

Dynamical self-arrest in symmetric and asymmetric diblock copolymer melts using a replica approach within a local theory

Sangwook Wu

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, USA
(Received 12 July 2008; revised manuscript received 27 October 2008; published 27 March 2009)

We investigate dynamical self-arrest in a diblock copolymer melt using a replica approach within a self-consistent local method based on dynamical mean-field theory (DMFT). The local replica approach effectively predicts $(\chi N)_A$ for dynamical self-arrest in a block copolymer melt for symmetric and asymmetric cases. We discuss the competition of the cubic and quartic interactions in the Landau free energy for a block copolymer melt in stabilizing a glassy state depending on the chain length. Our local replica theory provides a universal value for the dynamical self-arrest in block copolymer melts with $(\chi N)_A \sim 10.5 + 64N^{-3/10}$ for the symmetric case.

DOI: [10.1103/PhysRevE.79.031803](https://doi.org/10.1103/PhysRevE.79.031803)

PACS number(s): 83.80.Uv, 81.05.Kf

I. INTRODUCTION

A diblock copolymer melt is a polymer in which two segments of simple monomers are joined together by covalent bonds. Despite its simple structure, it has attracted many researchers for the last decades presumably because it shows various morphological changes such as the lamellar phase, bcc phase, and fcc phase in the process of the disorder-order transition. The equilibrium properties of a diblock copolymer melt have been well studied in the framework of mean-field theory. Leibler, for example, obtained a universal value $(\chi N)_{\text{MST}} \sim 10.5$ for microphase separation transition (MST) for a diblock copolymer melt in the weak segregation limit [1]. χ is the Flory-Huggins interaction parameter and N is the degree of polymerization. The mean-field solution predicts that the order-disorder transition of a lamellar phase for the composition $f=0.5$ is second order. However, when the temperature approaches the temperature of the order-disorder transition region, the composition fluctuation plays an important role. The Fredrickson-Helfand theory with the fluctuation effect incorporated demonstrates that the order-disorder transition of the lamellar phase for the composition $f=0.5$ is first order. This is quite consistent with the experimental result: $(\chi N)_{\text{MST}} \sim 10.5 + 41\bar{N}^{-1/3}$ [2]. The origin of the correction term to $(\chi N)_{\text{MST}}$ arises from a fluctuation-induced first-order transition. Interestingly, the fluctuation-induced first-order transition is known to be a characteristic of the ‘‘Brazovskii universality class’’ [3,4]. Leibler and co-workers [1,5] have demonstrated that the Hamiltonian for the block copolymer melt reduces to the Hamiltonian for the ‘‘Brazovskii universality class.’’

The competition between short-range and long-range interactions induces a frustration, which generates an exponentially large number of metastable states in a self-generated glass system [6]. In the case of the diblock copolymer melt, there also exists a competition between short-range and long-range interaction. The short-range interaction comes from the excluded volume due to nearest-neighbor monomers. On the other hand, the long-range interaction originates from the connectivity between two different chains, which does not allow macroscopic phase separation [5,7]. This implies the possibility of a kinetic trap of the diblock copolymer melt

due to the numerous local minima states at a specific condition, leading to dynamical self-arrest of the diblock copolymer melt. Although it was not developed for the particular case of the diblock copolymer melt, the frozen nonergodic state (kinetic trap in the local minima) of the ‘‘Brazovskii universality class’’ has been implemented for symmetric (in the absence of the cubic interaction in the Brazovskii-type Hamiltonian) [8] and asymmetric (in the presence of the cubic interaction in the Brazovskii-type Hamiltonian) cases [9].

A frozen nonergodic state for a diblock copolymer has been verified from a temperature quenching experiment for the disordered state in the nearly symmetric system of poly(ethylene-propylene)-poly(ethyl-ethylene) (PEP-PEE) ($f=0.55$) [4]. The quenched state shows a macroscopically isotropic pattern for small angle neutron scattering (SANS) data and also shows a large elastic modulus G at low frequencies and slow relaxation. This nonequilibrium state demonstrates a frozen-ergodic state, for which molecular rearrangement is suppressed similar to a ‘‘pattern glass’’ [4]. For the case of dynamical self-arrest in a block copolymer melt, the function $(\chi N)_A$ [10] was studied using perturbation theory within the framework of the self-consistent screening approximation (SCSA) method [8,11,12]. Since the perturbative expansion is performed in terms of the inverse of the scaled degree of polymerization, \bar{N} [12], the perturbative description for dynamical self-arrest becomes reliable for longer, symmetric chains. For an effective description of dynamical self-arrest in a diblock copolymer melt with short and asymmetric chains, however, a new approach beyond conventional perturbation theory is required. The objective of this paper, then, is to apply the local replica approach based on DMFT [13] to the case of dynamical self-arrest of a block copolymer melt beyond the perturbative regime, and to develop a reason after prediction of the critical value, $(\chi N)_A$.

