

Curvature Determination of Spinodal Interface in a Condensed Matter System

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Laser scanning confocal microscopy has been used to study the time evolution of a three dimensional spatially bicontinuous structure of a phase-separated polymer blend undergoing the late stage of spinodal decomposition, as a model example of condensed matter systems. Both the mean and Gaussian curvatures of the interface between two coexisting phases have been directly measured for the first time from the reconstructed 3D image. The Gaussian curvature is negative, clearly demonstrating that the interface of the bicontinuous structure is anticlasic, while the mean curvature is close to zero. Self-similar growth of the structure is inferred from the time evolution of the average radius of curvature of the interface. [S0031-9007(97)02588-X]

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If a mixture is rapidly quenched from the single phase state to the spinodal region of the phase diagram by changing thermodynamic variables such as temperature, the thermodynamically unstable mixture separates, via “spinodal decomposition” (SD), into two phases; it forms bicontinuous two-phase structure during the course of SD, if the volume fraction of one of the phases is close to 0.5 (isometric case) [1]. Over the past decade a number of scattering studies [2–4] have been made on the dynamics of SD, including the time evolution of structural properties, such as characteristic wavelength of the phase-separated structure. Bicontinuous structures are formed in a variety of condensed atomic and molecular systems. They are commonly formed transiently in binary mixtures of polymer blends, simple fluid mixtures, metallic alloys, and inorganic glasses [1]. In other cases, equilibrium bicontinuous structures are formed, for example, in microemulsions [5] (where the structures are spatially disordered), lyotropic cubic phases of amphiphilic systems [6], and microphase-separated block copolymers [7] (both spatially ordered).

Estimates of the Gaussian curvatures of interfaces in polymer blends [8] and microemulsions [9] have been derived assuming the validity of the Gaussian random wave model [10]. This model, however, is based on a number of assumptions: It assumes Gaussian disorder, and for convenience the mean curvature of the interface (or its area average) is taken to equal zero. More recently, a couple of attempts have been made to measure curvatures of the bicontinuous structures. A small-angle neutron scattering (SANS) experiment with a contrast variation method has been carried out for three-component microemulsions, which yielded the mean curvature, H , of the interface between water and oil of the system [11]. However, in practice, smearing effects due to the interpenetration of oil or water into the surfactant monolayer and

experimental errors made the measurement of the Gaussian curvature K of the system too difficult to implement. Besides these scattering approaches, attempts have been made to characterize interfacial curvatures for a computer simulated phase-separated bicontinuous structure of binary mixtures containing surfactants [12] and for a polymer blend in two-dimensional space [13].

To date, however, no direct measurements of the curvatures of the spinodal interface have been reported. *Direct measurement* of the interfacial curvatures for a *real experimental system* is now possible, due to the recent development of 3D imaging by the use of laser scanning confocal microscopy (LSCM) [14]. These data capture the local structure of the interface, as well as its global topology, and are thus of central importance to the physics of the system undergoing decomposition.

The mixtures studied consisted of polybutadiene (PB) and poly(styrene-*ran*-butadiene) (SBR). The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of PB were, respectively, 5.7×10^4 and 1.6 (M_w denotes the weight-average molecular weight). M_n and M_w/M_n for SBR were 7.1×10^4 and 1.2, respectively. The styrene content in SBR polymer was 20% by weight. Anthracene was attached to PB for contrast enhancement for LSCM [15] (two anthracene molecules per PB chain on average). The SBR/PB blend exhibits an upper critical solution temperature type phase diagram [16]. A mixture of SBR and PB (50/50 wt % composition) was dissolved in toluene to form ca. 7 wt % solution and then cast into a film by evaporating the solvent at room temperature. The as-prepared film containing the phase-separated structure was then homogenized by mechanical mixing [17] and placed between coverslips.

