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Theory of phase separation for a solution of tridisperse rod-like particles

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Abstract

Within the Onsager theory, we study solutions of polydisperse thin hard rods. An approximate method by Odijk is used numerically to determine the orientational distribution functions in the nematic phase in a straightforward way. Next, the coexistence relations are used in determining phase transitions. In coexisting nematic phases equality of osmotic pressure implies equal overall number density. A procedure is developed to locate equal chemical potentials between nematic phases of tridisperse systems. For length ratios larger than 3, we find phase diagrams showing nematic three-phase regions, critical points, critical end points and as a limit a tricritical point. The mechanism is not due to excluded-volume effects but to the interplay between orientational entropy and entropy of mixing. At higher concentrations the phase diagram is independent of concentration. Below a certain concentration, coexistence with an isotropic phase intervenes. © 1997 Elsevier Science B.V.

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1. Introduction

Barry Ninham has contributed significantly to many aspects of the theory and stimulated experiment of the interactions between colloidal particles. Twenty years ago Barry, together with Jacob Israelachvili, summarized the growth of intermolecular force theory over the 50-year period 1926–1976 in a pictorial essay entitled: 'The Great Colloid Schism' [1]. Barry and Jacob retrace the progress of intermolecular forces, both theory and experiment, from the days of Young and Maxwell, to Langmuir, through London, Debye, Derjaguin, Lifshitz, and on to 1976. They argue that after Langmuir, theories and concepts developed along three separate routes. This trichotomy centred around the different emphases placed on short-range forces, long-range forces, and statistical mechanics in various colloidal and biological phenomena. In discussing the lonesome road of statistical mechanics they summarized their point of view as follows [1]: "... a knowledge of the interaction free energy between two atoms or particles, taken in isolation, may tell us little of the properties of an ensemble of such particles. Thus the first moral to be learned from statistical mechanics is that the existence of a minimum in the two-particle interaction free energy in the associated or ordered state does not guarantee the formation of this state. Conversely, the existence of an associated or ordered state does not necessarily imply that the particles are sitting at a separation where there is a minimum in the two-particle interaction free energy".

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A striking example of this statement is provided by the isotropic-nematic phase transition in suspensions of rod-like colloidal particles, such as Tobacco Mosaic Virus [2]. Here Onsager [3] provided irrefutable proof that this transition can be explained on the basis of a hard-rod interaction, which of course does not show any minimum in the two-particle interaction free energy. The nematic phase arises due to the fact that although it has a lower orientational entropy than the isotropic phase, the rods are packed more efficiently in the nematic phase, leading to an increase of 'available volume', the associated increasing entropy of which outweighs the loss of configurational entropy. We may therefore term this an entropy-driven phase transition which is due to a balance of two entropic terms. The phase transition between the isotropic and the anisotropic phase in dispersions of plate-like clay particles first observed by Langmuir [4] has the same origin [3,5,6].

Entropy-driven phase transitions do not only occur in dispersions of anisometric hard particles. Another system showing an entropy-driven phase transition between an isotropic and an ordered state is the hard-sphere system. This existence of this transition was first suggested by Kirkwood [7]. About two decades later the computer simulations of Alder and Wainwright provided the first firm evidence for this transition [8]. Hoover and Ree determined the coexisting densities [9]. Again the stability of the ordered phase is due to an "available volume entropy". The freezing transition has been observed experimentally in systems of (almost) hard colloidal particles by several workers [10,11].

An even richer phase behaviour is observed in mixtures of hard particles. Mixtures of hard spheres have received the most attention so far. Experiments using colloidal hard spheres with size ratios of 0.61 and 0.58 between the small and large particles have yielded the striking observation that in addition to crystals consisting of only one of the two components, the more complex crystal structures AB_2 and AB_{13} can be obtained (with A the larger type of sphere) [12,13]. Recent computer simulations have confirmed the thermodynamic stability of these crystalline phases [14,15]. Mixtures of rod-like particles with different lengths have also attracted considerable attention both theoretically [16–21] and experimentally [22–26]. Above a critical length ratio two nematic phases are predicted to form [16,19–21]. This has indeed been observed experimentally [22–26]. According to the analysis of Vroege and Lekkerkerker [20] the nematic–nematic phase transition does not involve changes in excluded volume but a balance between orientational entropy and entropy of mixing.

