

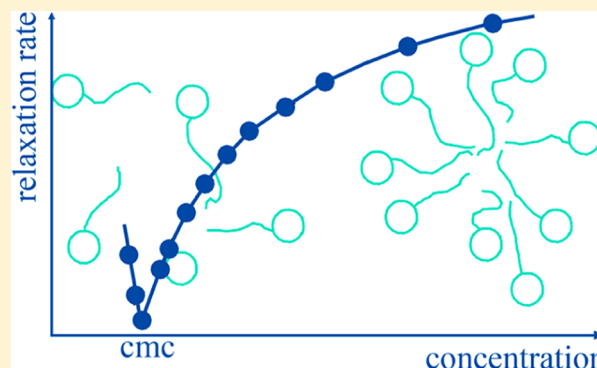
# Fluctuations Near the Critical Micelle Concentration. I. Premicellar Aggregation, Relaxation Rate, and Isentropic Compressibility

Jayanta K. Bhattacharjee<sup>\*,†</sup> and Udo Kaatz<sup>\*,‡</sup>

<sup>†</sup>Harish-Chandra Research Institute, Chhatnag Road, Jhusi, Allahabad 211019, India

<sup>‡</sup>Drittes Physikalisches Institut, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany

**ABSTRACT:** A thermodynamic model including fluctuations of micelle sizes has been derived to describe solution properties of amphiphile systems close to the critical micelle concentration. Owing to the consideration of an affinity field in the free energy of the system, the model is capable of featuring experimental findings that are incorrectly reflected by established theories of the micelle formation and disintegration kinetics. In conformity with experiments, the thermodynamic theory predicts the onset of micellar structure formation already at amphiphile concentrations below the critical micelle concentration. It also applies well for the distinctive concentration dependency of the relaxation rate of monomer exchange and likewise for the sound velocity and thus the isentropic compressibility variations with concentration. Comparison of the theoretical predictions is made with special emphasis to short-chain surfactant systems, which allowed for reliable measurements in the range below the critical micelle concentration.



## 1. INTRODUCTION

The unusual behavior of solutions of amphiphiles in water has fascinated and likewise confused scientists for the past 100 years.<sup>1</sup> Over this period of time, numerous studies, both experimental and theoretical, have been directed toward the spontaneous self-assembly of amphiphilic molecules into mesoscopic aggregates. Nevertheless, the dynamics of the aggregate formation and disintegration is still today a topic of considerable interest.<sup>1–9</sup> Such interest does not only spring from scientific curiosity but also from the need of a better understanding of the molecular processes in various domains of applications, including such diverse fields as medicine and biochemical research, food, paper, and plastics production, as well as materials processing and oil recovery.<sup>2–6</sup>

It is well established that many amphiphiles build micellar aggregates when their concentration  $c$  exceeds a limiting value, the critical micelle concentration (cmc). Normally, almost spherically shaped micelles are first formed above the cmc. Solutions of such globular micelles at  $c$  clearly above the cmc, occasionally called “proper micelle systems”, are appropriately understood now. Experimental findings relating to the kinetics of micelle formation and disintegration<sup>10–24</sup> can be primarily represented in terms of theoretical approaches<sup>25–27</sup> that rest upon the Aniansson–Wall isodesmic reaction model.<sup>28–30</sup> This prominent model is based on the probabilities for a monomer  $A_1$  to meet an aggregate  $A_{i-1}$  made of  $i-1$  monomers and to form an aggregate  $A_i$ ,  $i = 1, 2, 3, \dots$ , and, vice versa, for an aggregate  $A_i$  to disintegrate into a monomer and an aggregate  $A_{i-1}$ . Hence it proceeds from a scheme of coupled chemical equilibria  $A_{i-1} + A_1 \leftrightarrow A_i$ , with forward and reverse rate

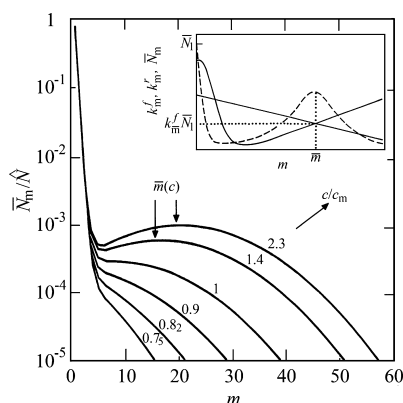
constants  $k_i^f$  and  $k_i^r$ , respectively, and with equilibrium constants  $K_i = k_i^f/k_i^r$ . Aniansson and Wall postulated identical reaction volumes  $\Delta V_i$  for all steps of the coupled reaction scheme and assumed an obvious distribution of aggregate sizes. The concentration of monomers was supposed to equal the cmc, the concentrations of oligomers were to be small, and those of micelles were to follow a Gaussian distribution. The small concentrations in the oligomer region provoke two relaxation processes in proper micelle systems. The one with smaller relaxation time  $\tau_p$ , typically on the order of nanoseconds to microseconds, represents the fast monomer exchange. The process with relaxation time  $\tau_s$ , on the order of milliseconds or seconds refers to the establishment of complete equilibrium after a small disturbance and involves a change in the concentration of micellar species.

At amphiphile concentrations  $c$  close to the cmc, however, the minimum in the oligomer region disappears in the size distribution of aggregates, as illustrated by some distribution functions displayed in Figure 1. These distribution functions have been obtained from numerical simulations, using a modified version<sup>31</sup> of the Teubner–Kahlweit–Aniansson–Wall model<sup>25–30</sup> of stepwise association and disintegration. In that version, instead of presuming the size distribution of micelles, reasonable assumptions are made on the forward and reverse rate constants. The dependencies of  $k_i^f$  and  $k_i^r$  upon the aggregation number  $i$ , as defined in the modified model,<sup>31</sup> are

