What is spinodal decomposition?

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Abstract

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A pair of partially miscible liquids, i.e. liquids that do not mix in all proportions at all temperatures, shows in a temperature-composition diagram a miscibility gap where phase separation occurs. Gibbs [1] showed that the condition for stability (or metastability) in respect to continuous change of phase is that the second derivative of the free energy of mixing to be positive. If negative, the system is unstable. If zero, the spinodal is defined. The free energy of mixing, $\Delta G^{\text{mix}}$, has the following general form:

$$\Delta G^{\text{mix}} = \Delta H^{\text{mix}} - T\Delta S^{\text{mix}}.$$ (1)

For the regular solution model [2] the entropy of mixing is the same as for the ideal mixing: $\Delta S^{\text{mix}} = -R(X_A \ln X_A + X_B \ln X_B)$, where $X_A$ and $X_B$ are the molar fractions of components A and B in the mixture ($X_A + X_B = 1$). However, the enthalpy of mixing may be written as $\Delta H^{\text{mix}} = X_A \beta$, where $\beta$ is an interaction parameter lumping the energy of mixing contribution [3]. Under these assumptions, eq.(1) becomes:

$$\Delta G^{\text{mix}} = X_A X_B \beta + RT(X_A \ln X_A + X_B \ln X_B).$$ (2)

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In the 1st row the solution has been brought, very carefully, in to the unstable region (compare also with Fig.2 to see the difference). The density of the system now has a wavy profile with maxima and minima around the average density. In the third row the expected diffusion process results to \( \frac{c_{A}^{inh}-c_{A}^{nh}}{c_{B}^{inh}-c_{B}^{nh}} \), however. Diffusion does not take place from left to right i.e. from lower to higher concentration (uphill). Diffusion is large in extent but small in degree; the arrows show the diffusion direction. As diffusion progresses the density increases until it reaches a point where becomes equal to the density of pure B (rows 3-5). Phase separation that occurs in this way is known as spinodal decomposition and the fingerprint of that mechanism is the uphill diffusion.

The miscibility-gap and spinodal-region boundaries are obtained by calculating the first and second derivatives of the free energy, respectively, and setting them equal to zero.

\[
\frac{T}{T_{c}} = 2 \frac{X_{A} - X_{B}}{\ln X_{A} - \ln X_{B}}; \quad \frac{T}{T_{c}} = 4X_{A}X_{B}; \quad T_{c} = \frac{\beta}{2R}.
\]

In Fig.1 (upper frame) it can be seen that the first derivative is zero at the two free energy minima corresponding to the two miscible phases and the second derivative is zero at the points of inflexion. Also, both derivatives are zero at the free energy maximum. For a series of temperatures, the locus of the free energy minima projected on a temperature-composition diagram defines the phase boundary and the locus of the points of inflexion the spinodal (see lower frame in Fig.1). The maxima coincide to the upper consolute temperature \( T_{c} \) at \( X_{B}=0.5 \). Phase separation occurs when the system is within the miscibility gap. If the system is in the metastable region the mechanism is by nucleation and growth.
growth whereas if it is in the unstable region by spinodal decomposition.

Figure 2 depicts the nucleation and growth mechanism [4]. Gibbs (Ref. 1 p.254) discussed the possibility of the formation of a fluid of different phase within any homogeneous fluid and showed that the work W required to form (by a reversible process) an heterogeneous globule in the interior of a very large mass having initially the uniform phase of the exterior mass will be:

\[ W = 4\pi r^3 \gamma - \frac{4}{3} \pi r^3 \Delta \rho, \quad (4) \]

where \( \gamma \) is the surface tension, \( r \) is the radius of the nucleus, and \( \Delta \rho \) is the hydrostatic pressure. In the case where a critical nucleus is formed the first derivative of eq.(4) becomes zero while the hydrostatic equilibrium is preserved; \( \Delta \rho = 2 \gamma r_{crit} \), where \( r_{crit} \) is the radius of the critical nucleus. When \( r > r_{crit} \) the nucleus grows and when \( r < r_{crit} \) it collapses because the pressure exerted by the surface is greater than \( \Delta \rho \). By introducing \( r_{crit} \) in eq.(4) the minimum work \( W_{min} \) required to form that critical nucleus is given as:

\[ W_{min} = \frac{4}{3} \pi r_{crit}^2 \gamma. \quad (5) \]

