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Computer Simulation of Copolymer–Copolymer and Copolymer–Homopolymer Mixtures with a Single Interaction Energy

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ABSTRACT: Interactions in copolymer–homopolymer (A_xB_{1-x}/B) and copolymer–copolymer (A_xB_{1-x}/A_yB_{1-y}) mixtures containing equal amounts of the two respective components were studied as a function of the copolymer compositions x and $|x - y|$, respectively, and of segmental interaction energies using computer simulations of chains on a planar square lattice. The effective interaction parameter χ_{blend} for regimes corresponding to miscibility was less strongly dependent on x (or $|x - y|$) than predicted by the mean-field square power rule, and the number of heterocontacts varied widely from that calculated by random mixing. In the immiscibility regime, the effective χ_{blend} becomes asymptotic as a result of phase separation.

Introduction

Numerical simulations of binary mixtures of homopolymers in either two[1,2] or three[3] dimensions have yielded considerable microscopic information on equilibrium lattice conformations and have permitted examination of the deviations from the mean-field treatment usually applied to such polymer blends. Such computer simulations can readily be performed for a range of interaction energies and have demonstrated effects of mixing, segregation, hole formation, etc., as a function of this parameter.[1-3]

Mixtures of random or near-random copolymers which have received substantial experimental investigation,[4-8] offer an opportunity of examining the effect of additional degrees of freedom in composition and in microsctructure

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and show effects that are peculiar to such systems. For example, it is known that if the intramolecular repulsive interactions between unlike moieties in a statistical copolymer are sufficiently large relative to the intermolecular interactions in the system, a miscible domain may appear for a range of copolymer compositions, even if all the segmental interactions in the system are repulsive. This effect was recognized early[4,5] and has been incorporated more recently into generalized mean-field Flory–Huggins (FH) treatments for copolymer containing blends.[7,8] These treatments are useful for the interpretation of results for a variety of binary and higher homopolymer/copolymer and copolymer/copolymer systems and with some modification and additional complexity can be extended to include the effect of deviations from random placements in the constituents of the mixtures, i.e., to take into account the microstructures of the respective chain(s).

This paper is concerned with the simplest possible case of copolymer blends, those which require the specification of only one type of interaction. This class includes the mixture of a homopolymer with a copolymer having one segment identical with that of the homopolymer (here denoted A_xB_{1-x}/B), and a mixture of two copolymers containing the same segments but of different compositions (denoted A_xB_{1-x}/A_yB_{1-y}). In the mean-field treatment, the thermodynamics of these systems is described by the well-known relations[4]

$$\Delta G/RT = (\phi_1/n_1)\ln\phi_1 + (\phi_2/n_2)\ln\phi_2 + \chi_{\mathrm{blend}}\phi_1\phi_2 \quad (1)$$

where

$$\chi_{\mathrm{blend}} = (x-y)^2\chi_{AB} \quad \text{for the } A_xB_{1-x}/A_yB_{1-y} \text{ system} \quad (2)$$

and

$$\chi_{\mathrm{blend}} = x^2\chi_{AB} \quad (3)$$

for the limiting case of the A_xB_{1-x}/B system. Here ΔG is the free energy of mixing per unit volume, in our case per one lattice site; n_1 and n_2 are respectively the number of segments per chain of components 1 and 2 of either segment A or segment B occupying one lattice site in the mixture; and χ_{blend} is the net interaction parameter for the blend, χ_{AB} being the segmental interaction parameter for the A/B blend. The phase behavior is in effect determined by the usual critical condition for χ_{blend}, i.e.,

