Triple Points in Solutions of Polydisperse Semiflexible Polymers

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When a mother solution of semiflexible polymers with differing molecular weights is forced to undergo phase transition, cloud and shadow curves emerge instead of a coexistence curve. For the first time, we calculate the cloud and shadow curves for an isotropic-nematic transition coupled to polydispersity and predict novel triple points. Because of the emergence of new triple points, polydispersity allows the occurrence of anisotropic phases at much lower polymer concentrations than for the monodisperse solutions.

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The collective behavior of semiflexible polymers with different molecular weights is a subject of great interest in the liquid crystal, polymer physics, and biophysics communities. Practical examples originate from biological processes like ordering of microtubules [1] which is pertinent to the shape and stability of the cell. Microtubules are self-assembled stiff objects with the size distribution arising from polymerization at the plus end [1]. Another example is actin polymerization [2] generating stiff objects. Thus, a fundamental problem in understanding this collective process is to study ordering in a polydisperse system of semiflexible polymers.

The ordering induced by stiff polymers with a fixed molecular weight is already quite complicated due to the combination of two different types of phase transitions. The stiffness of the polymer gives rise to the process of orientational ordering with the first order isotropic-nematic (IN) phase transition [3–6]. The process of phase separation typical of usual flexible polymers gets coupled to this ordering transition resulting in a phase behavior involving the existence of triple points and the second order critical points. This problem has already received considerable attention when the polymers are monodisperse [7,8].

On the other hand, the role of polydispersity in general is a very significant issue in complex fluids [9]. Phase separation induced by polydispersity for flexible polymers has been studied extensively [10–16]. The new feature of polydispersity needs the system to be characterized in terms of the cloud and shadow curves [12,13,16]. The cloud curve is the locus of all points on the temperature-density space which correspond to the first occurrence of the phase separation. The shadow curve is the locus of all those points which coexist with the points on the cloud curve. As a consequence of polydispersity the concept of the phase coexistence curve has to be modified. Only in the limit of a monodisperse system, the cloud curve and the shadow curve merge and form the coexistence curve. It is also well known that in the polydisperse case the critical point is no longer at the minimum of the cloud curve; rather, it is on the right branch of the cloud curve where the shadow curve intersects the cloud curve. The problem of polydispersity is highly nontrivial due to the existence of many different components owing to the size distribution of the polymer. Polydispersity brings in the additional complication of a multicomponent system which is worse for a continuous distribution in the molecular weight because of the existence of infinite degrees of freedom. For a bidisperse or a finite component system, it is theoretically possible to match the chemical potential of each species in the different phases and construct a multicomponent phase diagram. However, this prescription is of little use while dealing with a system with infinite components (continuous molecular weight distribution).

What is the effect of polydispersity in a system of semiflexible polymers undergoing isotropic-nematic transition? Although there has been some work [17–20] on this issue, the cloud and shadow curves have not yet been addressed. In this work, we combine the work of Warren [12] and our previous work on phase diagrams of semiflexible polyelectrolytes [8] to calculate the cloud and shadow curves for a collection of neutral semiflexible polymers with a Schulz distribution in molecular weight. We illustrate the phenomenon of splitting of a triple point by considering polydispersity in semiflexible polymers. We also find that it is possible to realize an anisotropic phase at a very low polymer concentration.

First, the free energy of a monodisperse solution of neutral semiflexible polymers is given, in terms of the monomer density (ϕ) and the orientational order parameter (S), as

$$f = \chi\phi(1-\phi) + \frac{\phi}{L}\ln(\phi) + (1-\phi)\ln(1-\phi) - \phi^2\frac{u}{6} + S^2\left(\frac{9\phi}{4\epsilon} - \frac{\phi^2 u}{3}\right) - \frac{9\phi}{4\epsilon}S^3 + \frac{27\phi}{4\epsilon}S^4, \tag{1}$$

where f is the free energy density in units of $k_B T$, L is the number of Kuhn segments per chain (proportional to molecular weight), χ is the Flory interaction parameter (related inversely to temperature), ϵ is the measure of the stiffness of the chain, and u is the strength of the anisotropic interaction [8,21]. The absolute temperature is denoted by T, while k_B is the Boltzmann constant. Only terms up to the fourth order in S are kept in Eq. (1) which is obtained by minimizing the free energy expression [Eq. (3.8)] of Ref. [8] with respect to all variables except the order parameter S. The order parameter S is given by