II. THEORY

A. Theory of block copolymer

We start from the effective Hamiltonian for a block copolymer melt (S diblock copolymer chains, each consisting of N segments) [2].

$$\begin{aligned} \mathcal{H}_{\text{block}} = & \frac{1}{2} \int_{\mathbf{q}} \Psi_{\mathbf{q}} \mathcal{G}_{\mathbf{q}}^{-1} \Psi_{-\mathbf{q}} + \frac{\Gamma_3}{3!} \int_{\mathbf{q}, \mathbf{q}'} \Psi_{\mathbf{q}} \Psi_{\mathbf{q}'} \Psi_{-\mathbf{q}-\mathbf{q}'} \\ & + \frac{\Gamma_4}{4!} \int_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} \Psi_{\mathbf{q}} \Psi_{\mathbf{q}'} \Psi_{\mathbf{q}''} \Psi_{-\mathbf{q}-\mathbf{q}'-\mathbf{q}''}, \end{aligned} \quad (1)$$

where $\Psi_{\mathbf{q}}$ corresponds to the Fourier transform of the density-fluctuation field, $\Psi(\mathbf{r})$. We set $k_B T$ to 1. $\int_{\mathbf{q}}$ denotes $\int \frac{d^3 \mathbf{q}}{(2\pi)^3}$ and the integration is performed over momentum space. Since we make the assumption that the system is incompressible, the total density of the system does not vary in space,

$$\rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) = \rho_0 = \frac{NS}{V}. \quad (2)$$

We set the persistence lengths of the A polymer, b , and the B polymer, b' , to $b'=b=1$ in our study. According to a Flory-Huggins lattice theory, ρ_0 is set to unity ($\rho_0 \sim b^{-3}$) [2]. The density fluctuation of the A block and B block, $\Psi_A(\mathbf{r})$ and $\Psi_B(\mathbf{r})$, are defined in terms of the density fields of the A and B blocks, ρ_A and ρ_B .

$$\Psi_A(\mathbf{r}) = \rho_A(\mathbf{r}) - f = \Psi(\mathbf{r}),$$

$$\Psi_B(\mathbf{r}) = \rho_B(\mathbf{r}) - (1-f) = -\Psi(\mathbf{r}). \quad (3)$$

Thus $\Psi(\mathbf{r}) > 0$ corresponds to an excess of A monomers whereas $\Psi(\mathbf{r}) < 0$ refers to an excess of B monomers. The higher vertex terms Γ_3 and Γ_4 denote $\Gamma_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$ and $\Gamma_4(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4)$. The third order vertex function $\Gamma_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$ vanishes unless $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 = 0$. The nonvanishing $\Gamma_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)$ is denoted as Γ_3 . As the fourth order vertex function $\Gamma_4(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4)$, $\Gamma_4(0, 0)$ is used for the lamellar phase. They can be obtained directly from Leibler's random-phase approximation (RPA) method [1]. The correlation function of the block copolymer melt can be expanded around the peak position of the scattering function. Then,

$$\mathcal{G}_{\mathbf{q}} = \frac{N}{\mathcal{F}^* - 2\chi N + \mathcal{F}^{**}(qR_0 - x^*)^2},$$

where $\mathcal{F}^* = \mathcal{F}(x^*, f)$ and $\mathcal{F}^{**} = \frac{1}{2} \frac{\partial^2 \mathcal{F}(x, f)}{\partial x^2} \Big|_{x=x^*}$. $q_0 R_0 = x^*$ and the composition value, f , is N_A/N . The strong peak of $\mathcal{G}_{\mathbf{q}}$ occurs at the dominant wave vector $|\mathbf{q}| = q_0$. \mathcal{F} is defined as $(S_{\mathbf{k}}^{BB} + S_{\mathbf{k}}^{AA} + 2S_{\mathbf{k}}^{AB}) / [S_{\mathbf{k}}^{AA} S_{\mathbf{k}}^{BB} - (S_{\mathbf{k}}^{AB})^2]$. $S_{\mathbf{k}}^{AA}$, $S_{\mathbf{k}}^{BB}$ and $S_{\mathbf{k}}^{AB}$ are correlation functions for the AA chain, BB chain, and AB chain, respectively. R_0 is the gyration length of the block copolymer melt. For example, for $f=0.5$, it holds $x^* \approx 1.95$ with $F(x^*, \frac{1}{2}) \approx 20.99$ and $\frac{1}{2} \frac{\partial^2 F(x, 1/2)}{\partial x^2} \Big|_{x=x^*} \approx 7.29$. The bare correlation function of the block copolymer melt can be transformed into a Brazovskii-type correlation function,

$$\mathcal{G}_{\mathbf{q}} = \frac{Z}{\varepsilon_0^2 q_0^2 + (q - q_0)^2}. \quad (4)$$

