

Microemulsions in the three-phase regime

H. Kleinert^{a),b)}

Physics Department, University of California at San Diego, La Jolla, California 92093

(Received 8 July 1985; accepted 5 September 1985)

Using a simple Landau free energy we determine the shape of the three-phase regime of a ternary mixture of water, oil, and tenside (microemulsion) in the space of concentrations and temperature x, y, τ . The boundaries at $x = 0$ (equal water and oil) and $y = 1$ (fixed tenside) are in excellent agreement with recent data of Kahlweit *et al.* and Shinoda *et al.* We also find satisfactory agreement for the temperature behavior of fluctuation phenomena such as the intensity of scattered light and the interfacial tensions.

Since the work of Griffith and Widom,¹ it has been known that the three-phase separation observed when adding salt to a ternary mixture of oil, water, and a tenside happens near a tricritical point. This point can be reached by changing pressures or the chemical composition of the constituents.² The addition of salt can efficiently be replaced by temperature.² Then the connodal triangle of the coexisting phases may be pictured as moving up and down in a prisma with the height corresponding to the temperature T . At some upper and lower values T_u and T_l , the triangles degenerate into lines (see Fig. 1) whose one end is critical. These ends mark the end points of critical lines of the two-phase regimes of the binary systems oil-tenside and oil-water, respectively.

Griffith proposed to describe such a system by a Landau free energy

$$f_{\text{pot}} = a_1x + a_2x^2 + a_3x^3 - \frac{3}{2}x^4 + x^6, \quad (1)$$

where x is an order parameter related to the oil in water concentration by, say, $c_{\text{ow}} = c_{\text{ow}}^0 + ax$ while x^2 gives the tenside concentration $c_T = c_T^0 + bx^2$. [The freedom of rescaling x and x^2 has been used to bring the last two terms $a_4x^4 + a_6x^6$ to the form $-\frac{3}{2}x^4 + x^6$. The parameter a_4 measures the distance from the tricritical point, say $a_4 \propto (p - p_c)$. Thus, in the normalization (1), the energy and the order parameters x and $y = x^2$ are measured in units of a_4/a_6^2 , $\sqrt{a_4/a_6}$, a_4/a_6 , respectively.] In the a_1, a_2, a_3 space, there are surfaces of two-phase coexistence which intersect in a line of three-phase coexistence.¹ We propose to parametrize this line as a function of some reduced temperature τ or salinity by the Ansatz

$$f_{\text{pot}} = \frac{1}{16}(4x^3 - 3x + \tau)^2 - \frac{1}{16}\tau^2 \\ = x^6 - \frac{3}{2}x^4 + \frac{1}{2}\tau x^3 + \frac{9}{16}x^2 - \frac{3}{8}\tau x. \quad (2)$$

This can be written as

$$f_{\text{pot}} = (x - x_1)^2(x - x_2)^2(x - x_3)^2, \quad (3)$$

where $x_{1,2,3}$ are the roots of the cubic equation

$$4x^3 - 3x + \tau = 0 \quad (4)$$

satisfying

$$x_1 + x_2 + x_3 = 0, \quad x_1x_2 + x_2x_3 + x_3x_1 = -\frac{3}{4}, \\ x_1x_2x_3 = -\frac{1}{4}\tau. \quad (5)$$

Equation (4) can be solved by setting $x = \cos \alpha$ and using the well-known identity

$$-4 \cos^3 \alpha + 3 \cos \alpha + \cos(3\alpha) = 0$$

to find, with $\gamma = \arccos \tau \in (\pi, 0)$ for $\tau \in (-1, 1)$:

$$x_1 = -\cos\left[\frac{1}{3}(\gamma + 2\pi)\right] \in (1, \frac{1}{2}), \\ x_2 = -\cos\left(\frac{1}{3}\gamma\right) \in (-\frac{1}{2}, -1), \\ x_3 = -\cos\left[\frac{1}{3}(-\gamma + 2\pi)\right] \in (-\frac{1}{2}, \frac{1}{2}). \quad (6)$$

