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# Polydispersity in liquid crystal systems

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# Polydispersity in liquid crystal systems

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Here we discuss the statistical mechanics of polydisperse liquid crystal systems. Three different kinds of liquid crystal systems are treated: nematic order in thermotropic Maier–Saupe-like systems and in lyotropic Onsager-like rod systems, and smectic order in a perfectly aligned hard rod fluid. In the first two cases we calculate the broadening of the isotropic-nematic transition. In the last case the suppression of smectic order is dealt with. We discuss the relationship between real systems and the models discussed in the paper.

## 1. Introduction

In this article we consider some aspects of the physics of multi-component liquid crystal systems. Binary mixtures of liquid crystals have been considered by a number of authors [1–3] but clearly the statistical mechanics of a liquid mixture becomes increasingly complicated as the number of components increases. In this situation a more attractive model system is the polydisperse limit—the limit of an infinite number of components. This approach has been used fruitfully by a number of authors to discuss phase equilibria in fluids [4, 5]. We shall consider liquid crystal systems with many components each of which is distinguished by an index $x$ which indicates some physical property. Examples of $x$ might be the length of a rod-like molecule, or the molecular weight of a polymer molecule. In each of the examples we use we shall spell out the precise meaning of the index $x$. Clearly in nature examples of such systems abound. While almost always $x$ is a discrete variable, in practice it is often more convenient to suppose $x$ to be a continuous variable; associated with $x$ is a probability distribution function, $p(x)$. In the limit of a very highly peaked distribution function (at $x_0$, say) the system becomes effectively a one component (or monodisperse) system. We shall find it useful to use the variance $\sigma^2$ of the distribution function, $p(x)$, as a perturbation parameter.

The classic works in the theory of nematic liquid crystals are the Maier–Saupe [6] theory of thermotropic liquid crystals and the Onsager [7] theory of lyotropic liquid crystal order. More recently [8] it has been realised that hard rod systems can also form a smectic phase. In §2, 3 and 4 we discuss in turn these three systems and their generalization to polydisperse situations. We concentrate on some specific features, namely, the nature of the order, its relation to the polydispersity in the ordered phase, and the effect of the polydispersity on the phase transition marking the onset of the liquid-crystalline order. Finally, in §5, we make some concluding remarks.

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## 2. Maier–Saupe theory

Let us consider a polydisperse system of molecules with an index $x$ which marks the different species of molecule. We shall suppose, in this example, that the orientational degrees of freedom are not affected by the index $x$. Consequently the orientational entropy $S(x)$ is given by

$$S(x) = -\int f(x, \Omega) \ln 4\pi f(x, \Omega)\, d\Omega, \tag{2.1}$$

where $f(x, \Omega)$ is the orientational distribution function for the species $x$. This is clearly a simple generalization of the usual Maier–Saupe formula [6]. Thus the total entropy per particle is

$$S = \int S(x) p(x)\, dx, \tag{2.2}$$

where $p(x)$ is the probability distribution function governing the frequency of $x$, and

$$\int p(x)\, dx = 1. \tag{2.3}$$

On the other hand we suppose that the effective interaction *is* dependent on the index $x$. Thus

$$U = -\tfrac{1}{2} \int u(x_1, x_2) \bar{P}_2(x_1) \bar{P}_2(x_2) p(x_1) p(x_2) dx_1 dx_2, \tag{2.4}$$

so that the index $x$ is defined by the interaction $u(x, x') = u(x', x)$, and $\bar{P}_2(x)$ is the orientational order parameter appropriate to molecules of index $x$

$$\bar{P}_2(x) = \int P_2 (\cos\theta) f(x, \Omega) d\Omega, \tag{2.5}$$

where $P_2(\cos\theta)$ is the second Legendre polynomial, as is usual in the liquid crystal literature. The total Helmholtz free energy (per particle) is now

$$A = u - TS = kT \int p(x) \ln p(x) dx + kT \int p(x) f(x, \Omega) \ln 4\pi f(x, \Omega) dx d\Omega$$
$$- \tfrac{1}{2} \int u(x, x') \bar{P}_2(x) \bar{P}_2(x') p(x) p(x') dx dx', \tag{2.6}$$

where the first term comes from the entropy of mixing of the polydisperse fluid.

In our work we shall concentrate on narrow distribution functions of the form

$$p(x) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left\{ -\frac{(x - x_0)^2}{2\sigma^2} \right\}. \tag{2.7}$$

The limit $\sigma \to 0$ corresponds to a pure $x_0$ system and we shall use as a perturbation parameter the standard deviation, $\sigma$, of the distribution.

### 2.1. *Ordering at low temperatures*

We first remind the reader of the conventional Maier–Saupe theory [6] corresponding to the free energy (2.6) in the limit of a pure system with

$$A = kT \int f(\Omega) \ln 4\pi f(\Omega) d\Omega - \tfrac{1}{2} u \bar{P}_2^2. \tag{2.8}$$

Minimizing with respect to $f(\Omega)$ yields

$$f(\Omega) = \frac{1}{4\pi Z} \exp\left\{\frac{u}{kT} \bar{P}_2 \, P_2 (\cos\theta)\right\}, \tag{2.9}$$

$$Z = \frac{1}{4\pi} \int \exp\left\{\frac{u}{kT} \bar{P}_2 P_2 (\cos\theta)\right\} d\Omega \tag{2.10}$$

and the orientation order parameter is given, self consistently, by

$$\bar{P}_2 = W[u\bar{P}_2/kT], \tag{2.11}$$

where the Maier–Saupe function $W(y)$ is given by

$$W(y) = \frac{d}{dy}[\ln Z(y)] \tag{2.12}$$

and, consistent with equation (2.10),

$$Z(y) = \frac{1}{4\pi} \int \exp\left[yP_2 (\cos\theta)\right] d\Omega. \tag{2.13}$$

The generalization of this theory to a polydisperse system comes from the minimization of the functional (2.6) with respect to $f(x, \Omega)$. We obtain

$$f(x, \Omega) = \frac{1}{4\pi Z(x)} \exp\left\{\frac{1}{kT} \int u(x, x')\bar{P}_2(x')p(x') \, dx' \, P_2 (\cos\theta)\right\}, \tag{2.14}$$

with a normalizing factor

$$Z(x) = \frac{1}{4\pi} \int d\Omega \exp\left\{\frac{1}{kT} \int u(x, x')\bar{P}_2(x')p(x') \, dx' \, P_2 (\cos\theta)\right\}. \tag{2.15}$$

Combining equations (2.14), (2.15) with the definitions in equations (2.5) and (2.11), we obtain a set of self-consistent equations for the order parameters $\bar{P}_2(x)$

$$\bar{P}_2(x) = W\left[\frac{1}{kT} \int u(x, x')p(x')\bar{P}_2(x') \, dx'\right], \tag{2.16}$$

$$\bar{P}_2 = \int p(x)\bar{P}_2(x) \, dx = \int p(x) \, W\left[\frac{1}{kT} \int u(x, x')p(x')\bar{P}_2(x') \, dx'\right]. \tag{2.17}$$