$$S = \frac{1}{8} + \frac{1}{2}\sqrt{\frac{8\epsilon u \phi}{81} - \frac{29}{48}} \quad \text{for } \phi > \phi_{\mathrm{IN}} = \frac{99}{16\epsilon u} \tag{2}$$

and 0 otherwise. The isotropic-nematic transition concentration is ϕ_{IN}. This free energy produces the same class of phase diagrams already reported in Ref. [8]. The characteristics of these phase diagrams (χ-ϕ plots) is the existence of a second order critical point at the bottom of the phase coexistence curve with a narrow chimneylike biphasic region which creates a triple point (Fig. 1). On the left of ϕ_{IN} the phase is isotropic, whereas for concentrations higher than ϕ_{IN} we have a nematic phase.

With the introduction of polydispersity, we extend the problem by following the procedure given by Warren [12]. The infinite degrees of freedom due to polydispersity is brought in by considering the chain number density (ρ) as another independent variable. For the parent solution, ρ is related to the first moment of the distribution function by $\langle L\rangle\rho = \phi$, where $\langle L\rangle$ is the average molecular weight. It is assumed [12] that the free energy due to polydispersity depends only on the first moment ($\langle L\rangle$). Thus f is modified for the polydisperse case as follows:

$$f = \chi\phi(1-\phi) + \rho\ln(\rho) + (1-\phi)\ln(1-\phi) - \phi^2\frac{u}{6} + S^2\left(\frac{9\phi}{4\epsilon} - \frac{\phi^2 u}{3}\right) - \frac{9\phi}{4\epsilon}S^3 + \frac{27\phi}{4\epsilon}S^4 - \alpha\rho\ln(\phi/\rho), \tag{3}$$

where α is related to the width of the size distribution which has been assumed to follow Schulz distribution [12]. In the limit of very high α we should recover the results for the monodisperse system. The second term, the entropy of mixing of the chains, in the free energy has been modified from the monodisperse case since ρ is now an independent variable. The last term in the free energy accounts for the polydispersity, and its origin can be found in Warren's work [12]. To simplify the problem, we assume that the isotropic-nematic transition concentration is not affected by the distribution function. In other words, we assume all chains have an aspect ratio greater than the critical aspect ratio needed to undergo the ordering transition. Thus, the order parameter S is still given by the same expression as before. The next step is to construct the binary phase diagrams in ρ-ϕ space for the given χ values. By definition, the points on the cloud curve have the same property as the mother solution; i.e., for the points on the cloud curve $\langle L\rangle\rho$ is equal to ϕ. The intersection of the ρ-ϕ phase diagrams with the physical line $\langle L\rangle\rho = \phi$ defines the points on the cloud curve. The coexisting phases are found by following the tie lines in ρ-ϕ space and thus we construct the shadow curve. A cartoon of the phase diagram constructed using the free energy stated above is shown in Fig. 2. Let the χ value corresponding to this diagram be χ_A. As expected, due to the first order transition there is a biphasic region in the phase diagram around $\phi = \phi_{\mathrm{IN}}$. The biphasic region

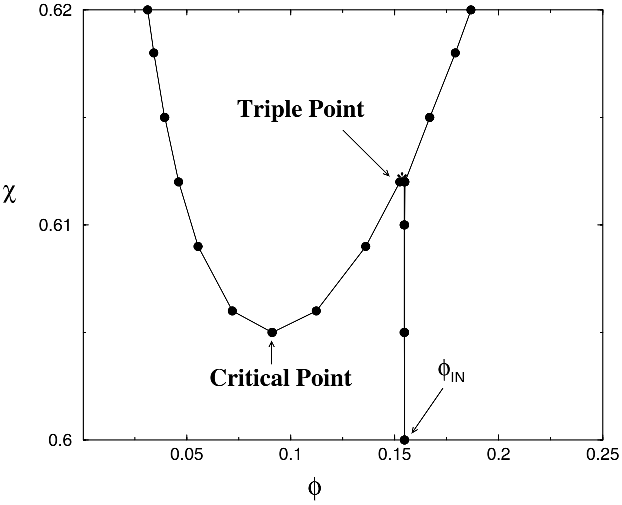

FIG. 1. χ-ϕ phase diagram for a monodisperse system with the molecular weight L being 100 and $\epsilon = 8000$ and $u = 0.005$. The biphasic region is very narrow and appears to be a line in the graph.