The points (x_i, y_i) with $y_i = x_i^2$ form the triangles of coexistence in the x, y plane (symmetric to the y axis for $\tau = 0$) (see Fig. 2). Algebraically, it is easier to parametrize the triangles as a function of x_1 . By letting x_1 vary from $1/2$ to 1 , we can calculate τ from Eq. (4) and x_2, x_3 from Eq. (5),

$$x_2 = -\frac{1}{2}x_1 \left[1 + \sqrt{1 + \tau/x_1^3} \right] \in (-1, -\frac{1}{2}), \quad (7)$$

$$x_3 = -\frac{1}{2}x_1 \left[1 - \sqrt{1 + \tau/x_1^3} \right] \in (\frac{1}{2}, -\frac{1}{2}).$$

It is now easy to find the boundary of the three phase regime. First we take the symmetric cut at $x = 0$ (cut A in Fig. 3). The inner boundary y_i is given by the intercept of the $x = 0$ line with the side lines 23 or 31 of the triangle, depending on the sign of x_3 :

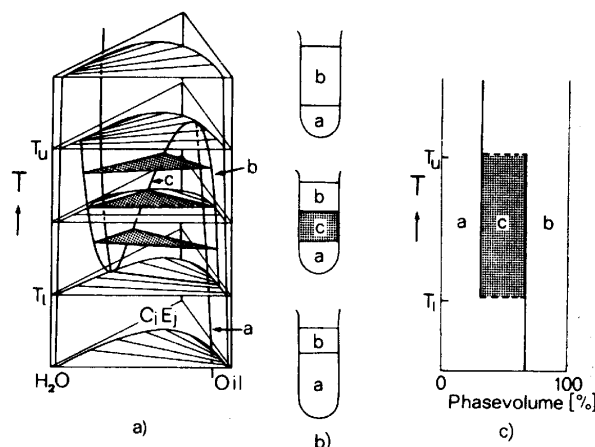


FIG. 1. The prisma in which to picture the phase diagram of a ternary system as a function of temperature. The triangles mark the coexisting phases (after Ref. 3, their Fig. 5).

^{a)}Supported in part by Deutsche Forschungsgemeinschaft under grant no. K1 256.

^{b)}On sabbatical leave from Institut für Theorie der Elementarteilchen, Freie Universität Berlin, Arnimallee 14, 1000 Berlin 33, Germany

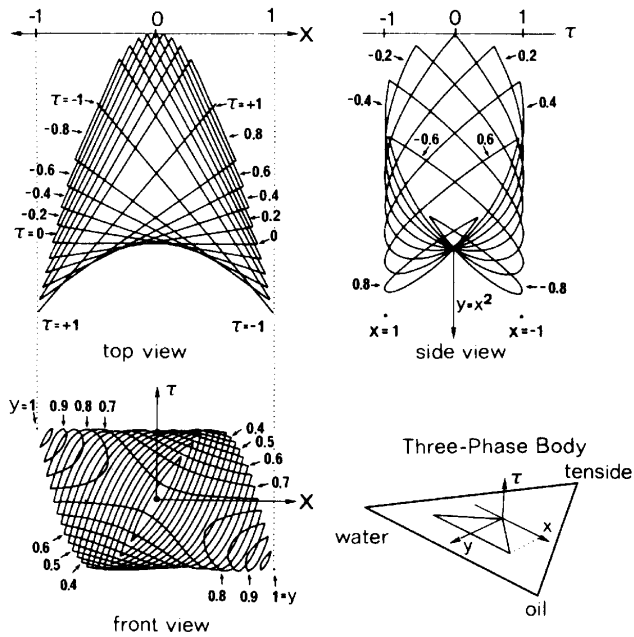


FIG. 2. The calculated boundaries of the three-phase regime within the prisma where x, y are the concentrations oil/water and tenside/(water + oil), respectively, and τ is the temperature, in reduced units.