We shall merely seek the leading order behaviour of the solutions to equation (2.16) and (2.17) in the limit $\sigma \to 0$. To do this we note

$$V(x) = \int u(x, x')p(x')\bar{P}_2(x') \, dx = \langle u(x, x')\bar{P}_2(x')\rangle \tag{2.18a}$$

$$= \langle u(x, x')\rangle \langle \bar{P}_2(x')\rangle + \langle (u(x, x') - \langle u(x, x')\rangle) (\bar{P}_2(x') - \langle \bar{P}_2(x')\rangle)\rangle, \tag{2.18b}$$

$$= u(x, x_0)\bar{P}_2 + O(\sigma^2), \tag{2.19}$$

Thus to order $\sigma^2$ error equations (2.16) to (2.19) yield

$$\bar{P}_2 = W\left[\frac{1}{kT} u(x_0, x_0)\bar{P}_2\right] \tag{2.20}$$

(the usual Maier–Saupe result for $\bar{P}_2$) and

$$\bar{P}_2(x) = W\left[\frac{1}{kT}u(x, x_0)\bar{P}_2\right]. \tag{2.21}$$

Equation (2.21) shows that, unsurprisingly, there is excess ordering on those components which couple more strongly to the order parameters, a trend which of course has been observed in studies of binary mixtures of liquid crystals [1].

### 2.2. *The onset of order*

Martire *et al.* [2] pointed out that, as a consequence of the phase rule, in binary mixtures of nematogens there is a range of temperatures over which there is coexistence between an isotropic and a nematic phase. In general, of course, at coexistence the compositions of the two phases of the binary mixture are different. These aspects of the nematic–isotropic phase transition are preserved in polydisperse mixtures. In general, at nematic–isotropic coexistence the probability distribution functions $p_N(x)$, $p_I(x)$ in the nematic and isotropic phases will not be the same. As a result if the distribution function $p(x)$ is prescribed there will be a range of temperatures over which the system phase separates into a proportion, $q$, in the nematic phase with

$$qp_N(x) + (1 - q)p_I(x) = p(x). \tag{2.22}$$

In this section we calculate the relationship between $p_N(x)$ and $p_I(x)$, and calculate the width of the nematic–isotropic coexistence region. We first make some elementary observations. In the limit $\sigma \to 0$ the system becomes monodisperse, and thus the width of the coexistence regime must also tend to zero. Secondly, in this model the molecules of type $x$ are distinguished, and *only* distinguished, by the function $u(x, x')$ which is not constant. It will be useful therefore to parametrize the non-constancy of $u(x, x')$ by making the expansion

$$\begin{aligned} u(x, x') = {} & u_0 + u_1\,[(x - x_0) + (x' - x_0)] + u_{21}\,[(x - x_0)^2 + (x' - x_0)^2] \\ & + u_{22}\,(x - x_0)(x' - x_0), \end{aligned} \tag{2.23}$$

where

$$u_0 = u(x_0, x_0), \tag{2.24 a}$$

$$u_1 = \frac{\partial u}{\partial x}(x_0, x_0) = \frac{\partial u}{\partial x'}(x_0, x_0), \tag{2.24 b}$$

$$u_{21} = \frac{1}{2}\frac{\partial^2 u}{\partial x^2}(x_0, x_0), \tag{2.24 c}$$

$$u = \frac{\partial^2 u}{\partial x \partial x'}(x_0, x_0). \tag{2.24 d}$$

The condition of weak polydispersity can now be quantified; it is that

$$\lambda_1 = \frac{\sigma u_1}{u_0} \ll 1, \tag{2.25 a}$$

$$\lambda_{2i} = \sigma^2\frac{u_{2i}}{u_0} \ll 1, \tag{2.25 b}$$

where the small parameters $\lambda_{ij}$ will be useful in the context of perturbation theory. We shall suppose, without loss of generality, that $u_1 > 0$; equivalently $\bar{P}_2(x)$ is an increasing function of $x$.

We can now define chemical potentials for each species by functional differentiation of equation (2.6)

$$\mu(x) = \frac{\delta A}{\delta p(x)} \tag{2.26}$$

and the grand thermodynamic potential (per particle) is

$$\Omega = A - \int \mu(x) p(x). \tag{2.27}$$

Now $\Omega = \Omega[\{p(x)\}]$ and, by the usual principles of density functional theory [5, 9], is a minimum at the equilibrium value of $p(x)$, provided that the constraint (2.3) of conserved probability is borne in mind. This constraint leads to new Lagrange parameter $\mu$, and now the condition for equilibrium in phase $\alpha$ is

$$\frac{\delta\Omega}{\delta p_\alpha(x)} = \mu_\alpha. \tag{2.28}$$

The conditions for equilibrium between two phases $\alpha$ and $\beta$ are now that

$$\mu_\alpha(x) = \mu_\beta(x), \tag{2.29}$$

$$\Omega_\alpha(x) = \Omega_\beta(x), \tag{2.30}$$

where the subscripts refer to the phases $\alpha$ and $\beta$. There is no condition, however, that $\mu_\alpha$ and $\mu_\beta$ should be equal. This arises essentially because the Maier–Saupe theory in its simplest form is a constant volume and constant density theory. When we relax this constraint, as we shall in the next section, a total chemical potential relation governs the relative densities in the two phases.

We now apply the relation (2.28) to coexisting nematic (N) and isotropic (I) phases to obtain

$$kT[\ln p_I(x) + 1] = \mu_I(x) + \mu_I \tag{2.31}$$

$$kT[\ln p_N(x) + 1] + kT\int f_N(x_1\Omega)\ln 4\pi f_N(x,\Omega)\,d\Omega$$
$$- \int u(x,x')p_N(x')\bar{P}_2(x)\bar{P}_2(x')\,dx' = \mu_N(x) + \mu_N. \tag{2.32}$$

Applying the definition (2.15) of $Z(x)$, and eliminating $\mu_N(x)$, $\mu_I(x)$ from equations (2.31) and (2.32) using equation (2.14) yields

$$p_N(x) = p_I(x) Z_N(x) \exp((\mu_N - \mu_I)/kT) \tag{2.33}$$

Now, because $\bar{P}_2(x)$ is an increasing function of $x$, $Z_N(x)$ is also an increasing function of $x$. Thus we expect that $p_N(x)$ peaks at a value of $x > x_0$.