$$\chi_{\mathrm{blend}} = \chi_c = 2/n \quad (4)$$

for the case of systems with equal numbers of segments per chain n of the two components. Comparing eq 2 or 3 with eq 4, it can be seen that there is a finite compositional difference $|x-y|_{\max}$ in the copolymer/copolymer case or a finite value $x_{\max}$ for A in the A_xB_{1-x}/B system which cannot be exceeded to retain miscibility, for given positive values of χ_{AB} and n. A characteristic feature of a copolymer–copolymer mixture in this approximation is that the miscibility is a function only of the difference in the composition $|x-y|$ and not of the absolute value of x or y. Both kinds of systems have been extensively investigated in this laboratory. For example, the study of mixtures of chlorinated polyethylene with components of different degrees of chlorination[9] showed the predicted maximum compositional difference and that the observed UCST (upper critical solution temperature) increased with increasing $|x-y|$ as required. Among the extensive studies of blends formed with halogenated polystyrenes, the present work is related to experiments carried out with blends (for example) of polystyrene with random copolymers of poly(styrene-*co*-*p*(*o*)-fluorostyrene)[10] or poly(styrene-*co*-*p*(*o*)-bromostyrene).[11] Thus, in the latter mixture, copolymers of *o*-bromostyrene and styrene containing over 36 mol % *o*-bromostyrene exhibited phase separation. Similarly copolymers of *p*-bromostyrene and styrene with a *p*-bromostyrene content of over 18 mol % *p*-bromostyrene were found to be immiscible with polystyrene at 200 °C.

A more complete theoretical model for describing polymer mixtures also contains a free volume term in addition to the interaction and entropy of mixing terms introduced in eq 1. In the present computer simulation study, we include a fixed fraction of unoccupied lattice sites (holes) and hold the segment volumes and chain lengths constant for both components; this permits the investigation of the effect of the segment interactions separately. In this way also, we restrict ourselves to systems exhibiting UCST behavior. The main focus in this study is the calculation of how the interactions are propagated in these mixtures without resorting to a mean-field approximation. We note also that with computer simulations we may readily study situations not normally attainable experimentally within the miscible and immiscible regimes.

It is noted that simulation calculations of systems containing copolymers inherently consume substantially more computer time than those of homopolymer mixtures. In following the reptation of homopolymer chains during the approach to equilibrium, it suffices to examine interactional changes only at the head and tail segments of the respective chains inasmuch as internal segments of the chain do not contribute to energy changes. In contrast, during the corresponding reptation of copolymer chains, energy changes may occur with respect to any segment along the chain. The present study, to our knowledge, presents the first numerical results obtained using reptation of copolymer chains in binary mixtures.

In spite of the growing number of off-lattice or continuum numerical studies,[12,13] lattice-based models[14-16] still provide a good approximation for the study of equilibrium thermodynamic behavior, which includes long-distance configurational properties of the chains. The simplicity of the treatment of the chains on a lattice is especially valuable for studying dense multichain systems. Although there are known to be some quantitative differences between the results obtained on different lattices, qualitative differences are not observed. It is also useful to note that the results on lattices with 90° bond angles correspond to much longer chains with more realistic bond angles.[17]

Theoretical Section

Computational Methodology. Linear statistical AB copolymer 20-segment chains were generated with ideal statistical copolymerization kinetics in a step-by-step procedure. The probability for the next segment in each step to be added into a growing chain was given by a fixed parameter p_1 for A segments and $p_2 \equiv 1 - p_1$ for B segments. These probabilities were held constant during the "copolymerization" and resulted in an assembly of chains of type A_xB_{1-x} with the same average composition x close to p_1 and always exactly specified in the computations. The computations, of course, allowed for the generation of a monodisperse system with each copolymer (or homopolymer) chain containing exactly 20 segments. The computational methodology used has been described in earlier contributions, ref 1–3, and is in major respects similar to other work in this area, ref 12–17.