$$y_i \frac{x_3 x_{1,2}^2 - x_{1,2} x_3^2}{x_3 - x_{1,2}} = -x_{1,2} x_3 \quad \text{for } x_3 \leq 0. \quad (8a)$$

Similarly, we find for the outer boundary

$$y_0 = \frac{x_1 x_2^2 - x_2 x_1^2}{x_1 - x_2} = -x_1 x_2. \quad (8b)$$

If we do not cut symmetrically but along a fixed value $x \neq 0$ (cut A' in Fig. 3) the intercepts are

$$y_i = -x_{1,2} x_3 + x(x_{1,2} + x_3) \quad \text{for } x_3 \leq x, \quad (9)$$

$$y_0 = -x_1 x_2 + x(x_1 + x_2) \quad \text{for } x_2 < x < x_1.$$

The resulting curves are shown in Fig. 2(b). If we take the $x = 0$ curve and scale its height vs length ratio appropriately, it fits *precisely* the data points obtained in Ref. 2 (see Fig. 4).

Let us calculate also the phase boundaries along a horizontal cut at fixed y (cut C in fig. 3). The left- and right-hand boundaries are

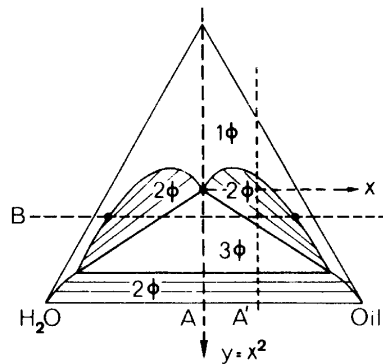


FIG. 3. The different cuts along which the data are conveniently taken.

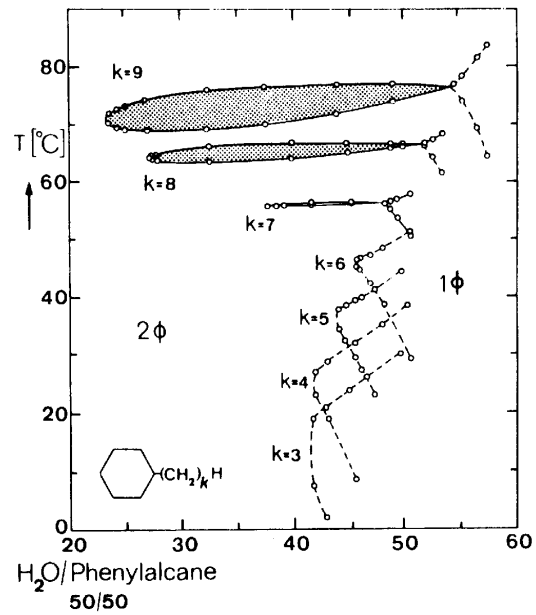


FIG. 4. Comparison of the calculated $x = 0$ cut of the three-phase regime with experiment of Ref. 2. The dashed curves through the tail ends are drawn to guide the eye.

$$\begin{aligned} x_l &= \frac{(x_2^2 - y)x_{3,1} - (x_{3,1}^2 - y)x_2}{x_2^2 - x_{3,1}^2} \\ &= \frac{x_2 x_{3,1}}{x_2 + x_{3,1}} + \frac{y}{x_2 + x_{3,1}} \quad \text{for } x_2^2 \leq y, \\ x_r &= \frac{(x_1^2 - y)x_{3,2} - (x_{3,2}^2 - y)x_1}{x_1^2 - x_{3,2}^2} \\ &= \frac{x_1 x_{3,2}}{x_1 + x_{3,2}} + \frac{y}{x_1 + x_{3,2}} \quad \text{for } x_1^2 \geq y. \end{aligned} \quad (10)$$