The bare mass $\varepsilon_0^2 = \frac{\mathcal{F}^* - 2\chi N}{\mathcal{F}^{**} x^{*2}}$ and normalization factor $Z = \frac{N}{\mathcal{F}^{**} R_0^2} = \frac{6}{\mathcal{F}^{**} b^2}$. The bare mass ε_0^2 controls the strength of phase segregation. The segment volume, η , is therefore set to unity ($\eta \sim b^3$). Thus, in our theory, N is replaced by $\bar{N} = Nb^6 \eta^{-2}$.

Introducing a new field variable, $\varphi(r) = Z^{-1/2} \Psi(r)$, the rescaled effective Hamiltonian for a block copolymer melt can be written as

$$\begin{aligned} \mathcal{H}_{\text{rescaled}} = & \frac{1}{2} \int_{\mathbf{q}} \varphi_{\mathbf{q}} \mathbf{G}_{\mathbf{q}}^{-1} \varphi_{-\mathbf{q}} + \frac{\nu}{3} \int_{\mathbf{q}, \mathbf{q}'} \varphi_{\mathbf{q}} \varphi_{\mathbf{q}'} \varphi_{-\mathbf{q}-\mathbf{q}'} \\ & + \frac{u}{4} \int_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} \varphi_{\mathbf{q}} \varphi_{\mathbf{q}'} \varphi_{\mathbf{q}''} \varphi_{-\mathbf{q}-\mathbf{q}'-\mathbf{q}''}. \end{aligned} \quad (5)$$

The rescaled bare correlation function $\mathbf{G}_{\mathbf{q}}^{-1}$ is defined as

$$\mathbf{G}_{\mathbf{q}} = \frac{1}{\varepsilon_0^2 q_0^2 + (q - q_0)^2}, \quad (6)$$

with rescaled vertex coefficients, $u = (1/6)(6/\mathcal{F}^{**})^2 \Gamma_4(0, 0)$ and $\nu = (1/2)(6/\mathcal{F}^{**})^{3/2} \Gamma_3$.

B. Replica approach

If the system becomes trapped in local metastable states for a very long time, it cannot explore the entire phase space. The breakdown of equilibrium, or so-called ergodicity breaking, occurs. One of the theoretical approaches that cope with this breakdown of equilibrium is replica theory. A simple procedure is used to calculate the self-averaging free energy for the system with random quenched disorder [14]. It introduces replicas (copies) of the system for averaging over the randomness of the logarithm of the partition function. The physical free energy is recovered in the limit of zero replicas ($m \rightarrow 0$) [15]. However, for the self-generated glass system without quenched disorder, the free energy is recovered by the analytic continuation of $m \rightarrow 1$ [16]. The long time correlation function is interpreted as the interaction between two different replicas with small attraction [17]. Following the scenario of self-generated glassiness [8,9,17] and the ansatz of one-step replica symmetry breaking (RSB) in $m \times m$ replica space [18], we construct the correlation function in replica space by a matrix with a diagonal part and an off diagonal part,

$$\begin{aligned} G_{\alpha\beta}(q) &= K(q) \delta_{\alpha\beta} + F(q), \\ \Sigma_{\alpha\beta}(q) &= \Sigma_K(q) \delta_{\alpha\beta} + \Sigma_F(q), \end{aligned} \quad (7)$$

where α and β are replica indexes that build the $m \times m$ replica matrix. $\Sigma_K(q)$ and $\Sigma_F(q)$ are self-energies corresponding to $K(q)$ and $F(q)$, respectively. $K(q)$ is a response function and $F(q)$ is an off-diagonal correlation function in replica space. Inverting the Dyson equation leads to

$$\begin{aligned} K(q) &= \frac{1}{(q - q_0)^2 + \kappa^2 q_0^2}, \\ mF(q) &= \frac{1}{(q - q_0)^2 + \varepsilon^2 q_0^2} - \frac{1}{(q - q_0)^2 + \kappa^2 q_0^2}, \end{aligned} \quad (8)$$

with $\kappa^2 q_0^2 = \varepsilon_0^2 q_0^2 - \Sigma_K(q)$ and $\varepsilon^2 q_0^2 = \varepsilon_0^2 q_0^2 - \Sigma_K(q) - m \Sigma_F(q)$. The $m \times m$ replica matrix of $G_{\alpha\beta}$ according to the one-step replica symmetry breaking ansatz is written as

$$G_{\alpha\beta}(q) = \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \\ \cdots & K(q)+F(q) & F(q) & F(q) & \cdots \\ \cdots & F(q) & K(q)+F(q) & F(q) & \cdots \\ \cdots & F(q) & F(q) & K(q)+F(q) & \cdots \\ & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (9)$$

