Correlations in Block Copolymers under Shear

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Introduction

Nonequilibrium methods for predicting the structural evolution and flow behavior of multicomponent, multiphase block copolymeric systems under realistic processing conditions are much less developed compared to their equilibrium counterparts. The main complications in the context of block copolymers arise from the fact that a dynamical description requires one to account for the explicit coupling between the single-chain dynamics and the accompanying evolution of the mesoscopic inhomogeneous density fields. One popular approximation to address this coupling invokes a *local equilibrium assumption* for the concentration fields.[1−3] In such a framework, it is assumed that the chain conformations relax instantaneously to an equilibrium value corresponding to the prevailing inhomogeneous concentration field. The evolution of the concentration fields is then assumed to be determined by a balance between the flow and a "local equilibrium" chemical potential. This technique has been employed in a variety of different contexts to address the shear-induced ordering,[2] structure factors under shear,[1] dynamics of spinodal decomposition of block copolymers, etc.[4]

Despite the success of the above approach, issues pertaining to chain stretching effects cannot be directly addressed by such methods.[1] Such viscoelastic effects have been demonstrated to be of importance in polymer solutions and blends, as well as in the contexts of block copolymers with more complicated molecular architectures.[5] The focus of this note is to probe the utility of a different approximation to address the influence of the chain dynamics on the self-assembly and structure of block copolymers. In the present model, we assume that *the chain conformations are in a steady state corresponding to the applied flow field* and utilize the anisotropic conformational characteristics of the chain (arising from a balance of the elasticity and the applied flow field) to discern the mesoscopic compositional features of the block copolymer. In this note we utilize this idea in conjunction with the random phase approximation (RPA) to derive and discuss the structure factor $S(\mathbf{q})$ and the characteristics of the ODT of a symmetric incompressible diblock copolymer melt under shear. Many earlier studies have successfully employed RPA to study both the static, dynamic structure factors and the ODT of diblock and multiblock copolymers.[6,7] In essence, the framework of RPA allows one to relate the structure factor $S(\mathbf{q})$ of the system of interacting block copolymer chains to the structure factor $S^0_{ij}(\mathbf{q})$ ($i, j = A, B$) of ideal, noninteracting chains. The latter quantities are typically computed by employing a microscopic model for the elasticity of the chains. Knowledge of the structure factor $S(\mathbf{q})$ enables one to analyze the stability of the homogeneous phase as well as the fastest growing unstable modes. In this note, our objective is to employ a similar idea to compute the structure factor $S(\mathbf{q})$ for a diblock copolymer under shear. Within the framework of a local steady-state assumption, this exercise involves the computation of the above correlation functions $S^0_{ij}(\mathbf{q})$ for the case of ideal, noninteracting chains *under shear* (cf. ref 8 for a similar approach, albeit in an equilibrium context). In the next section, we outline the results of such an exercise for both the case of Rouse and reptation models. To maintain brevity, we do not expound upon the details of the calculations, which are relatively straightforward. Subsequently, we discuss the physical implications of our results and some possible experimental consequences. To maintain the simplicity of the discussion, we restrict our analysis and the numerical results to a symmetric diblock copolymer in a simple shear of the form $(v_x, v_y, v_z) = (\dot{\gamma}z, 0, 0)$.

Analytical Expressions for $S^0_{ij}(\mathbf{q})$

Within the framework of RPA, the structure factor $S(\mathbf{q})$ is given by

$$S(\mathbf{q}) = W(\mathbf{q})/[\tilde{S}(\mathbf{q}) - 2\chi W(\mathbf{q})] \tag{1}$$

where χ denotes the Flory−Huggins interaction parameter, and

$$\tilde{S}(\mathbf{q}) = S^0_{AA}(\mathbf{q}) + S^0_{BB}(\mathbf{q}) + 2S^0_{AB}(\mathbf{q}) \tag{2}$$

and

$$W(\mathbf{q}) = S^0_{AA}(\mathbf{q})\, S^0_{BB}(\mathbf{q}) - (S^0_{AB})^2(\mathbf{q}) \tag{3}$$