**Received:** January 31, 2013

**Revised:** March 18, 2013

**Published:** March 18, 2013

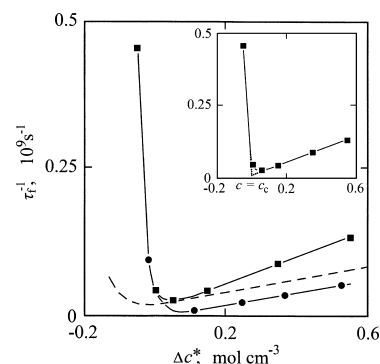


**Figure 1.** Equilibrium concentration  $\bar{N}_m$ , normalized to an amplitude  $\bar{N}$ , at some concentrations  $c$  around the cmc  $c_m$  shown in a logarithmic scale as a function of the aggregation number  $m$ .<sup>31</sup> The size distribution functions were obtained from numerical calculations based on a modified Teubner–Kahlweit theory. Parameter values corresponding with the *n*-heptylammonium chloride–water system were used in the simulation study.<sup>31</sup> In the inset, the dependencies of the forward ( $k_m^f$ ) and reverse ( $k_m^r$ ) rate constants upon  $m$  are presented. Also shown in a linear scale is the nearly Gaussian size distribution resulting from the rate constants.<sup>31</sup>

displayed in the inset of Figure 1. Also shown in the inset is the size distribution which, at  $c$  sufficiently above the cmc, results from the law of mass action.<sup>31</sup> Obviously, the definitions of the rate constants secure a nearly Gaussian distribution of micelle sizes for proper micelle system. Hence, at concentrations sufficiently above the cmc, the modified model is in conformity with the original ideas of Aniansson, Wall, Teubner, and Kahlweit. However, approaching the cmc from larger amphiphile concentrations, the relative maximum in the micelle size distribution function becomes less distinctive and, as mentioned before, the minimum in the oligomer region vanishes. As a consequence of absence of a relative minimum, the slow and fast relaxation processes of the original model merge.

In correspondence with experimental evidence,<sup>32–35</sup> the size distribution functions obtained from the simulation studies furthermore reveal the existence of small micelles and oligomeric structures at amphiphile concentrations below the cmc. They indicate, in addition, substantial deviations of the relaxation rate  $\tau_f^{-1}$  (Figure 2) from a linear dependence upon the concentration difference  $\Delta c^* = c - c_c$ , as predicted by the original micelle formation/disintegration theory if the concentration difference  $\Delta c = c - \text{cmc}$  is considered instead of  $\Delta c^*$  ( $\approx \Delta c$ ).<sup>25,26</sup> Although such deviations have been identified in a variety of experimental studies,<sup>14,16,18,19,22,32,34,35</sup> they have attracted little attention so far. Here  $c_c$  is the characteristic concentration as defined by the point of intersection when extrapolating a suitable parameter from below and above (Figure 2, inset). It will be shown below that, in general, this concentration may deviate from the cmc.

Figure 2 clearly also demonstrates a significant discrepancy between the experimental findings and the results from simulations of the modified isodesmic reaction scheme of micelle formation/disintegration. Evidently, this scheme is indeed able to indicate the general tendencies in the relaxation rates at and below the cmc, but it clearly fails to quantitatively model the striking behavior of the relaxation rates at  $c < \text{cmc}$ . Since the Teubner–Kahlweit–Aniansson–Wall model of



**Figure 2.** Relaxation rate  $\tau_f^{-1}$  of the fast relaxation process due to the monomer exchange versus concentration difference  $\Delta c^* = c - c_c$  for aqueous solutions of *n*-heptylammonium chloride<sup>35</sup> (■, HepACl,  $c_c = 0.45$  mol/L) at 25 °C and of triethylene glycol monohexyl ether<sup>32</sup> (●, C<sub>6</sub>E<sub>3</sub>,  $c_c = 0.1$  mol/L) at 17.5 °C. The  $\tau_f$  data are principal relaxation times of a distribution function controlling the fast relaxation processes. The dashed line reveals the results from the numerical calculations on the basis of the modified Teubner–Kahlweit model of the micelle formation/disintegration kinetics.<sup>31</sup> The inset illustrates the extrapolation from below and above to an intersection point, the concentration at which  $\Delta c^* = 0$ , i.e.,  $c = c_c$ .

stepwise association, in its original as well as in its modified form, is unable to properly account for the relaxation rates of amphiphile solutions near their cmc, it is an obvious attempt to consider the dynamics of such systems close to the cmc to be dominated by fluctuations. In this paper, we present a theoretical model that proceeds from a Landau approach in order to focus on the local fluctuations in the concentration of amphiphile species.

## 2. GENERAL DISPOSITION

Focusing on the concentration range near the cmc, denoted  $c_m$  in the following, let us build a Landau picture based on the manifold observations that at  $c > c_m$ , almost spherically shaped micelles with size distribution around a mean  $\bar{m}$  exist. Let us start with the generally accepted assumptions

$$\bar{m} = 0 \quad \text{at} \quad c < c_m \quad (1a)$$

and

$$\bar{m} \neq 0 \quad \text{at} \quad c > c_m \quad (1b)$$

Fluctuations around  $\bar{m}$  imply that the monomer concentration also fluctuates. Let us use the fluctuating micelle size  $m$  as the variable in the following. According to  $\phi = (\partial\phi)/(\partial m)m$ , it creates a fluctuating concentration  $\phi$ . Following Landau and Ginzburg<sup>36</sup> and keeping criteria 1a and 1b in mind, the fluctuation contribution to the free energy  $F$  can be written as

$$F = \int d^3r \left[ \frac{a}{2} m^2 + \frac{1}{2} (\vec{\nabla} m)^2 + \frac{b}{4} m^4 + \dots \right] \quad (2)$$

In this equation,  $b$  is a constant and

$$a = a_0(c_m - c) \quad (3)$$

where  $a_0 > 0$  is also a constant. We need to keep in mind that  $c_m$  is a function of temperature<sup>37–39</sup> and possibly also of pressure.

All thermodynamic properties will follow from the partition function

$$Z = \sum_{m(\vec{r})} e^{-F/k_B T} \quad (4)$$

with  $k_B$  denoting the Boltzmann constant. Since in our sphere of interest temperature will not change appreciably, we shall continue in units  $k_B T = 1$ . We first look at the mean field approximation. Within such approximation,  $Z$  is calculated for the  $m(\vec{r})$  that minimizes  $F$ . Obviously this approach leads to a spatially independent  $m$  ( $= \bar{m}$ ) and thus  $F$  reduces to

$$F = V \left[ \frac{a}{2} \bar{m}^2 + \frac{b}{4} \bar{m}^4 \right] \quad (5)$$

where  $V$  denotes the volume. Minimizing with respect to  $\bar{m}$  yields

$$\bar{m}[a + b\bar{m}^2] = 0 \quad (6)$$

i.e.,

$$\bar{m} = 0 \quad \text{or} \quad \sqrt{-a/b} \quad (7)$$

Clearly, for  $c < c_m$  we have  $a > 0$  (eq 3), and the only solution is  $\bar{m} = 0$ . Hence so far the mean field approximation predicts the average size of micelles to be zero at  $c < c_m$ , indicating that there appears to be no micelle formation. For  $c > c_m$ , the minimization gives

$$\bar{m} = \sqrt{\frac{a_0}{b}} (c - c_m)^{1/2} = \sqrt{\frac{a_0}{b}} \Delta c^{1/2} \quad (8)$$