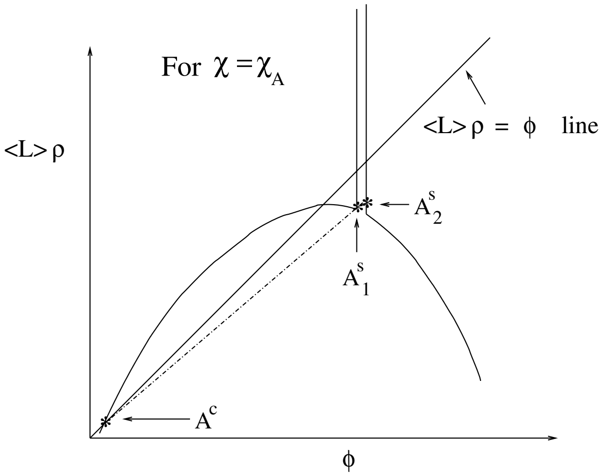

FIG. 2. Cartoon phase diagram for the polydisperse system in the $\langle L\rangle\rho$-ϕ space for $\chi = \chi_A$. The tie line, the dash-dotted line, going through the triple point intersects the $\langle L\rangle\rho = \phi$ physical line at A^c which is a point on the cloud curve, and it is a triple point since it coexists with two phases A_1^s and A_2^s.

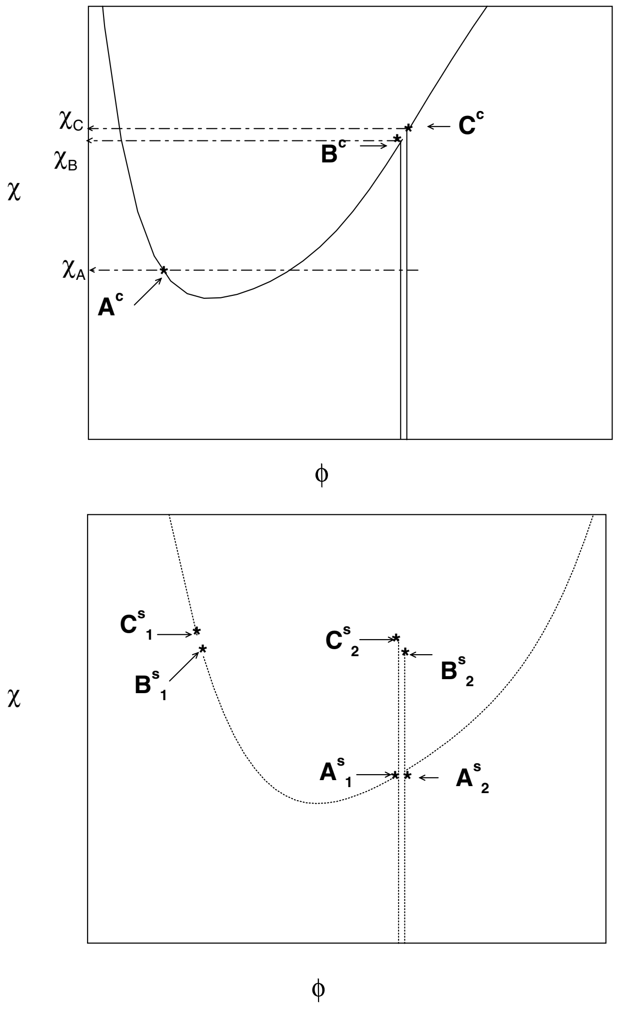

FIG. 3. (a) A typical cloud curve for a polydisperse system. The three triple points (A^c, B^c, and C^c) are shown in the graph by an asterisk (*). The corresponding χ values are denoted by χ_A, χ_B, and χ_C. (b) The full shadow curve is shown by dotted lines. The coexisting shadow phases for the three triple points A^c, B^c, and C^c are given by A^s_1, A^s_2; B^s_1, B^s_2; and C^s_1, C^s_2, respectively.

