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Notes

Determination of Dynamic and Thermodynamic Quantities from the Scaling Behavior during the Later Stages of Spinodal Decomposition

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Introduction

Phase separation following the mechanism of spinodal decomposition (SD) is often observed when a mixture of two components is transferred from the single into the two phase region. A maximum appears in scattering curves (intensity I versus scattering vector q). Investigations have been done both on systems with a lower critical solution temperature (LCST)[1-14] and on systems with an upper critical solution temperature (UCST).[1,2,15-22] According to Hashimoto,[2,6] different stages of spinodal decomposition can be distinguished: (1) during the early stage, only the amplitude of the fluctuation grows but the wavelength remains constant; (2) during the intermediate stage, both the wavelength and amplitude change; (3) during the transition stage or late stage 1, the amplitude reaches the equilibrium value but the domains as well as the interface profile are still developing; (4) in the final or late stage 2, only a domain growth is observable. While often the early stages of SD can be well described by the Cahn–Hilliard–Cook (CHC) theory,[23-26] which yields the mobility and the interdiffusion coefficient, the later stages follow so-called scaling laws for both the maximum position of the spinodal peak, $q_m(t,T)$, and the maximum intensity, $I_m(t,T)$, as functions of time, because the phase-separating system becomes self-similar with time.[27-29] A universal master curve describing the scaling behavior of all systems seems not to exist. But it has been shown for many systems that by using the maximum position $q_m(0,T)$ and the time $t_c(T)$, as obtained from the CHC analysis of the early stages, reduced values for both $q_m(t,T)$ and t can be defined as $Q_m(\tau) = q_m(t,T)/q_m(0,T)$ and $\tau = t/t_c(T)$. These quantities show coincidence (i.e., master curve behavior) for different temperature jump experiments of the same system. Hashimoto et al.[15,16] extended the idea of a master curve by allowing any arbitrary time as a reference time for the reduced time scale. They used that approach to investigate the validity of the scaling hypothesis in systems where no CHC analysis was possible, i.e., where no data on $q_m(0,T)$ and t_c were available. They further used this approach to determine $q_m(0,T)$ for temperature jumps where the early stages of SD could not be resolved by comparing with experimentally determined $q_m(0,T)$ of the early stages at a different temperature.[16]

In this paper it will be shown that quantities proportional to the interdiffusion coefficient $D(T)$ and the mobility $M(T)$ as functions of temperature as well as the activation energy E_a of such a system can be determined even in the case where experimental data of the early stages are not available. Further a procedure is proposed which can give access to the second derivative of the free energy of mixing of an "incompatible" blend.

Theoretical Background

Early Stage of SD: CHC Analysis. The early stage of SD is characterized by two features: (i) a maximum with a time-independent position $q_m(0,T)$ appears in the scattering curve and (ii) the intensity for a given q changes exponentially with time. These properties can be expressed by the CHC theory:

$$I(q,t,T) = I(q,\infty,T) + (I(q,0,T) - I(q,\infty,T))\exp(2R(q,T)t) \qquad (1)$$

with

$$R(q,T) = -M(T)q^2\left(\left(\frac{\partial^2 f_m}{\partial \phi^2}\right)_T + 2\kappa q^2\right) \qquad (2)$$

$R(q,T)$ is the amplification factor, $M(T)$ is the mobility (assumed to be q-independent in the CHC theory, while other theories take a q-dependence into account[26,30]), ϕ is the volume fraction of component 1, κ is the gradient energy coefficient (interfacial free energy density), f_m is the mean field free energy of mixing, $q = 4\pi/\lambda \sin(\theta/2)$ is the scattering vector, with λ being the wavelength of the radiation in the sample and θ being the scattering angle, and t is the time. From the slope of an Arrhenius plot of $M(T)$ ($\ln(M(T))$ vs $1/T$) the activation energy of the system can be obtained.

