Polydispersity and Ordered Phases in Solutions of Rodlike Macromolecules

Anne M. Bohle,[1] Robert Hołyst,[2] and Thomas Vilgis[1]

[1]*Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany*
[2]*Institute of Physical Chemistry PAS and College of Science, Department III, Kasprzaka 44/52, 01224 Warsaw, Poland*

We apply density functional theory to study the influence of polydispersity on the stability of columnar, smectic, and solid ordering in the solutions of rodlike macromolecules. For sufficiently large length polydispersity (standard deviation $\sigma > 0.25$) a direct first-order nematic-columnar transition is found, while for smaller σ there is a continuous nematic-smectic and first-order smectic-columnar transition. The length distribution of macromolecules changes neither at the nematic-smectic nor at the nematic-columnar transition. In the binary mixtures the nematic-smectic transition is also continuous. Demixing in the smectic phase is preempted by transitions to solid or columnar phases.

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It has been known for some time that concentrated solutions of DNA [1], polypeptides [2,3], polysaccharides [3], and hairy rod polymers [4] form columnar phases. It also has been observed that DNA in bacteriophages and sperm nuclei of sepia, trout, and salmon exhibit columnar ordering [1]. The activity of DNA (renaturation, transcription, or replication) can be enhanced in the condensed phase [5]. Also the condensed form of DNA can be used by nature to store genetic material in small volume and use it at the moment of cell cycle. Despite the accumulating body of experimental data, very little is known about the influence of various factors, such as attractive forces or polydispersity, on the stability of columnar ordering in macromolecular solutions. It is known that columnar ordering is preempted by smectic ordering in hard monodisperse rod systems [6], but can be stabilized in binary mixtures of rods of different length [7]. However, since in actual solutions the systems are characterized by the continuous distribution of molecular length, true monodisperse or bidisperse systems are rare. Here we fill this apparent gap and study, within density functional theory [8,9], the influence of polydispersity on columnar ordering.

A polydisperse system with continuous distribution of molecular masses (or length as is the case here) can be regarded as a mixture of infinitely many components. Thus, phase equilibria between two phases requires the equality of chemical potentials for molecules of all lengths, making the total number of equilibrium conditions infinite. Previous studies of polydisperse systems have employed bifurcation analysis [10] or expansion in the distribution function width [11] (valid for sharp distributions only), but, to date, no general approach is known. Here we establish the equilibrium conditions by a novel technique that does not involve expansion or assumption of the sharpness of the molecular length distribution.

We pose the following questions: What is the minimal degree of polydispersity necessary to stabilize the columnar phase? At what polydispersity is the smectic phase destabilized? Does polydispersity change the continuous nature of the nematic-smectic phase transition [12]? Are there any smectic phases in which rods of different lengths are demixed (completely demixed, or ordered in layers with varying widths)?

We consider a polydisperse system of hard, parallel cylinders of diameter D interacting via the hard core repulsion potential. The free energy of the system as a functional of the number density $\rho_0(\mathbf{r}, L)$, for a given length Ll (L is dimensionless), is given by the following formula (the free energy is in $k_B T$ units):

$$F[\rho] = \int dL \int d\mathbf{r}\, \rho_0(\mathbf{r}, L) \ln[\lambda^3 \rho_0(\mathbf{r}, L)] - 1$$
$$+ \int dL \int d\mathbf{r}\, \rho_0(\mathbf{r}, L) \Psi(v_0 \bar{\rho}_0(\mathbf{r}, L)), \quad (1)$$

