On critical dynamics of the smectic A to nematic phase transition

1978 J. Phys. A: Math. Gen. 11 2045

(http://iopscience.iop.org/0305-4470/11/10/021)

J. Phys. A: Math. Gen., Vol. 11, No. 10, 1978. Printed in Great Britain

On critical dynamics of the smectic A to nematic phase transition

Yasuhiro Shiwa

Department of Physics, University of California at San Diego, La Jolla, California 92093, USA

Received 6 March 1978

Abstract. A kinetic equation is derived for the slowly varying, large-scale critical fluctuations (gross variables) in a smectic A liquid crystal below a smectic A to nematic phase transition point using Kawasaki's formulation of the extended mode-coupling theory. Two kinds of variables, i.e. amplitude of the smectic A order parameter and a second-sound mode are chosen as gross variables. A time-correlation-function formalism applied to this kinetic equation yields no serious renormalisation of transport coefficients to indicate adequateness of the mean-field-type treatment to critical dynamics in the smectic A phase.

1. Introduction

Liquid crystals present a fascinating array of phase transitions associated with the orientational and spatial order of elongated organic molecules. Recently there has been considerable theoretical and experimental attention towards a smectic A–nematic transition.

In a smectic A liquid crystalline phase, bar-like molecules coalesce into equidistant planes; centres of mass form a one-dimensional sinusoidal density wave in the direction normal to the planes, while the centre-of-mass density in the plane is uniform as in a normal liquid. A nematic phase is characterised by a uniform centre-of-mass distribution but the molecules have their long molecular axes aligned along a specific direction labelled by a unit vector called a director. The orientational order survives the nematic to smectic A phase transition; the director is perpendicular to the smectic layers in the smectic A phase.

Microscopic theory (McMillan 1971, Lee *et al* 1973) has indicated that this phase transition could be of second order when the reduced temperature T_{NS}/T_{NI} (the ratio of nematic–smectic A to nematic–isotropic transition temperature) is small enough, i.e. when the nematic ordering is nearly saturated at T_{NS}. The centre-of-mass density is periodic in the direction perpendicular to the smectic layers in the smectic A phase. It can, therefore, be expanded in a Fourier series of wavevector $Q = 2\pi/L$, where L is the interlayer distance, whose first Fourier coefficient is proposed to be a smectic A order parameter. Thus defined the smectic A order parameter is complex having both amplitude and phase. Traditional, heuristic reasoning (de Gennes 1972, Brochard 1973, 1976, Jähnig and Brochard 1974) would then say that the critical exponents for the smectic A–nematic transition should be the same as those for superfluid ^{4}He which also has a complex order parameter. Indeed there is a strong analogy between them

0305-4770/78/0010-2045$02.00

regarding some physical features, but it is another problem whether or not the smectic A exhibits critical behaviour which is similar to that in superfluid helium. In fact, experimental observations are rather incompatible concerning the value of the critical exponents (see, for example, Chandrasekhar 1977).

The purpose of this paper is to investigate the effect of non-linear coupling among the critical fluctuations upon critical dynamical behaviour within the framework of Kawasaki's (extended) mode–mode coupling theory (Kawasaki 1976). If the transition should be helium-like at all, the mode-coupling mechanism would inevitably exert great influence upon critical dynamics of the smectic A phase. Our conclusion is that the mode coupling does not seriously affect critical dynamics indicating adequateness of a mean-field picture. This paper is divided into five sections of which this is the first. In § 2, after a brief summary of Kawasaki's formulation of constructing a kinetic equation, a proper set of dynamical variables called gross variables that enter the kinetic equation for the smectic A mesophase is determined. In § 3 the kinetic equations for these gross variables are derived. Applying Kawasaki's method to the kinetic equations obtained, § 4 discusses the renormalisation of the decay rate of critical fluctuations. This treatment indicates we have no mode coupling that seriously affects critical dynamics in the critical region. A few comments about the present approach are made in § 5.

2. Dynamical gross variables

2.1. Review of formulation

This subsection gives a brief summary of the mutilated kinetic equations for gross variables presented by Kawasaki (1976).

We denote a gross variable by a_j, and the corresponding phase function A_j, where j specifies wavevector as well as the type of the variable. If we retain only up to quadratic terms in the a's in the kinetic equation, the kinetic equation for $a_j(t)$ is written as

$$\frac{\mathrm{d}}{\mathrm{d}t} a_j(t) = \sum_l \left(\mathrm{i}\omega_{jl} - \frac{k_\mathrm{B}\zeta^0_{jl}}{\chi_l}\right) a_l + \frac{\mathrm{i}}{2}\sum_{l,m} \mathscr{V}_{jlm}(a_l a_m - \langle A_l A_m\rangle) + f_j, \tag{2.1}$$

where $\{\zeta^0_{jl}\}$ is the bare damping matrix, and f_j a random force acting on a_j.

Here the first-moment frequency matrix $\{\omega_{jl}\}$ and the mode-coupling coefficient $\mathscr{V}_{jlm}$ are given by

$$\omega_{jl} = -\mathrm{i}k_\mathrm{B}T\langle[A_j, A_l^+]\rangle/\chi_l, \tag{2.2}$$

$$\mathscr{V}_{jlm} = -\mathrm{i}k_\mathrm{B}T\left(\langle[A_j, A_l^+A_m^+]\rangle - \sum_p \frac{\langle[A_j, A_p^+]\rangle}{\chi_p}\langle A_p A_l^+ A_m^+\rangle\right)(\chi_l\chi_m)^{-1}, \tag{2.3}$$

respectively, with $\langle A_j\rangle = 0$ and $\langle A_i A_j^+\rangle = \delta_{ij}\chi_i$; $[X, Y]$ denotes the Poisson bracket of two phase functions X and Y, $\langle\ldots\rangle$ the equilibrium ensemble average.

The kinetic equation (2.1) is only valid over time scales which are much greater than microscopic times that characterise rapid molecular random processes.