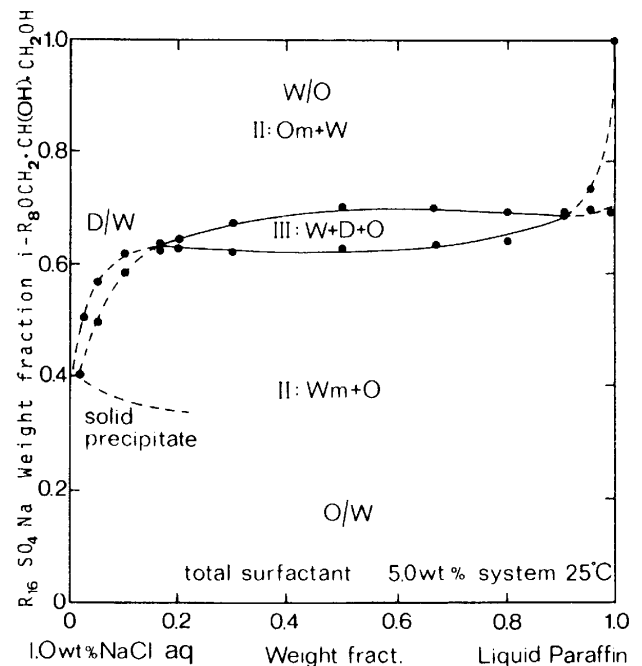


FIG. 5. Comparison of the calculated $y = 1$ curve with the data of Shinoda *et al.* (Ref. 4).

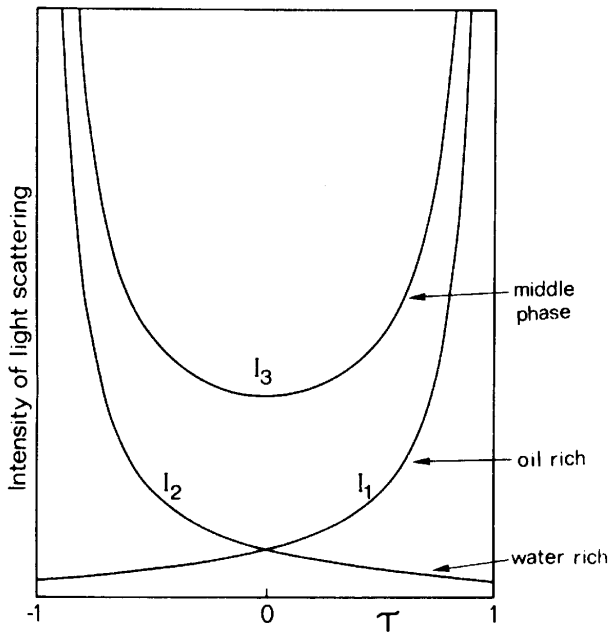


FIG. 6. The inverse curvature of the energy (3) at the three minima which determine the strength of the long-wavelength correlation of the order parameter x (= concentration) and thus the scattering of light as well as relaxation times.

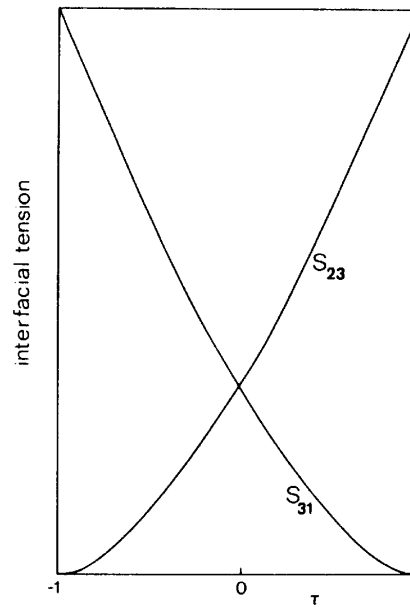


FIG. 8. The path taken by the solutions of the field equation (15) which yield the interfacial tension.