A binary system of 11 chains of each component was then loaded onto a planar square lattice containing $L \times L$ sites, where $L = 22$. A single lattice site contains either segment A or segment B or a void. During the computation, periodic boundary conditions were imposed. The dimensions of the lattice exceeded the equilibrium end-to-end dimensions of a single chain in all cases. Together with the periodic boundary conditions, this largely suppressed spatial finite size effects. In addition, some of the calculations were carried out using a larger lattice with $L = 44$ (and a total of 88 chains) and yielded results not significantly different from those for which $L = 22$. The equilibrium number of heterocontacts, $\bar{N}_{AB}$, was used as a key descriptor of the thermodynamic state of the system, and these values were obtained with an experimental scatter of about ±5% in the equilibrium values. The initial configuration for the Monte Carlo computation of mixtures was the completely ordered arrangement of parallel chains in an alternating homopolymer/copolymer order. Simulations were also performed for a reference state consisting simply of pure copolymer chains and holes. All mixtures studied contained a 1:1 ratio of the respective components; thus, each component had a concentration, ϕ, in site fraction units of 0.4545. The composition, x or y, of the copolymer chains was the principal parameter varied during the study. The equilibrium thermodynamic properties were obtained as previously described for a binary mixture of homopolymers[1,2] by imposing energetic constraints on the random reptation of the chains until the system attained equilibrium. Typically 4×10^6–1.6×10^7 chain moves were performed depending on the system. Each lattice site was permitted to contain either one segment or zero segments, a single interaction energy, ϵ_{AB}, between A and B segments was counted in the total energy of the system whenever A and B segments occupied adjacent sites, and A–B contact could be either intra- or intermacromolecular. As usual,[12-17] segment–hole interaction energies are ignored in this approximation; the presence of holes, however, affects the entropic contributions in the simulation (see below). Thermodynamic averages were obtained by applying the Metropolis rules[18] to each new configuration; the 9% void space in the system facilitated reptation in this dense, entangled medium. The void concentration was chosen to be consistent with the nature of a dense polymer system and may be compared with void contents used in similar studies, i.e., 0.2 (ref 16) and 0.024 (ref 15). In future work, the effects of varying this parameter will be examined. The equilibrium in the system was established by balancing the entropic contributions arising from the different configurations attained by moving the chains and the applied interactional energy, ϵ_{AB}, contributions. This procedure thus optimizes the free energy in the simulation. Equilibration of each state was preceded by an initial intermixing period during which the interaction energy, ϵ_{AB}, was held equal to zero.

Comparison with Mean-Field Theory. As before, the average number of heterocontacts, $\bar{N}_{AB}$, in the system was computed as the major thermodynamic variable. In actual experimental studies, the variable of primary interest in blends is the quantity χ_{blend} defined by eq 1. The relation between $\bar{N}_{AB}$ and χ_{blend} for copolymer mixtures can be obtained by first considering the binary homopolymer A/B mixture.[1,2] The mean-field interactional term for a given χ_{blend} is given by the product of the concentrations, $\phi_A\phi_B$, and χ_{blend}. In the simulation studies, the average overall number of interactions $\bar{N}_{AB}(\epsilon'_{AB})$ is a function of the reduced energy difference ϵ'_{AB} ($\epsilon'_{AB} = \epsilon_{AB}/kT$). Equating these two representations, we obtain

$$\chi_{\text{blend}}\phi_A\phi_B = \epsilon'_{AB}\bar{N}_{AB}(\epsilon'_{AB})/N \tag{5}$$

where N is the total number of sites in the system. Note that χ_{blend} and $\bar{N}_{AB}(\epsilon'_{AB})$ are free-energy parameters, while ϵ'_{AB} is the energy parameter. With some modification, this analysis can also be used for mixtures of copolymers. However, in the latter case, there are thermodynamic interactions between different A, B monomer units both in the mixture and in the pure copolymer. This implies that a different reference state for mixing properties is required in comparison with that used for homopolymer blends. For the most general case of a binary copolymer blend, represented as A_xB_{1-x}/C_yD_{1-y}, one obtains

$$\begin{aligned}\chi_{\text{blend}}\phi_1\phi_2 = (1/N)\{&\epsilon'_{AB}\bar{N}_{AB} + \epsilon'_{AC}\bar{N}_{AC} + \epsilon'_{AD}\bar{N}_{AD} + \\ &\epsilon'_{BC}\bar{N}_{BC} + \epsilon'_{BD}\bar{N}_{BD} + \epsilon'_{CD}\bar{N}_{CD} - \\ &\phi_1\epsilon'_{AB}(\bar{N}_{AB})_{co,x} - \phi_2\epsilon'_{CD}(\bar{N}_{CD})_{co,y}\}\end{aligned} \tag{6}$$

where the subscripts 1 and 2 designate the respective copolymer components in the mixture, $\bar{N}_{AC}$, $\bar{N}_{AD}$, etc., have definitions analogous with $\bar{N}_{AB}$, and we recall that $\phi_1 + \phi_2 = 0.909$. The first six terms on the right-hand side of eq 6 are accounted for by interactions in the mixture, while the last two negative terms are obtained from the reference state consideration of the pure copolymer (eigher A_xB_{1-x} or C_yD_{1-y}) on a lattice under the same conditions as those used in the mixture. $(\bar{N}_{AB})_{co,x}$ and $(\bar{N}_{AB})_{co,y}$ are, therefore, the number of heterocontacts in the pure copolymer melt at the copolymer compositions x and y, respectively. These terms arising from the pure copolymer are essential for the existence of the "repulsion effect" in the AB/CD system. The general relation 6 reduces in the present case for a mixture of two copolymers with the same monomers but with different copolymer compositions, i.e., A_xB_{1-x}/A_yB_{1-y}, to