2.2. Gross variables for the smectic A

De Gennes (1972, 1973) proposed that the order parameter for a smectic A phase be defined by a density wave along a constant direction which we take to be the z direction (perpendicular to the smectic layers), i.e.

$$\rho(\boldsymbol{r}) = \rho_0 + \mathrm{Re}[\psi(\boldsymbol{r}) \exp(\mathrm{i}Qz)]. \tag{2.4}$$

Here $L = 2\pi/Q$ is the smectic layer spacing and $\psi(\boldsymbol{r}) = \psi_0(\boldsymbol{r}) \exp[-\mathrm{i}Qu_z(\boldsymbol{r})]$ is a complex smectic A order parameter; u_z represents a displacement of the layer in the z direction, and in the smectic A phase $\langle\psi_0\rangle = \psi_{00} \neq 0$.

We choose phase functions corresponding to the A_i's to be Fourier components of the two-component smectic A order parameter or its magnitude $\psi_Q(\boldsymbol{k})$ and its phase, i.e. the displacement $u_z(\boldsymbol{k})$ of the smectic layer, and dilatation $\theta(\boldsymbol{k})$, and the local velocity $\boldsymbol{v}(\boldsymbol{k})$ giving the flow of matter, which are defined by

$$O(\boldsymbol{k}) = V^{-1/2} \int \mathrm{d}r\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} O(\boldsymbol{r}) \tag{2.5}$$

with $O(\boldsymbol{r}) = \psi_Q(\boldsymbol{r})$, $u_z(\boldsymbol{r})$, $\theta(\boldsymbol{r})$ or $\boldsymbol{v}(\boldsymbol{r})$, and V being volume of the system. Here

$$\psi_Q(\boldsymbol{r}) = (\psi_0(\boldsymbol{r}) - \psi_{00}) \cos(Qz), \tag{2.6a}$$

$$\theta(\boldsymbol{r}) = \partial u_z(\boldsymbol{r})/\partial z + \boldsymbol{\nabla}_\perp \cdot \boldsymbol{u}_\perp(\boldsymbol{r}), \tag{2.6b}$$ †

and

$$\boldsymbol{v}(\boldsymbol{r}) = \rho_0^{-1} \boldsymbol{p}(\boldsymbol{r}), \tag{2.6c}$$

with $\boldsymbol{p}(\boldsymbol{r})$ being the local momentum density.

In the smectic A phase, the broken symmetry is translational, i.e. a small translation along the normal to the layers produces a different, but equivalent, state of the system; u_z is a symmetry-breaking variable while v_z is a symmetry-restoring variable. Coupling of the symmetry-breaking variable to the flow is known to give rise to a so called second-sound mode (de Gennes 1969, Martin *et al* 1972, Jähnig 1975). We shall simply neglect thermal variables. The orientational displacements of molecules, that is, the director fluctuations, are also ignored, which means we assume orientational order has been saturated at $T \simeq T_{\mathrm{NS}}$.

In the next subsection we will determine the linear combination of the gross variables u_z, θ, $\boldsymbol{v}$ which is an eigenfunction of the second-sound mode (to be referred to as ESSM), to which we couple the amplitude of the order parameter, ψ_Q.

2.3. *Second-sound mode*‡

To construct ESSM we first have to know a frequency matrix (2.2) in the restricted phase space spanned by the gross variables u_z, θ and $\boldsymbol{v}$. Let us start from the orthogonalised set of gross variables $\{u_z(\boldsymbol{k}), \tilde{\theta}(\boldsymbol{k}), \boldsymbol{v}(\boldsymbol{k})\}$, where

$$\tilde{\theta}(\boldsymbol{k}) = \theta(\boldsymbol{k}) + \frac{\chi_{u\theta}(\boldsymbol{k})}{\chi(\boldsymbol{k})} u_z(\boldsymbol{k}) \tag{2.7}$$

with

$$\chi(\boldsymbol{k}) = \beta\langle|u_z(\boldsymbol{k})|^2\rangle \qquad \text{and} \qquad \chi_{u\theta}(\boldsymbol{k}) = \beta\langle u_z(\boldsymbol{k})\theta(-\boldsymbol{k})\rangle = -\chi_{u\theta}(-\boldsymbol{k}),$$

β/k_{B} being temperature.

† The second term represents the transverse dilatation and should be regarded as a definition of the transverse displacement of the layer.

‡ The author owes this part to Professor Kawasaki's unpublished note.

Poisson brackets for these variables are given in appendix 1; making use of these yields the frequency matrix of the form

$$
\mathrm{i}\boldsymbol{\omega}(\boldsymbol{q}) = \begin{array}{c} \\ u_z \\ \tilde{\theta} \\ v_z \\ v_x \\ v_y \end{array}
\begin{array}{c} \begin{array}{ccccc} u_z & \tilde{\theta} & v_z & v_x & v_y \end{array} \\
\begin{pmatrix}
0 & 0 & 1 & 0 & 0 \\
0 & 0 & \mathrm{i}\alpha q_z & \mathrm{i}q_x & \mathrm{i}q_y \\
-1/\rho_0\chi(\boldsymbol{q}) & \mathrm{i}\alpha q_z/\rho_0\chi_{\tilde{\theta}}(\boldsymbol{q}) & 0 & 0 & 0 \\
0 & \mathrm{i}q_x/\rho_0\chi_{\tilde{\theta}}(\boldsymbol{q}) & 0 & 0 & 0 \\
0 & \mathrm{i}q_y/\rho_0\chi_{\tilde{\theta}}(\boldsymbol{q}) & 0 & 0 & 0
\end{pmatrix}\end{array} . \tag{2.8}
$$

Here,

$$
\chi_{\tilde{\theta}}(\boldsymbol{q}) = \beta\langle|\tilde{\theta}(\boldsymbol{q})|^2\rangle \qquad \text{and} \qquad \alpha \equiv 1 - \frac{\mathrm{i}\chi_{u\tilde{\theta}}(\boldsymbol{q})}{q_z\chi(\boldsymbol{q})}, \tag{2.9}
$$

and we have used the relation $\beta\langle v_\alpha(\boldsymbol{q})v_\beta(-\boldsymbol{q})\rangle = \rho_0^{-1}\,\delta_{\alpha\beta}$. We should note that the first row of the above matrix $\boldsymbol{\omega}$ represents a permeation process (Helflich 1969, Martin *et al* 1972, Jähnig 1975) of molecules through the smectic layers: $du_z/dt = v_z +$ dissipative terms.