The curves $(x_i, y_i), (x_r, y_r)$ for $\tau \in (-1, 1)$ are plotted in Fig. 2(c). Figure 5 shows that the $\tau = 0$ cut (C in Fig. 3) compares well with the experimental data of Shinoda *et al.*⁴

For a further comparison with experimental data let us now study fluctuations around the three minima by adding a gradient energy and postulating the local energy density

$$f = \frac{1}{2}(\partial x(\mathbf{r}))^2 + f_{\text{pot}}(x(\mathbf{r})), \quad (11)$$

where x is now a function of the space variables \mathbf{r} and the length scale has been normalized to unity. Then the long-wavelength correlation functions in momentum space are given by the inverse curvatures at the three minima

$$\langle x(\mathbf{k})x(\mathbf{k}) \rangle|_{k=0} = (\frac{1}{2}f''_{\text{pot}}(x_{1,2,3}))^{-1}. \quad (12)$$

Since

$$\begin{aligned} \frac{1}{2}f''_{\text{pot}}(x) = & [(x - x_1)^2(x - x_2)^2 + (23) + (31)] \\ & + 12x(x - x_1)(x - x_2)(x - x_3), \end{aligned}$$

we find the inverse curvatures in the minima $i = 1, 2, 3$ to be $(x_i - x_j)^2(x_i - x_k)^2$ ($ijk = \text{cyclic}$). They are observable via the intensities I_i of scattered light (or the relaxation time t_i). In the middle phase we find

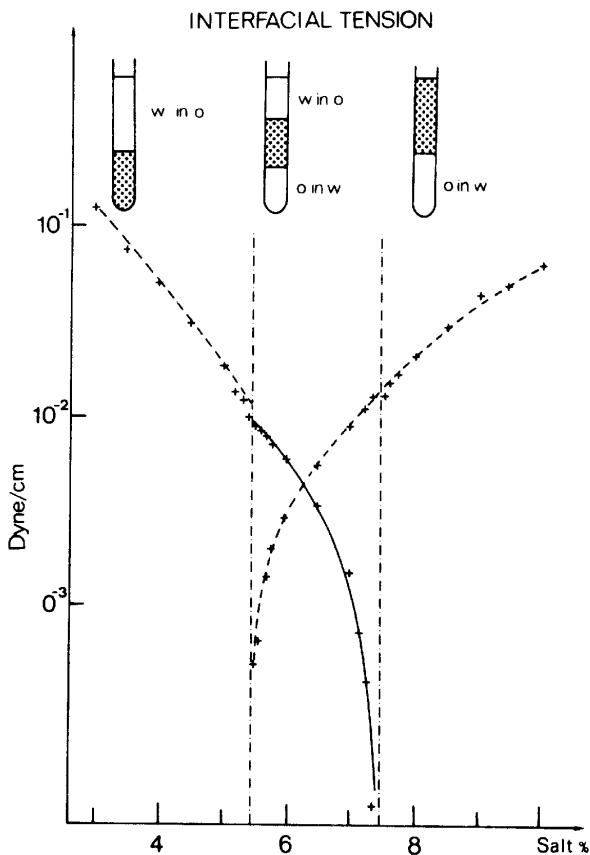


FIG. 7. Comparison of our curve for I_3 with the experimental data of Ref. 5 (their Fig. 4).

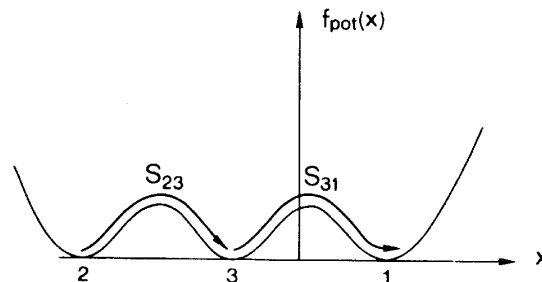


FIG. 9. The interfacial tension as a function of τ .

