phi) = 1$$

$g^{(2)}(|\underline{r}|, \omega\delta)$ is the pair correlation function, which is approximately expressed in two terms:

$$(6.5) \quad g^{(2)}(|\underline{r}|, \omega\delta) = g_0^{(2)}(|\underline{r}|) + g_2^{(2)}(|\underline{r}|) P_2(\omega\delta)$$

Here $g_0^{(2)}(|\underline{r}|)$ describes correlations in isotropic liquid and may be used in consideration of the nematic phase, $g_2^{(2)}(|\underline{r}|)$ is the correlation function of the nematic phase and both $g_0^{(2)}(|\underline{r}|)$ and $g_2^{(2)}(|\underline{r}|)$ may be used for the smectic phase.

Assuming the axial symmetry of the system on the average and substituting (6.2) into (6.3), with the use of (6.4 - 6.5) we get:

$$(6.6) \quad \ln \lambda \cdot g(\underline{r}, \Theta, \Phi) = \alpha_0 + 2\alpha_1 (\cos 2\pi x + \cos 2\pi y + \cos 2\pi z) \sigma + \beta_0 P_2(\cos \Theta) \eta + 2\beta_1 P_2(\cos \Theta) (\cos 2\pi x + \cos 2\pi y + \cos 2\pi z) \tau$$

$$\alpha_0 \equiv \alpha_{000} \quad \beta_0 \equiv \beta_{000} \quad \alpha_{100} \equiv \alpha_1 \quad \beta_{100} \equiv \beta_1$$

Here the approximation for the Fourier transforms $\alpha_{l_1 l_2 l_3}$ and $\beta_{l_1 l_2 l_3}$ was also made in / see (5.4 - 5.5) /

$$(6.7) \quad \alpha_{l_1 l_2 l_3} = \beta_{l_1 l_2 l_3} = 0 \quad \text{for } |l_1|^2 + |l_2|^2 + |l_3|^2 > 1$$

The parameters σ, η and τ , appearing in (6.6) are defined as :

$$\sigma \equiv \frac{1}{4\pi} \int d\Omega \cdot S_{100}(\Theta)$$

$$(6.8) \quad \eta \equiv \frac{1}{4\pi} \int d\Omega \cdot P_2(\cos\Theta) S_{000}(\Theta)$$

$$\tau \equiv \int d\Omega P_2(\cos\Theta) S_{100}(\Theta)$$

σ and η represent the translational and orientational order parameters, τ is the mixing order parameter.

The Fourier coefficients $\alpha_{l_1 l_2 l_3}$ and $\beta_{l_1 l_2 l_3}$ are defined:

$$(6.9) \quad \alpha_{l_1 l_2 l_3} = -\frac{\beta}{\mathcal{V}} \int d^3r [V(|\underline{r}|) g_0^{(2)}(|\underline{r}|) + \frac{1}{5} W(|\underline{r}|) g_2^{(2)}(|\underline{r}|)] \cdot \exp[2\pi i(l_1 x + l_2 y + l_3 z)]$$

$$\beta_{l_1 l_2 l_3} = -\frac{\beta}{\mathcal{V}} \int d^3r [W(|\underline{r}|) g_0^{(2)}(|\underline{r}|) + V(|\underline{r}|) g_2^{(2)}(|\underline{r}|) + \frac{2}{7} W(|\underline{r}|) g_2^{(2)}(|\underline{r}|) \cdot \exp[2\pi i(l_1 x + l_2 y + l_3 z)]$$

One can calculate the mean internal energy, the entropy and other thermodynamic functions in terms of the order parameters. For instance the mean internal energy U is given:

$$(6.10) \quad \beta U = -\alpha_0 + 6\alpha_1 \sigma^2 - \beta_0 \eta^2 - 6\beta_1 \tau^2$$

The equation (6.6) was solved numerically for σ and with the conditions : $\tau = 0$, $\beta_1/\beta_0 = 1/80$, $\beta_0/\alpha_1 = 6$ the results are shown in Fig. 3.

The equation (6.6) admits three types of solutions:

1/

- i/ $\sigma = \eta = \tau = 0$; no order, the isotropic liquid phase
- ii/ $\sigma = 0, \eta \neq 0$; orientational order only, the nematic phase
- iii/ $\sigma \neq 0, \eta \neq 0$; orientational and translational order, the smectic A phase
 $\tau = 0$

The transition is of the first order.

In the theory of smectics, even the simple and general form of the two-body potential (6.1) makes the more precise calculations extremely difficult. McMillan [13,14] proposed the model, in which the mean field approximation has been used to calculate the one-particle simplified potential.

In this model, the anisotropic part of the two-body interaction potential is:

$$(6.11) \quad V_{12}(r_{12}, \cos \theta) = -\left(V_0 / N r_0^3 \pi^{3/2} \right) \exp \left[-\left(\frac{r_{12}}{r_0} \right)^2 \right] P_2(\cos \theta)$$

where r_{12} is the distance between centers of mass and r_0 is of the order of the length of the rigid section of the molecule / and is fixed for homologues series / .

