# Comparison of the pseudospinodal to the transition from metastability to instability in a binary-liquid mixture

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In recent work, Tanaka *et al.*[1] studied the transition from metastability to instability in an off-critical quench of a binary-liquid mixture. Both the kinetic behavior and morphology of the quenched system gave consistent evidence for a diffuse metastable to unstable crossover region. This supports theoretical implications[2,3] that in nonmean field systems the free energy barrier to nucleation in quenched systems becomes of the order of a few $k_BT$ well before the spinodal is reached; the spinodal being the line where this barrier is zero and below which the system is unstable to any fluctuation.

The purpose of this Note is to compare the observed quench depth to the pseudospinodal.[4,5] As temperature is varied along an off-critical isochore, a given parameter $X$ will display divergent behavior identical to that observed along the critical isochore except that the singular temperature is $T_s(\rho)$ rather than the critical temperature $T_s$ as described in

$$X = X_0\{[T - T_s(\rho)]/T_c\}^{-x}. \tag{1}$$

In Eq. (1) $X_0$ and $x$ are the critical amplitude and exponent found on the critical isochore and $\rho$ represents either density in a one component system or concentration in a binary system. $T_s(\rho)$ represents the pseudospinodal curve where $T_s(\rho_c) = T_c$. If $X = K_T$, the isothermal compressibility (susceptibility), one finds $K_T \to \infty$ along the pseudospinodal, a characteristic of the classical spinodal curve which separates the metastable and unstable regions for mean field systems.

In earlier work[6] we have used Eq. (1) with $X = K_T$ combined with a general form for the scaling equation of state to derive an equation of state from which a pseudospinodal curve can be calculated. We found the pseudospinodal is given by

$$\Delta\rho = B_s t_s^{\beta}, \tag{2}$$

where $t_s = [T_c - T_s(\rho)]/T_c$, $\beta$ is the coexistence or binodal curve exponent, and $B_s \simeq 0.63\, B_b$, where $B_b$ is the binodal curve amplitude. It was found that the derived equation of state and the pseudospinodal reduced to the mean field forms when mean field exponents were used. Hence the pseudospinodal in Eq. (2) is a generalization of the mean field spinodal for the nonmean field case under the deriving assumptions. A study of off-critical data for a variety of liquid systems[7] substantiated Eq. (2) with $\beta \simeq 1/3$ and $B_s/B_b = 0.66 \pm 0.13$. We shall now compare both the theoretical and empirical pseudospinodals to the quench of Tanaka *et al.*

Tanaka *et al.* used a system with a critical point at 156 °C and quenched off critical where the coexistence or binodal curve temperature was $T_b = 150$ °C. We write $\delta T_b = T_c - T_b = 6$ °C. One can show from Eq. (2) and its binodal analogue, $\Delta\rho = B_b t_b^{\beta}$ where $t_b = \delta T_b/T_c$, that

$$\delta T_s = \delta T_b (B_b/B_s)^{1/\beta}, \tag{3}$$

where $\delta T_s = T_c - T_s$. Equation (3) was used to calculate $\delta T_s$ with the above values of $B_s/B_b$ and $\beta = 1/3$. The results are compared to the quench in Fig. 1 which is a reproduction of Fig. 5 of Tanaka *et al.* with our results included. One sees the pseudospinodal lies at the lower edge of the diffuse transition regime discovered by Tanaka *et al.*[1] It lies along the upper edge of the unstable region in the region of the spinodal where a quench would be definitely unstable.

This comparison suggests that extrapolation of equilibrium properties into the metastable and unstable regimes below the coexistence curve, inherent in the pseudospinodal assumption, can successfully describe the limit of stability of a liquid system. The pseudospinodal acts not only as a convenient way to characterize data[5,7,8] but also appears to be an operationally valid generalization of the mean field concept of a spinodal.

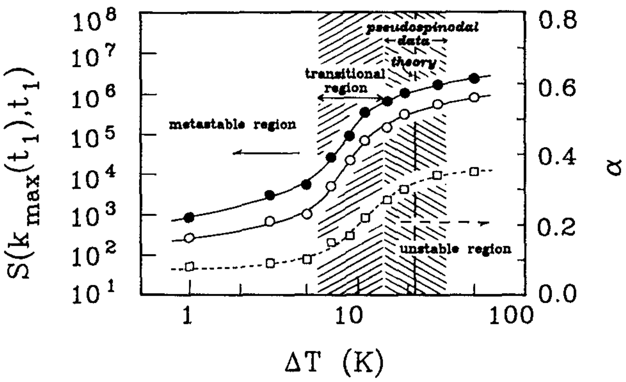


FIG. 1. Reproduction of Fig. 5 from Tanaka *et al.*, Ref. 1. $\Delta T$ is the quench depth in their experiment. The regions marked "metastable," "transitional" (positively sloped cross-hatched), and "unstable" are their findings. Added to their figure is the negatively sloped cross-hatched region corresponding to pseudospinodal data and the bold vertical line which represents a theoretical value for the position of the pseudospinodal for this quench.

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[1] H. Tanaka, T. Yokokawa, H. Abe, T. Hayashi, and T. Nishi, Phys. Rev. Lett. **65**, 3136 (1990).
[2] J. S. Langer, Physica **73**, 61 (1974).
[3] K. Binder, Phys. Rev. A **29**, 341 (1984).
[4] G. B. Benedek, in *Polarisation Matie et Rayonnement*, Livre de Jubile en l'honneur du Prof. A. Kastler (Presses Universitaires de Paris, Paris, 1968).
[5] B. Chu, F. J. Schoenes, and M. E. Fisher, Phys. Rev. **185**, 219 (1969).
[6] C. M. Sorensen and M. D. Semon, Phys. Rev. A **21**, 340 (1980).
[7] J. Osman and C. M. Sorensen, J. Chem. Phys. **73**, 4142 (1980).
[8] C. M. Sorensen, J. Phys. Chem. **92**, 2367 (1988).