Figure 3 depicts the spinodal decomposition mechanism [5]. Cahn and Hilliard [6] utilize the van der Waals equation for the energy of binary mixture [7] to develop a model for spinodal decomposition through Fick’s law of diffusion.

\[ \frac{\partial C_B}{\partial t} = \left\{ M \left( \frac{\partial^2}{\partial C_B^2} \right)_{T,D} \right\} \nabla^2 C_B - 2M \gamma \nabla^4 C_B, \quad (6) \]

where \( f \) is the free energy density of homogeneous material of composition e.g. C_B, \( M \) is a positive constant [8], and \( \kappa \) is a positive parameter. The first term on the right hand side of eq.(6) is the classical diffusion equation where the coefficient of \( \nabla^2 C_B \) is the diffusion coefficient \( D \). Since \( M > 0 \) the sign of \( D \) will be determined by the sign of \( \frac{\partial f}{\partial C_B} \). When \( \frac{\partial f}{\partial C_B} < 0 \) the solution is stable, \( D > 0 \), and diffusion (if any) occurs downhill. When \( \frac{\partial f}{\partial C_B} > 0 \) the solution has crossed the spinodal and is unstable, \( D < 0 \), and diffusion takes place uphill. It is noted, however, that the second term on the right hand side of eq.(6) (i.e. the fourth-order term) stabilizes the system against short distance scale fluctuations when \( \frac{\partial^2 f}{\partial C_B^2} < 0 \). Uphill diffusion and consequently spinodal decomposition requires a large enough distance scale fluctuation (i.e. to move mass over long distances).

In this note an elementary review on the concept of spinodal decomposition was given. The nucleation and growth mechanism was also presented. Comparing the two processes it is evident that nucleation is large in degree and small in extent while spinodal is small in degree and large in extent. In Fig.2 and 3 the evolution of the density profiles at various stages of the processes was drawn. It is noted that spinodal decomposition results to a high interconnectivity of the two phases. However, the morphology of the resulted separation is only an indication that spinodal decomposition has taken place [9]. Nucleation may also produce high interconnectivity [10]. Besides, fractal morphology is possible to be induced by both processes. For instance a fractal flake that grows is an example of a fractally nucleation process whereas a twin-dragon Peano curve that thickens is an example of a fractally spinodal process [11].

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References

3. For the ideal solution the enthalpy of mixing is zero.
5. IUPAC definition of spinodal decomposition: A clustering reaction in a homogeneous, supersaturated solution (solid or liquid) which is unstable against infinitesimal fluctuations in density or composition. The separation is only an indication that spinodal decomposition has taken place [9]. Nucleation may also produce high interconnectivity [10]. Besides, fractal morphology is possible to be induced by both processes. For instance a fractal flake that grows is an example of a fractally nucleation process whereas a twin-dragon Peano curve that thickens is an example of a fractally spinodal process [11].
7. J.D.van der Waals, The thermodynamic theory of capillarity flow and showed that the work W required to form (by a reversible process) an heterogeneous globule in the interior of a very large mass having initially the uniform phase of the exterior mass will be:
9. J.D.van der Waals, The thermodynamic theory of capillarity flow under the hypothesis of a continuous variation in density, Verhandelingen der Koninklijke Nederlandsche Akademie van Wetenschappen te Amsterdam 1, 1 (1893).
10. M is related to the interdiffusion coefficient. For a binary system \( J_\mu = M(\mu_B - \mu_A) \), where \( J \) and \( \mu \) are respectively the flux and the chemical potential of e.g. the B component and M is the mechanical mobility. Changes in the concentration in the given by taking the divergence of the flux: \( \nabla \cdot J_B = -V J_B \).