Equation 2 contains the so-called interdiffusion coefficient $D(T)$ which describes the uphill diffusion during spinodal decomposition:

$$D(T) = -M(T)\left(\frac{\partial^2 f_m}{\partial \phi^2}\right)_T \qquad (3)$$

Using the random phase approximation of de Gennes,[26,31] one can express the gradient energy coefficient by

$$\kappa = \frac{1}{6}\left(\frac{\langle R_{g,1}^2\rangle}{N_1\phi} + \frac{\langle R_{g,2}^2\rangle}{N_2(1-\phi)}\right)$$

where $R_{g,i}$ is the radius of gyration of component i and N_i is the degree of polymerization of component i. $\partial^2 f_m/\partial\phi^2$ can be expressed in terms of the Flory–Huggins–Staverman theory,

$$\left(\frac{\partial^2 f_m}{\partial \phi^2}\right)_T = \frac{1}{N_1\phi} + \frac{1}{N_2(1-\phi)} + \left(\frac{\partial^2 \Gamma}{\partial \phi^2}\right)_T \qquad (4)$$

where f_m is the Flory–Huggins–Staverman free energy[32-36] of mixing and Γ is the interaction function. $\partial^2 f_m/\partial\phi^2$ can be directly obtained from the intercept of an Ornstein–Zernike plot of the scattering data ($1/I(q)$ versus q^2),

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$$\left(\frac{\partial^2 f_m}{\partial \phi^2}\right)_T = \frac{c}{I(q=0,T)} \qquad (5)$$

where c is the contrast factor for the particular type of scattering experiment. From eq 1 it follows that a plot of $\ln(I(q,t,T) - I(q,\infty,T))$ versus t yields $R(q,T)$, and from eqs 2 and 3 it follows that a plot of $R(q,T)/q^2$ versus q^2 yields mobility from the slope if the radii of gyration are known and the interdiffusion coefficient as the intercept.

Setting eq 2 equal to 0 yields $q_c(T)$, above which concentration fluctuations decay and below which concentration fluctuations increase. Differentation of eq 2 with respect to q yields $q_m(0,T)$, i.e., the scattering vector corresponding to the wavelength of maximal growth of concentration fluctuation (correlation length $\Lambda(0,T)$), which is not a function of time during the early stages:

$$q_c(T) = 2^{1/2} q_m(0,T) = \left(\frac{D(T)}{2M(T)\kappa}\right)^{1/2} = \left(-\frac{1}{2\kappa}\left(\frac{\partial^2 f_m}{\partial \phi^2}\right)_T\right)^{1/2} \qquad (6)$$

To compare the spinodal decomposition of different temperature jumps or different systems, it is useful to define a reference or critical time $t_c(T)$ which allows for a normalization of the absolute time scale by using $t/t_c(T)$ instead of t. $t_c(T)$ is defined proportional to the time $t_{\Lambda(0,T)}$ a particle needs to move across a distance to the correlation length $\Lambda(0,T) = 2\pi/q_m(0,T)$:

$$t_c(T) = \frac{t_{\Lambda(0,T)}}{4\pi^2} = \frac{1}{D(T)\, q_m^{\,2}(0,T)} \qquad (7)$$

Late Stages of SD: Scaling Analysis. After some time in a SD process the maximum of the scattering curve starts to move toward smaller q; i.e., the correlation length increases. In this intermediate stage nonlinear behavior of the time evolution of the structure function becomes important[28] and leads to a crossover from exponential growth to a power law behavior for the enlargement of the amplitudes. There the concentration fluctuations have reached the value equal to the coexistance curve and the phase-separating domains still grow in size to reduce the interface between the coexisting phases. This power law behavior characterizes the late stage, and for the growth of $q_m(t,T)$ and $I(q_m(t,T))$

$$q_m(t,T) \propto t^{-\alpha} \qquad (8)$$

$$I(q_m(t,T)) \propto t^{\beta} \qquad (9)$$

are found experimentally. For the intermediate stages of SD one finds

$$\beta > d\alpha \qquad (10)$$

while for the late stages

$$\beta = d\alpha \qquad (11)$$

is found, with d being the dimensionality of the system (usually $d = 3$).