The first term in Eq. (1) is exact and represents the configurational entropy of the polydisperse system. The second term is the excess free energy determined by the interparticle interactions. Here Ψ is the excess free energy density of the homogeneous system and $\bar{\rho}_0(\mathbf{r}, L)$ is the weighted density, defined by

$$\bar{\rho}_0(\mathbf{r}, L) = \int dL' \int d\mathbf{r}'\, w(\mathbf{r} - \mathbf{r}', L + L')\rho_0(\mathbf{r}', L'),$$
$$(2)$$

where the weight function $w(\mathbf{r} - \mathbf{r}', L + L')$ is normalized according to

$$\int d\mathbf{r}\, w(\mathbf{r} - \mathbf{r}', L + L') = 1. \quad (3)$$

The weighted density [Eq. (2)] represents the influence of the total density of particles on the density of rods of length L at point $\mathbf{r}$. The normalized length distribution of the cylinders is given by $g(L) = N^{-1} \int d\mathbf{r}\, \rho_0(\mathbf{r}, L)$, where N is the number of particles in the system.

Now we make the following approximations. First, for the weight function we choose the normalized Mayer function, i.e.,

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$$w(\mathbf{r} - \mathbf{r}', L + L') = \frac{\Theta((L + L')l/2 - |z - z'|)}{(L + L')l} \frac{\Theta(D - |\mathbf{r}_\perp - \mathbf{r}'_\perp|)}{\pi D^2}$$

$$= f_1(L + L', |z - z'|)f_2(D, |\mathbf{r}_\perp - \mathbf{r}'_\perp|), \tag{4}$$

where Θ is the Heaviside step function. This weight function implies that the free energy of a system with columnar ordering does not depend on the degree of polydispersity. Second, we employ a decoupling approximation, i.e., $\rho_0(\mathbf{r}, L) = \rho(\mathbf{r})g(L)$. The density distribution $\rho(\mathbf{r})$ is approximated by a Gaussian function centered at the sites of the Bravais lattice characteristic for the given phase [8,13–17]. We assume that $g(L)$ is given by the Gaussian distribution, characterized by the mean value L_0 and the standard deviation σ. It turns out that the mean length L_0 scales out. Finally, the excess free energy density for the homogeneous system is approximated by the Carnaham-Starling equation as in Ref. [6], i.e., $\Psi(\eta) = \eta(4 - 3\eta)/(1 - \eta)^2$, where $\eta = \rho v_0$, ρ is the average number density, and $v_0 = (1/4)\pi D^2 l L_0$ is the mean volume of the cylinders.

The phase diagram obtained from the above outline is shown in Fig. 1. It encompasses the nematic, smectic,

columnar, and solid phases. For $\sigma \gtrsim 0.25$ there is a direct first-order phase transition to the columnar phase. The chemical potential as a function of L for the nematic and columnar phases can be written in the form

$$\mu(L) = \ln[g(L)] + \mu_0, \tag{5}$$

It is central to our approach that for at least one of the phases in equilibrium $g(L)$ may be calculated as a function of $\mu(L)$, as is the case for Eq. (5). In the nematic phase μ_0 is given by

$$\mu_0^{\mathrm{nem}} = \ln(\lambda^3 \rho^{\mathrm{nem}}) + \Psi(v_0 \rho^{\mathrm{nem}})$$

$$+ v_0 \rho^{\mathrm{nem}} \Psi'(v_0 \rho^{\mathrm{nem}}) \tag{6}$$

and in the columnar phase by

$$\mu_0^{\mathrm{col}} = \frac{\int d\mathbf{r}_\perp \, \rho^{\mathrm{col}}(\mathbf{r}_\perp) \ln[\lambda^3 \rho^{\mathrm{col}}(\mathbf{r}_\perp)]}{\int d\mathbf{r}_\perp \rho^{\mathrm{col}}(\mathbf{r}_\perp)}$$

$$+ \frac{\int d\mathbf{r}_\perp [\rho^{\mathrm{col}}(\mathbf{r}_\perp)\Psi(v_0 \rho^{-\mathrm{col}}(\mathbf{r}_\perp)) + v_0 \rho^{\mathrm{col}}(\mathbf{r}_\perp)\rho^{-\mathrm{col}}(\mathbf{r}_\perp)\Psi'(v_0 \rho^{-\mathrm{col}}(\mathbf{r}_\perp))]}{\int d\mathbf{r}_\perp \, \rho^{\mathrm{col}}(\mathbf{r}_\perp)}. \tag{7}$$