The diagonal elements $K(q)+F(q)$ in replica space correspond to the equilibrium, liquid state correlation function. It is determined only by ε , which is dependent only on the liquid state correlation length of $\frac{1}{\varepsilon q_0}$. In a similar way, the response function $K(q)$ is determined by the correlation length $\frac{1}{\kappa q_0}$. The off-diagonal part, $F(q)$, corresponds to the correlation function in nonequilibrium state and characterizes long time correlations, $\lim_{t \rightarrow \infty} \lim_{t' \rightarrow \infty} \langle \Psi_{\mathbf{q}}(t) \Psi_{-\mathbf{q}}(t+t') \rangle$. The combination of two dimensionless order parameters, ε and κ , defines the Lindemann length [8] as $\lambda^{-1} = \frac{\sqrt{\kappa^2 - \varepsilon^2}}{2} q_0$. If the system is in the equilibrium state, when the replica index m goes to 1, the off-diagonal part, $F(q)$, goes to 0 ($\kappa = \varepsilon$). However, if the system is in the nonequilibrium state, $F(q)$ is nonzero even if the replica index m goes to 1 ($\kappa \neq \varepsilon$). In the liquid state, the Lindemann length diverges ($\kappa \rightarrow \varepsilon$). On the other hand, in a glassy state ($\kappa \neq \varepsilon$), the system is frozen with finite Lindemann length.

C. Local replica approach within the DMFT

The emergence of glassiness in a glass-forming material is due to strong local interaction [8]. We construct a replica theory within the framework of DMFT, which enables us to deal with the glassy behavior due to a strong local interaction. Following the DMFT scheme [13], we first construct the correlation function in replica space for the effective description of the dynamical self-arrest in the original problem with the assumption that the self-energy is momentum independent. In strongly correlated systems, the assumption of a momentum independent self-energy dramatically simplifies the dynamics, describing states far from the perturbative regime [13,19]. We then set up an auxiliary local problem corresponding to the original problem by mapping the original one onto the local one. In this case, we have the same momentum independent self-energy in both the original and the auxiliary local problems. The two functionals $\Phi[\bar{G}]$ and $\Phi[\mathcal{G}]$ [20], which are the sum of skeleton diagrams of the free energy in the original and the local problems, become identical in the local theory [13]. \bar{G} and \mathcal{G} are the correlation functions in the original and local problems. The functional derivative of the functional $\Phi[\bar{G}]$ with respect to \bar{G} gives a self-energy. Thus, the same functionals and the same correlation functions ensure the same self-energy in the original and local problems. Such an identity for two functionals guarantees us the equivalence of solving the original and the local problems if we set $\bar{G} = \mathcal{G}$ [13]. If the self-energy, Σ , is momentum independent, the renormalized correlation function has the form

$$G(q) = \frac{1}{(q - q_0)^2 + \varepsilon^2 q_0^2}, \quad (10)$$

with $\varepsilon^2 = \varepsilon_0^2 - q_0^{-2} \Sigma > 0$. A momentum-averaged correlation function gives us

$$\bar{G} = \int \frac{d^3 q}{(2\pi)^3} G(q) = \frac{q_0}{2\pi\varepsilon}. \quad (11)$$

Averaging the response function and off-diagonal correlation function over momenta gives

$$\bar{K} = \int \frac{d^3 q}{(2\pi)^3} K(q) = \frac{q_0}{2\pi\kappa},$$

$$\bar{F} = \int \frac{d^3 q}{(2\pi)^3} F(q) = \frac{q_0}{2\pi m} \left(\frac{1}{\varepsilon} - \frac{1}{\kappa} \right). \quad (12)$$