We use equation (2.15) to find an approximate relation between $p_N(x)$, $p_I(x)$ in a more tractable form. From equation (2.33)

$$\ln p_N(x) = \ln p_I(x) + \ln Z_N(x) + \frac{(\mu_N - \mu_I)}{kT}, \tag{2.34}$$

where from equation (2.15) and (2.18)

$$Z_N(x) = \frac{1}{4\pi}\int \exp\left\{\frac{V(x)}{kT}P_2(\cos\theta)\right\} d\Omega. \tag{2.35}$$

We now constrain the probability distribution functions $p_N(x)$ and $p_I(x)$ to be of the form

$$p_\alpha(x) = \frac{1}{(2\pi\sigma_\alpha^2)^{1/2}}\exp\left\{-\frac{(x-x_{\alpha 0})^2}{2\sigma_\alpha^2}\right\}. \tag{2.36}$$

Using the form (2.36) we expand equation (2.34) around $x_{I0}$ to obtain

$$-\ln\sigma_N - \frac{(x-x_{N0})^2}{2\sigma_N^2} = -\ln\sigma_I - \frac{(x-x_{I0})^2}{2\sigma_I^2} + \frac{u_I}{kT}\bar{P}_2^2(x-x_{I0}) + \frac{(\mu_N-\mu_I)}{kT} + \dots, \tag{2.37}$$

where the remaining terms on the right hand side of equation (2.37) are small with respect to the terms present from relation (2.25 *b*). If we make the further supposition that $\sigma_N = \sigma_I$ then equation (2.37) yields

$$\frac{(x_{N0}-x_{I0})}{\sigma} = \frac{u_I\sigma}{kT}\bar{P}_2^2, \tag{2.38}$$

where $\bar{P}_2$ and $T$ can be taken from the monodisperse Maier–Saupe theory at isotropic–nematic coexistence [6], thus yielding

$$\frac{(x_{N0}-x_{I0})}{\sigma} \cong 0{\cdot}881\,\lambda_I + \text{higher order terms}, \tag{2.39}$$

with $\lambda_I$ as defined in equation (2.25 *a*).

Finally we use this result to calculate the range of nematic–isotropic coexistence for a polydisperse fluid with the probability distribution $p(x)$ given by equation (2.7). This we calculate by noting that the upper limit of this range, $T_{NI}$, is given by the condition $p_I(x) = p(x)$, whereas at the lower limit, $T_{N2}$, $p_N(x) = p(x)$; these conditions correspond to the proportion of nematic phase $q = 0$, 1 respectively. Using the usual Maier–Saupe theory

$$T_{NI1} = 0{\cdot}2202\,u(x_0, x_0) + \alpha\sigma^2, \tag{2.40}$$

where the $\alpha\sigma^2$ is a secular shift in the phase transition due to the polydispersity. $T_{N2}$ is calculated for the isotropic distribution function $p_I(x)$ in coexistence with $p_N(x) = p(x)$. If we use the ansatz (2.36) this has mean $x_{I0}$ given by equation (2.39)

$$x_{I0} = x_0 - 0{\cdot}881\left[\frac{u_I}{u_0}\right]\sigma^2 \tag{2.41}$$

and

$$T_{NI2} = 0{\cdot}2202\,u(x_{I0}, x_{I0}) + \alpha\sigma^2. \tag{2.42}$$

We shall not concern ourselves with the magnitude of the secular shift. However comparison of equations (2.40) and (2.42) shows that the region of nematic–isotropic coexistence is given by, to lowest order in $\sigma$,

$$\frac{\Delta T}{T_{\mathrm{NI}}} = \frac{T_{\mathrm{NI1}} - T_{\mathrm{NI2}}}{T_{\mathrm{NI}}} \simeq 1{\cdot}76\left[\frac{u_1\sigma}{u_0}\right]^2 = 1{\cdot}76\,\lambda_1^2, \tag{2.43}$$

where we have used the expansion (2.23) to evaluate $u(x_1, x_2)$ in the neighbourhood of $(x_0, x_0)$. The crucial feature of equation (2.43) is that the coexistence regime shrinks to zero *both* in the limit of monodispersity ($\sigma \to 0$) *and* in the limit of identical particles, constant $u(x, x)$, for which $u_1 = 0$.

## 3. Onsager theory: ordering in a polydisperse mixture of rods

We consider a solution in which rods of length $L$ and fixed diameter $D$ are placed in a solvent with concentration $c' = N/V$ (total number of rods $N$, volume $V$), and with a distribution function $p(L)$. The related problem of a solution of rod-like micelles was treated by McMullen *et al.* [10]; Odijk [11] has also drawn attention to this problem. We suppose that the lengths are normally distributed around some mean, $L_0$, with standard deviation $\sigma$,

$$p(L) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp - \frac{(L - L_0)^2}{2\sigma^2}. \tag{3.1}$$

This distribution function must be wrong close to $L = 0$, because rods cannot have negative length. So long as $(\sigma/L_0) \ll 1$ this cannot be important and will not affect the calculations. For some purposes it will be convenient for us to discuss the distribution function of normalized lengths

$$x = 1 + y = L/L_0. \tag{3.2}$$

Then

$$p(y) = \frac{1}{(2\pi s^2)^{1/2}} \exp - \frac{y^2}{2s^2}, \tag{3.3}$$

where

$$s = \sigma/L_0 \tag{3.4}$$

is the normalized standard deviation.

### 3.1. *Onsager–Odijk theory*

Because we use monodisperse systems as a reference point in our perturbation theory for polydisperse systems it is useful to remind the reader of the basic structure of Onsager's theory of lyotropic ordering [7]. Odijk [11] has shown that most of the main features of the Onsager theory can be derived using a simple variational ansatz and we shall follow this treatment.

The free energy $\Delta A$ associated with a rod concentration $c'$ at an orientational distribution, $f(\Omega)$, is

$$\frac{\Delta A}{NkT} = \frac{\mu_0}{kT} - 1 + \ln c' + \int f(\Omega) \ln 4\pi f(\Omega)\, d\Omega + B_2 c', \tag{3.5}$$

where the orientational entropy is given by

$$S = -\int f(\Omega) \ln 4\pi f(\Omega)\, d\Omega = -\Sigma\,[f(\Omega)] \tag{3.6}$$

and the second virial coefficient is given by

$$B_2 = -\frac{1}{2}\int \beta(\Omega, \Omega')f(\Omega)f(\Omega')\,d\Omega d\Omega', \tag{3.7}$$

with

$$\beta_1(\Omega, \Omega') = -2L^2D|\sin\gamma(\Omega, \Omega')| \tag{3.8}$$

and $\gamma(\Omega, \Omega')$ the angle between $\Omega$ and $\Omega'$. If

$$b = \pi/4\, L^2D \tag{3.9}$$

and a scaling is introduced, such that

$$c = bc', \tag{3.10}$$

$$\varrho = \frac{4}{\pi}\langle|\sin\gamma(\Omega, \Omega')|\rangle. \tag{3.11}$$

then

$$\frac{\Delta A}{NkT} = \text{const} + \ln c + \Sigma\,(f) + c\varrho(f). \tag{3.12}$$

We observe that in the isotropic phase $\varrho = 1$.