The mixture was annealed at about 100 °C for various times t ($t = 22, 44, 70, 114.8, 254.5$ h), all characteristic of late stage SD. The mixtures were subsequently observed

by LSCM (Carl Zeiss, LSM410) with a 364 nm laser at room temperature. Sixty image slices (256×256 pixels) with $0.5 \mu\text{m}$ increments along the optical axis of the microscope (the z axis) were recorded using an oil-immersed $\times 40$ objective. Each slice covered an area of $80 \mu\text{m} \times 80 \mu\text{m}$ in the lateral x - y plane, thus the pixel length L was $0.3125 \mu\text{m}$. All optical slices were at least $20 \mu\text{m}$ distant from the coverslips, to avoid possible surface effects on the structure. The raw images were subjected to the “binarization” with an appropriate threshold to obtain a 3D reconstruction of the interface between the SBR and the PB components [15]. We have used the “marching cubes algorithm” [18] to model the interface by contiguous polygons; this allows normal vectors at the vertices of the polygons to be determined, which are used for estimation of the curvatures [19]. The interfacial area was estimated by summing the area of the polygons, from which the interfacial area per unit volume, $\Sigma(t)$, was estimated. The volume fraction of one of the phases was also measured to ensure the image analysis is accurate: We note that the volume fraction of the SBR-rich phase remained 0.5 over the entire time of our experiment, as expected.

Figure 1 shows the 3D LSCM image constructed from the optical sections collected at $t = 70$ h, after image processing: the interface towards SBR-rich domain is colored by blue, while the other side by yellow. Clearly, the phase-separated structure is bicontinuous. Apart from rescaling of the characteristic “wavelength” of the interface with time t , all other images appear similar to that of Fig. 1.



FIG. 1(color). 3D image of the SBR/PB phase-separated structure 70 h after the onset of SD (box size: $30 \times 30 \times 30 \mu\text{m}^3$ in size). Depth resolution was $0.65 \mu\text{m}$ so that interpolation was not required in stacking the LSCM 2D sections. The characteristic wavelength, Λ_m , was $12.1 \mu\text{m}$.

The structure factor, $S(q, t)$, defined by $I(q, t)/C$ where $I(q, t)$ is the scattering function and C the factor related to absolute scattering intensity was obtained from the LSCM image by 3D Fourier transformation of spatial correlation function of the image contrast where $\text{PB} = 1, \text{SBR} = 0$. Here the wave number is defined: $q = 2\pi j/NL$ ($j = 0, 1, 2, \dots, N/2; N = 256$). To assess the validity of this image construction, we have compared this structure factor with simulated and experimental ones. The LSCM-deduced $S(q, t)$ was in excellent quantitative agreement [14,20] with that obtained from a computer simulation using the time-dependent Ginzburg-Landau (TDGL) equation [21] and with that measured by light scattering (LS) from a mixture of PB and polyisoprene (PI) in the late stage SD [2].

The interfacial curvatures were deduced from the variation of surface area by parallel displacement. A parallel surface to the interface is formed by translating the interface along its normals by an equal distance everywhere on the interface, as schematically depicted in Fig. 2. The area of the parallel surface, $A(d)$, and that of the interface, $A(0)$ depend on the interfacial curvatures, thus [22,23]

$$A(d) = A(0)(1 + 2\langle H \rangle d + \langle K \rangle d^2), \quad (1)$$

where d is a signed displacement of the parallel surface from the interface: It is positive if the direction of the normals points to a specific phase (the SBR-rich phase say), and negative otherwise. Since the curvatures of the surface vary from point to point, we introduce the area-averaged mean curvature, $\langle H \rangle$, and Gaussian curvature, $\langle K \rangle$,

$$\langle H \rangle = \frac{1}{2} \frac{\iint (k_1 + k_2) da}{\iint da}, \quad \langle K \rangle = \frac{\iint k_1 k_2 da}{\iint da}, \quad (2)$$

where da is the area element of the interface and k_1 and k_2 are the principal curvatures of the interface at a point of interest. $\langle H \rangle$ and $\langle K \rangle$ can be determined from Eq. (1) by measuring $A(d)$ with various displacements d . We refer to this scheme as a “Parallel Surface Method

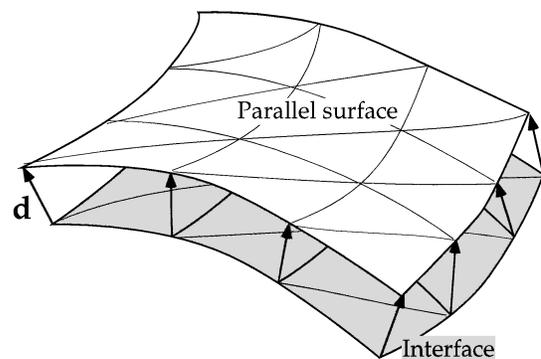


FIG. 2. Schematic diagram of a parallel surface (shown by white surface) at displacement d from the interface (shown by grey surface) between the SBR-rich and PB-rich phases. The arrows indicate displacement vectors from the interface.