Now we can readily obtain the secular equation for $\mathrm{i}\boldsymbol{\omega}$:

$$
\omega\left[\omega^4 + \omega^2\rho_0^{-1}\left(\frac{q_\perp^2 + \alpha^2 q_z^2}{\chi_{\tilde{\theta}}(\boldsymbol{q})} + \frac{1}{\chi(\boldsymbol{q})}\right) + \frac{q_\perp^2}{\rho_0^2\chi_{\tilde{\theta}}(\boldsymbol{q})\chi(\boldsymbol{q})}\right] = 0 \tag{2.10}
$$

with $q_\perp^2 = q^2 - q_z^2$.

Equation (2.10) gives three eigenmodes of different type, one of which is a damped hydrodynamic shear mode $\omega = \omega_3 = 0$; the others are $\omega = \pm\omega_j(\boldsymbol{q}) \equiv \mathrm{i}s_j(\hat{q})q$ $(j = 1, 2)$, where the velocities s_j are roots of the equation

$$
(\rho_0 s^2)^2 - \rho_0 s^2\left(\frac{1 + (\alpha^2 - 1)\hat{q}_z^2}{\chi_{\tilde{\theta}}(\boldsymbol{q})} + \frac{1}{q^2\chi(\boldsymbol{q})}\right) + \frac{\hat{q}_\perp^2}{q^2\chi_{\tilde{\theta}}(\boldsymbol{q})\chi(\boldsymbol{q})} = 0 \tag{2.11}
$$

with $\hat{q}_z = q_z/q$ and $\hat{q}_\perp = q_\perp/q$.

If, in equation (2.11), we adopt the expressions for the mean-square fluctuations:

$$
\chi^{-1}(\boldsymbol{q}) = \bar{B}q_z^2, \qquad \chi_{\tilde{\theta}}^{-1}(\boldsymbol{q}) = A \qquad \text{and} \qquad \chi_{u\tilde{\theta}}^{-1}(\boldsymbol{q}) = A\bar{B}q_z/\mathrm{i}C \tag{2.12}
$$

with elastic constants† A, B, C, and $\bar{B} \equiv B - C^2/A > 0$, which are given by the familiar free energy of deformation due to de Gennes (1969), we will find the well known equation (de Gennes 1969, Martin *et al* 1972, Jähnig 1975):

$$
(\rho_0 s^2)^2 - \rho_0 s^2(A + \bar{B}\cos^2\phi) + A\bar{B}\sin^2\phi\cos^2\phi = 0 \tag{2.13}
$$

with ϕ being the angle between $\boldsymbol{q}$ and z axis. Here we have put $\alpha = 1 + C/A \simeq 1$, since $A \gg C$ (Liao *et al* 1973). Thus we see equation (2.11) gives what are called the first- and the second-sound modes (ω_1 and ω_2).

† The elastic constants A, B, and C are related to the usual elastic moduli C_{ij} by $A = C_{11}$, $B = C_{33} + C_{11} - 2C_{13}$ and $C = C_{11} - C_{13}$.

Then it is straightforward to obtain the eigenvector $(A_+^1(\boldsymbol{q}), A_-^1(\boldsymbol{q}), A_+^2(\boldsymbol{q}), A_-^2(\boldsymbol{q}), A^3(\boldsymbol{q}))$, corresponding to the eigenmodes $(\omega_1(\boldsymbol{q}), -\omega_1(\boldsymbol{q}), \omega_2(\boldsymbol{q}), -\omega_2(\boldsymbol{q}), \omega_3(\boldsymbol{q}))$, of the form

$$\begin{aligned} &A_+^l = a_l u_z + b_l\tilde{\theta} + c_l v_z + \mathrm{d}_l v_x + e_l v_y, \qquad A_-^l = (A_+^l)^*, \qquad l = 1, 2, \\ &A^3 = a_3 u_z + b_3\tilde{\theta} + c_3 v_z + d_3 v_x + e_3 v_y, \end{aligned} \tag{2.14}$$

where parameters a_m, b_m, c_m, d_m, and e_m $(m = 1, 2, 3)$ are to be djxined.

At this point we shall note the fact that the first-sound velocity is finite at T_{NS}; this mode remains at high frequency and is not expected to have any serious influence on critical behaviour if attention is confined to phenomena occurring in the frequency range $\omega \ll s_2\xi^{-1}$ (ξ, characteristic correlation length). This, as well as the experimentally verified (plausible) relation (Liao *et al* 1973) $A \gg \bar{B}$ (which also means $\omega_1 \gg \omega_2$), allow us to take the limit of a weak coupling between the first- and the second-sounds. Hence, we might take only ESSM, i.e. $A_\pm^2(\boldsymbol{q})$, as our dynamical gross variable. The normalised ESSM, $A_\pm(\boldsymbol{q}) \equiv A_\pm^2(\boldsymbol{q})$, are given after some manipulations by

$$\begin{aligned} A_+(\boldsymbol{q}) &= \frac{\mathrm{i}}{(2\chi(\boldsymbol{q}))^{1/2}} u_z(\boldsymbol{q}) - \frac{1}{(2\chi(\boldsymbol{q}))^{1/2}} \frac{\hat{q}_z}{q} \tilde{\theta}(\boldsymbol{q}) + \left(\frac{\rho_0}{2}\right)^{1/2} \left(\hat{q}_\perp v_z(\boldsymbol{q}) - \frac{\hat{q}_z}{\hat{q}_\perp} (\hat{\boldsymbol{q}}_\perp \cdot \boldsymbol{v}_\perp(\boldsymbol{q}))\right), \\ A_-(\boldsymbol{q}) &= A_+^*(\boldsymbol{q}), \end{aligned} \tag{2.15}$$