Then, we obtain the momentum averaged correlation function in replica space,

$$\bar{G}_{\alpha\beta} = \bar{K} \delta_{\alpha\beta} + \bar{F}. \quad (13)$$

Next, we map our original problem into a local one, which depends only on the microscopic-length scale $1/q_0$. The auxiliary local Hamiltonian is given as

$$\mathcal{H} = \frac{1}{2} \sum_{\alpha\beta} \mathcal{J}_{\alpha\beta} \phi_\alpha \phi_\beta + \sum_{\alpha} \left(\frac{u q_0^{-3}}{3} \phi_\alpha^3 + \frac{u q_0^{-3}}{4} \phi_\alpha^4 + h \phi_\alpha \right). \quad (14)$$

The correlation function in the local problem is given as

$$\mathcal{G}_{\alpha\beta} = (\mathcal{J}_{\alpha\beta} - q_0^{-1} \Sigma_{\alpha\beta})^{-1}. \quad (15)$$

The correlation function, $\mathcal{G}_{\alpha\beta}$, does not depend on momentum or position. The Weiss field, a single-site effective field [13] in replica space, is given as

$$\mathcal{J}_{\alpha\beta} = \mathcal{J} \delta_{\alpha\beta} - \mathcal{C}. \quad (16)$$

From Eqs. (13) and (15), the Weiss field is expressed in terms of ε and κ ,

$$\mathcal{J} = \frac{2\pi\kappa + \varepsilon_0^2 - \kappa^2}{q_0},$$

$$\mathcal{C} = \frac{2\pi(\kappa - \varepsilon) + \varepsilon^2 - \kappa^2}{m q_0}. \quad (17)$$

The external field, h , guarantees $\langle \phi \rangle = 0$ for the liquid state. In the case of the liquid state, the replica index is not required. By solving the self-consistent nonlinear algebraic equations for ε , Eq. (18), we can obtain a solution for the liquid state,

$$\frac{q_0}{2\pi\varepsilon} = \frac{\int_{-\infty}^{\infty} d\phi \phi^2 e^{-\mathcal{H}}}{\mathcal{Z}},$$

$$0 = \frac{\int_{-\infty}^{\infty} d\phi \phi e^{-\mathcal{H}}}{\mathcal{Z}}, \quad (18)$$

where $\mathcal{H} = \frac{1}{2}\mathcal{J}\phi^2 + (\frac{uq_0^3}{3}\phi^3 + \frac{uq_0^3}{4}\phi^4 + h\phi)$ and $\mathcal{Z} = e^{-\mathcal{H}}$ [9]. In the liquid state, since $\kappa \rightarrow \varepsilon$, \mathcal{J} reduces to $\frac{2\pi\varepsilon + \varepsilon_0^2 - \varepsilon^2}{q_0}$. The off-diagonal Weiss field, \mathcal{C} , goes to 0. For fixed q_0 , v , u , and ε_0^2 , we obtain ε and h from a liquid solution. Finally, we can determine \bar{K} and \bar{F} for a given \mathcal{J} and \mathcal{C} such that $\mathcal{G}_{\alpha\beta} = \bar{G}_{\alpha\beta}$ is satisfied. By a simple algebra [9], we find a self-consistent equation for \bar{F} in the local problem (in terms of the Weiss field) and the original problem (averaged over momentum),

$$\begin{aligned} \bar{F} &= -\frac{1}{\mathcal{Z}(1)} \int \frac{d\lambda}{\sqrt{2\pi\mathcal{C}}} e^{-\lambda^2/2\mathcal{C}} \Omega(\lambda) \log \Omega(\lambda) \\ &\quad \times (\mathcal{C}^{-1} \langle \phi \rangle_{\lambda} + \langle \phi^2 \rangle_{\lambda}) \\ &= \frac{q_0}{2\pi} \left(\frac{1}{\varepsilon} - \frac{1}{\kappa} \right), \end{aligned} \quad (19)$$

where $\mathcal{Z}(m)$ is the partition function. The partition function, $\mathcal{Z}(m) = \int d^m \phi e^{-\sum_{\alpha=1}^m \mathcal{H}[\phi_{\alpha}] + (1/2)\mathcal{C}(\sum_{\alpha} \phi_{\alpha})^2}$, can be transformed into $\mathcal{Z}(m) = \int \frac{d\lambda}{\sqrt{2\pi\mathcal{C}}} e^{-\lambda^2/2\mathcal{C}} \Omega(\lambda)^m$ by a Hubbard-Stratonovich transformation leading to the elimination of the coupling between different replicas. $\mathcal{Z}(1)$ is the partition function at $m=1$. The terms $\langle \phi \rangle_{\lambda}$ and $\langle \phi^2 \rangle_{\lambda}$ are defined as