Now assume that the molecules are preferentially oriented in the z direction and their centers of mass sit on planes parallel to the $x - y$ plane, with the interplanar distance d , intersecting the z -axis at $0, \pm d, \pm 2d$ etc. Thus the average, test molecule would feel the mean field, one-particle potential of the form:

$$(6.12) \quad \overline{V_1(z, \cos \theta)} = -V_0 \left[\eta + \sigma \cdot \alpha \cdot \cos(2\pi z/d) \right] P_2(\cos \theta)$$

Here η and σ are the order parameters, as yet undetermined. α is the physical parameter entering the theory. It can vary between 0 and 2 and should increase with increasing the chain length.

Then the one-particle distribution function can be written in the form

$$(6.13) \quad g(z; \cos \theta) = \exp[-\beta \overline{V_1(z, \cos \theta)}] \cdot Z^{-1}$$

The selfconsistent equation for the potential gives the defining equations for the order parameters σ and η . Recalculating the mean-field one-particle potential with the use of (6.11) and (6.13) we get the equations for the order parameters :

$$(6.14) \quad \begin{aligned} \eta &= \langle (P_2(\cos \theta)) \rangle = \langle \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \rangle_g \\ \sigma &= \langle \left(\cos(2\pi z/d) \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \right) \rangle_g \end{aligned}$$

Eqs. (6.14) solved self-consistently for η and σ admit three types of solutions, giving then the description of the possible phases in the rod-like molecule system. Again we can distinguish the isotropic liquid when $\eta = \sigma = 0$, the nematic phase when $\sigma = 0$, $\eta \neq 0$, there is orientational order only and the smectic A phase when $\sigma \neq 0$,

$\eta \neq 0$, both translational and orientational order exist. The free energy F , calculated in terms of the order

parameters has the form :

$$(6.15) \quad F = \frac{1}{2} N V_0 (\eta^2 + \alpha \sigma^2) - N k_B T \ln \left\{ \int_0^1 dz \int_0^{2\pi} d\omega \exp \left[\left(\frac{V_0}{k_B T} \right) (\eta + \alpha \sigma \cos \frac{2\pi z}{d}) \cdot P_2(\cos \omega) \right] \right\}$$

Minimizing the free energy we get the equations for the order parameters. The equations (6.14) were solved numerically. For the calculations, two physical parameters have to be assumed : V_0 and α .

The transition temperatures as a function of the parameter are shown in the phase diagram in Fig. 4.

For $\alpha < 0.98$ the nematic - isotropic transition temperature is $T_{NI} = 1$ /in the reduced units of $0.2202 V_0$, $t = T/T_{NI}$ / and the entropy change at the transition is $S_{NI} = 0.429 R_0 / R_Q = 8.31$ J/deg mole/. The smectic A - nematic phase transition is second order for $\alpha < 0.70$ and is first order for $0.70 < \alpha < 0.98$. The entropy change at the smectic A - nematic transition increases from 0 at $\alpha = 0.70$ to $1.18 R_0$ at $\alpha = 0.98$.

The theoretical phase diagram in Fig. 4, calculated on the basis of McMillan model can be compared with the experimental phase diagram in Fig. 2. Apparently, the agreement of the theory with the experiment is quite satisfactory. Another comparison of the theory with the experiment is depicted in Fig. 5. Here the entropy change ΔS_{SN} is plotted versus T_{SN} / T_{NI} . The solid curve is theoretical and the circles and triangles are experimental. The theory here predicts correctly the qualitative trend and the order of magnitude of ΔS_{SN} , however the values of ΔS_{SN} are overes-

estimated. That disagreement between the theoretical and experimental values on the phase diagram motivated further investigations. Lee et al [16,17] improved the McMillan model by using the pair potential instead of the simplified one-molecule potential.

That modified version gave better results and the obtained phase diagram and transition entropies agree qualitatively and quantitatively with experiment remarkably well.

/see Ref. [16,17]/.

The McMillan model, considering its all approximations, describes comparatively well the isotropic - nematic - smectic A phase transition. Introduced order parameters : η - the orientational one and σ , which can be interpreted as the amplitude of a density wave in the direction of the nematic preferred axis, describe the various phases of liquid crystals. The nematic phase is described by an orientational order parameter η ; the smectic A phase is described by η and σ . The most interesting fact - the possibility of a second order smectic A - nematic phase transition for $T_{SN} / T_{NI} < 0.87$ /see Fig. 4 / is predicted by that theoretical model, also by the improved Lee et al model. However, the experimental results seem not to give the clear answer to that question. To confirm that prediction one would have to do very accurate specific heat measurements, the full specific heat curves found experimentally have been published for a few cases only.

7. Conclusions

The presented molecular theory of the liquid crystals phase transitions is based upon the mean field approximation. The integral equation for the one-particle distribution function (3.9), derived on the basis of the statistical mechanics, is used in the form:

$$(7.1) \quad g(x) = \text{const} \exp \left[-\beta \int dx' V(x, x') g(x') g(x, x') \right]$$

$$(x = r, \theta, \phi)$$

in Kobayashi model,

or

$$(7.2) \quad g(x) = \text{const} \cdot \exp \left[-\beta \overline{V(x)} \right]$$

in McMillan model.