$$\chi_{\text{blend}} = (\epsilon'_{AB}/\phi_1\phi_2N)[\bar{N}_{AB} - \phi_1(\bar{N}_{AB})_{co,x} - \phi_2(\bar{N}_{AB})_{co,y}] \tag{7}$$

and for a mixture of a homopolymer and a copolymer with a common segment, i.e., A_xB_{1-x}/B, to

$$\chi_{\text{blend}} = (\epsilon'_{AB}/\phi_1\phi_2N)[\bar{N}_{AB} - \phi_1(\bar{N}_{AB})_{co,x}] \tag{8}$$

Equations 7 and 8 correspond to eq 2 and 3 for the mean-field treatment and are employed below to evaluate χ_{blend} for our mixtures. It is noted also that a principal difference between copolymer mixtures with single interactions as compared to mixtures involving several nonequivalent interactions is that it is not possible to change the sign of χ_{blend} by changing the composition of the copolymer (see eq 2 and 3), as is in principle possible in mixtures with more than one type of interaction.

Results and Discussion

Figures 1 and 2 show the results of calculations of the reduced number of A–B interactions per site, $\bar{N}^{r}_{AB} \equiv \bar{N}_{AB}/N$ and $(\bar{N}^{r}_{AB})_{co,x} \equiv (\bar{N}_{AB})_{co,x}/N$, as a function of the copolymer composition x. Also shown is the calculation corresponding to random mixing based on the relation $N(z - 2)\phi_i\phi_j$ for the number of contacts. In this expression, z represents the coordination number of the lattice (in this case $z = 4$ for a planar square lattice), and i and j are the segmental indexes in the interaction. For a segment belonging to copolymer 1 in the blend, the concentration is given as $\phi_i = \phi_1x$ where x is the content of segment i in the copolymer. For this illustrative calculation, we have chosen two different reduced interactions: $\epsilon'_{AB} = -1$ and $+1$, which according to previous work[1,2] are values that correspond respectively to configurations lying well within the miscible and immiscible regimes in the simple binary A/B mixture. We note that the result for $\epsilon'_{AB} = 0$ is coincident within experimental error for $\epsilon'_{AB} = +1$. First in Figure 1, $(\bar{N}^{r}_{AB})_{co,x}$ is shown for the one-component copolymer A_xB_{1-x} as a function of composition x: this will be the reference state for the mixtures discussed below. Surprisingly, the curve corresponding to unfavorable in-

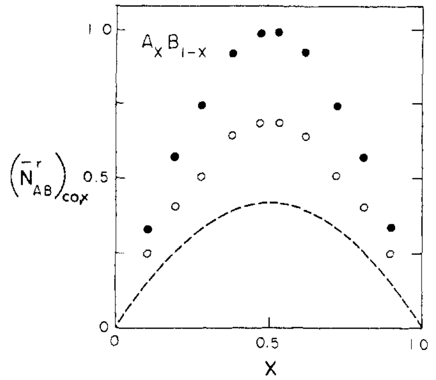

Figure 1. Number of heterocontacts in a pure statistical copolymer (A_xB_{1-x}) melt at two different interactions: $\epsilon'_{AB} = 1$ (○) and −1 (●). The overall site concentration of segments is 0.909. The dashed curve represents athermal random mixing.

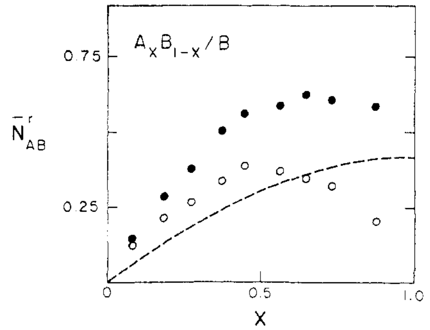

Figure 2. Number of heterocontacts in an A_xB_{1-x}/B mixture containing equal numbers of chains (see text). Symbols are the same as in Figure 1.