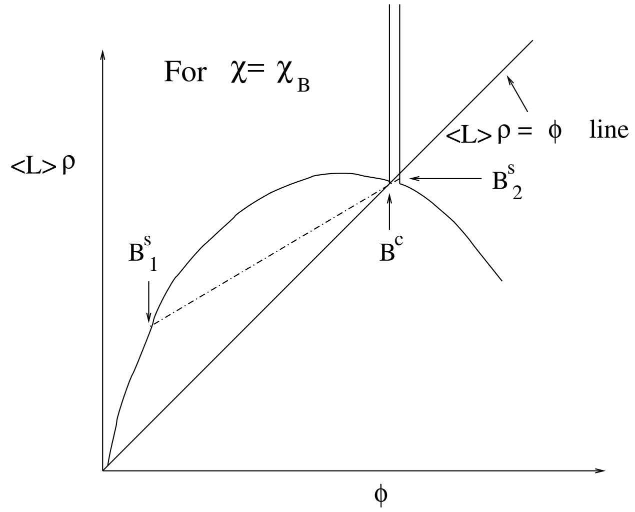

FIG. 4. The $\langle L \rangle \rho$-ϕ phase diagram for $\chi = \chi_B$. The triple point is denoted by B^c and it lies on the physical line. The two coexisting phases are B^s_1 and B^s_2.

in practice is much narrower than the one shown in the cartoon. The rest of the phase diagram remains similar to the flexible polymer case [12]. It is important to notice that the tie lines (dash-dotted lines) are not horizontal. As a consequence of the biphasic region we get a triple point in the $\langle L \rangle \rho$-ϕ phase diagram for each χ. Sometimes there is more than one triple point on the cloud curve [Fig. 3(a)] which can be explained by looking up the corresponding $\langle L \rangle \rho$-ϕ phase diagrams for respective values of χ. The triple point shown by A corresponds to the situation when the tie line going through the triple point in the $\langle L \rangle \rho$-ϕ phase diagram intersects the physical line and the intersection point (A^c) is on the phase boundary and it is on the left of ϕ_{IN}. This immediately suggests A^c coexists with A^s_1 and A^s_2 giving rise to two points on the shadow curve [see Fig. 3(b)]. Thus, A^c is a triple point on the cloud curve. Now, with an increase in χ we reach two special values of χ, $\chi = \chi_B$ and $\chi = \chi_C$, which gives rise to triple points B^c (Fig. 4) and C^c (Fig. 5), respectively. The overall cloud curve thus looks like the one shown in Fig. 3(a), and the shadow curve is shown in Fig. 3(b). It is also worth mentioning that, due to the existence of the triple points, there are discontinuities in the shadow curve which is a known effect of polydispersity [15]. However, in reality the chimney region is very narrow and it looks almost like a line. It is almost impossible to distinguish the two triple points B^c and C^c. A typical phase diagram ($\epsilon = 8000$, $u = 0.005$, $\alpha = 2$, and $\langle L \rangle = 100$) is presented in Fig. 6. As expected, the critical point is located

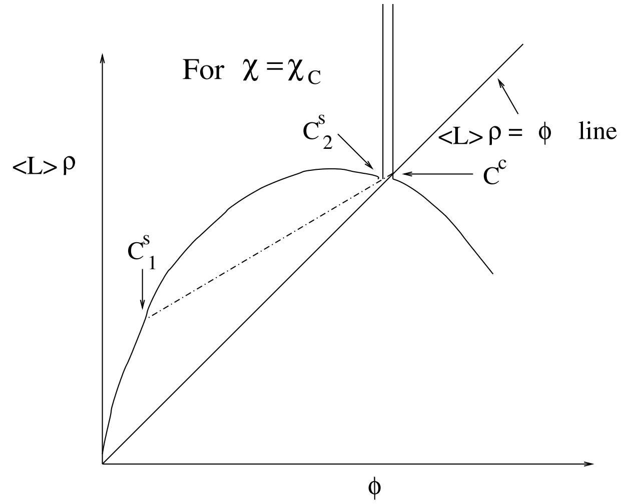

FIG. 5. The $\langle L \rangle \rho$-ϕ phase diagram for $\chi = \chi_C$. The tie line, shown by the dash-dotted line, through the triple point intersects with the physical line at the point C^c which is on the right branch of the biphasic region. Thus, it is the triple point on the cloud curve. The two coexisting phases are C^s_1 and C^s_2.

