Self-Consistent Field Theory of Disordered Block-Copolymers

Gabriele Migliorini
Department of Mathematics and Statistics
University of Reading
RG6 6AX Reading, United Kingdom

(Dated: January 17, 2011)

We derive the mean-field theory of disordered block-copolymers composed of two monomeric species, combining Edwards’ functional method with the replica technique of disordered systems. In the absence of disorder we recover the canonical self-consistent field theory of inhomogeneous polymers. In the presence of sequence disorder the theory can be regarded as a comprehensive, novel self-consistent treatment of copolymer melts, unifying the weak- and strong-inhomogeneous regimes. In particular, we study the stability of the microphase separation transition in a melt of diblock-copolymers, composed of $N$ monomers and equal A-B-volume fraction, against the disruptive effect of disorder. We obtain a phase diagram in terms of the relevant parameters, namely the rescaled Flory-Huggins parameter $\chi N$ and disorder strength $p$.

The interplay between topological and energetic effects in linear heteropolymeric systems is a central problem in soft-condensed matter and biophysics. Heteropolymers composed of two monomeric species include for example block-copolymers, alternating $(AB)_n$ multiblock copolymers and random copolymers [1][2][3]. Polymer chains composed of several monomeric species include random heteropolymers, biopolymers as well as proteins, that are comprised of twenty amino-acids [4][5][6].

Block-copolymer melts undergo an order-disorder transition at which spatially periodic, coexisting microdomains of similar chemical composition form. In particular, mean-field theory [5][8] predicts that a melt of diblock-copolymers with an equal A- and B-volume fraction undergoes a second order phase transition at which a lamellar phase (L) occurs. For different values of the A- and B-volume fraction, diblock-copolymers are known to present in addition other morphologies, characterized by periodic two- and three-dimensional spacial orderings, e.g. body-centered-cubic (bcc), hexagonally ordered cylindrical (hex) and bicontinuous gyroid (G) [9] and mean-field predicts all transitions to be first order in this case [10]. Different microphase orderings, induced by the appropriate choice of molecular weight and chain architecture during synthesis, have different thermal and mechanical properties. Consequently, block-copolymers find several applications in surfactant systems, as well as microelectronic systems and nanotechnology.

The phenomenon of microphase separation in systems of block-copolymer melts have been explained, within the weak-segregation approximation, more than thirty years ago [8]. A self-consistent, mean-field theory of block-copolymer systems for the gaussian chain model, beyond the weak-segregation approximation, has been formulated [1][10] and, despite the high computational cost required to solve the corresponding equations, it represents to date the leading method to investigate quantitatively block-copolymer morphologies. The phase diagram in terms of the Flory-Huggins parameter $\chi$, the degree of polymerization $N$ and A-block volume fraction $f$ has been obtained and represents one of the crowning achievements of self-consistent field theory [10].

![FIG. 1. The phase diagram of a disordered diblock-copolymer melt with equal A- B-volume fraction $f = 1/2$, and disorder strength $p$, in terms of the relevant parameters, namely the rescaled Flory-Huggins parameter $\chi N$ and disorder strength, $p$. The solid line represents the second-order phase boundary between the lamellar (L) and disordered (D) phases.](image)

In this letter we study the effect of quenched disorder on the equilibrium properties of block-copolymers [11]. The equilibrium mean-field theory here introduced does not describe the effects of self-generated disorder, that plays an important role in dynamical mean-field theories of polymer melts and glassy systems [12][13].

The study of condensed-matter systems that possess quenched disorder [14] represents a relatively old, yet rapidly evolving frontier of modern science. The mean-field theory of spin-glasses [15][16] has been extended to a variety of different problems, including the one of chemically disordered polymeric systems, firstly at the phenomenological level [17], and later from the microscopic...
point of view \cite{18}. Quenched disorder in polymeric systems may occur to be fixed in space, when studying the behavior of macromolecules \cite{19}, manifolds \cite{20} and directed polymers in random media \cite{21} or might instead characterize the sequence of monomeric units.