This relation implies that for  $c > c_m$ , the size starts from zero ( $c = c_m$ ) and grows as  $c$  increases. At this point we notice that at  $c = c_m$ , most likely a finite value of  $\bar{m}$  exists already in the system. This  $\bar{m}$  may be small but nonzero, as it is caused by an affinity for forming micelles, resulting predominantly from hydrophobic or, more generally, solvophobic interactions and related to a chemical potential. This affinity, which is reflected by the chemical reactions going on within the system, will be considered by an affinity field  $\mu$ . If  $\mu$  is included in the free energy, eq 2 will now contain a symmetry breaking term and will appear as

$$F = \int d^3r \left[ \frac{a}{2} m^2 + \frac{1}{2} (\vec{\nabla} m)^2 + \frac{\mu}{3} m^3 + \frac{b}{4} m^4 \right] \quad (9)$$

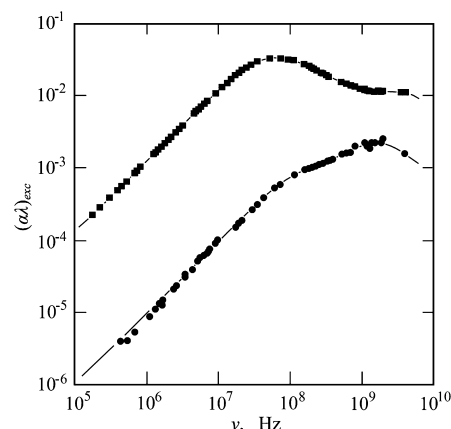
In the mean field theory, the analogue of eq 6 is now

$$\bar{m}[a + \mu\bar{m} + b\bar{m}^2] = 0 \quad (10)$$

giving extrema at

$$\bar{m} = 0 \quad \text{or} \quad \bar{m} = \frac{-\mu \pm \sqrt{\mu^2 - 4ab}}{2b} \quad (11)$$

These finite extrema in the mean aggregation number exist at  $a \leq \mu^2/(4b)$ . Hence they come into existence already at  $a = \mu^2/(4b)$ , i.e., at  $c < c_m$ . This result profoundly changes the simple picture provided by eq 8, which predicts a nonvanishing  $\bar{m}$  to exist only at  $c > c_m$ . The typical behavior of solutions with molecularly dispersed solutes does not continue until  $c_m - c = 0$  but will stop already at  $a_0(c_m - c) = \mu^2/(4b)$ . This feature is illustrated by Figure 3, which shows that ultrasonic excess attenuation with comparatively small amplitude exists already at an amphiphile concentration of 0.7 mol/L, whereas the characteristic concentration of that system is  $c_c = 1.1$  mol/L and the cmc may be even larger, as will be argued below.



**Figure 3.** Ultrasonic excess attenuation per wavelength  $(\alpha\lambda)_{\text{exc}}$  versus frequency  $\nu$  for aqueous solutions of *n*-hexylammonium chloride at 25 °C and at two amphiphile concentrations<sup>40</sup> (●, 0.7 mol/L; ■, 1.0 mol/L =  $c_m$ ). Here  $(\alpha\lambda)_{\text{exc}} = \alpha\lambda - B\nu$ , where  $\alpha$  is the sonic attenuation coefficient,  $\lambda$  the wavelength of the sonic field within the liquid, and  $B$  the coefficient of the less interesting high-frequency contributions to the ultrasonic attenuation.

This interesting behavior can be sensitively seen in the correlation function  $G(r_{12})$  of fluctuations. Using the quadratic part in the free energy (eq 9) to construct the correlation function, the usual Ornstein – Zernike form<sup>41</sup>

$$G_{\text{OZ}}(r_{12}) = \text{const.} \frac{\exp(r_{12}/\xi)}{r_{12}} \quad (12)$$

follows, with correlation length given by

$$\xi = \xi_0(c_m - c)^{-1/2} \quad (13)$$

In principle this correlation length will diverge at  $c = c_m$ . However, as noted above, the smallest  $c_m - c$  that can be reached by the system is  $\mu^2/(4a_0b)$  so that there is a maximum value  $\xi_{\text{max}}$  of  $\xi$ . The nonlinear terms in the free energy will change the exponent in the power law of the correlation length (eq 13) in the usual manner<sup>42</sup> and we will finally have

$$\xi = \xi_0(c_m - c)^{-\tilde{\nu}} \quad (14)$$

and

$$\xi_{\text{max}} = \xi_0 \left( \frac{\mu^2}{4a_0b} \right)^{-\tilde{\nu}} \quad (15)$$

with  $\tilde{\nu} = 0.63^{43,44}$  denoting the universal critical exponent of  $\xi$ .

We will now consider the specific heat of the amphiphile system. In a constant pressure physical situation, the specific heat

$$C_p = -T \frac{\partial^2 F}{\partial T^2} \quad (16)$$

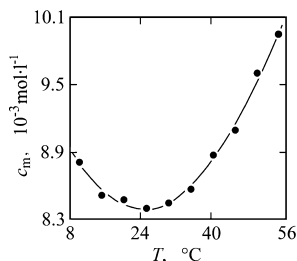
is given by the second derivative of the free energy  $F$  with respect to temperature  $T$  and  $F$  follows from eq 4 as

$$F = -\ln Z \quad (17)$$

At first sight, one may think that this model does not have a specific heat. However, as mentioned before,<sup>37–39</sup> there is a smooth temperature dependence of the cmc. For a popular surfactant system as an example, the temperature effect in  $c_m$  is

illustrated by Figure 4. Keeping this dependence in mind, the derivative of  $Z$  with respect to  $T$  gives the expression

$$C_p = a_0^2 \left( \frac{dc_m}{dT} \right)^2 \int d^3r_{12} \langle m^2(\vec{r}_1) m^2(\vec{r}_2) \rangle \quad (18)$$



**Figure 4.** Dependence of the cmc  $c_m$  of solutions of sodium dodecylsulfate in water upon temperature  $T$ .<sup>45</sup>