In this paper we show that solutions of tridisperse rod-like particles display an even richer phase behaviour including the possibility of a three-nematic-phase region bordered by three two-phase regions, which in turn could display critical points upon changing the length ratios of the rod-like particles involved. The three-phase region can collapse via a critical end point. Also, the possibility of a collapse of two critical points in the form of a tricritical point is possible for one specific combination of lengths.

2. Formalism

We start with a solution of thin hard rods all having the same diameter D but with different lengths L_j ($j=1,2,3\cdots$; for the sake of clarity we use increasing subscript numbers to denote increasingly longer rods). The volume of the system is V and the number of rods of type 'j' is denoted as N_j. Onsager [3] described the nematic phase of a dilute solution of long thin rods in terms of functions $f_j(\theta)$ which describe the distribution of angles θ of the rods of type j with the director. The occurrence of an isotropic state (with f_j constant) or a nematic state (with a peaked distribution) is caused by competition between orientational entropy and translational entropy. Onsager defined σ_j as a measure for the orientational entropy

$$\sigma_j \equiv \int f_j(\theta) \ln[4\pi f_j(\theta)] \, d\Omega \tag{1}$$

which acquires its minimum value of 0 in the isotropic state but increases as the orientational entropy decreases. $d\Omega$ indicates integration over all angles. The relevant part of the translational entropy derives from the two-particle interaction

in the form of the excluded volume between two thin hard rods (with length L_j and L_k) which depends on their mutual angle γ

$$v_{\text{excl}} \sim 2DL_jL_k|\sin\gamma| \tag{2}$$

A measure for the average excluded volume interaction between rods of type j and k is given by the average of its angular dependence

$$\rho_{jk} \equiv \frac{4}{\pi}\iint |\sin\gamma| f_j(\theta) f_k(\theta')\,\mathrm{d}\Omega\mathrm{d}\Omega' \tag{3}$$

which is 1 in the isotropic state and more favourable (between 0 and 1) in the nematic state. The total Helmholtz free energy F of a polydisperse system may be written in terms of these parameters as

$$\frac{F}{\sum_j N_j k_B T} \simeq \text{cst} + \ln c - 1 + \sum_j x_j \ln x_j + \sum_j x_j\sigma_j + c\sum_{j,k} q_j q_k x_j x_k \rho_{jk} \tag{4}$$

where k_B and T have their usual meaning of Boltzmann's constant and absolute temperature. In this equation $x_j \equiv N_j/\sum_i N_i$ is the mole fraction of rods of type j and c is the total number density of rods rendered dimensionless by relating it to the average excluded volume b between two of the shortest rods in the isotropic state

$$c \equiv b\frac{\sum_j N_j}{V} \equiv \frac{\pi}{4}L_1^2 D\frac{\sum_j N_j}{V}. \tag{5}$$

Since c is related to the excluded volume of two of the shortest rods, the excluded volume terms in Eq. (4) which involve longer rods are multiplied by $q_j\, q_k$, with

$$q_j \equiv L_j/L_1. \tag{6}$$

Once expression (4) for the free energy is known, we must minimize it with respect to the orientational distribution at given c and set of mole fractions $\{x_j\}$. One way of doing this is using a trial function with one or more variational parameters. A convenient choice for the angular distribution of rod j in the nematic state is the Gaussian trial function [27,18]

$$f_j(\theta) \equiv \frac{\alpha_j}{4\pi}\exp\left(-\frac{1}{2}\alpha_j\theta^2\right) \quad 0 \le \theta \le \pi/2$$
$$\equiv \frac{\alpha_j}{4\pi}\exp\left[-\frac{1}{2}\alpha_j(\pi-\theta)^2\right] \quad \pi/2 \le \theta \le \pi \tag{7}$$

which gives good qualitative results for the isotropic–nematic phase transition for monodisperse rods and is getting more accurate as the phase is more highly ordered. α_j is the variational parameter of this trial function. To determine its value we must know the expressions for σ_j and ρ_{jk} obtained by substituting Eq. (7) in Eqs. (1) and (3):

$$\sigma_j \sim \ln\alpha_j - 1 \tag{8}$$

$$\rho_{jk} \sim \frac{4(\alpha_j+\alpha_k)^{1/2}}{(2\pi)^{1/2}\alpha_j^{1/2}\alpha_k^{1/2}} \tag{9}$$

which are the first terms of asymptotic expansions valid for large α_js. Using these expressions in Eq. (4) and minimizing with respect to α_i we obtain an equation which can be reduced to the form [27]

$$\alpha_i = \frac{4c^2}{\pi}\left[q_i\sum_k x_k q_k\left(\frac{2}{1+\alpha_i/\alpha_k}\right)^{1/2}\right]^2. \tag{10}$$