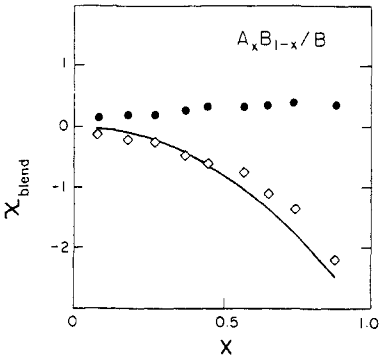

Figure 3. Effective interaction parameter χ_{blend} as a function of composition x of the copolymer in an A_xB_{1-x}/B mixture for $\epsilon'_{AB} = 1$ (●) and −1 (◇). The solid curve is the mean-field prediction for $\epsilon'_{AB} = -1$ using the appropriate value of χ_{AB} from the binary homopolymer mixture.[1,2]

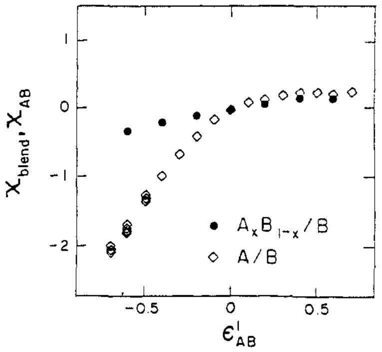

Figure 4. Effective χ_{blend} in the blend A_xB_{1-x}/B at fixed $x = 0.54$ and χ_{AB} in a binary A/B mixture as a function of reduced interaction energy ϵ'_{AB}.

teractions lies above that calculated for random mixing, apparently reflecting the segregation of polymer chains in a two-dimensional system.[1,2] In the absence of an energetic attraction between chains, the chains must segregate from each other in a manner analogous to that shown in athermal systems. In addition, because of this segregation, there is an enhanced probability for intrachain contacts which most probably increases $(\bar{N}^r_{AB})_{co,x}$ above the random value.

Figure 2 shows results for the A_xB_{1-x}/B mixture. Random mixing predicts a continuous increase of $\bar{N}^r_{AB}$ with x as the latter parameter increases from zero to its maximum value at $x = 1$, which represents the A/B mixture. The Monte Carlo results show that $\bar{N}^r_{AB}$ reaches a maximum at $x < 1$. Again this reflects the tendency of the chains to segregate. The curve corresponding to the immiscibility condition $\epsilon'_{AB} = +1$ reaches a definite maximum around $x \simeq 0.5$, reflecting the maximal interaction probability within the copolymer chain. The decrease in $\bar{N}^r_{AB}$ for $x > 0.5$ reflects both the decreasing concentration of B segments in the copolymer chain together with the lowered probability for A segments to form contacts with homopolymer B in an interchain contact. While the results yield useful information about the present two-dimensional system, it should be recalled[19] that in three-dimensional systems strong excluded volume effects do not exist, the chains interpenetrate readily, and the systems follow the mean-field theory more precisely. Thus, as before, the observed propagation of interactions calculated here in effect applies most correctly to polymer monolayers.

The results in Figure 3 are for the effective χ_{blend} as a function of the composition x in an A_xB_{1-x}/B mixture obtained by applying eq 8 to $\bar{N}^r_{AB}$ values obtained for the mixture and $(\bar{N}^r_{AB})_{co,x}$ for the pure copolymer. It can be seen that in the miscibility regime, $\epsilon'_{AB} = -1$, the system follows the square power dependence, eq 3, relatively closely. The solid curve was obtained by using eq 3 with the value of $\chi_{AB} = -3.3$, which corresponds to the χ_{AB} found[1,2] in a binary A/B system of equal chain length at $\epsilon'_{AB} = -1$. The "experimental" curve shows a slightly less steep dependence on the square power rule,[11] which can again be ascribed to the tendency of the chains to segregate. The effect of a change in the copolymer composition parameter x on the interchain parameter χ_{blend} seems to be hindered by the segregation tendency. With an unfavorable interaction, $\epsilon'_{AB} = 1$, the system is nominally immiscible. Large concentration fluctuations are found, and the system obviously cannot follow the random mixing rule; χ_{blend} values therefore attain an asymptotic value. One can observe from relation 8 that χ_{blend} should increase with increasing $\bar{N}^r_{AB}$; however, with demixing, unfavorable contacts are not likely to form, even when changes in the copolymer composition might favor an increase in $\bar{N}^r_{AB}$ simply because of the presence of more A segments. This compensation results in the observed leveling off of χ_{blend} values at higher x.