This is the usual expression that one finds for critical phenomena, except that it now includes term  $dc_m/dT$  in the prefactor. It shows that our model will not give an extra contribution to the specific heat near  $c = c_m$ , if  $c_m$  does not depend upon  $T$ . The analysis of this specific heat follows the usual path in the treatment of critical phenomena,<sup>42,46</sup> except that one needs to stop at finite  $\Delta c$ . From our expression for the free energy, we get

$$C_p = C_0(c_m - c)^{-\alpha_0} \quad (19)$$

for  $c < c_m$ , and the divergence at  $c = c_m$  will be stopped because of the finite  $c_m - c = \mu^2/(4ba_0)$  that can be reached, as discussed before. The critical exponent  $\alpha_0$  ( $= 0.11^{44,47,48}$ ) is the universal exponent that governs regular critical systems, such as critically demixing binary liquids. It is the finite frequency specific heat  $C_p(c, \nu)$  that controls the sound attenuation in these systems ( $\nu$  = frequency). To set the stage for that, we need to understand the dynamics of  $m(\vec{r})$ . For that purpose, we prescribe the usual Langevin dynamics<sup>42</sup> for  $m(\vec{r}, t)$  by

$$\frac{\partial m}{\partial t} = -\Gamma \frac{\partial F}{\partial m} + \Xi \quad (20)$$

which is

$$\frac{\partial m}{\partial t} = -\Gamma[am - \nabla^2 m + \mu m^2 + bm^3] + \Xi \quad (21)$$

In these equations,  $\Xi$  denotes usual Gaussian noise with delta function correlation. Due to the aggregate formation/disintegration processes that may alter the concentration of micellar species in the system, we did not use an overall conservation law so far. The only overall conservation law is that the number of amphiphile molecules in the systems is constant. Hence, at any instant, the sum  $\sum_m m \bar{N}_m$  of the number of monomers and of the number of molecules within aggregates is conserved but not the sum of the number of monomers and of micellar aggregates.

Working in the linear approximation, we note that the relaxation time  $\tau_c$  ( $= \Gamma^{-1}(c < c_m)$ ), following from eq 21 for the regime below the cmc, diverges as

$$\tau_c \propto (c_m - c)^{-1} \quad (22)$$

with the exception that it never reaches infinity as  $c_m - c$  never reaches zero. Hence, in correspondence with a maximum correlation length (eq 15), there is a maximum relaxation time

$$\tau_{c_{\max}} \propto \left( \frac{\mu^2}{a_0 b} \right)^{-1} \quad (23)$$

In the regime above the cmc, i.e.,  $a < 0$ , the finite  $\bar{m}$  has to be considered, and it is common to write the aggregation number as

$$m = \bar{m} + \delta m \quad (24)$$

where  $\delta m$  is the fluctuation around  $\bar{m}$ . The free energy of eq 9 is now

$$\begin{aligned} F &= \int d^3r \left[ \frac{a}{2} (\bar{m} + \delta m)^2 + \frac{\mu}{3} (\bar{m} + \delta m)^3 + \frac{b}{4} (\bar{m} + \delta m)^4 \right] \\ &\quad + \int d^3r \frac{1}{2} (\nabla \delta m)^2 \\ &= \int d^3r \left[ \frac{a}{2} \bar{m}^2 + \frac{\mu}{3} \bar{m}^3 + \frac{b}{4} \bar{m}^4 \right] \rightarrow F_0 = \text{constant} \\ &\quad + \int d^3r \delta m [a\bar{m} + \mu\bar{m}^2 + b\bar{m}^3] \rightarrow \text{zero} \\ &\quad + \int d^3r (\delta m)^2 \left[ \frac{a}{2} + \mu\bar{m} + \frac{3}{2}b\bar{m}^2 \right] + \int d^3r (\delta m)^3 \left[ \frac{\mu}{3} + b\bar{m} \right] \\ &\quad + \frac{b}{4} \int d^3r (\delta m)^4 + \frac{1}{2} \int d^3r (\nabla \delta m)^2 \\ &= F_0 + \int d^3r \left[ \frac{a}{2} + \mu\bar{m} + \frac{3}{2}b\bar{m}^2 \right] (\delta m)^2 + \frac{1}{2} \int d^3r (\nabla \delta m)^2 \\ &\quad + \int d^3r \left[ \frac{\mu}{3} + b\bar{m} \right] (\delta m)^3 + \frac{b}{4} \int d^3r (\delta m)^4 \end{aligned} \quad (25)$$

At minimum  $F$  and finite  $\bar{m}$ , we have  $a + \mu\bar{m} + b\bar{m}^2 = 0$  as shown before (eq 10). Therefore,

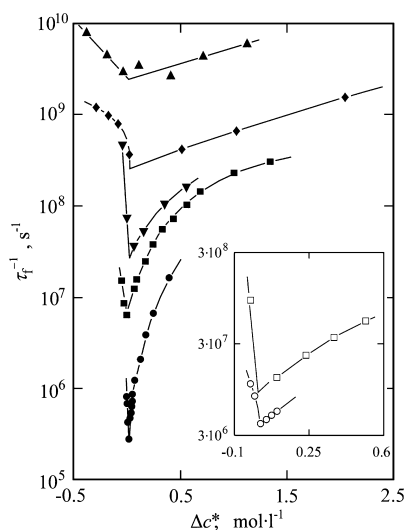
$$\begin{aligned} F &= F_0 + \int d^3r \left[ \frac{1}{2} b\bar{m}^2 + \frac{a}{2} \right] (\delta m)^2 + \frac{1}{2} \int d^3r (\nabla \delta m)^2 \\ &\quad + \int d^3r \left[ \frac{\mu}{3} + b\bar{m} \right] (\delta m)^3 + \frac{b}{4} \int d^3r (\delta m)^4 \end{aligned} \quad (26)$$

We note that the relaxation rate  $\tau_c^{-1}$  ( $= \Gamma(c > c_m)$ ) in the dynamics of the system above the  $c_m$  is now inversely proportional to the coefficient of the  $(\delta m)^2$  term and thus

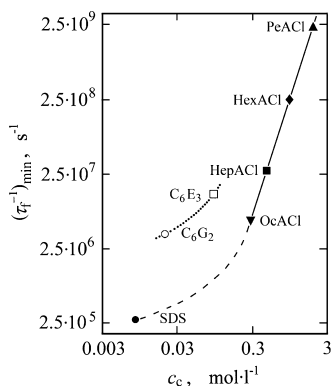
$$\tau_c^{-1} \propto [b\bar{m} + |a|] = [b\bar{m} + a_0 \Delta c] \quad (27)$$