and satisfy the relations

$$\begin{aligned} &\beta\langle A_\alpha(\boldsymbol{q}) A_\beta^*(\boldsymbol{k})\rangle = \delta_{\alpha\beta}\, \Delta(\boldsymbol{q}-\boldsymbol{k}), \\ &\langle [A_\alpha(\boldsymbol{q}), A_\beta^*(\boldsymbol{k})]\rangle = \delta_{\alpha\beta}\, \Delta(\boldsymbol{q}-\boldsymbol{k}) \mathrm{i}\omega_2(\boldsymbol{q}) \operatorname{sgn} \alpha + \mathrm{O}(\bar{B}/A), \end{aligned} \tag{2.16}$$

where $\Delta(\boldsymbol{q})$ is a generalised Kronecker delta: $\Delta(\boldsymbol{q}) = 1$ for $\boldsymbol{q} = 0$, $= 0$ otherwise.

3. Kinetic equation

We can now set up the kinetic equations for an orthogonal set of gross variables $\{\psi_Q(\boldsymbol{q}), A_+(\boldsymbol{q}), A_-(\boldsymbol{q})\}$ in the smectic A phase according to the prescription described in § 2.1.

Poisson brackets given in appendix 1 yield the frequency matrix

$$\mathrm{i}\boldsymbol{\omega}(\boldsymbol{q}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \mathrm{i}\omega_2^0(\boldsymbol{q}) & 0 \\ 0 & 0 & -\mathrm{i}\omega_2^0(\boldsymbol{q}) \end{pmatrix}, \tag{3.1}$$

where $\omega_2^0(\boldsymbol{q})$ is the unrenormalised second-sound frequency, and $\omega_2^0(\boldsymbol{q}) = \bar{B}\hat{q}_\perp\hat{q}_z q$ if the relations (2.12) were used.

Let us now turn to the mode-coupling coefficients $\mathscr{V}_{jlm}$, namely,

$$\begin{aligned} &\mathscr{V}_{jlm} = \mathscr{V}^{\mathrm{G}}(jlm) + \mathscr{V}^{\mathrm{NG}}(jlm), \\ &\mathrm{i}\mathscr{V}^{\mathrm{G}}(jlm) \equiv \frac{\langle [A_j, A_l^+ A_m^+]\rangle}{\chi_l \chi_m}, \\ &\mathrm{i}\mathscr{V}^{\mathrm{NG}}(jlm) \equiv -\sum_p \frac{\langle [A_j, A_p^+]\rangle}{\chi_p} \frac{\langle A_p A_l^+ A_m^+\rangle}{\chi_l \chi_m}. \end{aligned} \tag{3.2}$$

As we show in appendix 2, the non-vanishing set of $\mathscr{V}^{\mathrm{G}}$'s are

$$\mathrm{i}\mathscr{V}^{\mathrm{G}}(\psi_Q(\boldsymbol{q})\psi_Q(\boldsymbol{k})A_+(\boldsymbol{q}-\boldsymbol{k})) = -\mathrm{i}(2\rho_0 V)^{-1/2} qz(\hat{\boldsymbol{q}}, \widehat{\boldsymbol{q}-\boldsymbol{k}}),$$
$$\mathrm{i}\mathscr{V}^{\mathrm{G}}(\psi_Q(\boldsymbol{q})A_+(\boldsymbol{k})\psi_Q(\boldsymbol{q}-\boldsymbol{k})) = -\mathrm{i}(2\rho_0 V)^{-1/2} qz(\hat{\boldsymbol{q}}, \hat{\boldsymbol{k}}),$$
$$\begin{aligned}\mathrm{i}\mathscr{V}^{\mathrm{G}}&(A_+(\boldsymbol{q})\psi_Q(\boldsymbol{k})\psi_Q(\boldsymbol{q}-\boldsymbol{k}))\\ &= -\mathrm{i}(2\rho_0 V)^{-1/2}\left(\frac{kz(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}})}{\chi_\psi(\boldsymbol{k})} + \frac{|\boldsymbol{q}-\boldsymbol{k}|z(\widehat{\boldsymbol{q}-\boldsymbol{k}}, \hat{\boldsymbol{q}})}{\chi_\psi(\boldsymbol{q}-\boldsymbol{k})}\right)\\ &= -\mathrm{i}\mathscr{V}^{\mathrm{G}}(A_-(\boldsymbol{q})\psi_Q(-\boldsymbol{k})\psi_Q(\boldsymbol{k}-\boldsymbol{q})),\end{aligned} \tag{3.3a}$$

and

$$\mathrm{i}\mathscr{V}^{\mathrm{G}}(A_+(\boldsymbol{q})A_+(\boldsymbol{k})A_+(\boldsymbol{q}-\boldsymbol{k})) = -\mathrm{i}(8\rho_0 V)^{-1/2} qV(\boldsymbol{q}, \boldsymbol{k}) = -\mathrm{i}\mathscr{V}^{\mathrm{G}}(A_-(\boldsymbol{q})A_-(\boldsymbol{k})A_-(\boldsymbol{q}-\boldsymbol{k})),$$

where

$$z(\boldsymbol{x}, \boldsymbol{y}) = x_z y_\perp - \frac{y_z}{y_\perp}(\boldsymbol{x}_\perp \cdot \boldsymbol{y}_\perp) \qquad \text{and} \qquad \chi_\psi(\boldsymbol{q}) = \beta\langle|\psi_Q(\boldsymbol{q})|^2\rangle. \tag{3.3b}$$

We have not written down $\mathscr{V}^{\mathrm{G}}(AAA)$ explicitly since this term can be neglected as we shall see later; suffice it to say that $V(\boldsymbol{q}, \boldsymbol{k})$ takes the asymptotic form $V(\boldsymbol{q}, \boldsymbol{k}) \to \hat{V}(\hat{\boldsymbol{q}}, \hat{\boldsymbol{k}})$ as $q/k \to 0$.

