Spinodal Decomposition of Homopolymer Blends:
Geometrical Properties of the Interface

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The spinodal decomposition (SD) of the homopolymer blends has been studied by the
numerical integration of the Cahn-Hilliard-Cook equation with the Flory-Huggins-de Gennes
free energy functional. The scaling dependences for the surface area density, Euler characteristics density, average Gaussian and mean curvatures of the blend interface have been found.
In the shallow and asymmetric quenches the topological transformation from the bicontinuous to droplet morphology has been observed. The influence of the thermal fluctuations on
the curvature distribution has been investigated.

When a homogeneous binary mixture is quenched into the unstable part of its
miscibility gap, the spinodal decomposition (SD) takes place, which manifests in
the spontaneous growth of the concentration fluctuations that leads the system to
the two-phase state. 1) Most of the previous studies 2) have been concerned with the
evaluation of the quantities that can be measured by the scattering techniques, for
example, the average domain size, \( R_g \), which is extracted from the structure factor. Less attention has been paid to the quantitative characterization of the interface
morphology. 3) 4) However, morphology indeed determines macroscopic properties
of the blend. The connectivity of the domains could affect not only mechanical
properties but also diffusive transport and electric conductivity. The time evolution
of the interface that appears in the spinodally decomposing homopolymer blends is
the main object of the present research.

The quantity that describes the surface topology is the genus, \( g \), and the Euler characteristics, \( \chi_{\text{euler}} = 2(1 - g) \). For a closed surface, the genus is simply
the number of holes in the surface. Thus, a sphere has \( g = 0 \) (\( \chi_{\text{euler}} = 2 \)), a torus
\( g = 1 \) (\( \chi_{\text{euler}} = 0 \)), and a pretzel \( g = 2 \) (\( \chi_{\text{euler}} = -2 \)). Figure 1 presents
the time evolution of the Euler characteristics density, \( \chi_{\text{euler}}/V \), for different quench
conditions. For the blends of the average composition \( \phi_0 = 0.5, 0.45, 0.4 \) and 0.375,
the Euler characteristics increases monotonically from the initially large negative
value and remains negative for all times studied. The negative Euler characteristics
indicates that interface in these blends is bicontinuous. The time evolution of
the morphology is characterized by the progressive growth of the average domain size
\( R_g \sim \tau^{0.25} \) for \( \phi_0 = 0.5 \) accompanied by the decrease of the domains connectivity. For the symmetric blends \( \phi_0 = 0.5 \) the Euler characteristics increases as \( \tau^{0.75} \)
regardless of the quench temperature and remains negative (Fig. 1(b)). In the
asymmetric mixtures the exponent depends on the average volume fraction and the
final quench temperature. In some cases, the Euler characteristics approaches zero at the late times ($\phi_0 = 0.36, T = 15^\circ\text{C}$) or even becomes positive for $\phi_0 = 0.35$ at $T = 15, 25^\circ\text{C}$ and $\phi_0 = 0.4$ at $T = 40^\circ\text{C}$ (Fig. 1(a)). This implies the droplet morphology, while the close to zero values correspond to some intermediate morphology where the droplets with complex topology are present (the final state in this simulation is still far from the equilibrium where only one big spherical droplet is formed).

![Fig. 1. (a) The plot of the Euler characteristics density, $\chi_{euler}/V$, versus time, $\tau$. (b) The plot of $\log(-\chi_{euler}/V)$ versus $\log(\tau)$. Symmetric ($\phi_0 = 0.5$) blends at $T = 15^\circ\text{C}$ ($\triangle$); $25^\circ\text{C}$ ($\Delta$); $40^\circ\text{C}$ ($\nabla$); $54^\circ\text{C}$ (♦). Asymmetric blends: $\phi_0 = 0.45$ at $T = 15^\circ\text{C}$ (filled squares); $\phi_0 = 0.4$ at $T = 15^\circ\text{C}$ (×); $25^\circ\text{C}$ (+); $40^\circ\text{C}$ (♦); $\phi_0 = 0.375$ at $T = 15^\circ\text{C}$ (filled diamonds); $\phi_0 = 0.36$ at $T = 15^\circ\text{C}$ (+); $\phi_0 = 0.35$ at $T = 15^\circ\text{C}$ (◦); $25^\circ\text{C}$ (squares). The critical temperature is $T = 62^\circ\text{C}$.

We have found that the interface area density, $S/V$, scales with time as $\tau^{-0.25}$ for the symmetric blends independent of the final quench temperature. Therefore, the average Gaussian curvature which is related to the surface area and Euler characteristics by the Gauss-Bonnet theorem, increases as $\tau^{0.5}$. The average mean curvature remains close to zero for the symmetric blend. For the symmetric blends the homogeneity index, $HI$, defined as $HI = [-S^3/(2\pi\chi_{euler}V^2)]^{1/2}$, is constant at the late times. This suggests that at the level of the integral geometry quantities, the dynamic scaling hypothesis for the evolution of the interface morphology holds in quenched critical systems. However, the distribution functions of the local curvatures scaled with the interface density do not exhibit universal scaling if the local thermal undulations of the interface are taken into account. The scale of the thermal undulations does not depend on the progress of the SD and therefore the scaled curvature distribution functions broaden with the time.

References