Theoretical approaches explaining these power laws were given by Binder,[27] Langer et al.,[28] and Furukawa.[29] They introduced the idea of scaling laws for demixing processes after some initial transient time following a temperature jump, so that only a single length scale $\Lambda(t,T) = 2\pi/q_m(t,T)$ is established. All physical quantities should depend on time t only through this length scale. $\Lambda(t,T)$ is a measure of the domain size of the morphology. Asymptotically, the morphology of the phase-separating domains is expected to become self-similar in time. Details of the structure such as interface thickness or curvature of the interfaces, which play a role for the question of self-similarity of the whole structure factor, are not important for the following discussion, since these length scales are much smaller than $\Lambda(t,T)$ and for our considerations we need only to focus our attention on $\Lambda(t,T)$ or $q_m(t,T)$, respectively.

Discussion

For systems where the CHC analysis is possible, direct determination of the mobility M, the interdiffusion coefficient D, and the activation energy E_a is possible. Feng et al.[37] used that approach to investigate the nature of the interdiffusion coefficient of a thermodynamically unstable polymer blend.

However, even if the early stages of SD cannot be resolved experimentally, there is access to these quantities nevertheless. A necessary condition is that besides the late stages a part of the intermediate stages of SD can be investigated, because this leads to a transient time dependence of the exponent α in eq 8, i.e., a curvature in the plot $\ln(q_m(t,T))$ vs $\ln(t)$. A master curve of this plot is created by choosing arbitrarily a reference temperature T_r characterized by a reference time t_r and a reference value for q_m, q_r. All curves are now shifted both horizontally ($\ln(a(T))$) and vertically ($\ln(z(T))$) to yield the best coincidence (Figure 1). Notice that both shift factors $a(T)$ and $z(T)$ are well defined for a given reference temperature T_r, since there is only one way to get superposition in the master curve. In the case of time-independent α arbitrary shifting would be possible, which yields no information. The obtained values $a(T)$ are proportional to the unknown times $t_c(T)$ (the proportionality factor depends only on t_r), and the values $z(T)$ are proportional to $q_m(0,T)$ (the proportionality factor depends only on q_r):

$$a(T) = k_t(t_r)\, t_c(T) \qquad (12)$$

$$z(T) = k_q(q_r)\, q_m(0,T) \qquad (13)$$

The shift factors in eqs 12 and 13 are not dimensionless, as compared to the similar quantities in ref 16. We can thus rewrite eq 7 in terms of $a(T)$ and $z(T)$ to give

$$D'(T) = \frac{1}{a(T)\, z^2(T)} \qquad (14)$$

By comparison with eq 6 we can define $M'(T)$, which is proportional to the mobility $M(T)$:

$$M'(T) = \frac{1}{a(T)\, z^4(T)} \qquad (15)$$

Using eqs 14 and 15 we can also obtain the temperature dependences of $D'(T)$ and $M'(T)$, which are directly proportional to the temperature dependences of $D(T)$ and $M(T)$.

Such an analysis should enable investigations of the nature of diffusion coefficients and mobilities for all systems, independent of the observation of the early stages of SD. A more quantitative comparison between different systems should be possible by using similar conditions such as an identical temperature difference between T_r and the spinodal.