The equilibrium density distribution in the columnar phase $\rho^{\mathrm{col}}(\mathbf{r}_\perp)$ is a sum of Gaussian functions centered at the sites of a hexagonal lattice. The lattice constant and the width of the Gaussian peaks are obtained from minimization of the functional [Eq. (1)] with respect to these variables. It can be seen directly that the distribution function does not change at the nematic-columnar coexistence. The densities at coexistence, normalized by the density at close packing ($\eta_{\mathrm{cp}} = \pi/2\sqrt{3} \sim 0.907$), are determined as follows: $\eta^{\mathrm{nem}}/\eta_{\mathrm{cp}} = 0.36$ and $\eta^{\mathrm{col}}/\eta_{\mathrm{cp}} = 0.43$, independent of the polydispersity of the system.

For standard deviations $\sigma < 0.25$ we find a continuous transition from the nematic to the smectic phase. The length distribution does not change the continuous nature

of the transition. This result is in agreement with computer simulations by Stroobants [7], who found a continuous nematic-smectic transition for a binary mixture of long and short spherocylinders. This result is not at all obvious. In principle one might expect that the nematic-smectic transition could be accompanied by the separation of rods, similar to the isotropic-nematic transition. In the latter case the longer rods are more abundant in the nematic than in the isotropic phase [10,11,18,19]. By analogy, we could expect the length distribution to narrow at the nematic-smectic transition and consequently to change the continuous nature of the transition. The transition has been studied as follows. First we have calculated the chemical potential of the smectic phase. It reads

$$\mu^{\mathrm{sm}}(L) = \ln[g^{\mathrm{sm}}(L)] + \frac{\int dz \, \rho^{\mathrm{sm}}(z) \ln[\lambda^3 \rho^{\mathrm{sm}}(z)]}{\int dz \, \rho^{\mathrm{sm}}(z)} + \frac{\int dz \, \rho^{\mathrm{sm}}(z)\Psi(v_0 \rho^{-\mathrm{sm}}(z, L))}{\int dz \, \rho^{\mathrm{sm}}(z)}$$

$$+ \frac{\int dz \int dz' \int dL' f_1(L + L', |z - z'|)\rho^{\mathrm{sm}}(z')v_0 \rho^{\mathrm{sm}}(z)g^{\mathrm{sm}}(L')\Psi'(v_0 \rho^{-\mathrm{sm}}(z', L'))}{\int dz \, \rho^{\mathrm{sm}}(z)}, \tag{8}$$

where f_1 is defined in Eq. (4). Then we have equated nematic and smectic chemical potentials:

$$\mu^{\mathrm{nem}}(L) = \mu^{\mathrm{sm}}(L). \tag{9}$$

It follows immediately that for the known distribution function $g^{\mathrm{sm}}(L)$ the distribution function $g^{\mathrm{nem}}(L)$ is trivially determined at coexistence by Eq. (5), i.e.,

$$g^{\mathrm{nem}}(L) = \exp[\mu^{\mathrm{sm}}(L) - \mu_0^{\mathrm{nem}}]. \tag{10}$$