$$\begin{aligned} \langle \phi \rangle_{\lambda} &= \frac{\int d\phi e^{-[1/2\mathcal{J}\phi_a^2 + (uq_0^{-3}/3)\phi_a^3 + (uq_0^{-3}/4)\phi_a^4 + (h+\lambda)\phi_a]} \phi}{\Omega(\lambda)}, \\ \langle \phi^2 \rangle_{\lambda} &= \frac{\int d\phi e^{-[1/2\mathcal{J}\phi_a^2 + (uq_0^{-3}/3)\phi_a^3 + (uq_0^{-3}/4)\phi_a^4 + (h+\lambda)\phi_a]} \phi^2}{\Omega(\lambda)}, \end{aligned} \quad (20)$$

for $m \rightarrow 1$ in Eq. (19). In Sec. IV, we investigate the nontrivial solution of \bar{F} for fixed q_0 , v , u , f , and N . It provides us a solution for the long time correlation indicating the dynamical self-arrest of the diblock copolymer.

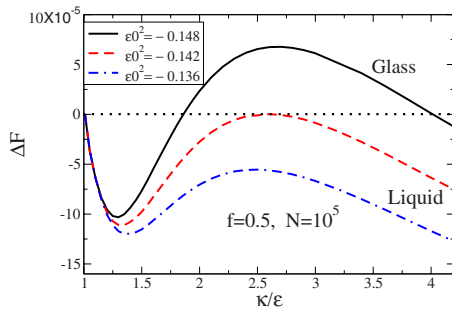


FIG. 1. (Color online) The solution for the self-consistent equation, Eq. (19), for different (ε_0^2) in the case $f=0.5$ and $N=10^5$. ΔF is defined as $-\frac{1}{\mathcal{Z}(1)} \int \frac{d\lambda}{\sqrt{2\pi\mathcal{C}}} e^{-\lambda^2/2\mathcal{C}} \Omega(\lambda) \log \Omega(\lambda) (\mathcal{C}^{-1} \langle \phi \rangle_{\lambda} + \langle \phi^2 \rangle_{\lambda}) - \frac{q_0}{2\pi} \left(\frac{1}{\varepsilon} - \frac{1}{\kappa} \right)$.

TABLE I. The coefficients for the rescaled higher vertex terms for different composition value f .

f	x^*	$N\Gamma_4(0,0)^a$	Nu	$N\Gamma_3^b$	Nv
0.1	2.36	28035.0	410.89	-1297.03	-929.4
0.2	2.11	2098.99	98.94	-182.31	-92.77
0.3	2.01	499.18	43.22	-55.32	-23.43
0.4	1.96	212.22	25.91	-18.81	-6.60
0.5	1.95	156.56	21.57	0	0

^aReference [1].

^bReference [2].

III. RESULT

The coefficients of the cubic and the quartic terms, Γ_3 and Γ_4 , for diblock copolymer melts are listed in Table I. The coefficients for the rescaled higher vertex terms for different composition value f are listed in Table I.

By solving the self-consistent equation, Eq. (19), we can determine a critical bare mass $(\varepsilon_0^2)_A$ for dynamical self-arrest which indicates that the glassiness has set in.

For instance, Fig. 1 shows the nontrivial solutions for $f=0.5$, $N=10^5$, and $u/q_0=1.177 \times 10^{-2}$ with different (ε_0^2) . We find there is only one solution for a critical glassiness, no solution for a liquid phase, and two nontrivial solutions for the glass phase. The critical nontrivial solution for dynamical self-arrest is found at $(\varepsilon_0^2) = -0.142$. Then, $(\chi N)_A$ can be obtained from the relation of $(\varepsilon_0^2)_A = \frac{f^* - 2(\chi N)_A}{f^* - x^*}$ for the onset of dynamical self-arrest of diblock copolymer melts [i.e., $(\chi N)_A = 12.45$]. Also, we find $\varepsilon_A = 0.132$ from the solution of Eq. (18) and $\kappa = 0.361$ from Fig. 1 ($\kappa/\varepsilon \sim 2.6$). In this manner, we can find all the nontrivial solutions for dynamical self-arrest of diblock copolymer melts for different chain length. Figure 2 shows $(\chi N)_A$ vs degree of polymerization number N for the lamellar phase. $(\chi N)_A$ is obtained from the critical nontrivial solution for dynamical self-arrest of the lamellar phase. The line corresponds to a fit of the nontrivial critical solution. It provides a universal value $[(\chi N)_A \sim 10.5 + 64N^{-3/10}]$ for a symmetric chain over a wide range of chain length ($10^2 - 10^7$). The transition to dynamical self-arrest is compared to the Brazovskii-Helfand-Fredrikson transition. Figure 3 shows a dynamical self-arrest of diblock copolymer melts depending on chain length for different composition