Figure 4 shows the dependence of χ_{blend} on ϵ'_{AB} for a selected copolymer composition, $x = 0.54$, in an A_xB_{1-x}/B mixture. For comparison, the results for an A/B homopolymer system are also shown. According to eq 3, the values of χ_{blend} should be $1/x^2 \cong 3.4$ times smaller than those of χ_{AB}. It was found that in the miscibility region both χ_{AB} and χ_{blend} decrease with ϵ'_{AB} but that the average ratio is 4.6. In the immiscible region, a leveling off of the χ's occurs due to demixing and eq 3 does not describe the situation accurately.

Figure 5 is analogous to Figure 3 for the system A_xB_{1-x}/A_yB_{1-y}. Again, in the miscible region, the numerical calculations agree with the mean-field square power rule,

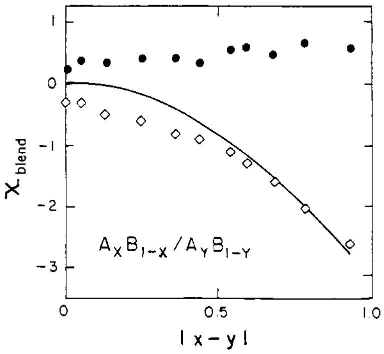

Figure 5. Effective χ_{blend} as a function of the composition difference $|x - y|$ in an A_xB_{1-x}/A_yB_{1-y} system. Symbols are the same as in Figure 3. The solid curve is the mean-field prediction for $\epsilon'_{AB} = -1$ using the same χ_{AB} as in Figure 3.

eq 2, relatively well. In the immiscible region, $\epsilon'_{AB} = 1$, an asymptotic leveling off of χ_{blend} is observed with increasing $|x - y|$. The finite limits observed for χ_{blend} as $|x - y| \rightarrow 0$ for both ϵ'_{AB} values is an artifact that arises from the use of a finite number of copolymer chains used in this calculation, compositional fluctuations around the average value of x or y can remain uncompensated, and the two components can be thermodynamically slightly nonequivalent even for $|x - y| \equiv 0$; hence, a residual finite value of χ_{blend} is observed. The fluctuations become more important for small values of $|x - y|$, and we expect computations for larger systems to agree more closely with the mean-field results especially for small values of $|x - y|$. We would like to emphasize also that only the difference $|x - y|$ has a physical meaning for the mixing properties in this system. Only this variable was systematically changed in the present calculations; the individual x and y values were chosen arbitrarily.

Conclusions

The results for the first computer simulation of a mixture containing copolymers have been presented. Agreement with the mean-field theory was observed in some cases. However, as before, a detailed interpretation of the interaction shows deviation from the random mixing rule; some deviation from mean-field theory originates from the fact that the system considered here is two-dimensional. In a miscible mixture, the present results and the extended FH treatment are in reasonable accord. Close agreement with the square power rules corresponding to eq 2 and 3 was obtained without using the mean-field approximation in a broad composition range usually not covered by experiment. In the immiscible regime with large concentration fluctuations, the interactions do not follow random mixing and relations 2 and 3 are not obeyed. It is important to point out specifically where mean-field treatments begin to fail. Thus, there are examples where the mean-field treatment has been used and random mixing is not guaranteed. A specific example relevant to copolymer blends is the A_xB_{1-x}/C system containing a miscibility window due to an A–B repulsion. Here the interaction parameters χ_{AC} and χ_{BC} are extracted in effect from the regions outside the miscibility regime and thus might be affected by an inadequacy of the mean-field treatment.

It has been commonly concluded that mean-field theory works reasonably well in dense polymer systems since to a good approximation the segment density can be considered uniform. Here we find that high density is a necessary but not always a sufficient condition. In systems with large concentration fluctuations, such as immiscible polymer mixtures, the simple mean-field treatment with random mixing obviously becomes inapplicable.

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