In the above equations, $S^0_{ij}(\mathbf{q})$ denote the correlation functions of the ideal noninteracting chains. In this section, we outline the analytical expressions for $S^0_{ij}(\mathbf{q})$ arising as a result of analyzing Rouse and reptation models. As a preliminary to the analytical expressions, we express $S^0_{ij}(\mathbf{q})$ in terms of monomer correlation functions $\hat{S}^0_{ij}(\mathbf{q}, s, s')$ as (in units wherein the monomer indices are normalized by N)

$$S^0_{ij}(\mathbf{q}) = N^2 \int_0^1 ds \int_0^1 ds'\, \alpha_i(s)\, \alpha_j(s')\, \hat{S}^0_{ij}(\mathbf{q}, s, s') \tag{4}$$

where $\alpha_p(s)$ enforces the identity of the component (set appropriately to 0 in the different blocks of the chain, that is, $\alpha_A(s) = 1$, $0 < s < f$, etc.). In both the Rouse and the reptation models the monomer correlation functions, $\hat{S}^0_{ij}(\mathbf{q}, s, s')$ can be written as

$$\hat{S}^0_{ij}(\mathbf{q}, s, s') = \exp[-{}^1/_2 \mathbf{q}\cdot\sigma(s, s')\cdot\mathbf{q}] \tag{5}$$

For the Rouse model, a standard normal-mode analysis[9] can be effected to yield the following expressions (in length units nondimensionalized by $N^{1/2}b$):

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$$\sigma_{xx}(s,s') = \frac{|s-s'|}{3} + \frac{\pi^4(\dot{\gamma}\tau_1)^2(5(s+s')(s+s'-2)[s(s-1)+(s'-1)s'] + |s-s'|^3)}{720} \quad (6)$$

$$\sigma_{xz}(s,s') = \frac{\dot{\gamma}\tau_1\pi^2(s-s')^2[3(2-s-s')(s+s') - 2|s-s'|]}{144} \quad (7)$$

In the above equation $\tau_1 = 2N\zeta R_g^2/\pi^2 k_B T$ denotes the relaxation time of the first Rouse mode.

For the case of entangled polymers, it is more appropriate to employ the reptation model.[9] In this work, we utilize a simple version of the Doi−Edwards reptation model. Within this framework, the components of the tensor $\boldsymbol{\sigma}(s,s')$ are given by (D_* denotes the diffusivity of the chain along its contour)

$$\sigma_{xx}(s,s') = \frac{|s-s'|}{3} + \frac{(\dot{\gamma}\tau_r)^2\pi^4(5|s^2-s'^2| - 5|s^4-s'^4| + 2|s^5-s'^5|)}{2560} \quad (8)$$

$$\sigma_{xz}(s,s') = \frac{\dot{\gamma}\tau_r\pi^2|s-s'|[3(2-s-s')(s+s') - (s-s')^2]}{96} \quad (9)$$

wherein $\tau_r = 9\pi^2 R_g^2/4D_*$ denotes the time scale for reptation motion. The correlations in other directions are unaffected by shear and are identical in both the Rouse and the reptation models:

$$\sigma_{yy}(s,s') = \sigma_{zz}(s,s') = \frac{|s-s'|}{3} \quad (10)$$

and $\sigma_{xy}(s,s') = \sigma_{yz}(s,s') = 0$.

Validity of the RPA

Our discussion in this note has focused on the use of eq 1, the random phase approximation, for steady-state conditions resulting in the presence of an external flow. However, the random phase approximation is usually presented in the context of linear response theories and for small deviations from equilibrium.[10] Consequently, it is natural to query whether indeed such an approximation can be employed for steady-state flow situations and, if so, the regime of shear rates in which it is appropriate. A rigorous approach to answer this question has been laid out in the work of Fredrickson and Helfand, which employed a Martin−Siggia−Rose generating functional formalism to deduce the hydrodynamical effects on the dynamical correlation functions of polymer solutions.[11] We have effected an analysis along their lines (details omitted to preserve brevity) to discern that the dynamical RPA (as we have employed it) is valid as long as the single chain dynamical correlation and response functions are still related by the fluctuation dissipation theorem (FDT). In the presence of shear one can indeed confirm that the FDT is no longer exactly valid. However, an order of magnitude analysis suggests that the deviations from FDT are insignificant as long as the shear rate $\dot{\gamma}\tau_R \lesssim 1$, where