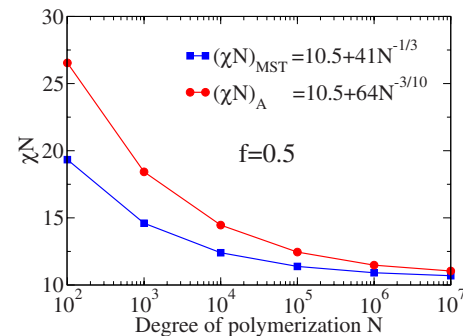


FIG. 2. (Color online) A universal value for the dynamical self-arrest $(\chi N)_A \sim 10.5 + 64N^{-3/10}$ of a symmetric diblock copolymer.

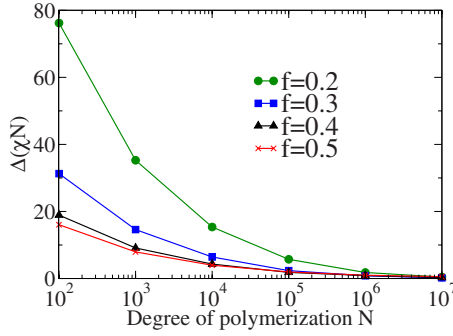


FIG. 3. (Color online) The chain length dependence of dynamical self-arrest for a diblock copolymer of different composition value f .

value f . $\Delta(\chi N)$ is defined as $\Delta(\chi N) = (\chi N)_A - (\chi N)_S$, a measure of $(\chi N)_A$ with respect to spinodal decomposition [12].

Our local replica calculation shows $(\chi N)_A$ tends to converge to $(\chi N)_S$, when the degree of polymerization N goes to ∞ . For a block copolymer melt with large chain length ($\sim 10^7$) and $f=0.5$, $(\chi N)_A=0.54$, as compared to ~ 0.28 in perturbation theory [12]. We expect these two $(\chi N)_A$ values from the different approaches would merge to one as the chain length increases ($\gg 10^7$).

Moreover, these two approaches show the same power law for chain length dependence ($N^{-3/10}$ for the symmetric chain [12]). As we expect, our result is compatible with the perturbation result for large and symmetric chains. However, it shows quite different features from the perturbative result for an asymmetric block copolymer melt, in which $\Delta(\chi N)$ takes on a negative value for the asymmetric chain ($f=0.3$) at chain length of 10^5 [12]. However, $\Delta(\chi N)$ based on a local replica approach exhibits a non-negative value for the entire composition value $f(0.2-0.5)$ and chain length $N(10^2-10^7)$.

Strikingly, we found that there exists a crossover region in which $(\chi N)_A$ for a symmetric chain becomes larger than the $(\chi N)_A$ for an asymmetric chain depending on chain length. $(\chi N)_A$ for an asymmetric chain is larger than $(\chi N)_A$ for a symmetric chain at the chain length of 10^4 (shown in the uppermost curve in Fig. 4). As chain length increases and reaches a certain value, N^* , however, $(\chi N)_A$ for $f=0.5$ becomes even larger than $(\chi N)_A$ for the asymmetric case.

Figure 5 clarifies the crossover region. $(\chi N)_A$ for $f=0.5$ is larger than the $(\chi N)_A$ for $f=0.4$ at the chain length of

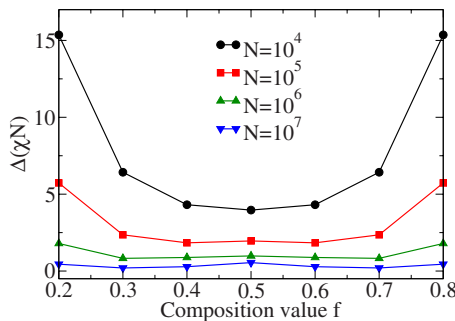


FIG. 4. (Color online) $\Delta(\chi N)$ vs composition value f for different chain lengths.

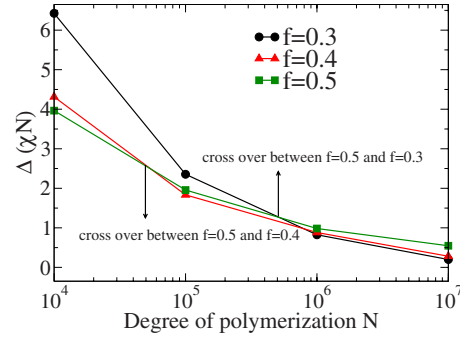


FIG. 5. (Color online) The crossover of $\Delta(\chi N)_A$ for symmetric chain and asymmetric chain at specific chain length. For $f=0.4$, the crossover value in the chain length, N^* , is approximately 5.1×10^4 and for $f=0.3$, approximately 5.1×10^5 .