The equation of state can be derived by taking thermodynamic derivatives of $\Delta A$, yielding for the osmotic pressure $\Pi$ and chemical potential $\mu$

$$\frac{\Pi}{kT} = c'(1 + pc), \tag{3.13}$$

$$\mu = \mu_0 + kT(\ln c' + \Sigma + 2c\varrho), \tag{3.14}$$

with $\mu_0$ the energy associated with inserting a rod particle in the solvent. The Odijk gaussian ansatz consists of supposing

$$f(\Omega) = f(\theta) = \frac{\alpha}{4\pi}\exp -\alpha\theta^2/2, \quad \left(0 < \frac{\pi}{2}\right)(\Omega \equiv -\Omega). \tag{3.15}$$

This ansatz is acceptable for well-ordered systems. For the isotropic phase we do not use it, merely noting that $\varrho = 1$, $\Sigma = 0$ in this case. For the nematic phase explicit substitution of the form (3.15) into the free energy (3.12) and subsequent minimization with respect to $\alpha$ yields (from equation (3.11))

$$\varrho = \frac{4}{(\pi\alpha)^{1/2}} \tag{3.16}$$

$$\Sigma\,(\alpha) = \ln\alpha - 1, \tag{3.17}$$

$$\alpha = \frac{4c^2}{\pi} \tag{3.18}$$

and hence

$$\varrho c = 2. \tag{3.19}$$

Coexistence between an isotropic phase at $c_{\mathrm{I}}$ and a nematic phase at $c_{\mathrm{N}}$ is thus established by equality of osmotic pressures and chemical potentials: from equations

(3.13) and (3.14) we have

$$c_{\mathrm{I}}(1 + c_{\mathrm{I}}) = 3c_{\mathrm{N}}, \tag{3.20}$$

$$\ln c_{\mathrm{I}} + 2c_{\mathrm{I}} = \ln c_{\mathrm{N}} + \Sigma(\alpha_{\mathrm{N}}) + 4, \tag{3.21}$$

$$= 3\ln c_{\mathrm{N}} + (3 + \ln 4/\pi). \tag{3.22}$$

Solving these coexistence equations yields $c_{\mathrm{N}} = 5{\cdot}12$, $c_{\mathrm{I}} = 3{\cdot}45$, and the coexistence osmotic pressure

$$\frac{\Pi_{\mathrm{coex}}}{bkT} = 3c_{\mathrm{N}} = 15{\cdot}36. \tag{3.23}$$

This compares with the exact answer of $c_{\mathrm{N}} = 4{\cdot}19$, $c_{\mathrm{I}} = 3{\cdot}29$ [12]. Finally we remark that the theory has been extended to multi-component mixtures. The equation of state in the nematic régime is always

$$\frac{\Pi}{kT} = 3c' \tag{3.24}$$

where $c'$ is the total concentration of rods, whatever the number of components. We have made some effort to go through these derivatives because this section forms the reference system for the polydisperse system under consideration.

### 3.2. *Free energy in the polydisperse rod system*

We consider a system of $N$ rods in volume $V$, with $c' = N/V$ distributed as before with probability $p(L)$ given by equation (3.1). The Helmholtz free energy is given by the analogues of equations (3.5) and (2.6)

$$\begin{aligned}\frac{\Delta A}{NkT} = &\int \frac{\mu_0(L)p(L)}{kT}\,dL - 1 + \ln c' + \int p(L)\ln p(L)\,dL \\ &+ \int p(L)f(L,\Omega)\ln 4\pi f(L,\Omega)\,d\Omega dL \\ &+ c'\int p(L)p(L')LL'D\,|\sin\gamma(\Omega,\Omega')|\,f(L,\Omega)f(L',\Omega')\,d\Omega d\Omega' dL dL'.\end{aligned} \tag{3.25}$$

### 3.3. *Ordering in the nematic phase*

The degree of order is determined by the parameter $\alpha$. The usual nematic order parameter $\bar{P}_2(\cos\theta)$ is related to $\alpha$ by

$$\bar{P}_2 = \langle \tfrac{1}{2}(3\cos^2\theta - 1)\rangle \approx 1 - \tfrac{3}{4}\langle\theta^2\rangle = 1 - \tfrac{3}{2}\alpha. \tag{3.26}$$

The gaussian approximation overestimates the nematic order (e.g. $\bar{P}_2 \approx 0{\cdot}95$ as opposed to the exact value of 0·79 at the nematic–isotropic coexistence) and this should be borne in mind when judging the spread of order induced by polydispersity.

It is necessary to minimize the free energy (3.25) with respect to the distribution function $f(L, \Omega)$ at constant $p(L)$. We make the Odijk gaussian ansatz

$$f(L,\Omega) = \frac{\alpha(L)}{4\pi}\exp - \tfrac{1}{2}\alpha(L)\theta^2. \tag{3.27}$$

The relevant part of the free energy (3.25) is now

$$\frac{\Delta A}{NkT} = \text{irrelevant terms} + \int p(L)\,[\ln \alpha(L) - 1] + \frac{4Dc'}{(2\pi)^{1/2}} \int p(L)p(L')LL' \left[\frac{1}{\alpha(L)} + \frac{1}{\alpha(L')}\right]^{1/2}. \tag{3.28}$$

We define $\alpha(x) = \alpha(L)$, with $x = L/L_0$ from equation (3.2). The equilibrium condition is

$$\frac{\partial \Delta A}{\partial \alpha(x)} = 0 \tag{3.29}$$

and after some algebra we obtain the self-consistent equation

$$\frac{\alpha^{1/2}}{x}(x) = 2(2/\pi)^{1/2} bc' \int x'\,p(x') \left[1 + \frac{\alpha(x)}{\alpha(x')}\right]^{-1/2}, \tag{3.30}$$

with $b = \pi/4\, L_0^2 D$, as in equation (3.9). An approximate solution of this equation can be found, in the limit of narrow distributions, by taking

$$\frac{\alpha^{1/2}}{x}(x) \approx 2(2/\pi)^{1/2} bc' \left\langle x' \left[1 + \frac{\alpha(x)}{\alpha(x')}\right]^{-1/2} \right\rangle, \tag{3.31}$$

$$\approx 2(2/\pi)^{1/2} bc' \langle x' \rangle \left[1 + \frac{\alpha(x)}{\langle \alpha(x') \rangle}\right]^{-1/2}, \tag{3.32}$$

$$\approx 2(2/\pi)^{1/2} bc' \left[1 + \frac{\alpha(x)}{\alpha(1)}\right]^{-1/2}. \tag{3.33}$$

In this limit, putting $c = bc'$ as in equation (3.10)

$$\alpha(1) = \frac{4c^2}{\pi} \tag{3.34}$$

in agreement with the monodisperse limit (3.18), and

$$\left[\frac{\alpha(x)}{\alpha(1)}\right]^2 + \left[\frac{\alpha(x)}{\alpha(1)}\right] - 2x^2 = 0. \tag{3.35}$$

Solving this equation we obtain

$$\alpha(x) \cong \frac{\alpha(1)}{2}\,[(8x^2 + 1)^{1/2} - 1]. \tag{3.36}$$

From this we obtain that $\alpha(x)$ and hence the order parameter, $\bar{P}_2(x)$, are, as we might reasonably expect, increasing functions of rod length. We also note that for $x = 0$, rods of zero length, there is no ordering, again consistent with intuition.

### 3.4. *The chemical potentials*

We rewrite the free energy (3.25) in a scaled form, following equation (3.12)

$$\frac{\Delta A}{NkT} = \frac{1}{kT}\int \mu_0(x)p(x)\,dx - 1 + \ln c' + \int p(x)\ln p(x)\,dx + \int p(x) f(x, \Omega) \ln 4\pi f(x, \Omega)\, d\Omega dx + c\,\langle xx'\varrho(x, x')\rangle_{x,x'}, \tag{3.37}$$

where

$$\varrho(x, x') = \frac{4}{\pi}\langle|\sin\gamma_{xx'}(\Omega, \Omega')|\rangle. \tag{3.38}$$

In the isotropic phase $\varrho(x, x') = 1\ \forall x, x'$. The *equation of state* in the isotropic phase is now

$$b\frac{\Pi}{kT} = c(1 + c), \tag{3.39}$$

as in the monodisperse case. Thus, in this approximation the equation of state by itself is not sufficient to betray polydispersity. We expect this result to carry over to the exact theory for low polydispersities, although clearly more study is required.