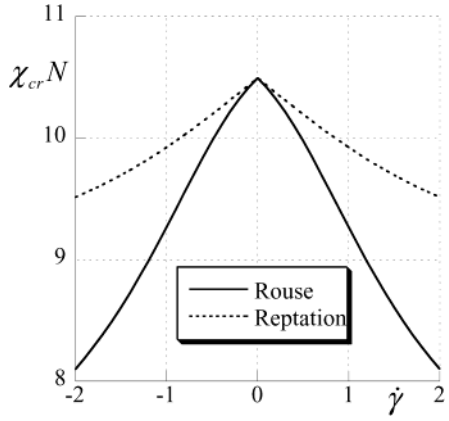

Figure 1. Critical temperatures of instability $\chi_{cr}N$ for Rouse and reptation models. τ_x denotes the characteristic relaxation time and represents τ_1 for the unentangled polymers (Rouse model) and τ_r for entangled polymers (reptation model).

τ_R is the characteristic relaxation time of the polymer. In situations wherein the shear rate is small enough for the preceding condition to hold, the RPA approach can be expected to be a reasonable approximation.

Numerical Results and Discussion

In this section, we discuss the physical implications of the results derived by a numerical evaluation of the quadratures involved in the expressions (eq 4).

The main focus of this note is to discern the manner in which chain stretching influences the spinodal temperature of the block copolymer. The mean-field ODT of the block copolymer corresponds to the critical temperature at which the value of the structure factor diverges for atleast one wave vector (the critical wave vector denoted as $\mathbf{q}^*$). Figure 1 displays the critical temperatures $\chi_{cr}N$ of this instability as a function of the shear rate $\dot{\gamma}$ for both the Rouse and reptation models. As one might expect, the critical temperature turns out to be an even function of the shear rate $\dot{\gamma}$ but, somewhat surprisingly, is *not an analytical function* at $\dot{\gamma} = 0$. This result can however be explained by considering the shear dependence of the critical wave vector $\mathbf{q}^*(\dot{\gamma})$. In the absence of shear, the structure factor $S(\mathbf{q})$ calculated from the above expressions (both Rouse and reptation models reduce to the same expression in the absence of shear) exhibits a spherical symmetry (displayed in Figure 2a), and consequently, the wave vector of the spinodal instability $\mathbf{q}^*(\dot{\gamma}=0)$ also exhibits a spherical degeneracy. In the presence of shear, however, this symmetry is destroyed (as is depicted in Figure 2b,c), and consequently one might expect that the wave vector corresponding to the spinodal instability also acquires a nontrivial phase angle. Figure 3a,b displays the magnitudes and the directions of this wave vector (in the XZ plane) as an explicit function of the shear rate for both Rouse and reptation models. As is evident, an infinitesimal shear breaks the isotropy of $\mathbf{q}^*$ and picks out the wave vector corresponding to an angle of $\pm\pi/4$ for a shear $\dot{\gamma} = \pm 0$. This result physically corresponds to the orientation of the chains at an angle of $\pi/4$ under the action of an infinitesimal shear. A reversal of the direction of the flow leads to an orientation orthogonal to the previous direction. Such an asymmetric destruction of the spherical degeneracy manifests in the nonanalytical dependence of the critical temperature $\chi_{cr}N$. The angle of the critical wave vector subsequently decreases as a monotonic function of the shear rate as