Hence for the region above the cmc, our model predicts a slower variation of the relaxation rate with respect to  $\Delta c$  than for the concentration range below the cmc, for which  $\tau_c^{-1} \propto a_0 |\Delta c|$  results (eq 22). This feature is clearly demonstrated by the experimental relaxation rate data  $\tau_f^{-1}$  for anionic, cationic, as well as nonionic surfactant systems displayed in Figure 5. These data also reveal a substantial variation of the minimum relaxation rates  $(\tau_f^{-1})_{\min} = \tau_f^{-1}(\Delta c^* = 0) = \tau_f^{-1}(\Delta c \approx 0)$  with the nature of the surfactant. Figure 6, in which the  $(\tau_f^{-1})_{\min}$  values are plotted versus the cmc  $c_m$ , evidences this finding in a suggestive manner. Our model predicts the minimum relaxation rates, in the regime above the cmc, to be reached at  $\Delta c = 0$  where  $b \propto (\tau_c^{-1})_{\min}/\bar{m}$ . Since, within a series of surfactants, the minimum relaxation rate tends to increase with cmc (Figure 6) and since simultaneously the mean aggregation number decreases, parameter  $b$  in the free energy of the amphiphile





**Figure 5.** Relaxation rate  $\tau_f^{-1}$  of the fast monomer exchange relaxation term in the ultrasonic spectra of aqueous solutions of some ionic (filled symbols,<sup>33</sup> 25 °C) and nonionic surfactants (open symbols), displayed versus concentration difference  $\Delta c^* = c - c_c$ :  $\blacktriangle$ , *n*-pentylammonium chloride (PeACl,  $c_c = 1.9$  mol/L);  $\blacklozenge$ , *n*-hexylammonium chloride (HexACl,  $c_c = 1.1$  mol/L);  $\blacktriangledown$ , *n*-heptylammonium chloride (HepACl,  $c_c = 0.45$  mol/L);  $\blacksquare$ , *n*-octylammonium chloride (OcACl,  $c_c = 0.27$  mol/L);  $\bullet$ , sodium dodecylsulfate (SDS,  $c_c = 0.0083$  mol/L);  $\square$ , triethylene glycol monoethyl ether<sup>32</sup> ( $C_6E_3$ , 17.5 °C,  $c_c = 0.12$  mol/L);  $\circ$ , *n*-hexyl- $\beta$ -D-maltopyranoside<sup>23</sup> ( $C_6G_2$ , 25 °C,  $c_c = 0.213$  mol/L).



**Figure 6.** Minimum relaxation rates  $(\tau_f^{-1})_{min}$  of aqueous surfactant solutions shown as a function of the characteristic concentration  $c_c$ . Data are taken from Figure 5 where also the abbreviated names of the surfactants are given.

system appears to be strongly correlated with the cmc. In the concentration range below the cmc the minimum relaxation rate is given by the maximum attainable relaxation time as expressed by eq 23. Therefore,  $(\tau_f^{-1})_{min} = \tau_{c_{max}}^{-1} \propto a_0 b \mu^{-1}$  and, combined with eq 15,  $(\tau_f^{-1})_{min} \propto \xi_{max}^{-1/\nu} = 1/\xi_{max}^{1.587}$  follows. Hence, according to our expectations, systems with high cmc are predicted to exhibit large minimum relaxation rates, logically accompanied by small maximum correlation lengths.

### 3. ISENTROPIC COMPRESSIBILITY AND SOUND VELOCITY

We will now consider the isentropic compressibility as the primary quantity for the study of interactions between sound and the liquids. Since we want to focus on the concentration range near the cmc, we need to know the compressibility only

for small  $|\Delta c|$  values. In the previous section it turned out that at  $|\Delta c| \simeq 0$  the amphiphile system is near a critical point. For the micelle formation, we can thus imagine a line of critical points,  $c_m(T)$ . It is the existence of these critical points from which an extra contribution to the specific heat  $C_p$  had followed above. We will pay careful attention to derivatives with respect to  $\Delta c$  which we will use as the scaled variable instead of the total amphiphile concentration  $c$ . All other variables will be assumed analytic. We start with the Gibbs free energy  $G = U + PV - TS$  and with the thermodynamic relationship

$$TdS = dU + PdV - \mu dc \quad (28)$$

in which  $\mu$  is the chemical potential corresponding to the amphiphile concentration  $c$ . We find

$$dG = -SdT + VdP + \mu dc \quad (29)$$

Although never explicitly stated, it is obvious that the critical concentration  $c_m$  corresponds to a critical pressure  $P_m$ . So we integrate eq 29 at constant  $T$  and, away from the critical line, we get

$$G = G_m + \int_{P_m}^P V dP + \int_{c_m}^c \mu dc \quad (30)$$

Since we are going to very close to criticality, i.e.,  $P \approx P_m$  and  $c \approx c_m$ , we can integrate eq 30, using the mean value theorem<sup>49</sup> to write

$$G = G_m + V_m \Delta P + \mu_m \Delta P \quad (31)$$

where  $V_m = V(c_m)$ ,  $\mu_m = \mu(c_m)$ , and  $\Delta P = P - P_m$ . We get the volume by calculating

$$\begin{aligned} V &= \left( \frac{\partial G}{\partial P} \right)_{T,c} = \left( \frac{\partial G_m}{\partial P} \right)_{T,c} + \frac{\partial V_m}{\partial P} \Delta P + V_m + \frac{\partial \mu_m}{\partial P} \Delta c \\ &\quad - \mu_m \frac{\partial c_m}{\partial P} \\ &= \left( \frac{\partial G}{\partial P} \right)_{T,c} + V'_m \Delta P + V_m + \mu'_m \Delta c - \mu'_m c'_m \end{aligned} \quad (32)$$

where primes denote derivatives with respect to pressure. We change the derivative with respect to  $P$  in the first term to a derivative with respect to  $\Delta c$  using the chain rule and get

$$\begin{aligned} \left( \frac{\partial G_m}{\partial P} \right)_{T,c} &= \left( \frac{\partial G_m}{\partial P} \right)_{T,\Delta c} + \left( \frac{\partial G_m}{\partial (\Delta c)} \right)_T \left( \frac{\partial (\Delta c)}{\partial P} \right)_T \\ &= G'_m - \left( \frac{\partial G_m}{\partial c} \right)_T \left( \frac{\partial c_m}{\partial P} \right)_T \\ &= G'_m - \mu'_m c'_m \end{aligned} \quad (33)$$