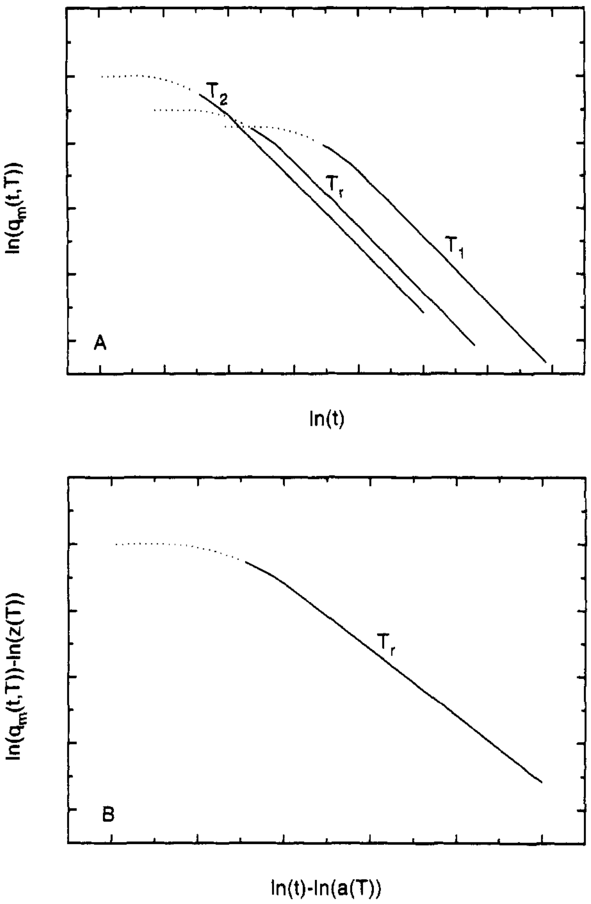

Figure 1. Solid lines represent measurable values of the later stages of SD and dotted lines represent the early stage and a part of the intermediate stage, which are not accessible by experiment. (A) Curves as obtained from experiment for one or different blends after different temperature jumps. T_r represents the chosen reference curve. T_1 and T_2 represent measurements at other temperatures or curves obtained from different blends. These curves are shifted both horizontally by $\ln(a(T))$ and vertically by $\ln(z(T))$ to coincide with the reference curve at T_r. (B) Master curve.

The activation energy E_a itself can be obtained directly from the slope of a plot $\ln(M'(T))$ vs $1/T$, independent of the choice of T_r.

While both dynamic and thermodynamic quantities contribute to the horizontal shift factor $a(T)$ (eqs 7 and 12), the vertical shift factor $z(T)$ is solely governed by thermodynamic properties (eqs 6 and 13).

From eq 6 it follows that $q_m(0,T)$ can be calculated if the temperature dependence of $\partial^2 f_m/\partial\phi^2$, the radii of gyration, and the degrees of polymerization are known, or vice versa. Higgins et al.[10] have shown that a linear extrapolation of $\partial^2 f_m/\partial\phi^2$ as a function of $1/T$ obtained from single phase data to the spinodal region can be done. Schwahn et al.[14] found for another blend deviations from linearity in the same plot around the spinodal temperature. However, it seems that both data sets show in common a point symmetry at $1/T_s$, which seems to justify an extrapolation from the single into the two phase region or in the opposite direction.

If two different blends show the same scaling behavior during the intermediate and late stages of SD, it is possible to shift them on one master curve. Supposing that from the first system $q_m(0,T_r)_1$ is known at the given reference temperature T_r of the master curve, the shift factor $z(T)$ of the second system directly yields its $q_m(0,T)_2$ at the temperature T and from eq 6 the second derivative of the free energy of mixing $(\partial^2 f_m/\partial\phi^2)_{2,T}$. This approach to determine $\partial^2 f_m/\partial\phi^2$ might be useful in cases where the early stages of SD are outside the length scales covered by light scattering and the contrast for other scattering techniques (X-ray, neutron) is not sufficiently large. This approach could also be useful for determination of $\partial^2 f_m/\partial\phi^2$ of incompatible blends, if they can be prepared as kinetically single phase blends by rapid solvent evaporation[3] or by mechanical homogenization.[16] "Incompatible" means that such a kinetically single phase blend is unstable between its glass transition and degradation temperature. Phase separation takes place as soon as such a blend is annealed above its glass transition temperature.

Conclusions

It was shown that quantities usually determined from an analysis of the early stages of SD are also accessible by using the scaling behavior of the later stages of SD. The creation of a master curve $\ln(q_m(t,T)) - \ln(z(T))$ versus $\ln(t) - \ln(a(T))$ yields two shift factors $z(T)$ and $a(T)$, respectively. $z(T)$ bears information about the second derivative of the free energy of mixing, $(\partial^2 f_m/\partial\phi^2)_T$. The shift factors $a(T)$ together with $z(T)$ yield information about the mobility, the interdiffusion coefficient, and the activation energy. The procedure described is especially valuable if early stages of SD are not measurable because they are too fast or outside the range of length scales covered by the particular experiment. To enable comparison between different studies, the reference state has to be chosen in a similar manner. For example, this can be a constant temperature difference between the spinodal temperatures and the chosen reference temperatures of the master curves.

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