In Kobayashi approach, to solve the eq. (7.1), one has to assume the form of the correlation function $g(x, x')$, with two-body anisotropic potential $V(x, x')$ taken in the form (6.1). In McMillan approach, the integral in the exponent appearing in (3.9) is interpreted as an average molecular field acting on a single molecule. Thus the effective mean-field one-particle potential $\overline{V(x)}$ is recalculated in the self-consistent method, using (7.2) and the two-body potential $V(x, x')$ (6.1).

Both approaches give the defining equations for the order parameters, describing the various phases in liquid crystals. The phase diagram and transition parameters can be calculated, giving the satisfactory agreement with the experiment.

The use of the mean field approximation neglects the fluctuations of the order parameters. That would be interesting to include this effect into the theory. Also the extension of this model to the more ordered smectics might give valuable results. The obvious truncation of the kernel K in the basic integral equation for the one-particle distribution function influences the developed theory and that question should be investigated in further work.

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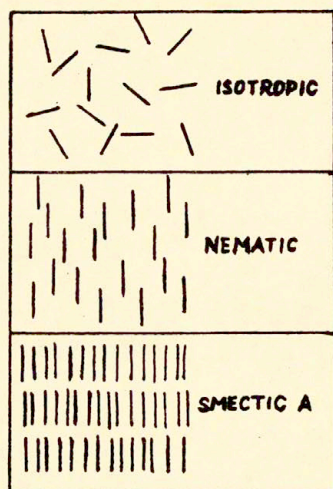


Fig. 1
Schematic representation of molecular ordering in
liquid crystals.

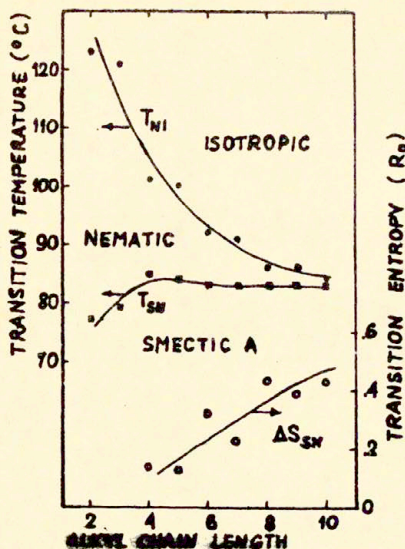


Fig. 2

Transition temperatures and transition entropy of 4-ethoxy-benzal-4-amino-n-alkyl- α methyl cinnamate versus alkyl chain length /Ref.[15]/

- nematic-isotropic transition temperature
- smectic A - nematic transition temperature
- smectic A - nematic transition entropy

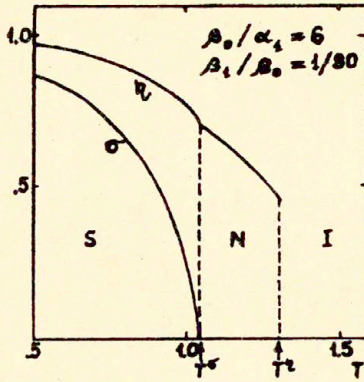


Fig. 3

Temperature dependence of orientational η and translational σ order parameters in Kobayashi model / Ref. [12]/

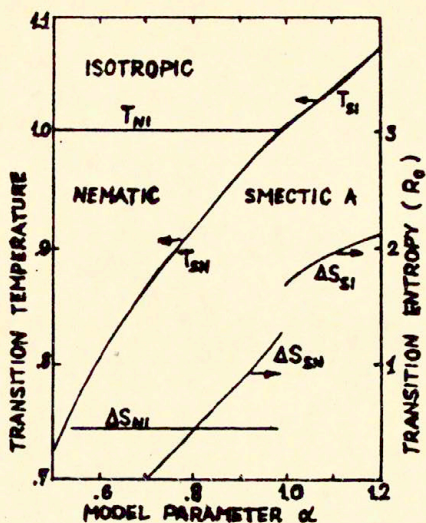


Fig. 4

Phase diagram for theoretical model parameter α in McMillan model / after Ref. [13] /

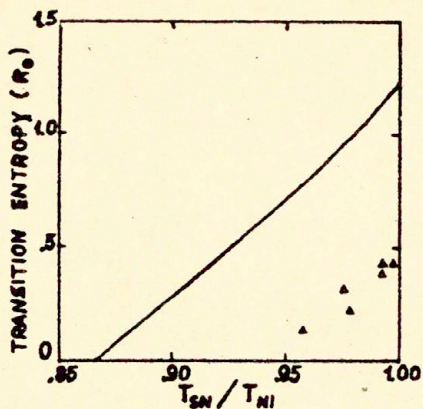


FIG. 5

Smectic A - nematic transition entropy versus ration of transition temperature T_{SN}/T_{NI}

- theoretical curve taken from Fig.3, McMillan model / Ref. [13] /
- Δ experimental data from Fig. 2 / Ref. [15] /