Now it is convenient to introduce a matrix Q_{ij} containing the ratios of the variational parameters of the different rods:

$$Q_{ij} \equiv \alpha_i/\alpha_j \tag{11}$$

A matrix equation for Q_{ij} is obtained by dividing two equations of type (10) [27]:

$$Q_{ij} = \left[\frac{q_i\sum_k x_k q_k(1+Q_{ik})^{-1/2}}{q_j\sum_l x_l q_l(1+Q_{jl})^{-1/2}}\right]^2. \tag{12}$$

This is an implicit equation for Q_{ij} and although we cannot obtain an explicit form for Q_{ij}, its value is easily found by iterating the above equation in the form given (starting with any matrix with positive elements).

At this point simple arguments concerning the c and $\{x_k\}$ dependence can considerably simplify the free energy in the nematic phase. Note that

Eq. (12) only contains the mole fractions $\{x_k\}$ and not the concentration c, which implies $Q_{ij}=Q_{ij}(\{x_k\})$. Since this in turn implies that the factor in parentheses on the right-hand side of Eq. (10) only depends on $\{x_k\}$, we find that the concentration dependence of all α_is remains quadratic as in the monodisperse case [3] and is only modified by a $\{x_k\}$-dependent factor.

As a consequence, ρ_{jk} scales like c^{-1} according to Eq. (9), which exactly compensates the linear c dependence of the excluded-volume term in the free energy (4). On the other hand, the factorization of α_i leads to a separation of σ_i into a term $2 \ln c$ and a term depending exclusively on $\{x_k\}$. Combined with the ideal translational entropy term, this reduces the c dependence of the total free energy of the nematic state to a simple term $3 \ln c$.

From this fact we immediately derive a very simple expression for the osmotic pressure in the nematic phase

$$\Pi^{(n)} \equiv -\left(\frac{\partial F}{\partial V}\right)_{\{N_k\},T} \sim \frac{k_B T}{b} 3c. \tag{13}$$

This asymptotic form for the osmotic pressure, which is 3 times the pressure from the ideal Van't Hoff's law, was already found by Onsager [3] for monodisperse and by Odijk [28] for polydisperse systems. Since a formal derivation of the osmotic pressure from (4) gives:

$$\frac{b\Pi}{k_B T} \simeq c + c^2 \sum_{j,k} q_j q_k x_j x_k \rho_{jk} \tag{14}$$

comparison with (13) leads to a very simple asymptotic expression for the excluded-volume term in the free energy (in the nematic state):

$$c \sum_{j,k} q_j q_k x_j x_k \rho_{jk} \sim 2 \tag{15}$$

The conclusion is: *in the nematic state the orientational distributions of all types of rods establish themselves in such a way that the average excluded volume per particle remains constant, irrespective of the concentration and the composition* (as was noted before by Odijk [28]). As a consequence, a nematic phase cannot lower its total excluded volume by separating into two or more nematic phases. Moreover, since equality of osmotic pressure in coexisting nematic phases requires equal overall number densities c (from Eq. (13), the translational entropy contribution to F is also constant. The driving force for a nematic–nematic phase separation can only be a trade-off between entropy of mixing and orientational entropy by changing the compositions of the phases at constant overall number densities.