The equilibrium properties of random AB copolymer melts have been studied in the weak-segregation approximation, by means of the replica \cite{22} and cumulant expansion methods \cite{23}. In these two studies, the effect of correlated disorder and the presence of finite size $A,B$ multiblocks have been considered in detail. An equivalent expression for the Landau-type density functional free-energy has been obtained with both methods and the corresponding phase diagram, in the weak-segregation limit, has been discussed. Related results have been obtained earlier, within the ground-state dominance approximation \cite{18}, in the case of uncorrelated sequence disorder.

We derive the self-consistent theory of disordered heteropolymers, that includes both the weak- and strong-segregation regimes \cite{22,24}, and apply it to the particular problem of disordered AB diblock-copolymers.

We consider the canonical formulation \cite{1} for a melt of $n_p$ block-copolymer monodisperse chains composed of $N$ segments, where the index $i = 1, \ldots, n_p$ labels each chain, where chains are characterized by $A$-block volume fraction $f$, where the total density of the system is $\rho_0$, where $\{r_i(s)\}$ are the monomer cartesian positions and where $\theta_i(s) = \pm 1$ are the occupation variables for segments $A$ and $B$ respectively, that occur to be disrupted with probability $p_{A,B}$, in each block independently. The total density for segments of both type $A$ and $B$ and the relative density of the two species are defined as

\[
\hat{\phi}(r) = \frac{N}{2\rho_0} \sum_{i=1}^{n_p} \int_0^1 ds \delta(r - r_i(s)),
\]

and depend on the quenched random occupation variables $\{\theta_i\}$, where each specific realization encode the presence of uncorrelated sequence disorder within each block \cite{2,3}. The model here introduced relates, without loss of continuity, the block-copolymer problem in the absence of disorder ($p_{A,B} = 0$), with the problem of random $AB$ copolymers ($p_{A,B} = 1/2$). The hamiltonian of the system is given by

\[
\mathcal{H}(\{\theta\}, \{r\}) = \frac{3}{2a^2N} \sum_{i=1}^{n_p} \int_0^1 ds |d(r_i(s))|^2
\]

\[+ \chi \rho_0 \int dr [\hat{m}^2(r) - \hat{\phi}^2(r)],
\]

where $\chi$ is the Flory-Huggins parameter, measuring the relative strength of the interaction between similar and dissimilar monomers, where we work in units of $k_BT$.

and where $aN^{1/2}$ is the statistical segment length of the Gaussian chain model.

We considered the case of uncorrelated disorder, so that the random occupation variables obey a binomial distribution in each block independently, with variance $\langle \theta_i(s)\theta_j(s') \rangle = 4\delta_{ij}\delta(s - s')p(1 - p)$, where $p = p_{A,B}$ for $s \leq f$ and $s \geq f$ respectively, and where we assume that monomers $A$ and $B$ are represented by statistical segments with the same size $aN^{1/2}$. The order parameter $M$ is defined as the amplitude of the relative density of the two monomeric species, $\hat{m}(r)$. According to the Markov model of random copolymerization \cite{23}, each block is characterized by its length and disorder strength, chemically wired during synthesis, i.e. an average copolymer composition $p_{A,B}$ (or mole fraction of monomers of type $A$ in block $B$ and vice versa).

\[
\text{FIG. 2. The order parameter } M \text{ obtained from self-consistent field theory, for different values of the rescaled Flory-Huggins parameter } \chi N \text{ and disorder strength. In the first plot (top) we show the order parameter } M \text{ as a function of disorder strength, for increasing values of the rescaled Flory-Huggins parameter } \chi N = 20, 25, 40, 80, 100 \text{ respectively. In the second plot (bottom) we show the order parameter } M \text{ as a function of } \chi N, \text{ for increasing values of disorder strength } p = 0, 0.05, 0.1, 0.15, 0.20.\n\]