$$I_3 \propto (x_3 - x_1)^2 (x_3 - x_2)^{-2}. \quad (13)$$

In the oil and water rich phases, on the other hand, we have

$$I_1 \propto (x_1 - x_2)^{-2} (x_1 - x_3)^{-2}, \quad (14)$$

$$I_2 \propto (x_2 - x_1)^{-2} (x_2 - x_3)^{-2}$$

as obtained by Kaufmann, Bardhan, and Griffiths.⁵ Due to Eq. (5) the intensities satisfy the sum rules

$$I_1^{1/2} + I_2^{1/2} - I_3^{1/2} = 0,$$

$$I_1^{-1/2} + I_2^{-1/2} - I_3^{-1/2} \propto \frac{2}{3} \quad (\text{i.e., } \propto \frac{2}{3} a_4/a_6).$$

For $\tau = -1(+1)$, the middle and the water rich (oil rich) phases become critical and the intensities $I_3, I_2(I_3, I_1)$ diverge. Near the critical point, the ratio of the diverging intensities is $1 + 2(\frac{2}{3})^{3/2} \sqrt{1 - |\tau|}$. In Fig. 6 we have shown these curves and in Fig. 7 we have compared the I_3 curve with experimental data of Pouchelon *et al.*⁵ Apart from a need for a slight asymmetry correction, the agreement is excellent.

A further available set of experimental data concerns the surface tension between the three phases within our free energy (12). It is obtained by calculating the energy per area of a "domain wall solution" $x_d(z)$ of the field equation⁶

$$\frac{d^2 x_d(z)}{dz^2} = f'_{\text{pot}}(x_d(z)) \quad (15)$$

which connects the minimum at i to that at j (see Fig. 8). Using the "constant of motion"

$$\frac{1}{2} \left(\frac{dx_d(z)}{dz} \right)^2 = x_{\text{pot}}(x_d(z)), \quad (16)$$

we can integrate

$$\begin{aligned} S_{ij} &= \int_{z_i}^{z_j} dz \left[\frac{1}{2} \left(\frac{dx_d}{dz} \right)^2 + f_{\text{pot}}(x_d(z)) \right] \\ &= \int_{x_i}^{x_j} dx \frac{dz}{dx} \left(\frac{dx_d}{dz} \right)^2 = 2 \int_{x_i}^{x_j} dx \sqrt{f_{\text{pot}}(x_d(z))} \quad (17) \\ &= \mp 2 \int_{x_i}^{x_j} dx (x - x_1)(x - x_2)(x - x_3) \quad \text{for } ij = \begin{Bmatrix} 31 \\ 23 \end{Bmatrix} \\ &= -2 \left[\frac{1}{4}(x_j^4 - x_i^4) - \frac{1}{3}(x_1 + x_2 + x_3)(x_j^3 - x_i^3) \right. \\ &\quad \left. + \frac{1}{2}(x_1 x_2 + x_2 x_3 + x_3 x_1)(x_j^2 - x_i^2) - x_1 x_2 x_3 (x_j - x_i) \right] \\ &= -2 \left[\frac{1}{4}(x_j^4 - x_i^4) - \frac{3}{8}(x_j^2 - x_i^2) + \frac{1}{4}\tau(x_j - x_i) \right]. \end{aligned}$$

Eliminating τ via (4) ($\frac{1}{4}\tau = -\frac{1}{2}(x_j^3 + x_i^3) + \frac{3}{8}(x_j + x_i)$), this becomes

$$\begin{aligned} S_{ij} &= \mp \frac{1}{2}(x_j - x_i)^3 x_k, \quad ij = \begin{Bmatrix} 31 \\ 23 \end{Bmatrix}, \\ S_{21} &= S_{31} + S_{23}. \quad (18) \end{aligned}$$

The curves plotted as a function of τ in Fig. 9. A comparison with experimental data of Pouchelon *et al.*⁷ is shown in Fig. 10. Again there is need of a small asymmetry correction. Otherwise the agreement is quite good.