The coexisting compositions must then be determined from the chemical potentials μ_i for the different components i:

$$\frac{\mu_i}{k_B T} \equiv \frac{1}{k_B T}\left(\frac{\partial F}{\partial N_i}\right)_{\{N_{k\neq i}\},V,T} = \ln c + \ln x_i + \sigma_i + 2cq_i \sum_k q_k x_k \rho_{ik} \tag{16}$$

In the nematic state we can rewrite this equation in terms of matrix elements Q_{ij} found from Eq. (12):

$$\frac{\mu_i^{(n)}}{k_B T} \sim 3 \ln c + \ln \frac{8}{\pi} - 1 + \ln x_i + 2 \ln[q_i \sum_j x_j q_j (1+Q_{ij})^{-1/2}] + 2 \frac{\sum_k x_k q_k (1+Q_{ik})^{1/2}}{\sum_l x_l q_l (1+Q_{il})^{-1/2}}. \tag{17}$$

We have now formulated a straightforward procedure to determine the thermodynamic properties in the nematic state at an arbitrary concentration c and composition $\{x_k\}$:

(1) Π follows immediately from c by means of Eq. (13);

(2) $\{\mu_k\}$ are found by first iterating Eq. (12) to determine $Q_{ij}(\{x_k\})$ and then applying Eq. (17). The corresponding expressions in the isotropic phase are found directly from Eqs. (14) and (16) with $\sigma_i=0$ and $\rho_{ik}=1$.

The problem in determining phase transitions in polydisperse thin rod systems is now shifted towards locating different $c,\{x_k\}$ with the same values for $\Pi,\{\mu_k\}$.

3. Nematic phases of tridisperse rods

For a tridisperse mixture we located the coexistence between different nematic phases by the

following procedure. From Eq. (13) we know we must work at equal c in that case so we only have to consider different compositions. In a composition triangle equi-μ_1 lines can be determined by applying a Newton–Raphson procedure for μ_1 as a function of x_2 at consecutive (fixed) x_3 values. To be stable with respect to demixing $\partial\mu_2/\partial x_3$ should be negative along such a line. For certain values of μ_1 this is always fulfilled. However, for other μ_1 values this monotonic decrease is interrupted by the occurrence of a local minimum and a local maximum respectively, enclosing an absolutely unstable region. The chemical potential μ_3 as a function of x_3 shows just the opposite behaviour because of the following Gibbs–Duhem relation:

$$x_2\left(\frac{\partial\mu_2}{\partial x_3}\right)_{T,\Pi,\mu_1} = -x_3\left(\frac{\partial\mu_3}{\partial x_3}\right)_{T,\Pi,\mu_1} \tag{18}$$

We can now locate two (possibly) coexisting compositions at our equi-μ_1 curve by requiring equal μ_2 and μ_3.

Similarly, (possibly) coexisting points can be located on equi-μ_2 and equi-μ_3 lines. Not every coexistence found in this way necessarily corresponds to a thermodynamically stable situation. To distinguish the stable from the metastable situations it has to be checked that there is not another phase equilibrium leading to a lower total free energy for the same overall composition. Two intersecting tie lines are necessarily unstable unless they intersect at a common end point, in which case the three remaining end points form a three-phase triangle. From the tie lines connecting stable coexisting points in the composition triangle, the total phase diagram may be constructed.

Some typical examples of the rich phase behaviour are shown in Fig. 1(a)–(c). For the ratio q_2/q_1 we always take 3.2. This is just above the critical length ratio 3.167 for which we first find a nematic–nematic transition in the bidisperse system [20]. On the q_1–q_2 axis we thus always have a nematic–nematic transition between $x_1=0.1438$ and $x_1=0.3080$, between which compositions we will find a two-phase area. Just above the q_1–q_2 axis the one- and two-phase areas on the axis will continue. Note, however, that this is barely visible in most figures since other phases intervene at a very small fraction of the longer rods. Since q_3 is by definition larger than q_2, there is also a (wider) nematic–nematic gap on the q_1–q_3 axis. We may now discern three cases for the length ratio q_3/q_2:

(1) $q_3/q_2>3.167$. Now the q_3/q_2 ratio is also larger than the critical length ratio, and a nematic–nematic transition is present on the q_2–q_3 axis. In the interior the three nematic–nematic transitions on the axes join to form a three-phase triangle, in which three nematic phases coexist. From Fig. 1(a) we see that below $x_2\simeq0.6$ only a minute quantity of longer rods (of type 3) leads to an expulsion of these rods to a new nematic phase: the one-phase areas are barely discernible in the plot.