The chemical potential $\mu(x)$ for each species $x$ can be determined from equation (3.37)

$$\mu(x) = \left[\frac{\partial\Delta A}{\partial N(x)}\right]_{V,T} \tag{3.40}$$

$$= \frac{1}{N}\left[\frac{\partial\Delta A}{\partial p(x)}\right]_{V,T}, \tag{3.41}$$

yielding

$$\frac{\mu(x)}{kT} = \frac{\mu_0}{kT} + \ln c' + \ln p(x) + \Sigma(x) + 2cx\,\langle x'\varrho(x, x')\rangle_{x'}, \tag{3.42}$$

where $\Sigma(x)$ is the entropy term in equation (3.37), defined by analogy with $\Sigma$ in equation (3.12). We first discuss the isotropic phase for which $\varrho(x, x') = 1$ and thus

$$\frac{\Delta\mu(x)}{kT} = \frac{\mu(x) - \mu_0(x)}{kT} = \ln p(x) + 2cx + \ln c'. \tag{3.43}$$

Using the gaussian form for $p(x)$ prescribed in equation (3.3) we obtain

$$\frac{\Delta\mu(x)}{k_B T} = [\ln c' + 2c] - [\tfrac{1}{2}\ln 2\pi + \ln s] - \frac{y^2}{2s^2} + 2cy. \tag{3.44}$$

The quantity $\Delta\mu(x)$ plays the role of a potential on particles of species $x$. It takes the form

$$\frac{\Delta\mu(x)}{kT} \sim \frac{-(y - y_0)^2}{2s^2}, \tag{3.45}$$

with

$$y_0 = 2cs^2. \tag{3.46}$$

The first two terms in $\mu(x)$, which govern the absolute magnitude, are, however, the same as in the monodisperse case (3.14).

We pass now to a discussion of the nematic phase. Now we have, in the Odijk gaussian approximation,

$$\Sigma\,(x) = \ln\alpha(x) - 1, \tag{3.47}$$

$$\varrho(x, x') = \frac{2}{\pi^{1/2}}\left(\frac{1}{\alpha(x)} + \frac{1}{\alpha(x')}\right)^{1/2}. \tag{3.48}$$

Then

$$\langle x'\varrho(x, x')\rangle_{x'} \approx \frac{2}{\pi^{1/2}}\left(\frac{1}{\alpha(x)} + \frac{1}{\alpha(1)}\right)^{1/2}, \tag{3.49}$$

$$= \frac{2}{[\pi\alpha(1)]^{1/2}}\left[1 + \left(\frac{\alpha(1)}{\alpha(x)}\right)\right]^{1/2}. \tag{3.50}$$

We now use equation (3.36) to obtain

$$\langle x'\varrho(x, x')\rangle_{x'} = \frac{4}{[\pi\alpha(1)]^{1/2}} \times \left[\frac{1}{2} + \frac{2}{(8x^2 + 1)^{1/2} - 1}\right]^{1/2}. \tag{3.51}$$

We bear in mind the result (3.34), that $\alpha(1)^2 = (4c^2)/\pi$. Then combining equations (3.42), (3.47) and (3.50) we obtain

$$\frac{\Delta\mu(x)}{kT} = \ln c' + \ln\alpha(1) - 1 + \ln\frac{\alpha(x)}{\alpha(1)} + 4x\left[\frac{1}{2} + \frac{1}{2}\frac{\alpha(1)}{\alpha(x)}\right]^{1/2}$$
$$+ \ln p(x). \tag{3.52}$$

It is now convenient to expand $\Delta\mu(x)$ in powers of $y = x - 1$, using equation (3.36) for $\alpha(x)$

$$\frac{\alpha(x)}{\alpha(1)} = \tfrac{1}{2}[(8x^2 - 1)^{1/2} - 1] \cong 1 + \frac{4}{3y} + \frac{2}{27}y^2 + \dots. \tag{3.53}$$

Hence

$$\ln\frac{\alpha(x)}{\alpha(1)} = \frac{4y}{3} - \frac{22}{27}y^2. \tag{3.54}$$

Using the form (3.3) for $p(x)$, and equation (3.34) for $\alpha(1)$,

$$\frac{\Delta\mu(x)}{kT} = \ln c' + \left[2\ln c + 3 + \ln\frac{4}{\pi}\right] - [\tfrac{1}{2}\ln 2\pi + \ln s] - \frac{y^2}{2s^2}$$
$$+ \left(\frac{4y}{3} - \frac{22}{27}y^2\right) + (\tfrac{8}{3}y + \tfrac{4}{27}y^2) + \dots, \tag{3.55}$$

$$= 3\ln c + \left[3 + \ln\frac{4}{\pi}\right] - (\tfrac{1}{2}\ln 2\pi + \ln s) - y^2/2s^2 + (4y - \tfrac{2}{3}y^2) - \ln b. \tag{3.56}$$

Close to $y = 0$ we now have

$$\frac{\Delta\mu(x)}{kT} \sim \frac{-(y - y_0')^2}{2s'^2}, \tag{3.57}$$

where

$$y_0' = 4s'^2 \tag{3.58}$$

and

$$\frac{1}{2s^2} + \frac{2}{3} = \frac{1}{2s'^2}. \tag{3.59}$$

### 3.5. *Phase equilibrium*

We can use the results for $\Delta\mu(x)$ to discuss isotropic–nematic phase coexistence, for at phase coexistence $\Delta\mu(x)$ is the same in each phase. In the same way as in our discussion in §2 we shall be interested in how the probability $p(x)$ differs between two coexisting phases, and how the isotropic–nematic phase transition is broadened (in this case as a function of osmotic pressure) when polydispersity is introduced. The general scenario is as follows. For a given $p(x)$ of gaussian form (3.3) there will be an osmotic pressure $\Pi^{(1)}_{\text{coex}}$ at which the isotropic phase coexists with the nematic phase with a probability distribution $p_{\text{N}}(x)$. As the osmotic pressure is further increased the distributions in the coexisting isotropic and nematic phase arrange themselves in such a way that the average probability is $p(x)$. At some higher osmotic pressure $\Pi^{(2)}_{\text{coex}}$ the nematic phase takes the probability distribution $p(x)$: for all higher osmotic pressures there is only a single nematic phase. Our purpose now is to calculate $\Pi^{(1)}_{\text{coex}}$ and $\Pi^{(2)}_{\text{coex}}$, and in particular the spread $\Pi^{(2)}_{\text{coex}} - \Pi^{(1)}_{\text{coex}} = \Delta\Pi$ which highlights the effect of the polydispersity on the phase diagram.