Hence eq 32 reads

$$V = G'_m + V_m + V'_m \Delta P - 2\mu'_m c'_m + \mu'_m \Delta c \quad (34)$$

We need to calculate the isentropic susceptibility

$$\chi_s = -\frac{1}{V^2} \left( \frac{\partial V}{\partial P} \right)_{S,c} \quad (35)$$

and take a differential of  $V$  for this purpose as we vary pressure:

$$\begin{aligned}
\delta V &= G''_m \delta P + 2V'_m \delta P + V''_m \Delta P \delta P \\
&\quad - (2\mu'_m c'_m + 2\mu''_m c''_m) \delta P + \mu''_m \Delta c \delta P \\
&\quad + \mu'_m \delta(\Delta c) \\
&= [G''_m + 2V'_m + V''_m \Delta P - 2\mu'_m c'_m - 2\mu''_m c''_m \\
&\quad + \mu''_m \Delta c] \delta P + \mu'_m \delta(\Delta c)
\end{aligned} \quad (36)$$

Imposing the entropy clamping condition for the variation  $\delta(\Delta c)$  we write

$$\delta S = \left( \frac{\partial S}{\partial(\Delta c)} \right)_P \delta(\Delta c) + \left( \frac{\partial S}{\partial P} \right)_{\Delta c} \delta P \quad (37)$$

and setting this equal to zero we get

$$\begin{aligned}
\delta S &= \left( \frac{\partial S}{\partial(\Delta c)} \right)_P \delta(\Delta c) + \left( \frac{\partial S}{\partial P} \right)_{\Delta c} \delta P \\
&= \left[ S'_m \left( \frac{\partial S}{\partial P} \right)_P^{-1} \frac{\partial T}{\partial c_m} \right] \delta P \\
&= \left[ TS'_m \left( \frac{\partial c_m}{\partial T} \right) C_p^{-1} \right] \delta P,
\end{aligned} \quad (38)$$

where  $C_p$  is again the specific heat at constant pressure. This relation allows us to write eq 36 at constant entropy as

$$\delta V = \left[ D_0 + \frac{TS'_m \mu'_m}{C_p} \frac{\partial c_m}{\partial T} \right] \delta P \quad (39)$$

At small  $\Delta c$  variation, parameter  $D_0$  is a constant. The quantity with stronger dependence upon  $\Delta c$  is the specific heat  $C_p$ .

Finally the sound velocity  $u$  follows from eq 39 as

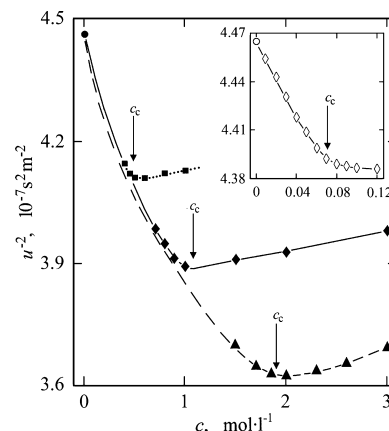
$$u^{-2} = u_0^{-2} + D/C_p \quad (40)$$

where  $u_0$  is a constant and  $D$  is proportional to the gradient  $dc_m/dT$ , indicating again that the coupling of the sonic field to the fluctuations in the amphiphile systems is strongly dependent on the temperature dependence  $c_m(T)$  of the cmc.

The sound velocity relation (eq 40) can be compared to experimental data (Figure 7). Experiments yielded a very small variation of  $u^{-2}$ , and thus of the isentropic compressibility  $\kappa_s = u^{-2}\rho^{-1}$ , at concentrations around the cmc. Our theoretical model relates this small effect to the specific heat, which is the quantity in eq 40 that varies but slightly with amphiphile concentration. In correspondence with the relaxation rate  $\tau_f^{-1}$  (Figure 5),  $C_p$ , and thus  $u^{-2}$ , and  $\chi_s$  exhibit a stronger variation for  $c < c_m$  than for  $c > c_m$ .

#### 4. CONCLUSIONS

A phenomenological Landau picture, which considers the tendency of amphiphile systems to form micelles by an extra affinity term in the free energy, exposes some fundamental features of surfactant solutions near their cmc  $c_m$ . First of all, consideration of a symmetry breaking affinity term clearly reveals an aggregate size distribution with finite mean aggregation number  $\bar{m}$  already at an amphiphile concentration below the cmc. The existence of micellar structures at  $c < c_m$  had been evidenced by several experiments in the past.<sup>32–35</sup> So far, however, attempts to extend the Aniansson–Wall isodesmic



**Figure 7.** Inverse squared sound velocity  $u^{-2}$  versus surfactant concentration  $c$  for aqueous solutions of *n*-heptylammonium chloride (■, HepACl<sup>35</sup>), *n*-hexylammonium chloride (◆, HexACl<sup>33</sup>), *n*-pentylammonium chloride (▲, PeACl<sup>33</sup>), and sodium dodecylsulfate (◇, SDS<sup>22</sup>) at 25 °C.

scheme of coupled reactions<sup>28–30</sup> had failed to explain the experimental findings satisfactorily. At  $c < c_m$ , the affinity field thus prevents fluctuations in the local concentration to increase until the cmc is reached. Rather, the increase in the fluctuations will be stopped at  $c_c$  where the formation of surfactant aggregates starts, offering a second pathway for minimizing the free energy and thus for approaching equilibrium. The concentration distance  $c_m - c_c$  is given by the affinity parameter and the other coefficients in the series representation of the free energy.

The distance  $c_m - c$  of the amphiphile concentration from the cmc governs the fluctuation correlation length  $\xi$  if the correlation function is assumed to follow the usual Ornstein–Zernike form and it also controls the specific heat at constant pressure. When analyzed along the path usually followed in the treatment of critical phenomena, it is found that the coupling of the fluctuations is provided by the temperature dependence  $dc_m/dT$  in the cmc. Since  $c_m(T)$  may feature a relative minimum (Figure 4) the contributions from fluctuations to the specific heat should noticeably depend upon temperature. To our knowledge, no systematic investigation into this temperature effect has been conducted so far.