The two microscopic density operators in equation (1) can be eliminated from the partition function, introducing the four, conjugate fields $\phi(r), m(r), u(r) \text{ and } v(r)$. The incompressibility condition of the melt is enforced introducing the total chemical potential $\xi(r)$. We average the partition function over the uncorrelated distribution of quenched random occupation variables in each block independently $\langle \theta_i(s) \rangle = \pm (1 - 2p_{A,B})$, according to the self-averaging hypothesis. Differently from the problem of self-interacting heteropolymers composed of many
monomeric species [3], where a replica symmetry broken scheme has to be introduced [6], the eigenvalue analysis of the AB copolymer free-energy shows that the replica symmetric solution is stable [18], so that the analytic continuation to the $n = 0$ limit is a simple task [22]. The self-consistent saddle point equations are given by

$$w(r) = 2\chi N\phi(r) + \xi(r) \quad \text{and} \quad v(r) = -2\chi Nm(r).$$

The conjugated density fields are given by

$$m(r) = \frac{1}{2Q} \int_0^1 d\epsilon \Theta(\epsilon) [1 - 2\mathcal{M}(r, s)] q(r, s) q^\dagger(r, s),$$

$$\phi(r) = \frac{1}{2Q} \int_0^1 ds q(r, s) q^\dagger(r, s),$$

(3) where the single-chain occupation variable, having performed the average over disorder, is simply given by $\Theta(s) = +1$ for $s < f$ and $\Theta(s) = -1$ for $s \geq f$ and where the single-chain polymer partition function is defined as $Q = \int dr q(r, s) q^\dagger(r, s)$. The two conjugated density fields in equation (3) are related to the forward propagator $q(r, s)$ via the modified diffusion equation,

$$\frac{\partial}{\partial s} q(r, s) = \left[-\frac{3}{2a^2 N} \nabla^2 - W(r, s)\right] q(r, s)$$

(4) and a similar modified diffusion equation applies for the backward propagator $q^\dagger(r, s)$. The self-consistent mean-field, given by $W(r, s) = \frac{1}{2} w(r) + \frac{1}{2} v(r) [1 - 2D(r, s)]$, has two contributions, associated to the two conjugated density fields $w(r)$ and $v(r)$ above and depends on the disorder strength $p_{AB}$ via

$$D(r, s) = \ln \left[1 + p(s) \left(e^{\mathcal{G}(r, s)} - 1\right)\right] / \mathcal{G}(r, s)$$

$$\mathcal{M}(r, s) = p(s) e^{\mathcal{G}(r, s)} / \left[1 + p(s) \left(e^{\mathcal{G}(r, s)} - 1\right)\right].$$

(5) The two functions in equation (5) are obtained averaging with respect to the binomial form of the disorder each term in the partition function and resumming the associated series and depend on the average, auxiliary mean-field $\mathcal{G}(r, s)$, containing four-propagator contributions [3], defined by

$$\mathcal{G}(r, s) = \Theta(s) \left[v(r) - \frac{1}{Q} \int dr' v(r') q(r', s) q^\dagger(r', s)\right].$$

(6)

In the absence of disorder, the saddle-point equations (5) reduce to canonical self-consistent field theory [10]. The modified diffusion equation (4) has been derived, within a replica symmetric ansatz for the many-body propagator $q(r_1, \cdots, r_n, s) = \prod_{\alpha=1}^n q(r_\alpha, s)$, following the principles of time-dependent mean-field Hartree-approximation [22].