(2) $3.167>q_3/q_2>2.30$. At the critical q_3/q_2 ratio 3.167 both nematic phases on the q_2–q_3 axis merge into a critical point, which then withdraws into the interior of the composition triangle for a still lower ratio. This is illustrated in Fig. 1(b). Note that at the same time the base of the three-phase triangle widens. The critical point moves closer and closer to its corresponding side of the three-phase triangle, which shrinks at the same time. By the time the critical point reaches the triangle, it is completely folded together and we end up with a line connecting a q_1-rich phase with a critical end point (see Fig. 1(c)).

(3) $2.30>q_3/q_2>1$. At lower q_3/q_2 ratios there is a smooth continuation from the nematic–nematic transition on the q_1–q_2 axis to that on the q_1–q_3 axis.

Another scenario to create a critical endpoint starting from Fig. 1(b) is to reduce the q_2/q_1 ratio. Now the base of the three-phase triangle shrinks. At $q_2/q_1=3.167$ the nematic–nematic transition on the q_1–q_2 axis vanishes into a critical point. This critical point then withdraws into the composition triangle and approaches the base of the three-phase triangle, which continues to shrink. Already at $q_2/q_1=3.13$ the two lower vertices coincide and form a critical endpoint; see Fig. 2. For lower q_2/q_1 ratios we now have a simple extension of the nematic–nematic transition at the q_1–q_3 axis (between a q_3-rich phase and a q_3-poor phase) into the interior of the composition triangle. The addi-

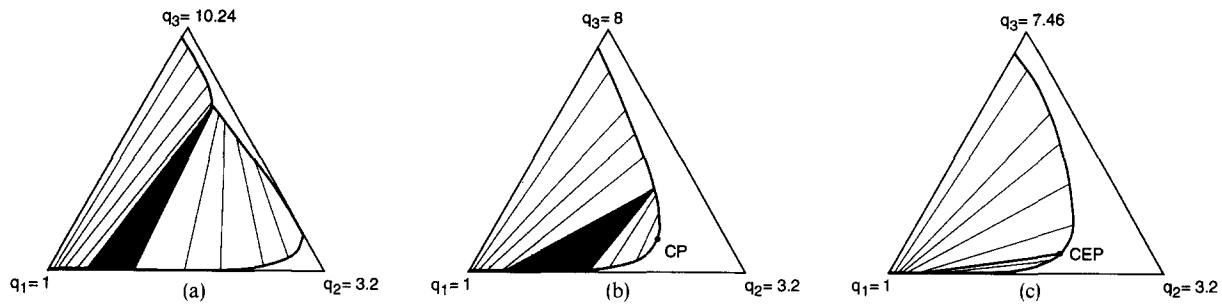

Fig. 1. Composition triangles for systems of different length ratios (indicated at the vertices). Thick lines represent phase boundaries. Thin lines are representative tie lines in two-phase areas. A three-phase region is indicated in grey. All phases are nematic. CP indicates a critical point, CEP a critical end point.

tion of component 2 reduces the difference between both phases, until they merge at a critical point (corresponding to CP in Fig. 2).

Above we noted that the addition of just a very small quantity of long rods may already lead to the appearance of an additional phase. This is reflected in the fact that two-phase regions lie extremely close to the base of the composition triangles in Figs. 1 and 2. To clarify the phase behaviour near the base, we also give more schematic drawings in Figs. 3 and 4, where the corresponding region is enlarged. There we see that the three-phase triangle is always bordered by three two-phase regions as it should be. The exact location of the vertices of the three-phase triangles is given in Table 1 in the next section.

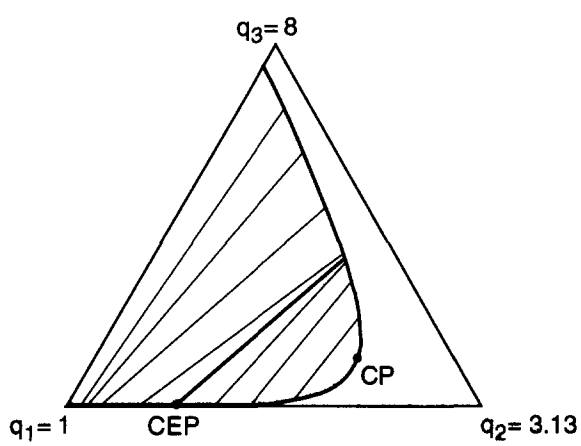

Fig. 2. Composition triangle for systems of different length ratios (indicated at the vertices). Thick lines represent phase boundaries. Thin lines are representative tie lines in two-phase areas. All phases are nematic. CP indicates a critical point, CEP a critical end point.