In the linear approximation, Langevin dynamics embracing Gaussian-noise-like fluctuations yield relaxation rates which decrease proportional to  $c_m - c$  at  $c < c_m$  and increase slower than proportional to  $c - c_m$  above the cmc. Both results, the prediction of finite relaxation rates at amphiphile concentrations below the cmc and the statement about the difference between the slopes of the relaxation rates, are in nice conformity with results from ultrasonic attenuation spectroscopy (Figure 5). The minimum relaxation rates adopted near the cmc depend significantly on the nature of the amphiphile (Figure 6) and, within the framework of our thermodynamic model, are again given by the coefficients in the expression for the free energy.

Around the cmc, the Gibbs free energy of the amphiphile system can be evaluated to show that the concentration dependence in the squared sound velocity  $u^{-2}$  (as well as of the isentropic compressibility) is controlled by the concentration dependence of the specific heat at constant pressure. A comparatively steep decrease, with  $(c_m - c)^{\alpha_0}$ , follows at  $c < c_m$ , where  $\alpha_0$  is the universal critical exponent of the specific

heat of critically demixing binary liquids. Like the relaxation rates (Figure 5), the absolute values of the slopes in the  $u^{-2}(c)$  relations are smaller at  $c < \text{cmc}$  than at  $c > \text{cmc}$  (Figure 7). Hence our fluctuation model features solutions properties near the cmc of amphiphile systems that are not represented by theories describing the kinetics of micelle formation and disintegration. It thus enables a reasonable understanding of striking characteristics of such systems at concentrations at which small clusters and premicellar aggregates are being formed.

## AUTHOR INFORMATION

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We gratefully acknowledge financial support by the International Office, Georg-August-Universität Göttingen.

## REFERENCES

- (1) Patist, A.; Kanicky, J. R.; Shukla, P. K.; Shah, D. O. Importance of Micellar Kinetics in Relation to Technological Processes. *J. Colloid Interface Sci.* **2001**, *245*, 1–15.
- (2) Rosen, M. J.; Kunjappu, J. T. *Surfactants and Interfacial Phenomena*; Wiley: Hoboken, NJ, 2012.
- (3) Zana, R., Ed. *Dynamics of Surfactant Self-Assemblies*; CRC Press: Boca Raton, FL, 2005.
- (4) Myers, D. *Surfactant Science and Technology*; Wiley: Hoboken, NJ, 2012.
- (5) Tadros, T. F. *Applied Surfactants, Principles and Applications*; Wiley-VCH: Weinheim, Germany, 2005.
- (6) Evans, D. F.; Wennerström, H. *The Colloidal Domain. Where Physics, Chemistry, and Biology Meet*; Wiley-VCH: New York, 1999.
- (7) Nyrkova, I. A.; Semenov, A. N. On the Theory of Micellization Kinetics. *Macromol. Theory Simul.* **2005**, *14*, 569–585.
- (8) Mohan, G.; Kopelevich, D. I. A Multiscale Model for Kinetics of Formation and Disintegration of Spherical Micelles. *J. Chem. Phys.* **2008**, *128*, 044905 DOI: 10.1063/1.2823729.
- (9) Hadgiivanova, R.; Diamant, H.; Andelman, D. Kinetics of Surfactant Micellization: A Free Energy Approach. *J. Phys. Chem. B* **2011**, *115*, 7268–7280, DOI: 10.1021/jp1073335.
- (10) Adair, D. A. W.; Reinsborough, V. C.; Plavac, N.; Valteau, J. P. Chemical Relaxations in Aqueous Micellar Solutions by Ultrasonic Spectroscopy. I. Alkali Metal Hexyl and Octyl Sulfates. *Can. J. Chem.* **1974**, *52*, 429–433.
- (11) Rassing, J.; Sams, P. J.; Wyn-Jones, E. Kinetics of Micellization from Ultrasonic Relaxation Studies. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1247–1258.
- (12) Lang, J.; Tondre, C.; Zana, R.; Bauer, R.; Hoffmann, H.; Ulbricht, W. Chemical Relaxation Studies of Micellar Equilibria. *J. Phys. Chem.* **1975**, *79*, 276–283.
- (13) Aniansson, E. A. G.; Wall, S. N.; Almgren, M.; Hoffmann, H.; Kielmann, I.; Ulbricht, W.; Zana, R.; Lang, J.; Tondre, C. Theory of the Kinetics of Micellar Equilibria and Quantitative Interpretation of Chemical Relaxation Studies of Micellar Solutions of Ionic Surfactants. *J. Phys. Chem.* **1976**, *80*, 905–922.
- (14) Adair, D. A. W.; Reinsborough, V. C.; Trendholm, H. M.; Valteau, J. P. Chemical Relaxations in Micellar Solutions by Ultrasonic Spectroscopy. II. Sodium Heptylsulfate and Hexylammonium Chloride Solutions. *Can. J. Chem.* **1976**, *54*, 1162–1167.
- (15) Diekmann, S. On the Micellization Kinetics of Sodium-Decylsulfate. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 528–532.
- (16) Hall, D. G.; Wyn-Jones, E. Chemical Relaxation Spectroscopy in Aqueous Surfactant Solutions. *J. Mol. Liq.* **1986**, *32*, 63–82.
- (17) Thomason, M. A.; Bloor, D. M.; Wyn-Jones, E. Ultrasonic Relaxation Associated with Monomer/Micelle Exchange of Nonionic Surfactants in Formamide. *J. Phys. Chem.* **1991**, *95*, 6017–6020.
- (18) Frindi, M.; Michels, B.; Levy, H.; Zana, R. Alkanediyl- $\alpha,\omega$ -bis(dimethylalkylammonium bromide) Surfactants. 4. Ultrasonic Absorption Studies of Amphiphile Exchange between Micelles and Bulk Phase in Aqueous Micellar Solutions. *Langmuir* **1994**, *10*, 1140–1145.
- (19) Frindi, M.; Michels, B.; Zana, R. Ultrasonic Absorption Studies of Surfactant Exchange between Micelles and the Bulk Phase in Aqueous Micellar Solutions of Amphoteric Surfactants. *J. Phys. Chem.* **1994**, *98*, 6607–6611.
- (20) Matsuoka, T.; Shibata, T.; Koda, S.; Nomura, H. Effect of Addition of Surfactant on Micelle-Monomer Exchange Process. *J. Mol. Liq.* **1995**, *65/66*, 337–340.
- (21) Nomura, H.; Koda, S.; Matsuoka, T.; Hiyama, T.; Shibata, R.; Kato, S. Study of Salt Effects on the Micelle-Monomer Exchange Process of Octyl-, Decyl-, and Dodecyltrimethylammonium Bromide in Aqueous Solutions by Means of Ultrasonic Relaxation Spectroscopy. *J. Colloid Interface Sci.* **2000**, *230*, 22–28.
- (22) Polacek, R.; Kaatz, U. Monomer Exchange Kinetics, Radial Diffusion, and Hydrocarbon Chain Isomerization of Sodium Dodecylsulfate Micelles in Water. *J. Phys. Chem. B* **2007**, *111*, 1625–1631.
- (23) Haller, J.; Kaatz, U. Ultrasonic Spectrometry of Aqueous Solutions of Alkyl Maltosides: Kinetics of Micelle Formation and Head-Group Isomerization. *Chem. Phys. Chem.* **2009**, *10*, 2703–2710.
- (24) Haller, J.; Kaatz, U. Monomer Exchange and Rotational Isomerization of Alkyl Monoglycosides in Water. *J. Phys. Chem. B* **2009**, *113*, 12283–12292.
- (25) Teubner, M. Theory of Ultrasonic Absorption in Micellar Solutions. *J. Phys. Chem.* **1979**, *83*, 2917–2920.
- (26) Kahlweit, M.; Teubner, M. On the Kinetics of Micellization in Aqueous Solutions. *Adv. Colloid Interface Sci.* **1980**, *13*, 1–64.
- (27) Lessner, E.; Teubner, M.; Kahlweit, M. Relaxation Experiments in Aqueous Solutions of Ionic Micelles. 1. Theory and Experiments on the System  $\text{H}_2\text{O}$ –Sodium Tetradecyl Sulfate– $\text{NaClO}_4$ . *J. Phys. Chem.* **1981**, *85*, 1529–1536.
- (28) Aniansson, E. A. G.; Wall, S. N. On the Kinetics of Step-wise Micelle Association. *J. Phys. Chem.* **1974**, *78*, 1024–1030.
- (29) Aniansson, E. A. G.; Wall, S. N. Kinetics of Step-wise Micelle Association. Correction and Improvement. *J. Phys. Chem.* **1975**, *79*, 857–858.
- (30) Aniansson, E. A. G. The Mean Lifetime of a Micelle. *Prog. Colloid Polym. Sci.* **1985**, *70*, 2–5.
- (31) Telgmann, T.; Kaatz, U. On the Kinetics of the Formation of Small Micelles. 2. Extension of the Model of Stepwise Association. *J. Phys. Chem. B* **1997**, *101*, 7766–7772.
- (32) Telgmann, T.; Kaatz, U. Monomer Exchange and Concentration Fluctuations of Micelles. Broad-Band Ultrasonic Spectrometry of the System Triethylene Glycol Monoheptyl Ether/Water. *J. Phys. Chem. A* **2000**, *104*, 1085–1094.
- (33) Kaatz, U. Kinetics of Micelle Formation and Concentration Fluctuations in Solutions of Short-Chain Surfactants. *J. Phys. Chem.* **2011**, *115*, 10470–10477.
- (34) LeBard, D. N.; Levine, B. G.; DeVane, R.; Shinoda, W.; Klein, M. L. Premicelles and Monomer Exchange in Aqueous Solutions above and below the Critical Micelle Concentration. *Chem. Phys. Lett.* **2012**, *522*, 38–42.
- (35) Telgmann, T.; Kaatz, U. On the Kinetics of the Formation of Small Micelles. 1. Broadband Ultrasonic Absorption Spectrometry. *J. Phys. Chem. B* **1997**, *101*, 7758–7765.
- (36) Ma, S. K., *Modern Theory of Critical Phenomena*, Benjamin/Cummings: Reading, MA, 1976.
- (37) Muller, N. Temperature Dependence of Critical Micelle Concentrations and Heat Capacities of Micellization for Ionic Surfactants. *Langmuir* **1993**, *9*, 96–100.
- (38) Chen, L. J.; Lin, S.-Y.; Huang, C.-C.; Chen, E.-M. Temperature Dependence of Critical Micelle Concentration of Polyoxyethyleneated Non-Ionic Surfactants. *Colloids Surf. A* **1998**, *135*, 175–181.