As to the non-Gaussian corrections $\mathscr{V}^{\mathrm{NG}}$, only the modes $\psi\psi A$, $AA\psi$, AAA participate in the (three-) mode coupling through a selection rule of the mode coupling arising from the time-reversal symmetry (Kawasaki 1976). However, $\mathscr{V}^{\mathrm{NG}}(\psi\psi A)$, $\mathscr{V}^{\mathrm{NG}}(\psi A\psi)$ and $\mathscr{V}^{\mathrm{NG}}(\psi AA)$ vanish since $\langle[\psi, \psi^*]\rangle = \langle[\psi, A^*]\rangle = 0$. Also $\mathscr{V}^{\mathrm{NG}}(A\psi\psi)$, $\mathscr{V}^{\mathrm{NG}}(AA\psi)$ and $\mathscr{V}^{\mathrm{NG}}(A\psi A)$ are negligible, because $\mathscr{V}^{\mathrm{NG}}(AA\psi) \propto \langle A(\boldsymbol{q})A^*(\boldsymbol{k})\psi_Q^*(\boldsymbol{q}-\boldsymbol{k})\rangle \simeq (\partial\langle|A(\boldsymbol{q})|^2\rangle/\partial\rho)_T\langle|\delta\rho(\boldsymbol{k})|^2\rangle = 0$ which follows from the formula (Schofield 1966):

$$\left(\frac{\partial X}{\partial Y}\right)_T = \lim_{\boldsymbol{q}\to 0}\frac{\langle\delta\rho(-\boldsymbol{q})X(\boldsymbol{q})\rangle}{\langle\delta\rho(-\boldsymbol{q})Y(\boldsymbol{q})\rangle}, \tag{3.4}$$

where $\delta\rho$ is a density fluctuation, and similarly for $\mathscr{V}^{\mathrm{NG}}(A\psi A)$ and $\mathscr{V}^{\mathrm{NG}}(A\psi\psi)$. Still more we simply assume $\mathscr{V}^{\mathrm{NG}}(AAA) \lessdot \mathscr{V}^{\mathrm{G}}(AAA)$. Hence, we may put $\mathscr{V} \cong \mathscr{V}^{\mathrm{G}}$.

Then we can easily get the kinetic equation from (2.1). Namely,

$$\begin{aligned}\dot{\psi}_Q(\boldsymbol{q}) = -\gamma^0(\boldsymbol{q})\psi_Q(\boldsymbol{q}) - \mathrm{i}(8\rho_0 V)^{-1/2} q \sum_{\boldsymbol{k}}{}' \, (z(\hat{\boldsymbol{q}}, \widehat{\boldsymbol{q}-\boldsymbol{k}})\psi_Q(\boldsymbol{k})A_+(\boldsymbol{q}-\boldsymbol{k})\\ + z(\hat{\boldsymbol{q}}, \hat{\boldsymbol{k}})A_+(\boldsymbol{k})\psi_Q(\boldsymbol{q}-\boldsymbol{k})) + f_{\boldsymbol{q}}^{\psi},\end{aligned} \tag{3.5a}$$

$$\begin{aligned}\dot{A}_+(\boldsymbol{q}) &= (\mathrm{i}\omega_2^0(\boldsymbol{q}) - q^2 D^0(\boldsymbol{q}))A_+(\boldsymbol{q})\\ &\quad - \mathrm{i}(8\rho_0 V)^{-1/2}\sum_{\boldsymbol{k}}{}'\left(\frac{kz(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}})}{\chi_\psi(\boldsymbol{k})} + \frac{|\boldsymbol{q}-\boldsymbol{k}|z(\widehat{\boldsymbol{q}-\boldsymbol{k}}, \hat{\boldsymbol{q}})}{\chi_\psi(\boldsymbol{q}-\boldsymbol{k})}\right)\psi_Q(\boldsymbol{k})\psi_Q(\boldsymbol{q}-\boldsymbol{k}) + f_{\boldsymbol{q}}^{A}.\end{aligned} \tag{3.5b}$$

Since $A_+^*(\boldsymbol{q}) = A_-(\boldsymbol{q})$, the equation for $A_-(\boldsymbol{q})$ is redundant. In equation (3.5), $\gamma^0(\boldsymbol{q})$ and $q^2D^0(\boldsymbol{q})$ are bare Onsager kinetic coefficients, and $\{f^\psi, f^A\}$ are random forces left out of $\{\psi, A\}$; in the sum $\Sigma_{\boldsymbol{k}}'$, k is restricted to be much smaller than the inverse microscopic distance ($\equiv \Lambda^{-1}$).

4. Renormalisation and critical dimensionality

Having obtained the kinetic equation, the next task is to deduce from it macroscopic behaviour near the critical point expressed in rather a general language. The time correlation functions seem to be most suitable for this purpose.

First we review briefly Kawasaki's formulation of time correlation functions (Kawasaki 1976). To solve the kinetic equations for gross variables and to determine behaviour of the set of time correlation functions, perturbation and renormalisation techniques are introduced. This method allows us to obtain a self-consistent set of equations for the time correlation functions of gross variables defined by

$$G_{jl}(t)=\langle A_j(t)A_l^+(0)\rangle/\chi_l. \tag{4.1}$$

We find, ignoring vertex corrections,

$$\frac{\mathrm{d}}{\mathrm{d}t}G_{jr}(t)=(\mathrm{i}\omega_j^0-\gamma_j^0)G_{jr}(t)-\sum_l\int_0^t \mathrm{d}s\ \Xi_{jl}(s)G_{lr}(t-s), \tag{4.2a}$$

with the memory kernel:

$$\Xi_{jl}(t)=\frac{1}{2}\sum_{mn}\sum_{m'n'}\frac{\chi_{m'}\chi_{n'}}{\chi_l}\mathscr{V}_{jmm}\mathscr{V}^*_{jm'n'}G_{mm'}(t)G_{nn'}(t), \tag{4.2b}$$

where $k_B\zeta^0_{jl}/\chi_l=\delta_{jl}\gamma^0_j$, and we put $\omega_{jl}=\delta_{jl}\omega^0_j$.