(PSM)” throughout this Letter. The interface of the SBR/PB mixture is modeled by elemental polygons, with the normal vectors $\mathbf{n}(|\mathbf{n}| = 1)$ at their vertices. New polygons, which represent the parallel surface displaced by a distance d from the interface, were computationally created by connecting the end of the displacement vectors, \mathbf{d} , that is given by $\mathbf{d} = d\mathbf{n}$. $A(d)$ was then measured by summing the area of the new polygons. The accuracy of this technique is dependent on the “grain size” of the polygonal approximation to the surface. We have chosen a sufficiently small grain size to ensure numerical stability of the resulting curvatures with changing grain sizes. Namely, the interfacial areas converged to a single number independent of elemental polygon area.

Fig. 3 shows $A(d)$ as a function of d for the SBR/PB mixture at $t = 70$ h. The volume sampled for the measurement was $62.5 \times 62.5 \times 30 \mu\text{m}^3$. The solid line in the figure represents the best fit of Eq. (1) to the data, from which $\langle H \rangle$ and $\langle K \rangle$ were determined. We note that the results slightly varied with size and the position of the image for the measurements, shown in the inset of Fig. 3. The averaged principal curvatures, $\langle k_1 \rangle$ and $\langle k_2 \rangle$ can be estimated by solving the quadratic equation, i.e., $x^2 - 2\langle H \rangle x + \langle K \rangle = 0$, where variable $x = \langle k_i \rangle$ ($i = 1$ or 2). From the data presented in the inset of Fig. 3, $\langle H \rangle$

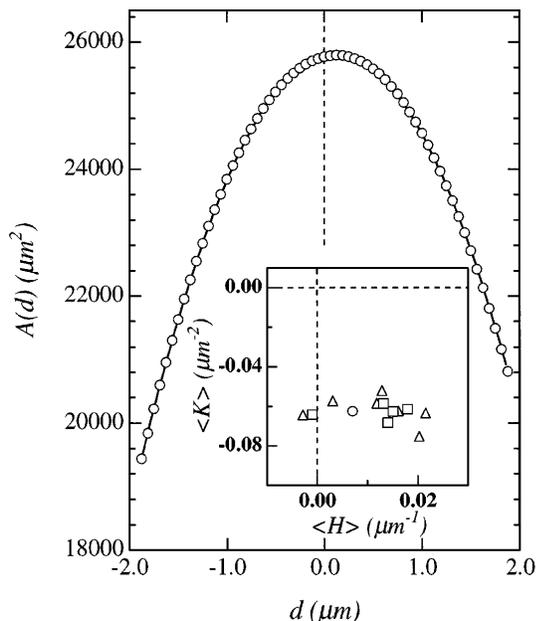


FIG. 3. The area of parallel surfaces, $A(d)$, plotted against the displacement from the interface, d for the phase-separated SBR/PB mixture at 70 h. The open circles represent the measurement ($62.5 \times 62.5 \times 30 \mu\text{m}^3$). The solid line shows the best fit to Eq. (1), which gave $\langle H \rangle \cong 0.0070 \mu\text{m}^{-1}$ and $\langle K \rangle \cong -0.062 \mu\text{m}^{-2}$. The inset shows the variation of the curvatures for different volume and portion of the LSCM image for the measurements. Triangles, squares, and a circle in the inset represent, respectively, the results obtained from the volume of $31.3 \times 31.3 \times 30 \mu\text{m}^3$, $46.9 \times 46.9 \times 30 \mu\text{m}^3$, and $62.5 \times 62.5 \times 30 \mu\text{m}^3$.

and $\langle K \rangle$ at $t = 70$ h were estimated to be $0.01 \mu\text{m}^{-1}$ and $-0.062 \mu\text{m}^{-2}$, respectively [24]. Thus we estimated $\langle k_1 \rangle \cong 0.26 \mu\text{m}^{-1}$ and $\langle k_2 \rangle \cong -0.24 \mu\text{m}^{-1}$.

The small positive value of $\langle H \rangle$ may reflect cylindrical (or spherical) domains that appear when a part of the domain breaks up in the course of SD. According to curvature distribution measurements, H was evenly distributed around zero [25]. The negative value of $\langle K \rangle$ clearly proves that the interface of the phase-separated polymer blend is, *on average*, anticlactic.