4. Coexistence with an isotropic phase

The phase behaviour becomes even richer when we also take into account the possibility of an isotropic phase. In that case the coexistence no longer takes place at equal overall number density $c^{(n)}$, but the osmotic pressure in the isotropic phase is now given by Eq. (14) with $\rho_{jk}=1$:

$$\frac{b\Pi^{(i)}}{k_B T} \simeq c^{(i)} + c^{(i)2}\left(\sum_j q_j x_j\right)^2. \tag{19}$$

Thus when one or more nematic phases are to be in equilibrium with an isotropic phase we have to equate Eqs. (13) and (19). This forms the additional coexistence relation required to also determine the values of the overall concentration in the isotropic phase $c^{(i)}$ and the overall concentration in all nematic phases $c^{(n)}$. Since this again complicates the procedure to find the coexisting phases, we restrict ourselves here to the isotropic phase which is in coexistence with the three-phase triangles in Figs. 1 and 2 as an example.

In that case it is justified to make the following assumption:

$$q_j x_j \ll 1 \quad j \geq 2 \tag{20}$$

This simplifies the coexistence relations considerably and enables us to determine the coexistence concentrations and composition of the isotropic

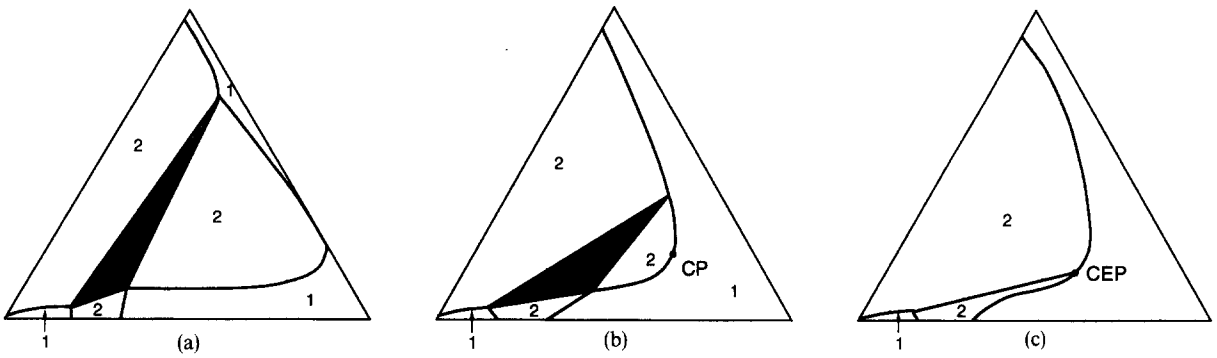

Fig. 3. A schematic representation of Fig. 1. The lower part is enlarged to show the existence of one- and two-phase areas near the axis. The numbers indicate the number of phases.

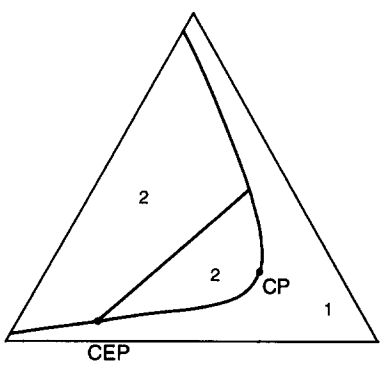

Fig. 4. A schematic representation of Fig. 2.

phase according to an extended version of the scheme described in references [18,20] for the bidisperse case. Some of the results are given in Table 1. Indeed, the composition in the coexisting isotropic phase is such that condition (20) is always satisfied: the longer species are expelled from the isotropic phase. The longest rods are virtually absent because of their very unfavourable excluded volume in the isotropic phase. The values of the coexisting concentrations are very similar to the corresponding bidisperse case of the two shortest species.