If we are allowed to make the Markoffian approximation to (4.2), equation (4.2a) reduces to the equation that determines the renormalised transport coefficients self-consistently. In particular, if a representation

$$G_{jl}(t)=\delta_{jl}\exp[(\mathrm{i}\omega_j-\gamma_j)t] \tag{4.3}$$

is used, we obtain

$$\gamma_j=\gamma_j^0+\frac{1}{2}\sum_{lm}\frac{\chi_l\chi_m}{\chi_j}|\mathscr{V}_{jlm}|^2\frac{1}{-\mathrm{i}(\omega_l+\omega_m)+\gamma_l+\gamma_m}, \tag{4.4}$$

which is what we observe in macroscopic measurements.

We apply the foregoing general theory to the smectic A phase discussed in § 3. We consider the following two types of propagators, one for amplitude of the smectic A order parameter denoted by $C_{\boldsymbol{q}}(t)$, and another for ESSM, $G_{\boldsymbol{q}}(t)$, defined by

$$C_{\boldsymbol{q}}(t)\equiv\beta\langle\psi_Q(\boldsymbol{q},t)\psi_Q^*(\boldsymbol{q},0)\rangle=\exp(-\gamma(\boldsymbol{q})t), \tag{4.5a}$$

$$G_{\boldsymbol{q}}(t)\equiv\beta\langle A_+(\boldsymbol{q},t)A_+^*(\boldsymbol{q},0)\rangle=\exp[(\mathrm{i}\omega_2(\boldsymbol{q})-q^2D(\boldsymbol{q}))t]. \tag{4.5b}$$

We arrive at the following coupled set of equations which corresponds to equation (4.4):

$$\gamma(\boldsymbol{q})=\gamma^0(\boldsymbol{q})+\frac{k_\mathrm{B}T}{8\rho_0}\frac{q^2}{\chi_\psi(\boldsymbol{q})}\int\frac{\mathrm{d}^dk}{(2\pi)^d}\frac{\chi_\psi(\boldsymbol{q}-\boldsymbol{k})z^2(\hat{\boldsymbol{q}},\hat{\boldsymbol{k}})}{-\mathrm{i}\omega_2(\boldsymbol{k})+k^2D(\boldsymbol{k})+\gamma(\boldsymbol{q}-\boldsymbol{k})}, \tag{4.6a}$$

$$D(\boldsymbol{q})=D^0(\boldsymbol{q})+\mathrm{Re}\bigg(\frac{k_\mathrm{B}T}{16\rho_0}q^{-2}\int\frac{\mathrm{d}^dk}{(2\pi)^d}\chi_\psi(\boldsymbol{k})\chi_\psi(\boldsymbol{q}-\boldsymbol{k})\bigg|\frac{kz(\hat{\boldsymbol{k}},\hat{\boldsymbol{q}})}{\chi_\psi(\boldsymbol{k})}+\frac{|\boldsymbol{q}-\boldsymbol{k}|z(\widehat{\boldsymbol{q}-\boldsymbol{k}},\hat{\boldsymbol{q}})}{\chi_\psi(\boldsymbol{q}-\boldsymbol{k})}\bigg|^2\frac{1}{\gamma(\boldsymbol{k})+\gamma(\boldsymbol{q}-\boldsymbol{k})}\bigg), \tag{4.6b}$$

$$\omega_2(\boldsymbol{q})=\omega_2^0(\boldsymbol{q})-\mathrm{Im}(\dots), \tag{4.6c}$$

where (...) is the same as the term in the large parentheses of equation (4.6*b*). To obtain this result the sum over $\boldsymbol{k}$ has been converted into a generalised d-dimensional integral with the upper cut-off Λ.

It is not possible to find an analytic solution to these equations. Yet when we restrict ourselves to the extreme critical regime ($q\xi \gg 1$), or more strictly $T = T_{\mathrm{NS}}$, equation (4.6) gives us the critical dimensionality d_c such that for the spatial dimensionality $d > d_c$, the mode-coupling contribution to the transport coefficients can be neglected, i.e. the conventional theory holds. We proceed based on the following set of approximations (Gunton and Kawasaki 1975, Kawasaki and Gunton 1977). First, we may neglect any dependence on ω_2 in equation (4.6). Secondly, at $T \simeq T_{NS}$ wavenumbers $\boldsymbol{k}$ much greater than $\boldsymbol{q}$ give the major contribution to the second terms of equation (4.6); we thus take the $\boldsymbol{q} \to 0$ limit in the integrand and introduce a lower cut-off ($\equiv cq$) which is proportional to q. Thus we get

$$\Gamma(\boldsymbol{q}) = \Gamma^0(\boldsymbol{q}) + \chi_\psi^{-1}(\boldsymbol{q}) \int_{\Lambda > k > cq} \mathrm{d}^d k \hat{A} \frac{\chi_\psi(\boldsymbol{k})}{k^2(D(\boldsymbol{k}) + \Gamma(\boldsymbol{k}))}, \tag{4.7a}$$

$$D(\boldsymbol{q}) = D^0(\boldsymbol{q}) + \int_{\Lambda > k > cq} \mathrm{d}^d k \, \hat{B} \left| \frac{\partial}{\partial \boldsymbol{k}} \frac{k}{\chi_\psi(\boldsymbol{k})} \right|^2 \frac{\chi_\psi^2(\boldsymbol{k})}{k^2 \Gamma(\boldsymbol{k})}. \tag{4.7b}$$

Here $\hat{A}$ and $\hat{B}$ represent anisotropic factors, the explicit forms of which are not necessary for our present purpose. To obtain this result we put $z(\hat{\boldsymbol{k}}, \hat{\boldsymbol{q}}) \simeq z(\widehat{\boldsymbol{q} - \boldsymbol{k}}, \hat{\boldsymbol{q}})$ for $q/k \ll 1$ and $\gamma(\boldsymbol{q}) = q^2 \Gamma(\boldsymbol{q})$.