The second equilibrium condition, i.e., the equality of pressure, combined with the normalization condition $\int dL \, g^{\mathrm{nem}}(L) = 1$ determines the coexisting densities. We have found further that for all degrees of polydispersity σ the nematic-smectic phase transition is continuous.
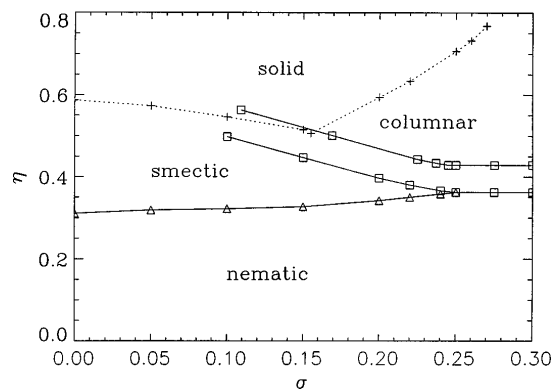
FIG. 1. Phase diagram for a polydisperse system of parallel rods interacting via hard core repulsive forces. The polydispersity of the rod lengths is modeled by a Gaussian distribution of standard deviation σ. Squares denote coexistence of phases, triangles a second-order phase transition, and crosses represent instabilities.

The same procedure has been applied to the columnar-smectic phase transition. In this case we have assumed a given length distribution function in the smectic phase and from the equality of chemical potentials [Eq. (5), (7),

and (8)] we could determine the distribution function in the columnar phase at coexistence with the smectic. This transition is first order, so the average volume fraction η jumps at the transition. The distribution function in the smectic is again assumed to be Gaussian. We characterize the distribution function in the columnar by its mean value and standard deviation in order to compare it to the distribution function in the smectic. It turns our that the change in the mean length is negligible. The standard deviation of the distributions is larger in the columnar than in the smectic This is the expected result, since the lamellar ordering in the smectic favors a sharp distribution whereas the columnar structure does not. For example, as seen in Fig. 1, a smectic phase with a polydispersity of $\sigma = 0.15$ at a packing fraction of $\eta/\eta_{cp} = 0.45$ is in equilibrium with a columnar structure of a polydispersity of $\sigma = 0.17$ at a packing fraction of $\eta/\eta_{cp} = 0.50$.

The dashed lines shown in Fig. 1 represent the instability of the smectic and columnar phases with respect to perturbations to a hexagonal solid. The phase characterized by the density distribution $\rho^i(\mathbf{r})$ is unstable with respect to the perturbation $\delta\rho^{(i,f)}(\mathbf{r})$ of the symmetry of the f phase if the following condition holds:

$$\int d\mathbf{r} \int d\mathbf{r}' \, \delta\rho^{(i,f)}(\mathbf{r})\delta\rho^{(i,f)}(\mathbf{r}') \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\bigg|_{\rho(\mathbf{r})=\rho^i(\mathbf{r})} = 0. \tag{11}$$

We have assumed that the perturbations can be expressed in the factorized form: $\delta\rho^{(i,f)}(\mathbf{r}) = \rho^i(\mathbf{r})\delta\rho^f(\mathbf{r})$, where $\delta\rho^f(\mathbf{r})$ describes the onset of the ordering specific for phase f and absent in phase i. For analysis of the columnar solid bifurcation we take $\delta\rho^f(\mathbf{r}) = \cos(kz)$ while for the smectic solid bifurcation we assume $\delta\rho^f(\mathbf{r}) = \sum_{n=1}^{3}\cos(\mathbf{k}_n\mathbf{r}_\perp)$, where $k_1 = (1, 1/\sqrt{3})k$, $k_2 = (-1, 1/\sqrt{3})k$, and $k_3 = (0, 2/\sqrt{3})k$ are the vectors spanning the first shell in the reciprocal space for the regular hexagonal lattice.

For large polydispersity the columnar phase is more stable than the solid phase. We expect this, since in the system of rods with continuous distribution of length, the particles do not fit well into the 3D structure involving ordering along the long axis of rods. This transition is expected to be first order, with the distribution function more strongly peaked in the solid. The smectic phase becomes slightly destabilized with respect to solid ordering if the polydispersity is increases. This can be understood as an indication that order in the z direction is least favored, so that even three-dimensional ordering is preferred.