- (39) Kim, H.-U.; Lim, K.-H. Description of Temperature Dependence of Critical Micelle Concentration. *Bull. Korean Chem. Soc.* **2003**, *24*, 1449–1454.
- (40) Hagen, R. Breitbandige Ultraschallabsorptionsspektroskopie an wässrigen *n*-Hexylammoniumchlorid-Lösungen im Frequenzbereich von 180 kHz bis 4.6 GHz. Diploma-Thesis; Georg-August-University, Göttingen, 1998.
- (41) Ornstein, L. S.; Zernike, F. Accidental Deviations of Density and Opalescence at the Critical Point of a Single Substance. *Proc. Acad. Sci. Amsterdam* **1914**, *17*, 793–806.
- (42) Bhattacharjee, J. K.; Kaatz, U.; Mirzaev, S. Z. Sound Attenuation Near the Demixing Point of Binary Liquids: Interplay of Critical Dynamics and Noncritical Kinetics. *Rep. Prog. Phys.* **2010**, *73*, 066601 DOI: 10.1088/0034-4885/73/6/066601.
- (43) Hohenberg, P. C.; Halperin, B. I. Theory of Dynamic Critical Phenomena. *Rev. Mod. Phys.* **1977**, *49*, 435–479.
- (44) Sengers, J. V.; Levelt Sengers, J. M. H. Thermodynamic Behavior of Fluids Near the Critical Point. *Annu. Rev. Phys. Chem.* **1986**, *37*, 189–222.
- (45) Goddard, E. D.; Benson, G. C. Conductivity of Aqueous Solutions of Some Paraffin Chain Salts. *Can. J. Chem.* **1957**, *35*, 986–991.
- (46) Binney, J. J.; Dowrick, N. J.; Fisher, A. J., Newman, M. *The Theory of Critical Phenomena: An Introduction to the Renormalization Group*; Oxford University Press: New York, 1992.
- (47) Rebillot, P. F.; Jacobs, D. T. Heat Capacity Analogy Near the Critical Point of Aniline-Cyclohexane. *J. Chem. Phys.* **1998**, *109*, 4009–4014.
- (48) Utt, N. J.; Lehmann, S. Y.; Jacobs, D. T. Heat Capacity of the Liquid–Liquid Mixture Nitrobenzene and Dodecane Near the Critical Point. *J. Chem. Phys.* **2007**, *127*, 104505 DOI: 10.1063/1.2766941.
- (49) Courant, R.; John, F. *Introduction to Calculus and Analysis*; Springer: New York, 1998.