We now adopt the anisotropic Ornstein–Zernike form for χ_ψ (Conrad *et al* 1977):

$$\chi_\psi(\boldsymbol{k}) = \frac{\chi_\psi(0)}{1 + k_z^2 \xi_\parallel^2 + k_\perp^2 \xi_\perp^2}, \tag{4.8}$$

where $\xi_\parallel$ and $\xi_\perp$ are the longitudinal and transverse correlation lengths, respectively, $\chi_\psi(0)$ being the susceptibility. Then it is not difficult to see that for $d > d_c = 2$ the mode-coupling contribution to $\Gamma(D)$, or $\delta\Gamma(\delta D)$, is negligible (even if we included the so far neglected term $\mathcal{V}(AAA)$), so that conventional theory is valid. In fact, $\delta\Gamma(\delta D) \sim \text{constant} \times q^{d-2}$, and we have no mode coupling in the small-$\boldsymbol{q}$ limit that seriously affects critical dynamics in the real smectic A phase.

5. Concluding remarks

We have investigated dynamics of critical fluctuations of a smectic A liquid crystal with a saturated nematic ordering near a second-order (or nearly second-order) smectic A–nematic transition.

First, the kinetic equations obeyed by critical fluctuations in the smectic A mesophase below T_{NS} have been derived using Kawasaki's formulation of the mode–mode coupling theory (the extended mode-coupling theory). The kinetic equations are then used to obtain self-consistent closed equations to determine renormalisation of the characteristic frequency (decay rate) of critical fluctuations. In particular in the critical regime, we have found non-linear mode coupling among critical fluctuations does not lead to serious renormalisation of their decay rates. Thus we might conclude that the mean-field theory is a very good approximation for the smectic A to nematic transition. Accordingly the smectic A liquid crystal has resemblance to an easy-axis antiferromagnet rather than to an isotropic antiferromagnet which has a close parallel with liquid helium near its λ transition; the point is that anisotropy alters critical behaviour drastically. In this respect an impetuous analogy between the smectic A and superfluid ^{4}He is superficial, at least as to its critical behaviour, although such a helium-type picture provides us with a fruitful insight into the physical properties of the smectic A outside the critical region (de Gennes 1974).

On the other hand, it should be emphasised that we have restricted ourselves to terms up to quadratic in critical fluctuation in the kinetic equation and that after such a special simplification the renormalisation technique has been applied. This notorious simplification remains an open question here too. Another problem pertinent to the mode-coupling theory is the assumption that gross variables we have taken to describe critical fluctuations in the smectic A form a complete set. Modification of critical dynamics through inclusion of additional variables such as energy density will be explained in the future.

We hope that experimental observations of pretransitional phenomena would enter fully into the critical region to confirm the prediction made here.

Acknowledgments

The author would like to express his sincere thanks to Professor K Kawasaki for hospitality and very enlightening discussions at the early stages of this research at Kyushu University. He is also grateful to Professor S Takada for his innumerable, patient comments and continual encouragement throughout the course of this work. This work is supported in part by the Rotary Foundation of Rotary International.

Appendix 1. Poisson brackets of gross variables

In this appendix we calculate Poisson brackets of our dynamical gross variables.

First, we write down the molecular expressions for them:

$$
\begin{aligned}
&\psi_Q(\boldsymbol{r}) \simeq \rho(\boldsymbol{r}) - [\rho_0 + \psi_{00}\cos(Qz)], \\
&\rho(\boldsymbol{r}) = \sum_\alpha m^\alpha \delta(\boldsymbol{r}-\boldsymbol{r}^\alpha), \\
&u_j(\boldsymbol{r}) = \sum_\alpha u_j^\alpha(\boldsymbol{r}-\boldsymbol{r}^\alpha), \\
&\theta(\boldsymbol{r}) = \sum_j u_{jj}(\boldsymbol{r}), \qquad u_{ij} = \tfrac{1}{2}(\nabla_i u_j + \nabla_j u_i), \qquad i, j = x, y, z, \\
&v_j(\boldsymbol{r}) = \rho_0^{-1} p_j(\boldsymbol{r}), \qquad p_j(\boldsymbol{r}) = \sum_\alpha p_j^\alpha \delta(\boldsymbol{r}-\boldsymbol{r}^\alpha), \qquad j = x, y, z.
\end{aligned}
\tag{A1.1}
$$

Here $\psi_{00} = \langle\psi_0\rangle$, $Q = 2\pi/L$, and we assume $|Qu_z| \ll 1$; m^α, $\boldsymbol{p}^\alpha$ and $\boldsymbol{u}^\alpha$ are, respectively, mass, local momentum and displacive degrees of freedom of the αth molecule at the point $\boldsymbol{r}^\alpha$. Here and in the following we shall always concentrate on fluctuations with long wavelengths ($k \ll Q$) and ignore the short wavelength quantities of the order of kL. By a straightforward evaluation we find non-vanishing Poisson-bracket relations among Fourier components of gross variables, which we list below:

$$[\psi_Q(\boldsymbol{q}), v_\alpha(\boldsymbol{k})] = -\mathrm{i}q_\alpha[\Delta(\boldsymbol{q}+\boldsymbol{k}) + (\rho_0 V^{1/2})^{-1}\psi_Q(\boldsymbol{q}+\boldsymbol{k})], \tag{A1.2a}$$

$$[u_z(\boldsymbol{q}), v_\alpha(\boldsymbol{k})] = \rho_0^{-1}\,\delta_{\alpha z}\Delta(\boldsymbol{q}+\boldsymbol{k}) - \mathrm{i}(\rho_0 V^{1/2})^{-1}q_\alpha u_z(\boldsymbol{q}+\boldsymbol{k}), \tag{A1.2b}$$