The functional given by Eq. (1) for the general case of a polydisperse system reduces to the binary mixture case for

$$\rho(\mathbf{r}, L) = \rho_1(\mathbf{r})\delta_{L,L_1} + \rho_2(\mathbf{r})\delta_{L,L_2}, \tag{12}$$

where $\delta_{i,j}$ is the Kronecker delta function. Using this density distribution, we are able to calculate the free energy of the nematic, smectic, and columnar phases

as well as the instabilities to solid ordering as before. Figure 2 shows the results for different ratios of the lengths of the rods. The phase diagram is calculated at the equivalence point, where the partial volume fractions of the two components are the same. Although the results are not completely comparable to those of Stroobants [7], who studied spherocylinders rather than cylinders, qualitative agreement can still be seen easily. As in the study of Stroobants, we observe the destabilization of the smectic order compared to the nematic, and stabilization of the columnar order with an increasing length ratio of the two components.
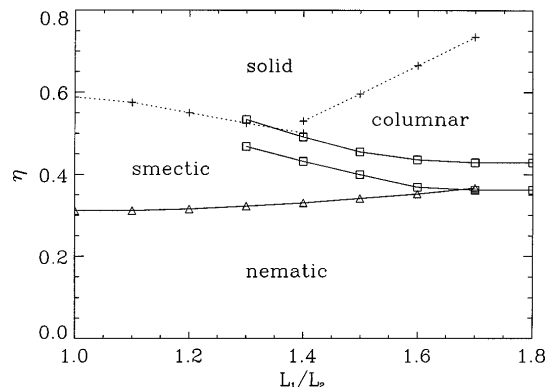

FIG. 2. Phase diagram for a two component system of length ratio L_1/L_2. Note the remarkable qualitative similarity to Fig. 1.

We now consider the possibility of demixing within the smectically ordered system. We look only for a separation of the complete system into one phase consisting mainly of long rods and another phase consisting mainly of short rods, since it can be shown that the free energy of such a system is comparable to that of smectics with alternating layers. In order to study the stability we check the partial derivatives $M_{ij} = \partial^2 F[\rho]/\partial\rho_i \partial\rho_j$, where ρ_i are the partial densities of the two components. It turns out that the matrix (M_{ij}) remains positive definite for all length ratios, compositions, and packing fraction, for which the smectic phase is stable. We also check for the possible coexistence between two smectic phases with widely varying composition, by equating the chemical potentials of both components as well as the pressure. Again we find no such coexistence in the smectic phase. This leads to the conclusion that demixed smectics or smectics with varying lamella widths are not found in binary systems under the present conditions.

A physical realization of our model is a dense polydisperse suspension of elongated colloidal particles stabilized against irreversible aggregation by surface-grafted polymer layers. In a good solvent the interactions between such colloidal particles can be approximated by hard core interactions [20,21].

In general, however, macromolecules in solutions interact via van der Waals forces, and, if they carry surface charges, also via screened Coulombic repulsion [20,22]. The influence of these complex interactions on the phase diagram is not known in general.

Different problems arise when the macromolecules are not rigid but semiflexible [23,24]. It should be noted as well that in self-assembling systems, when the length distribution is given by the thermodynamic conditions in a given phase [19,25], the equality of monomer chemical potential is sufficient to set the coexistence conditions between two phases.

Summarizing, by means of density-functional theory we have studied in detail the influence of polydispersity on phase equilibria in oriented rodlike macromolecular systems. For a Gaussian distribution of rods lengths we find three polydispersity regimes. For $0.15 > \sigma \geq 0$ we have the following sequence of phase transitions nematic-smectic-solid; for $0.25 > \sigma > 0.15$ we find the nematic-smectic-columnar and solid phases; for $0.27 > \sigma > 0.25$ we find direct nematic-columnar and columnar-solid transitions and for $\sigma > 0.27$ there are only nematic and columnar phases. We also find that polydispersity does not affect the continuous nature of the nematic-smectic phase transition. We do not find any evidence for demixed smectic phases. Our novel method for the study of polydispersity can be easily applied also to the isotropic-nematic phase transition [11].

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