We concentrate first on $\Pi^{(1)}_{\text{coex}}$. In general $p_{\text{N}}(x)$ and $p_{\text{I}}(x)$ at coexistence are connected through equation (3.42) and (3.52); at $\Pi^{(1)}_{\text{coex}}$ $p_{\text{I}}(x) = p(x)$. Rather than calculate the full form for $p_{\text{N}}(x)$ we parametrise it to be of the form

$$p_{\text{N}}(x) = \frac{1}{(2\pi s_{\text{N}}^2)^{1/2}} \exp - \frac{(y - y_{\text{N}})^2}{2s_{\text{N}}^2}, \qquad (3.60)$$

which has mean length $L_n = L_0(1 + y_{\text{N}})$ and variance $\sigma_{\text{N}}^2 = L_0^2 s_{\text{N}}^2$. Coexistence now occurs between the isotropic and nematic phases with scaled densities $c_{\text{I}}$ and $c_{\text{N}}$, and using equations (3.44) and (3.56) we obtain

$$\begin{aligned} &\ln c_{\text{I}} + 2c_{\text{I}} - \frac{y^2}{2s^2} + 2c_{\text{I}}y + \ln s \\ &= 3\ln c_{\text{N}} + \left(3 + \ln\frac{4}{\pi}\right) + \ln s_{\text{N}} - \frac{(y - y_{\text{N}})^2}{2s_{\text{N}}^2} + [4(y - y_{\text{N}}) - \tfrac{4}{3}(y - y_{\text{N}})^2]. \end{aligned} \qquad (3.61)$$

We now compare terms of orders 0, 1, 2 in $y$ in this equation; this yields

$$\frac{1}{2s^2} = \frac{1}{2s_{\text{N}}^2} + \frac{2}{3}, \qquad (3.62)$$

$$(2c_{\text{I}} - 4) = \frac{y_{\text{N}}}{s_{\text{N}}^2}, \qquad (3.63)$$

$$\ln c_{\text{I}} + 2c_{\text{I}} + \ln s = 3\ln c_{\text{N}} + \left(3 + \ln\frac{4}{\pi}\right) + \ln s_{\text{N}} - \frac{y_{\text{N}}^2}{2s_{\text{N}}^2} + 4y_{\text{N}} - \tfrac{4}{3}y_{\text{N}}^2. \qquad (3.64)$$

This must be solved in conjunction with the condition of equality of osmotic pressures, which from equation (3.39) and (3.40) is still identical with the monodisperse condition (3.20)

$$c_{\text{I}}(1 + c_{\text{I}}) = 3c_{\text{N}}. \qquad (3.65)$$

We solve equation (3.62) through (3.65) using perturbation theory around the coexistence conditions (3.20) and (3.21) for a monodisperse system. To lowest order in $s^2$, using the solutions of equations (3.20) and (3.21)

$$y_{\mathrm{N}} \approx 2\cdot 90 s^2, \tag{3.66}$$

$$s_{\mathrm{N}}^2 \approx s^2 (1 + \tfrac{4}{3} s^2). \tag{3.67}$$

The nematic phase, thus, has on average longer rods, and the distribution is also wider. Equation (3.64) is now

$$\ln c_{\mathrm{I}} + 2c_{\mathrm{I}} = 3 \ln c_{\mathrm{N}} + \left(3 + \ln \frac{4}{\pi}\right) + 10\cdot 81 s^2, \tag{3.68}$$

yielding

$$c_{\mathrm{I}} = 3.45(1 - 0\cdot 45 s^2), \tag{3.69a}$$

$$c_{\mathrm{N}} = 5\cdot 12(1 - 4\cdot 05 s^2) \tag{3.69b}$$

and hence

$$\Pi_{\mathrm{coex}}^{(1)} = \Pi_{\mathrm{coex}}^{\mathrm{mono}} (1 - 4\cdot 05 s^2). \tag{3.70}$$

To find $\Pi_{\mathrm{coex}}^{(2)}$ we need only use the results (3.66) through (3.70) bearing in mind that now the isotropic phase has

$$p_{\mathrm{I}}(x) = \frac{1}{(2\pi s_{\mathrm{I}}^2)^{1/2}} \exp\left(-\frac{(y - y_{\mathrm{I}})^2}{2 s_{\mathrm{I}}^2}\right), \tag{3.71}$$

but that the distributions $p_{\mathrm{I}}(x)$ and $p(x)$ are related in the same way as $p(x)$ and $p_{\mathrm{N}}(x)$. Thus we obtain

$$y_{\mathrm{I}} \approx -2\cdot 90 s^2, \tag{3.72}$$

$$s_{\mathrm{I}}^2 \approx s^2(1 - \tfrac{4}{3} s^2), \tag{3.73}$$

indicating, once again, a nematic phase with longer rods and a wider distribution.

The results (3.69) remain true, except that now the mean length of the rods in the isotropic phase is shorter. If we keep the same scaling as in the rest of the problem we must correct for this, obtaining for the coexistence concentrations $c_{\mathrm{I}}'$ and $c_{\mathrm{N}}'$

$$c_{\mathrm{I}}' = \frac{b}{b_{\mathrm{I}}} c_{\mathrm{I}}, \quad c_{\mathrm{N}}' = \frac{b}{b_{\mathrm{I}}} c_{\mathrm{N}}, \tag{3.74}$$

where

$$b_{\mathrm{I}} = \frac{\pi}{4} \langle L \rangle^2 D \tag{3.75}$$

and

$$\langle L \rangle = L_0 (1 - 2\cdot 90 s^2) \tag{3.76}$$

is the mean length in the isotropic phase. Thus we obtain

$$c_{\mathrm{I}}' \approx 3\cdot 45(1 - 0\cdot 45 s^2)(1 + 5\cdot 80 s^2), \tag{3.77a}$$

$$c_{\mathrm{N}}' \approx 5\cdot 12(1 - 4\cdot 05 s^2)(1 + 5\cdot 80 s^2) \tag{3.77b}$$

and hence

$$\Pi_{\mathrm{coex}}^{(2)} = \Pi_{\mathrm{coex}}^{\mathrm{mono}} (1 - 4\cdot 05 s^2)(1 + 5\cdot 80 s^2). \tag{3.78}$$

Finally comparing equations (3.70) and (3.78) we obtain the width of the coexistence region as a function of the polydispersity

$$\frac{\Delta\Pi}{\Pi_{\text{coex}}} = \frac{\Pi^{(2)}_{\text{coex}} - \Pi^{(1)}_{\text{coex}}}{\Pi_{\text{coex}}} \approx 5{\cdot}80\, s^2 + O(s^4). \tag{3.79}$$

## 4. Smectic order in hard rod systems

There has been much debate over the years as to the crucial physical mechanism governing smecticity. Systems with orientational fluctuations supressed might be expected to exhibit the minimal conditions for smectic phase formation. However, a simple scaling argument is sufficient to show that aligned hard ellipsoids cannot form a smectic A phase. Stroobants *et al.* have performed simulations in which aligned spherocylinders form a smectic phase [8]. In this section we discuss smectic A formation in a polydisperse mixture of aligned cylinders with the same diameter but varying lengths.