$$[\tilde{\theta}(\boldsymbol{q}), v_\alpha(\boldsymbol{k})] = \mathrm{i}\rho_0^{-1}q_\alpha\{[1 - \mathrm{i}\delta_{\alpha z}\chi_{u\theta}(\boldsymbol{q})/(q_z\chi(\boldsymbol{q}))]\,\Delta(\boldsymbol{q}+\boldsymbol{k}) - \mathrm{i}V^{-1/2}(q_\beta u_\beta(\boldsymbol{q}+\boldsymbol{k}) - \mathrm{i}\chi_{u\theta}(\boldsymbol{q})\chi^{-1}(\boldsymbol{q})u_z(\boldsymbol{q}+\boldsymbol{k}))\}, \tag{A1.2c}$$

$$[v_\alpha(\boldsymbol{q}), v_\beta(\boldsymbol{k})] = -\mathrm{i}(\rho_0 V^{1/2})^{-1}(q_\beta v_\alpha(\boldsymbol{q}+\boldsymbol{k}) - k_\alpha v_\beta(\boldsymbol{q}+\boldsymbol{k})), \tag{A1.2d}$$

where as usual summation over repeated indices is implied and $\Delta(\boldsymbol{q}-\boldsymbol{k}) = 1$ for $\boldsymbol{q} = \boldsymbol{k}$, $= 0$ otherwise.

Finally, combination of (2.15) with (A1.2) yields Poisson brackets for ψ_Q and the A's:

$$[\psi_Q(\boldsymbol{q}), A_\pm(\boldsymbol{k})] = -\mathrm{i}(\rho_0/2)^{1/2}qz(\hat{\boldsymbol{q}}, \hat{\boldsymbol{k}})[\Delta(\boldsymbol{q}\pm\boldsymbol{k}) + (\rho_0 V^{1/2})^{-1}\psi_Q(\boldsymbol{q}\pm\boldsymbol{k})], \tag{A1.3}$$

where

$$z(\hat{\boldsymbol{q}}, \hat{\boldsymbol{k}}) = \hat{q}_z\hat{k}_\perp - (\hat{\boldsymbol{q}}_\perp \cdot \hat{\boldsymbol{k}}_\perp)\hat{k}_z/\hat{k}_\perp, \tag{A1.4}$$

and in particular, $z(\hat{\boldsymbol{q}}, \pm\hat{q}) = 0$, $z(-\hat{\boldsymbol{q}}, \hat{\boldsymbol{k}}) = z(\hat{\boldsymbol{q}}, -\hat{\boldsymbol{k}}) = -z(\hat{\boldsymbol{q}}, \hat{\boldsymbol{k}})$.

Appendix 2. Mode-coupling coefficients

This appendix is devoted to the calculation of the mode-coupling coefficients $\mathscr{V}^G$ defined in (3.2).

The first three of (3.3*a*) can be obtained by a simple application of (3.2) with (A1.3). To get $\mathscr{V}^G(AAA)$ we proceed as follows. Although (A1.2*c*) is more involved to use, the following consideration helps to simplify it. Take two variables $X(\boldsymbol{k})$ and $Y(\boldsymbol{k})$ which are Fourier transforms of local density variables $X(\boldsymbol{r})$ and $Y(\boldsymbol{r})$. Then (Kawasaki 1976)

$$[X(\boldsymbol{k}), Y(\boldsymbol{k}')] = [X(\boldsymbol{k}+\boldsymbol{q}), Y(\boldsymbol{k}'-\boldsymbol{q})] + \mathrm{O}(qr_0), \tag{A2.1}$$

if the range of interaction, r_0, is short enough compared with k^{-1} and k'^{-1}. Consequently, if $\boldsymbol{q}$ is an arbitrary wavevector with $qr_0 \ll 1$, we have

$$[X(\boldsymbol{k}), Y(\boldsymbol{k}')] \simeq [X(\boldsymbol{k}+\boldsymbol{q}), Y(\boldsymbol{k}'-\boldsymbol{q})]. \tag{A2.2}$$

Using this approximation, we obtain

$$[\tilde{\theta}(\boldsymbol{q}), v_\alpha(\boldsymbol{k})] = -\mathrm{i}(\rho_0 V^{1/2})^{-1}q_\alpha\tilde{\theta}(\boldsymbol{q}+\boldsymbol{k}) \tag{A2.3}$$

apart from the term including $\Delta(\boldsymbol{q}+\boldsymbol{k})$ which turns out not to contribute to $\mathscr{V}$. Then we find, after a straightforward but lengthy calculation, that $\mathscr{V}^G(AAA)$ takes the form given in (3.3*a*).

References

Brochard F 1973 *J. Physique* **34** 411–22
—— 1976 *J. Physique* **37** C3 85–9
Chandrasekhar S 1977 *Liquid Crystals* (Cambridge: Cambridge University Press) pp 304–10

Conrad H M, Stiller H H, Frischkorn C G B and Shirane G 1977 *Solid St. Commun.* **23** 571–5
de Gennes P G 1969 *J. Physique* **30** C4 65–71
—— 1972 *Solid St. Commun.* **10** 753–6
—— 1973 *Molec. Cryst. Liquid Cryst.* **21** 49–76
—— 1974 *The Physics of Liquid Crystals* (Oxford: Clarendon) pp 273–325
Gunton J D and Kawasaki K 1975 *J. Phys. A: Math. Gen.* **8** L9–12
Helflich W 1969 *Phys. Rev. Lett.* **23** 372–4
Jähnig F 1975 *J. Physique* **36** 315–24
Jähnig F and Brochard F 1974 *J. Physique* **35** 301–13
Kawasaki K 1976 *Phase Transitions and Critical Phenomena* vol. 5A, eds C Domb and M S Green (New York: Academic) pp 165–403
Kawasaki K and Gunton J D 1977 *Progress in Liquid Physics* ed. C A Croxton (New York: Wiley) to be published
Lee F T, Tan H T, Shih Y M and Woo C W 1973 *Phys. Rev. Lett.* **31** 1117–20
Liao Y, Clark N A and Pershan P S 1973 *Phys. Rev. Lett.* **30** 639–41
Martin P C, Parodi O and Pershan P S 1972 *Phys. Rev.* A **6** 2401–20
McMillan W L 1971 *Phys. Rev.* A **4** 1238–46
Schofield P 1966 *Proc. Phys. Soc.* **88** 149–70