$\sim 5.1 \times 10^4$ and $f=0.3$ at $\sim 5.1 \times 10^5$. The cubic term that originates from asymmetry ($f \neq 0.5$) contributes greatly to the stabilization of the glassy phase in the diblock copolymer melt as it does in the Brazovskii class [9]. However, asymmetry of the block copolymer melt also increases the magnitude of the quartic term simultaneously, as shown in Table I, which provides an additional entropy with the diblock copolymer melt. Presumably, this entropy drives the diblock copolymer melt to escape from a local minimum. Thus, additional entropy works against the stability of the glassy state and so the system recovers to the liquid state. Interestingly, the competition between the cubic (stabilizing the glassy state), $v/q_0^{3/2}$, and quartic (destabilizing the glassy state) term, u/q_0 , determines the overall stabilization of the diblock copolymer melt. Additionally, since the rescaled cubic and the quartic terms have chain length dependency, the stability of the glassy state in the diblock copolymer exhibits a sensitive chain length dependence as seen in the crossover region.

IV. CONCLUSION

We have investigated the dynamical self-arrest of a block copolymer melt using a replica approach based on local theory. According to our previous result, the perturbation theory breaks down for extremely small coupling constants u/q_0 and v/q_0 ($\sim 10^{-4}$) [9]. Converting this to polymer language, the perturbation is effective only for $N > 10^9$ for $f=0.5$ [$u=21.57/N$ and $q_0=(6/N)^{1/2}x^*$]. The local replica theory is quite effective in predicting dynamical self-arrest of the block copolymer melts, especially for asymmetric and relatively short chains beyond the perturbation limit. For a more accurate agreement of theory with experimental data, we will need to accommodate the stiffness effect for polymer chains in the diblock copolymer case ($b'/b \neq 1$). The magnitude of the two higher vertex terms will presumably be changed for different chain stiffness, which could play an important role in determining the stabilization of the glassy phase for diblock copolymer melts.

ACKNOWLEDGMENTS

The author would like to thank Dr. J. Schmalian and Dr. L. G. Pedersen for useful discussions.

- [1] L. Leibler, *Macromolecules* **13**, 1602 (1980).
- [2] G. H. Fredrickson and E. Helfand, *J. Chem. Phys.* **87**, 697 (1987).
- [3] S. A. Brazovskii, *Sov. Phys. JETP* **41**, 85 (1975).
- [4] F. S. Bates, J. H. Rosedale, and G. H. Fredrickson, *J. Chem. Phys.* **92**, 6255 (1990).
- [5] T. Ohta and K. Kawasaki, *Macromolecules* **19**, 2621 (1986).
- [6] J. Schmalian and P. G. Wolynes, *Phys. Rev. Lett.* **85**, 836 (2000).
- [7] C. B. Muratov, *Phys. Rev. Lett.* **78**, 3149 (1997).
- [8] H. Westfahl, Jr., J. Schmalian, and P. G. Wolynes, *Phys. Rev. B* **64**, 174203 (2001).
- [9] S. Wu, J. Schmalian, G. Kotliar, and P. G. Wolynes, *Phys. Rev. B* **70**, 024207 (2004).
- [10] The subscript A in the $(\chi N)_A$ means the onset of dynamical self-arrest.
- [11] A. J. Bray, *Phys. Rev. Lett.* **32**, 1413 (1974).
- [12] C. Z. Zhang and Z. G. Wang, *Phys. Rev. E* **73**, 031804 (2006).
- [13] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, *Rev. Mod. Phys.* **68**, 13 (1996).
- [14] S. F. Edwards and P. W. Anderson, *J. Phys. F: Met. Phys.* **5**, 965 (1975).
- [15] V. Dotsenko, *An Introduction to the Theory of Spinglasses and Neural Networks* (World Scientific, Singapore, 1994).
- [16] M. Mézard and G. Parisi, *Phys. Rev. Lett.* **82**, 747 (1999).
- [17] R. Monasson, *Phys. Rev. Lett.* **75**, 2847 (1995).
- [18] G. Parisi, *J. Phys. A* **13**, 1101 (1980).
- [19] D. Vollhardt, in *Correlated Electron System*, edited by V. J. Emery (World Scientific, Singapore, 1993).
- [20] G. Baym, *Phys. Rev.* **127**, 1391 (1962).