In conclusion we see that the simple free energy (6) extended by a gradient term [Eq. (11)] is capable of explaining the temperature behavior of the shape of the three-phase coexistence regime, the size of the fluctuations in each phase, and the interfacial tensions. It will be an important task to relate the parameters of the free energy to the microscopic properties of the system.

The author is grateful to Professor M. Kahlweit for an inspiring seminar which triggered this research and to Dr. T. Hofsäss, Dr. M. Teubner, and Dr. R. Strey for several illuminating discussions.

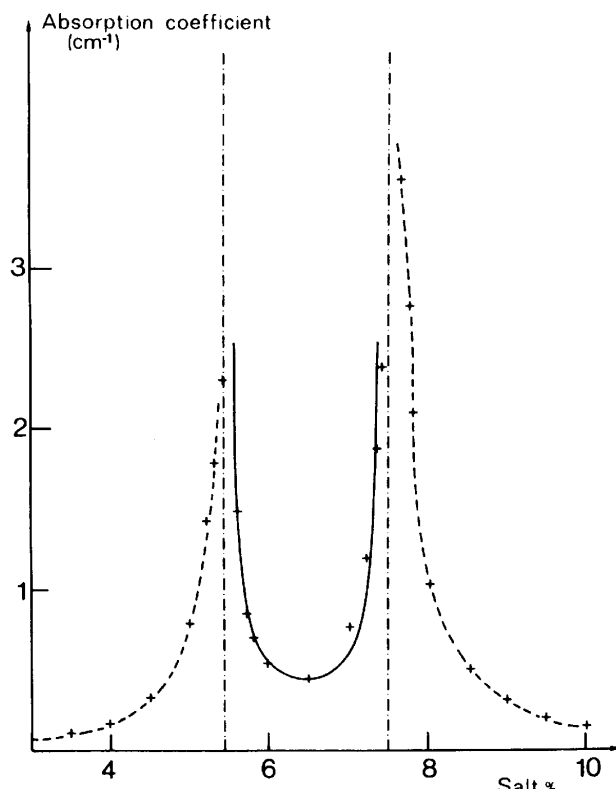


FIG. 10. Comparison of the calculated interfacial with data of Pouchelon *et al.* (Ref. 5). Some disagreement is due to the fact that the experimental system is not completely symmetric under $\tau \rightarrow -\tau$.

¹R. B. Griffiths, *J. Chem. Phys.* **60**, 195 (1974); R. B. Griffiths and B. Widom, *Phys. Rev. A* **8**, 2173 (1973); see also J. R. Fox, *J. Chem. Phys.* **69**, 12231 (1978); R. B. Griffiths and B. Widom, *Phys. Rev. A* **8**, 2173 (1973); see also J. L. Salager, *J. Colloid. Interface. Sci.* **105**, 21(1985).

²M. Kahlweit and R. Strey, *Angew. Chem.* (to be published).

³M. Kahlweit, E. Lessner, and R. Strey, *J. Phys. Chem.* **88**, 1937 (1984) (their Fig. 10).

⁴K. Shinoda, H. Kunieda, T. Arai, and H. Saijo, *J. Phys. Chem.* **88**, 5126 (1984) (their Fig. 5).

⁵M. Kaufman, K. K. Bardhan, and R. B. Griffiths, *Phys. Rev. Lett.* **44**, 77 (1980).

⁶This is the standard technique of J. S. Langer, *Physica* **73**, 61 (1974); B. Widom, *J. Chem. Phys.* **67**, 872 (1977); D. J. Klinger, M. Fisher, and B. Widom, *J. Phys. Chem.* **87**, 2841 (1983).

⁷A. Pouchelon, J. Meunier, D. Langevin, D. Chatenay, and A. M. Cazabat, *Chem. Phys. Lett.* **76**, 277 (1980) (their Fig. 2).