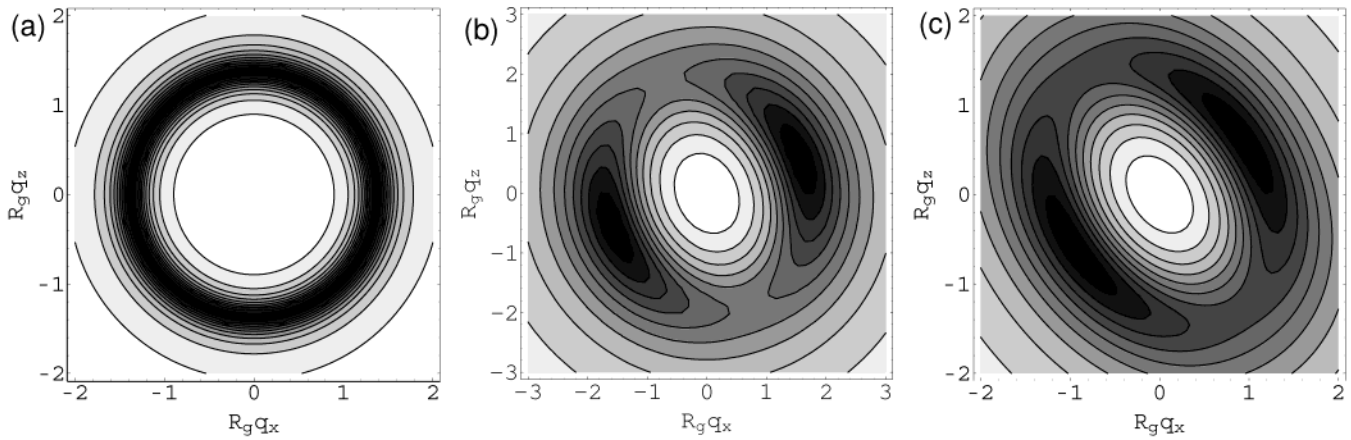

Figure 2. Structure factor $S(\mathbf{q})$ for (a) $\dot{\gamma} = 0$; (b) $\dot{\gamma}\tau_1 = 1$, $\chi N = 7.5$ for the Rouse model; and (c) $\dot{\gamma}\tau_r = 1$, $\chi N = 7.5$ for the reptation model.

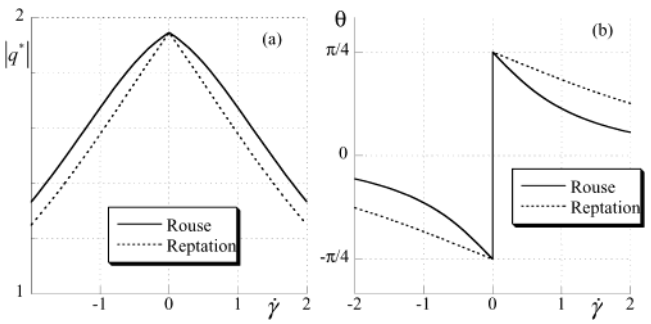

Figure 3. (a) Magnitude and (b) phase angle of the critical wave vector $\mathbf{q}^*$, for both Rouse and reptation models. θ is the angle between $\mathbf{q}^*$ and the direction of the flow (x-axis).

a result of the stretching and orientation of the chains along the plane of the shear.

It is of interest to discuss the nature of the above-determined critical temperature and its possible experimental consequences. In the absence of shear, the critical temperature is usually interpreted as a spinodal or a critical point (RPA by itself cannot distinguish between first- and second-order phase transitions) with the critical wave vector $\mathbf{q}^*$ representing the wave vector of the fastest growing fluctuation mode.[6] In the absence of shear, the latter further serves to define the wavelength of the long-range ordered structure resulting below the ODT (corresponding to a lamellar phase for the symmetric diblock copolymer). Our analysis in this note was motivated by the hypothesis that, near the critical point (or spinodal) wherein the susceptibility is very large, even weak shear flows should have a substantial effect on the collective structure factor. The results displayed in Figure 3 confirm such speculations by indicating that, in the presence of shear, there exists a critical temperature $\chi_{cr}N$ below which the chain stretching effects can lead to an instability in the directions corresponding $q^{(x)}$, $q^{(z)} \neq 0$, which arises from the stretching and orientation of the chains due to the flow. However, in the presence of a simple shear flow, all long-range fluctuations and correlations in the direction of flow are convected by the flow, and consequently, the only long-ranged ordered structures that can survive correspond to those with wave vectors homogeneous in the direction of flow, that is, with $q^{(x)} = 0$. Therefore, while the instability of the homogeneous phase usually signals microphase segregation, the instabilities predicted in the present situation do not correspond to long-range order. In fact, in the present approximation, the fluctuations with $q^{(x)} = 0$ are unaffected by shear and become unstable at a temperature identical to the critical temperature in the absence of shear, and consequently, the mean-field ODT, namely, the temperature at which the first signatures of long-ranged order appears, is not altered by the shear flow. Therefore, our results suggest that the stretching effects caused by the shear flow can lead to instabilities (that do not lead to long-range order) that can *amplify* the density fluctuations in some directions with $|\mathbf{q}^*| \approx R_g^{-1}$ (the magnitudes and the phase angles of which are displayed in Figure 3), such that, upon reducing the temperature below $\chi_{cr}N$, the intensity corresponding to the unstable mode $\mathbf{q}^*$ would grow in time in a manner reminiscent of a spinodal decomposition.