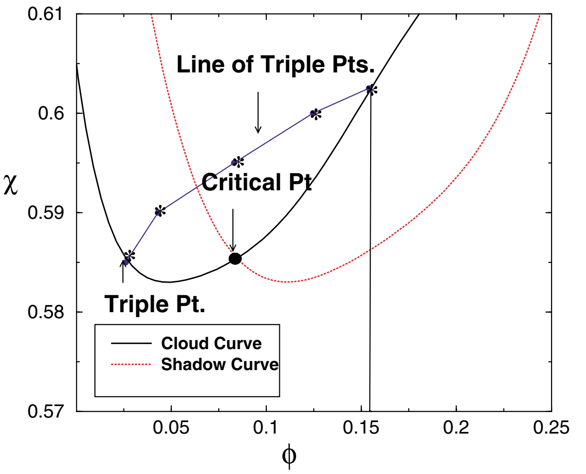

FIG. 6 (color online). Cloud and shadow curves are shown for a polydisperse system with $\alpha = 2$, $\langle L \rangle = 100$, $\epsilon = 8000$, and $u = 0.005$. The shadow curve is shown by the dotted line. The narrow biphasic region almost looks like a line. The narrow chimneylike region for both the cloud and the shadow curve are almost indistinguishable. The critical point is shown by ●. The two triple points on the right branch are very close and appear to be only one triple point. Triple points are shown by asterisks (*). The line joining the asterisks is the line of triple points.

where the shadow and the cloud curve intersect each other. It is not possible to distinguish between the two triple points located on the right branch of the cloud curve. Thus for all practical purposes, for the given value of the stiffness, we can assume that there are two triple points: one is on the left branch of the cloud curve while the other one is on the right branch of the curve. It is very instructive to compare the polydisperse phase diagram (Fig. 6) with the monodisperse phase diagram (Fig. 1) keeping all the parameters the same. The region of miscibility gets significantly reduced with the increase of polydispersity as expected [12]. Splitting of the triple point as a result of polydispersity has an interesting effect in terms of the onset of the anisotropic phase. There exists one triple point on the left branch of the cloud curve corresponding to very low concentration which has a shadow in the anisotropic phase. This implies that it is possible to realize an anisotropic phase at a very low concentration just by controlling the degree of polydispersity even if $\phi_{\rm IN}$ is quite high. The location of $\phi_{\rm IN}$ is simply determined by the stiffness of the chain. In the limit of the monodisperse case, the tie line in the $\langle L \rangle\rho$-ϕ phase diagram merges with the physical line because the allowed phases have only one molecular weight. This implies that all the triple points merge into one triple point for a monodisperse solution as expected [8].

Another interesting feature of the system is that for any χ value between the two triple points there exist a special value of the density at which the physical line intersects the tie line through the triple point in $\langle L \rangle\rho$-ϕ space for that value of χ. Thus, we get a line (line joining the "*" in Fig. 6) of triple points for the density and χ value between the two triple points. This line ends at the two triple points on the cloud curve.

In summary, we show that the triple point of a solution with monodisperse semiflexible chains is split into two by polydispersity. The appearance of the new triple point at a lower concentration permits the occurrence of a nematic phase at a very low concentration. These results are relevant to many biological systems where ordering of stiff polymers is coupled to the polymerization mechanism. We have not considered the effect of electrical charge or temperature dependent polydispersity on the calculated phase diagrams. Splitting of the triple point due to polydispersity can also be viewed from a more general perspective relevant to other problems of critical phenomena with triple points and polydispersity.

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