The work of Stroobants *et al.* [8] has inspired numerous theoretical studies [13–16] all of which are able, with greater or lesser accuracy, to predict the density at which the nematic phase becomes unstable with respect to smectic fluctuations. The best treatment is due to Mulder [13] and we begin our exposition below with a summary of his theory. In this theory the smectic A–nematic transition is second order. The crucial effect of the polydispersity is to reduce the susceptibility $\chi_{\text{Max}}(k)$ to smectic fluctuations at the smectic wavenumber $k$, while at the same time widening the peak of $\chi(k)$. This postpones the smectic transition to higher densities. For sufficiently high polydispersity in this system we might expect the smectic A phase to disappear entirely, leaving a high density columnar phase. The columnar phase is essentially a two dimensional crystallization in the plane perpendicular to the rods. A number of authors [17, 18] have observed that crystallization is postponed in polydisperse hard sphere systems, and the phenomenon we describe is, of course, directly analogous to this. In that case the high density phase is a glass. We might expect that if orientational fluctuations were reintroduced into this model the true high density phase would be a kind of smectic glass.

Our task in this section is to describe what happens to the phase transition as a function of polydispersity. We choose a particle distribution function exactly as in the last section: particles with diameter $D$ and length $L = L_0 x = L_0(1 + y)$ with $p(L)$, $p(y)$ given as in equation (3.1) and (3.3).

### 4.1. *The monodisperse system*

A liquid is unstable with respect to fluctuations with wave-number $k$ when the structure factor $S(\mathbf{k}) = [1 - \varrho c(\mathbf{k})]^{-1}$ diverges, where $\varrho$ is the liquid density and $c(\mathbf{k})$ is the direct correlation function. In hard particle fluids a good approximation for the direct correlation function $c(\mathbf{r})$ is [19, 20]

$$\begin{aligned} c(\mathbf{r}_{12}) &= -\frac{1}{(1-\eta)}, && \text{if particles 1, 2 overlap,} \\ &= 0, && \text{otherwise,} \end{aligned} \tag{4.1}$$

where $\eta$ is the packing fraction, the volume occupied by fluid particles. In this case the particles are cylinders aligned in the $z$ direction. Thus

$$\eta = \frac{\pi D^2 L}{4}\varrho \tag{4.2}$$

and

$$\begin{aligned} c(\mathbf{r}) = c(x, y, z) &= -\frac{1}{(1-\eta)} \quad \text{if } |z| \leqslant L,\, x^2 + y^2 \leqslant D^2, \\ &= 0 \text{ otherwise.} \end{aligned} \tag{4.3}$$

We seek an instability with wavenumber $\mathbf{k} = k\hat{\mathbf{z}}$ then

$$c(0, 0, k) = -\frac{\pi D^2}{(1-\eta)}\int_{-L}^{L} \exp(ikz)\, dz, \tag{4.4}$$

$$= -\frac{2\pi D^2}{(1-\eta)k}\sin kL. \tag{4.5}$$

Hence

$$\varrho c(\mathbf{k}) = -\frac{8\eta}{1-\eta}\frac{\sin kL}{kL}. \tag{4.6}$$

The susceptibility $S(\mathbf{k})$ has a maximum for the same value of $\mathbf{k}$ as $\varrho c(\mathbf{k})$: this occurs when

$$\frac{k_0 L}{2\pi} = 0{\cdot}715 \tag{4.7}$$

and

$$\frac{\sin k_0 L}{k_0 L} = -0{\cdot}217. \tag{4.8}$$

The instability to a smectic A phase thus occurs when

$$\varrho c(\mathbf{k}_0) = -\frac{8\eta}{1-\eta}\frac{\sin k_0 L}{k_0 L} = 1 \tag{4.9}$$

or when

$$\frac{\eta}{\eta_{\text{cp}}} = \eta_{\text{c}}^* = 0{\cdot}402, \tag{4.10}$$

where $\eta_{\text{cp}} = 0{\cdot}906$ is the packing fraction at close packing. The wavelength of the smectic wave

$$\frac{\lambda}{L} = \frac{2\pi}{k_0 L} = 1{\cdot}398. \tag{4.11}$$

We compare equations (4.10), (4.11) with the simulation results of Stroobants *et al.* [8], for which

$$\eta_{\text{c}}^* \approx 0{\cdot}39, \quad \lambda/L = 1{\cdot}28. \tag{4.12}$$

### 4.2. *The polydisperse system: formal theory*

We discuss the stability of a uniform equilibrium

$$\varrho(\mathbf{r}; x) = \varrho(x) = \varrho p(x) \tag{4.13}$$

where $x$ is the index of polydispersity. We consider small fluctuations in the density

$$\delta\varrho(\mathbf{r}, x) = \sum_k \delta\varrho(\mathbf{k}, x) \exp(i\mathbf{k}.\mathbf{r}). \tag{4.14}$$

The correct thermodynamic potential is the grand thermodynamic potential $\Omega$ [9]; then close to uniform equilibrium

$$\Omega[\varrho + \delta\varrho] = \Omega[\varrho] + \delta\Omega, \tag{4.15}$$

where

$$\delta\Omega = \frac{1}{2}\int \delta\varrho(\mathbf{r}, x)\, \delta\varrho(\mathbf{r}', x')\left[\frac{\delta(x - x')\delta(\mathbf{r} - \mathbf{r}')}{\varrho(x)} - c(\mathbf{r}, \mathbf{r}'; x, x')\right] d\mathbf{r}d\mathbf{r}'\, dxdx' \tag{4.16}$$

which is more conveniently expressed in reciprocal space:

$$\delta\Omega = \frac{1}{2}\sum_{\mathbf{k},\mathbf{k}'}\int \delta\varrho(\mathbf{k}, x)\delta\varrho^*(\mathbf{k}, x')\left[\frac{\delta(x - x')}{\varrho(x)} - c(\mathbf{k}; x, x')\right] dxdx'. \tag{4.17}$$

This expression is not in normal form—it contains terms non-diagonal in $x$, $x'$. It can be converted into an expression in normal form by solving the eigenvalue equation

$$\int\left[\frac{\delta(x - x')}{\varrho(x)} - c(\mathbf{k}, x, x')\right] f(x')dx' = \varepsilon f(x). \tag{4.18}$$

When the lowest eigenvalue of this equation $\varepsilon_0 = 0$, the form (4.17) is no longer positive definite, and the uniform state (4.13) becomes unstable. An estimate of $\varepsilon_0$ can be made using the trial function $f(x) = p(x)$. This gives an upper bound for $\varepsilon_0$, yielding

$$\varepsilon_0 \approx \int p(x)p(x')\left[\frac{\delta(x - x')}{\varrho p(x)} - c(\mathbf{k}, x, x')\right] dxdx' \tag{4.19}$$

$$= \frac{1}{\varrho} - \int p(x)p(x')c(\mathbf{k}; x, x'). \tag{4.20}$$

Defining $\bar{c}(\mathbf{k}) = \int p(x)p(x')c(\mathbf{k}; x, x')\, dxdx'$, we obtain as a criterion for instability to the smectic phase therefore the condition

$$\varrho\bar{c}(\mathbf{k}) = 1, \tag{4.21}$$

where it is assumed that $\mathbf{k}$ is evaluated at the maximum of $\varrho\bar{c}(k)$.