It is of interest to stress the connection of our work to other studies addressing similar issues. Other works have also unearthed qualitatively similar shear-induced enhancements in fluctuations in the context of polymer solutions. However, these effects (known as a Reynolds effect) arise as a result of the concentration dependence of the viscosity.[12,15] In contrast, the instabilities predicted in our research arise from the orientation and stretching of the chains and its coupling to the shear flow. The approximation and the method of analysis we have employed are qualitatively different from the approach adopted in many other works analyzing the effect of shear on the structural characteristics of block copolymers.[1,2] Most of those approaches adopt the local equilibrium assumption which enables one to start from a mesoscopic Landau−Ginzburg like diffusion equation with an appropriate convection term and in effect considers the effect of convection and suppression of density fluctuations by the flow field (such an effect is commonly termed as a Maxwell effect) for situations wherein the chain conformations relax instantaneously to their equilibrium statistics corresponding to the fluctuating concentration fields (extensions to include other slow variables have also been proposed; cf. for instance, ref 15). In terms of the results, three main features distinguish the present research from the conclusions of the previous studies: (i) The incorporation of chain stretching effects is shown to lead to an increase in fluctuations in some directions (Figure 3). This contrasts with the conclusions of the previous works (at the same level of approximation), wherein shear flow is predicted to only suppress fluctuations. (ii) The local equilibrium approximation predicts that the spinodal is unchanged (in the second-order non-Hartree

approximation) in the presence of shear flows. In contrast, the present approach predicts that the chain stretching effects can lead to a modulation of the spinodal (albeit see the discussion in the following paragraph). However, as pointed out earlier, these instabilities do not correspond to the occurrence of long-range order. (iii) In our analysis, the shift in the maximum value of $S(\mathbf{q})$ can be shown to be an increase, with a magnitude proportional to $|\dot{\gamma}|$ at small shear rates (as is also visible in the nonanalyticity of results in Figure 1). In contrast, local equilibrium approaches predict a decrease in the scattering intensity (i.e., a suppression of fluctuations) for all wave vectors except $q^{(x)} = 0$, with a magnitude proportional to $\dot{\gamma}^2$.