We consider a system of block-copolymers with equal $A$-$B$-volume fraction and the particular case of a symmetric disorder strength within the two blocks, $p_{AB} = p$. To solve numerically the associated saddle-point equations [3]-[6] we used the real-space, one-dimensional Crank-Nicholson algorithm, in combination with a simple mixing technique. For any given value of the rescaled Flory-Huggins parameter we find the optimal value of the domain spacing $d$ that minimizes, according to a standard one-dimensional minimization routine, the free-energy for different given values of disorder strength and rescaled Flory-Huggins parameter $\chi N$. Typically we used $10^3$ points along both the spacial and temporal grids, though higher values $5 \times 10^3$ have been used to check accuracy of our results in the strong-segregation regime.

In Fig. 1 we present the phase diagram of disordered block-copolymers with $A$-block volume fraction $f = 1/2$. The solid thick line represents the second order phase boundary separating the lamellar (L) and disordered (D) phases. As expected, lamellar order (L) is inhibited by the presence of disorder, but persists in the low temperature region, at large values of the disorder strength.

In Fig. 2 we show the values of the order parameter $M$, for different values of disorder strength (top panel) and rescaled Flory-Huggins parameter $\chi N$ (bottom panel), corresponding to horizontal and vertical scans in the phase diagram of Fig. 1. The order parameter $M$ is observed to depend on disorder. The location of the second-order phase boundary between the lamellar (L) and disordered (D) phases in the phase diagram Fig. 1 corresponds to the onset of points where the order parameter vanishes, as in Fig. 2. The expected asymptotic form $M = (1 - 2p)$, shown as a dashed line in the
top panel, is found to agree very well with the numerical results obtained within self-consistent field theory, in the intermediate segregation region $\chi N \gtrsim 60$ and at small values of disorder strength $p \lesssim 0.2$, while deviations from the strong-stretching results are described by self-consistent field theory, as in Fig. 3. The asymptotic form we derived above for the order parameter $M$, scales as the effective block-size in the presence of uncorrelated disorder and numerical self-consistent field theory is observed to approach exactly this simple form.

In Fig. 3 we plot the domain spacing $d$, characterizing lamellar order (L), as a function of the rescaled Flory-Huggins parameter $\chi N$. Domain spacing is observed to depend on the disorder strength, but not at the order-disorder transition, i.e. along the second-order phase boundary in the phase diagram, and as shown by the black filled squared boxes. In the strong-segregation limit the domain spacing of pure, non-disordered block-copolymers approaches the asymptotic form $d \propto (\chi N)^{1/6}$ [24]. In fact, we observe that the domain spacing of disordered block-copolymer systems appears to cross-over to the same universal asymptotic form, shown by the dashed line. The calculation of a global phase diagram, in the space of disorder strength $p$, block $A$ volume fraction $f$, and rescaled Flory-Huggins parameter $\chi N$ can be addressed within the present theory, and the issue of the stability of other block-copolymer morphologies, beyond the one-dimensional lamellar (L) ordering here discussed, and the nature of the phase transition within the mean-field approximation and in the presence of quenched disorder is an open interesting problem.

The important role of fluctuation effects, in the framework of one-loop Hartree approximation [23,24], as well as momentum space renormalization-group theory [27], have been considered in the absence of disorder and corrections to the mean-field phase diagram of pure block-copolymer melts have been discussed [28,29]. The effect of thermal fluctuations in random copolymer systems have been discussed, within the weak-segregation approximation [18]. A model of block-copolymer systems with equal $A-B$-volume fraction $f = 1/2$, in the presence of gaussian distributed Flory-Huggins interaction values, characterized by an average $\chi$ and disorder strength $\Delta \chi$, and the corresponding phase diagram have been discussed recently within renormalization-group theory [20]. It has been argued that the presence of disorder changes the nature of the transition at a critical value of disorder strength and lamellar order becomes unstable at values of $\Delta \chi / \chi_s \simeq 0.1$, where $\chi_s \simeq 10.495$ is the order-disorder transition in the absence of sequence disorder.

We observed that, within the mean-field theory approximation, lamellar ordering persists to large values of disorder strength, for any value of the Flory-Huggins parameter our algorithm can reach, and we in fact expect lamellar ordering to persist at low enough temperatures, for any value of disorder strength.