The condition (4.21) is in fact a *bound* on the stability of the uniform nematic phase. The assumption is that the non-uniform state has the same probability distribution as the uniform state. We note finally that condition (4.21) was used by McRae and Haymet [17] in their discussion of crystallization in polydisperse systems, although without the justification given here.

### 4.3. *The polydisperse system: calculations*

From equations (4.6) and (4.21) the condition for instability of the uniform nematic phase is

$$\frac{8\eta F}{1-\eta}(kL_0) + 1 = 0, \tag{4.22}$$

where

$$F(kL_0) = \int p(x)p(x')\frac{\sin\,[kL_0\,(x+x')/2]}{kL_0}\,dx\,dx' \tag{4.23}$$

is evaluated at its first minimum. In the case that $p(x)$ takes the gaussian form (see equations (3.3)) $[y = x - 1]$

$$p(x) = \frac{1}{(2\pi s^2)^{1/2}}\left(\exp - \frac{y^2}{2s^2}\right),$$

$F(kL_0)$ can be evaluated analytically, although we point out that for very large $s$ $p(0) \neq 0$ in the gaussian form, and this may affect the usefulness of the calculation. We first evaluate equation (4.23). We define

$$v = \frac{1}{\sqrt{2}}(y + y')$$

and (4.24)

$$w = \frac{1}{\sqrt{2}}(y - y').$$

Then

$$y^2 + y'^2 = v^2 + w^2 \tag{4.25}$$

and

$$F(kL_0) = \frac{1}{(2\pi s^2)^{1/2}}\int_{-\infty}^{\infty}\exp\left(-\frac{v^2}{2s^2}\right)\frac{\sin\left[kL_0\left(1+\frac{1}{\sqrt{2}}v\right)\right]}{kL_0}\,dv, \tag{4.26}$$

$$= \frac{1}{(2\pi s^2)^{1/2}}\int_{-\infty}^{\infty}\exp\left(-\frac{v^2}{2s^2}\right)\frac{\sin kL_0}{kL_0}\cos\left(\frac{kL_0 v}{\sqrt{2}}\right)dv, \tag{4.27}$$

$$= \frac{1}{(2\pi s^2)^{1/2}}\int_{-\infty}^{\infty}\exp\left[-\frac{v^2}{2s^2} + \frac{ikL_0 v}{\sqrt{2}}\right]\frac{\sin kL_0}{kL_0}\,dv, \tag{4.28}$$

$$= \left[\frac{\sin kL_0}{kL_0}\right]\int_{-\infty}^{\infty}\frac{1}{(2\pi s^2)^{1/2}}\exp\left[-\frac{1}{2s^2}\left(v - \frac{ik_0 Ls^2}{\sqrt{2}}\right)^2\right] \times \exp\left[-\frac{k_0^2 L_0^2 s^2}{4}\right]dv, \tag{4.29}$$

$$= \frac{\sin kL_0}{kL_0}\exp - \left[\frac{k_0 L_0 s}{2}\right]^2. \tag{4.30}$$

We first discuss the wavelength at which instability occurs,

$$F'(kL_0) = \frac{\cos kL_0}{kL_0} - \frac{\sin kL_0}{(kL_0)^2}\left[1 + \frac{(kL_0 s)^2}{2}\right] \tag{4.31}$$

and the condition

$$F'(kL_0) = 0 \tag{4.32}$$

yields

$$\frac{\tan kL_0}{kL_0} = \left\{1 + \frac{(kL_0 s)^2}{2}\right\}^{-1}. \tag{4.33}$$

The $s = 0$ solution of this equation is given in equation (4.7); we seek a perturbative solution close to $k_0 L = 4{\cdot}493$, yielding

$$k(s) = k_0 + \delta k$$

and

$$\delta k L_0 = -2{\cdot}25 s^2. \tag{4.34}$$

This indicates a *reduction* in the critical wavenumber, or an *increase* in the wavelength over what might be expected by taking the mean length of rods in the polydisperse system. There is, however, a limit in the increase in $\lambda$; even for very large $s$ $\lambda/L < 2$, from the form of equation (4.30).

The exponential term in equation (4.30) clearly reduces the absolute magnitude of $F(kL_0)$ dramatically, and hence from equation (4.22), *postpones* the onset of smecticity to higher densities. An estimate of this reduction can be obtained by substituting in equation (4.30) the solution (4.8) yielding for the critical density

$$\frac{\eta_c(s)}{\eta_c(0)} \approx \exp(10 s^2). \tag{4.35}$$

Now a maximum value for $\eta_c(s)$ is the close-packing density for a two dimensional fluid $\eta \approx 0{\cdot}906$; this gives a maximum value for $s$ of about 0·30 to destroy all smecticity. In practice this is likely to be a gross overestimate. Nevertheless the effect does not seem to be as great as that predicted for crystallization [17].

## 5. Final remarks

In this paper we have taken three of the simplest models of liquid crystal behaviour, and generalized them to polydisperse mixtures. On the whole we have confined our interest to weak polydispersity, in such a way that the effects of turning on polydispersity could be exhibited analytically. The models are, of course, soluble in the strong polydisperse limit too, but only at the expense of a great deal of numerical work which might not increase understanding of the physical processes involved.

The Maier–Saupe system which we discuss in §1 might be regarded as a model for thermotropic liquid crystal formation in a solution of colloidal ellipsoids. The Onsager system discussed in §2 is perhaps appropriate to viral mixtures—we recall that the Onsager picture has been fruitfully used to discuss nematic formation in tobacco mosaic virus solutions. Both these nematic systems develop a region of two phase coexistence at nematic onset in polydisperse systems, a consequence of the Gibbs phase rule. In retrospect it is not surprising that this two phase region has a width proportional to the variance of the polydispersity distribution function and we could perhaps for some purposes model polydisperse systems as effective two component mixtures, at any rate in the weak polydispersity limit. The smectic system shows a dramatic postponement of smectic onset with polydispersity, again a conclusion which is consistent with intuition. Polydisperse rods do not fit into layers as easily as do rods of the same length.

Are models of polydispersity appropriate to discussing liquid crystal formation in small molecules? Many liquid crystal forming substances are made from molecules which have a rigid backbone with some alkyl end chains. Such molecules are traditionally thought of as being in some sense on average cylindrical. It might be possible to take into account the real shapes as being polydisperse departures from cylindrical symmetry. In this case, of course, the calculations would have to be performed with an order parameter that takes into account the biaxiality, and not just with the usual $\bar{P}_2$, as is done in this paper. However, such polydispersity is *variable*—it is coupled with the interparticle statistical mechanics. Another example of variable polydispersity arises in a system of rod-like micelles [10]. The statistical mechanics of variable polydispersity is closely related to that of the *fixed* polydispersity considered here. There are crucial differences, however, in particular in the variable polydisperse case there is not necessarily a two phase coexistence region at a phase transition. We return to this problem elsewhere [21]. Finally we note that the most common form of polydispersity in familiar systems lies perhaps in polymeric systems, the polydispersity index being either the molecular weight or the chain flexibility. This kind of problem can be treated using the framework developed in this paper, and is currently under investigation.

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