While our discussion focused exclusively on the shear-induced chain stretching and its effects on the correlations under shear, experimental situations are expected to involve an interplay between the stretching-induced increase in fluctuations (predicted in this note) and the convection-induced suppression of fluctuations (arising in local equilibrium approximations). A rigorous way to incorporate features representative of both approximations and also clarify the distinction between the different approaches would be to implement a projection operator analysis to project out the appropriate slow variables in the different limits.[16,17] We plan to undertake and present the details of such efforts (along with the exact results of the dynamical field theory approach employing the Martin−Siggia−Rose formalism) in a future publication. However, even in the absence of such analyses, it is possible to offer some speculative arguments at a qualitative level. It is evident that in the absence of interactions ($\chi = 0$) our results are exact, and there is an increase in collective density fluctuations arising from the shear-induced stretching effects. To consider the combined influence of shear and interactions, let us choose a representative wave vector, say $\mathbf{q}'$, whose scattering amplitude is predicted to diverge in our analysis at χ'. To render the divergence of $S(\chi,\mathbf{q}')$ explicit, let us at the outset consider the functional form of $S(\chi,\mathbf{q}')$ in relation to the equilibrium spinodal temperature $\chi^0_{cr} \equiv \chi_{cr}(\dot{\gamma}=0)$. If we restrict our analysis to small shear rates, it is evident from Figure 1 that $\chi' \sim \chi^0_{cr} - C|\dot{\gamma}|$, where C denotes a constant. Therefore, in the regime near χ^0_{cr}, the scattering function $S(\chi,\mathbf{q}')$ can be written as $S(\chi,\mathbf{q}') \sim (\chi^0_{cr} - \chi)^{-1}(1 + C(\chi^0_{cr} - \chi)^{-1}|\dot{\gamma}|)$. This expression reiterates the main claim of this research and suggests that, in the proximity of χ^0_{cr} wherein the susceptibility is very large, even weak shear flows could render the chain stretching effects substantial and lead to an increase in the collective structure factor $S(\chi,\mathbf{q}')$. However, to incorporate the effects predicted in the local equilibrium approximations, note that the imminent divergence of this stretching-induced fluctuations also leads to a corresponding increase in the relaxation time of the fluctuations (due to the critical retardation effects) and therefore to an enhancement in the role of shear in convecting and, hence, suppressing such fluctuations. Indeed, when the collective relaxation time $\tau(\mathbf{q}')$ increases to a magnitude such that $\dot{\gamma}\tau(\mathbf{q}') > 1$, the shear-induced Maxwell effect kicks in to convect and suppress the density fluctuations.[1] Therefore, the following behavior is expected to result due to the interplay between the Maxwell effect and the shear-induced stretching effects: For wave vectors $\mathbf{q}^*$ (displayed in Figure 3a,b), the collective density correlations are expected to be enhanced at small shear rates (defined by $\dot{\gamma}\tau(\mathbf{q}^*) < 1$) and/or sufficiently far from the critical temperature $\chi_{cr}(\mathbf{q}^*)$, due to the stretching effects induced by the shear. On the other hand, at higher shear rates and/or closer to the spinodal temperature $\chi_{cr}(\mathbf{q}^*)$, the critical retardation effects render the Maxwell effects dominant and consequently suppress the fluctuations and thereby prevent the divergence of the structure factor $S(\mathbf{q}^*)$. Therefore, under the combined influence of stretching and convection of fluctuations, we expect that the spinodal temperature to be unchanged from its mean-field value χ^0_{cr} but however expect that the scattering functions to show some interesting, nonmonotonic behavior as a function of shear rate and temperature. In addition to the effect on the static structure factor, we also expect that such occurrence would influence and broaden the regime of pretransitional fluctuations.[14] It is to be cautioned that the above arguments are at a mean-field level and do not include the effects of self-consistent Hartree fluctuations. Therefore, the above reasoning should at best be viewed as speculative but one that we hope will nevertheless spur appropriate experiments.

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References and Notes

(1) Fredrickson, G. H. *J. Chem. Phys.* **1986**, *85*, 5306.
(2) Cates, M. E.; Milner, S. T. *Phys. Rev. Lett.* **1989**, *62*, 1856.
(3) Fraaije, J. G. E. M. *J. Chem. Phys.* **1993**, *99*, 9202.
(4) Qi, S. Y.; Wang, Z. G. *Phys. Rev. Lett.* **1996**, *76*, 1679.
(5) Viglid, M. E.; et al. *Macromolecules* **2001**, *34*, 951.
(6) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(7) Erukhimovich, I. Ya.; Semenov, A. N. *Sov. Phys. JETP* **1986**, *28*, 149. Semenov, A. N.; et al. *Macromolecules* **1997**, *30* 6280.
(8) Gurovich, E. *Phys. Rev. Lett.* **1995**, *74*, 482.
(9) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986.
(10) Hansen, J.-P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press: San Diego, 1986.
(11) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1990**, *93*, 2048.
(12) Bruinsma, R.; Rabin, Y. *Phys. Rev. A* **1992**, *45*, 994.
(13) Pistoor, N.; Binder, K. *Colloid Polym. Sci.* **1988**, *26* 132. Qiu, F.; et al. *J. Chem. Phys.* **1998**, *108*, 9529. Luo, K. F.; Yang, Y. L. *J. Chem. Phys.* **2001**, *115*, 2818.
(14) Barrat, J. L.; Fredrickson, G. H. *J. Chem. Phys.* **1991**, *95*, 1281.
(15) Helfand, E.; Fredrickson, G. H. *Phys. Rev. Lett.* **1989**, *62*, 2468. Milner, S. T. *Phys. Rev. Lett.* **1991**, *66*, 1477.
(16) Kawasaki, K.; Sekimoto, K. *Physica* **1987**, *143*, 349.
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