To visualize these four-phase equilibria one could construct a prism with the composition triangle as a base plane and a perpendicular concentration axis. In this representation, the four-phase region forms an irregular tetrahedron with its lower corner at $c^{(i)}$ and $x_1 \simeq 1$ and its upper side formed by the nematic three-phase triangle at a height $c^{(n)}$ (parallel to the base of the prism). This four-phase region is bordered by four three-phase regions, of which we only determined the nematic–nematic–nematic region whose composition happens to be invariant with concentration. The other

Table 1
The coexisting concentrations and compositions of the four-phase equilibrium for selected length ratios

Phase	c	x_1	x_2	x_3
$q_1=1$ $q_2=3.2$ $q_3=10.24$				
I	3.37	1	$2.35\ 10^{-5}$	$7.2\ 10^{-24}$
N_1	4.92	0.856	0.144	$2.17\ 10^{-6}$
N_2	4.92	0.680	0.319	$1.52\ 10^{-4}$
N_3	4.92	0.0545	0.267	0.678
$q_1=1$ $q_2=3.2$ $q_3=8$				
I	3.38	1	$2.29\ 10^{-5}$	$7.1\ 10^{-18}$
N_1	4.93	0.879	0.121	$4.76\ 10^{-5}$
N_2	4.93	0.564	0.428	$8.50\ 10^{-3}$
N_3	4.93	0.153	0.499	0.347
$q_1=1$ $q_2=3.2$ $q_3=7.46$				
I	3.38	1	$2.22\ 10^{-5}$	$1.7\ 10^{-16}$
N_1	4.93	0.894	0.106	$7.6\ 10^{-5}$
$N_2=N_3$	4.93	0.339	0.568	0.093
$q_1=1$ $q_2=3.13$ $q_3=8$				
I	3.36	1	$3.49\ 10^{-5}$	$9.2\ 10^{-18}$
$N_1=N_2$	4.89	0.751	0.248	$6.7\ 10^{-4}$
N_3	4.89	0.131	0.446	0.423

three nematic–nematic–isotropic regions border the other sides of the tetrahedron.

5. Discussion

As a conclusion we may state that the very simple system of polydisperse thin hard rods shows a very extensive phase behaviour with a possibility of several nematic phases. However, contrary to intuition, the mechanism of the separation in different nematic phases is not a direct consequence of excluded volume effects, since the excluded volume is coupled to the orientational distributions in such a way that the total excluded volume (15) remains constant irrespective of phase separation. Since demixing is always unfavourable for the entropy the gain in entropy has to be found in the orientational entropy. When we look at the phase enriched in the longer rods in a bidisperse system, the orientational distributions of both types of rods will be narrowed because of the higher excluded volume (2) when longer rods are involved. Therefore in this phase the orientational entropy is also reduced! The gain of entropy is found in the phase enriched in smaller rods, where wider orientational distributions are allowed with a concomitant increase in orientational entropy. This is also the reason why a small quantity of the longest rods in a tridisperse system is expelled to a separate phase.

The same mechanism is at work in tridisperse systems. When all length ratios lie above the critical value of 3.167, there will be a (bidisperse) transition on every axis in the composition triangle. These continue into the interior where they form a three-phase triangle. If one of the ratios is lowered below the critical value, the transition on the axis vanishes but survives for some time in the interior, now ending in a critical point. The transition vanishes altogether when the corresponding two vertices of the three-phase triangle coincide forming a critical endpoint. The length of the longest rod may be lowered substantially below the critical ratio with the second longest before this happens, whereas for the second longest the transition in the interior vanishes almost immediately. For one very special combination of lengths (near $q_1=1$, $q_2=3.1$, $q_3=7.4$) all vertices of the three-phase triangle may coincide, forming a tricritical point.

We want to stress that our paper is based on the Gaussian approximation, which for the isotropic–nematic transition is known to be only of qualitative value [27,29]. Another point of concern is that the Gaussian form of the trial function in the case of polydispersity even leads to a clear inconsistency (if it were the exact form a relation $Q_{ij}=q_i/q_j$ would be found [29] instead of Eq. (12)). Recent work by Van Roij and Mulder [30] shows, however, that for nematic phases the basic mechanism of phase separation is described well by the Gaussian method and even leads to semiquantitative agreement in the bidisperse case (within 1%).

No experiments to test our theory have been reported yet. Some qualitative support for the formation of two nematic phases was discussed in references [20,17]. Since our theory is restricted to very thin rods because of the second virial approximation used, only qualitative value must be expected for explaining experiments. The same goes for the neglect of any flexibility of the particles [27]. It is clear, however, that polydisperse rod systems may show a very rich phase behaviour even on the basis of only the simplest hard interactions.

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