Figure 4(a) shows the time dependence of $\langle H \rangle$ and $\langle K \rangle$ determined by the PSM. $\langle K \rangle$ at various t remains negative, demonstrating that the interface is hyperbolic regardless of t . $|\langle K \rangle|$ decreased with t due to rescaling of the area-averaged mean radius defined as $\langle R(t) \rangle \equiv (|\langle R_1 \rangle| + |\langle R_2 \rangle|)/2$ with $|\langle R_i \rangle| \equiv |1/\langle k_i \rangle|$ ($i = 1$ or 2) as the bicontinuous structure grows. $\langle H \rangle$ remained close to zero irrespective of time.

Figure 4(b) shows a double-logarithmic plot of a reduced curvature scaled by the characteristic length of the structure, $\langle R(t) \rangle / \Lambda_m(t)$, as a function of time. Here the

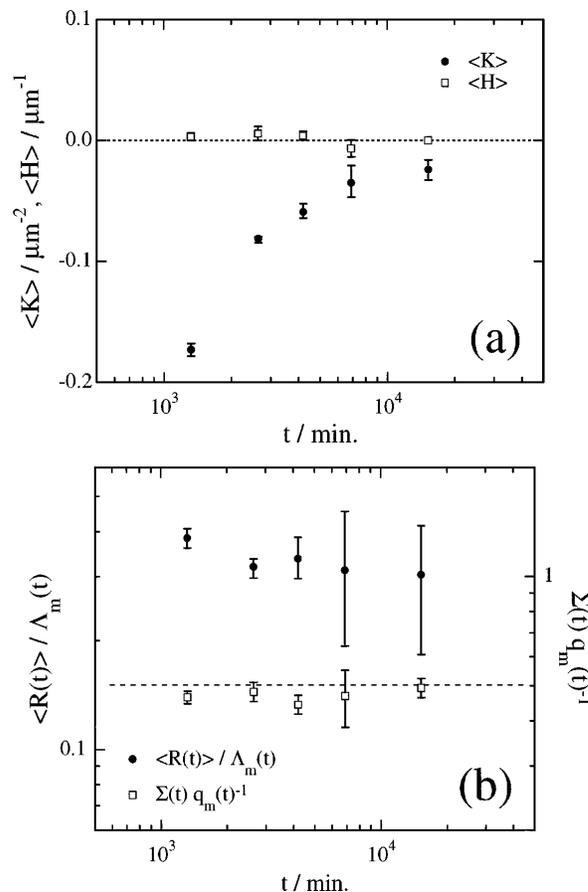


FIG. 4. (a) Time evolution of the mean, $\langle H \rangle$, and Gaussian, $\langle K \rangle$, curvatures. (b) Time evolution of the reduced radius, $\langle R(t) \rangle / \Lambda_m(t)$ (left axis) and $\Sigma(t) q_m(t)^{-1}$ (right axis). Dotted line for the right axis represents the value obtained from LS and the computer simulation (Ref. [27]).

characteristic length, $\Lambda_m(t)$, is equal to $\Lambda_m(t) \equiv 2\pi/q_m(t)$, where $q_m(t)$ is the wave number at the maximum intensity of $S(q, t)$, deduced from the LSCM image. A relation of $\langle R(t) \rangle / \Lambda_m(t) \cong 0.3$ holds throughout the time scale of these experiments. It is generally accepted that the phase-separated structure rescales with time by the factor $\Lambda_m(t)$ (i.e., “dynamical self-similarity” [26]). The fact that $\langle R(t) \rangle$ —which can only be obtained from the real-space method described here—has exactly the same growth rate as $\Lambda_m(t)$ is consistent with the idea of dynamical self-similarity. The time evolution of a dimensionless variable, $\Sigma(t)q_m(t)^{-1}$, is plotted in Fig. 4(b). The variables reach a plateau value of 0.5 (dotted line), in good agreement with the value found for the PB/PI mixture and the computer simulation of late stage SD [27].

In summary, direct evaluation of the average local geometry of the interface in a phase-separated bicontinuous structure has been done for the first time, using LCSM. The inferred (average) Gaussian curvature clearly demonstrated that the interface of the structure is—on average—hyperbolic. In addition, the ratio of the mean radius of curvature of the interface to the characteristic length of the structure was found to be constant irrespective of time, demonstrating that the dynamical scaling hypothesis holds in the late stage SD.

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