This research was funded by EPSRC under grant number EP/F068425/1. I acknowledge discussion with Alexei Likhtman and Pawel Stasiak.

[1] E. Helfand, J. Chem. Phys. 62, 999 (1975).
[2] P.G. de Gennes, Faraday Discuss. Chem. Soc. 68, 96 (1979).
[3] S.P. Obukhov, J. Phys. A 19, 3655 (1986).
[4] T. Garel and H. Orland, Europhys. Lett. 6, 307 (1988); ibid. 6, 597 (1988).
[5] E.I. Shakhnovich and A.M. Gutin, Biophys. Chem. 34, 187 (1989); E.I. Shakhnovich and A.M. Gutin, J. Phys. (France) 50, 1843 (1989).
[6] V.S. Pande, A.Yu. Grosberg, and T. Tanaka, Rev. Mod. Phys. 72, 259 (2000).
[7] S.F. Edwards, Proc. Phys. Soc. 88, 265 (1966).
[8] L. Leibler, Macromolecules 13, 1602 (1980).
[9] F. S. Bates, M.F. Shultz, A.K. Chandra, S. Forster, J.H. Rosedale, K. Almdal and K. Mortensen, Faraday Discuss. 98, 7 (1994).
[10] M.W. Matsen and M. Schick, Phys. Rev. Lett. 72, 2660 (1994).
[11] S.V. Panyukov and S.I. Kuchanov, J. Phys. II (France) 2, 1973 (1992).
[12] M. Dzero, J. Schmalian and P.G. Wolynes, Structural Glasses and Supercooled Liquids: Theory, Experiments and Applications, edited by P.G. Wolynes, John Wiley and Sons (2010).
[13] C.-Z. Zhang and Z.-G. Wang, Phys. Rev. E 73, 031804 (2006); S. Wu, Phys. Rev. E 79, 031803 (2009).
[14] S.F. Edwards and P.W. Anderson, J. Phys. F: Met. Phys. 5, 965 (1975).
[15] D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. 35, 1792 (1975).
[16] G. Parisi, Phys. Rev. Lett. 43, 1754 (1979).
[17] J.D. Bryngelson and P.G. Wolynes, Proc. Natl. Acad. Sci. U.S.A. 84, 7524 (1987).
[18] C.D. Sfatos, A.M. Gutin and E. Shakhnovich, Phys. Rev. E 48, 465 (1993); ibid. 51, 4727 (1995); E.G. Timoshenko, Yu.A. Kuznetsov and K.A. Dawson, Phys. Rev. E 57, 6801 (1998).
[19] S. Stepanov, A.V. Dobrynin, T.A. Vilgis and K. Binder, J. Phys. I 6, 837 (1996).
[20] M. Mézard and G. Parisi, J. Phys. I (France) 1, 809 (1991).
[21] V. Dotsenko, Europhys. Lett. 90, 20003 (2010).
[22] G. H. Fredrickson and S. T. Milner, Phys. Rev. Lett. 67, 835 (1991).
[23] G. H. Fredrickson, S.T. Milner and L. Leibler, Macromolecules 25, 6341 (1992).
[24] A.N. Semenov, Macromolecules 22, 2849 (1989).
[25] S. Stepanov, Macromolecules 28, 8233 (1995).
[26] S. A. Brazovskii, Sov. Phys. JETP 41, 85 (1975).
[27] P.C. Hohenberg and J.B. Swift, Phys. Rev. E 52, 1828 (1995).
[28] G. H. Fredrickson and L. Leibler, Macromolecules 22, 1238 (1989); H. Tang and K.F. Freed, J. Chem. Phys. 94, 7554 (1991).
[29] A. von der Heydt, M. Müller and A. Zippelius, Macromolecules 43, 3161 (2010).
[30] H. Westhöft Jr. and J. Schmalian, Phys. Rev. E 72, 011806 (2006).