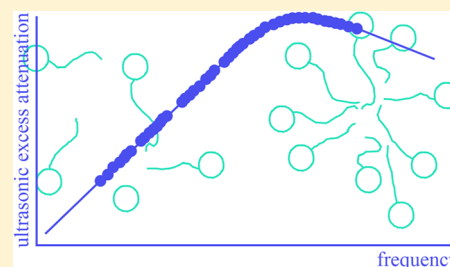


# Fluctuations Near the Critical Micelle Concentration. II. Ultrasonic Attenuation Spectra and Scaling

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**ABSTRACT:** Based on a thermodynamic model of amphiphile solutions derived in the first part of the paper, the ultrasonic attenuation of such systems has been considered theoretically, including fluctuations of local concentrations and micelle sizes. At amphiphile concentrations smaller than the critical micelle concentration (cmc), scaling behavior in terms of the concentration distance to the cmc is predicted by theory, in fair agreement with experimental evidence. The scaling function in the sound attenuation below the cmc reveals the unsymmetric broadening in the spectra that clearly emerges from measurements when approaching the cmc. The shape of the scaling function corresponds to the experimental spectra of solutions with comparatively large cmc as well as with the relaxation spectral function of the unifying model of non-critical concentration fluctuations. Above the cmc, an additional relaxation term is predicted in correspondence with the Landau–Khalatnikov term in the sound attenuation of superfluid helium. This term is difficult to verify by measurements because, in the relevant frequency range, other processes may also contribute the ultrasonic attenuation spectra.



## 1. INTRODUCTION

The organization of small molecules into aggregated structures is of paramount importance in many fields of basic science as well as numerous applications. Much attention has thus been directed toward amphiphile solutions with finite phase transitions in which fluctuations in the local concentrations are limited due to the formation of aggregates, such as micelles.<sup>1–4</sup> Micelles are naturally not frozen structures but permanently exchange molecules with the intermicellar bulk phase. The kinetics of exchange has been the focus of a variety of experimental and theoretical investigations of which some are mentioned in part I of this paper.<sup>5</sup> Among the experimental methods used, ultrasonic spectroscopy and its time domain analogues, pressure jump and temperature jump relaxation techniques,<sup>6</sup> contributed much to our present knowledge of the micelle formation/disintegration kinetics. Based on the Aniansson–Wall isodesmic reaction model<sup>7–9</sup> of micelle formation and by some analogy with the Becker–Döring treatment of nucleation,<sup>10–12</sup> Kahlweit and Teubner developed a theory of ultrasonic relaxation<sup>13–17</sup> that allows for a satisfactory description of the micelle formation/disintegration kinetics of proper micelle systems well above the critical micelle concentration (cmc). It predicts two relaxation processes with discrete relaxation times that are assigned in a suggestive manner to two modes in the establishment of thermal equilibrium after a small disturbance. The fast process with relaxation time  $\tau_f$ , normally explored by ultrasonic attenuation spectroscopy, is due to the monomer exchange between micelles and the bulk phase. It leaves the concentration of micellar aggregates unaltered. The slow relaxation with large relaxation time  $\tau_s$  refers to the establishment of complete

equilibrium after a small disturbance. It involves a change in the concentration of the micellar aggregates and is typically investigated by pressure jump and temperature jump techniques.

Approaching the cmc, however, the fast ultrasonic relaxation process is no longer governed by a discrete relaxation time. Rather it is subject to a relaxation time distribution that is particularly broad at and close to the cmc. For two cationic surfactant systems, this result is illustrated by Figure 1 where the relaxation time distribution function corresponding with the ultrasonic spectra of some aqueous solutions of *n*-hexylammonium chloride<sup>18</sup> and *n*-heptylammonium chloride<sup>19</sup> are shown. Here the relaxation time distribution  $G(r)$  is defined by

$$(\alpha\lambda)_{\text{exc}}(\nu) = A \int_{-\infty}^{\infty} G(r) \frac{\omega\tau}{1 + (\omega\tau)^2} dr \quad (1)$$

where the ultrasonic excess attenuation spectrum

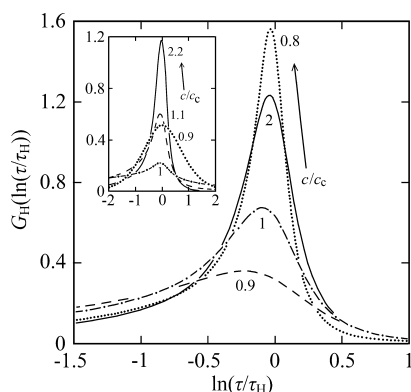
$$(\alpha\lambda)_{\text{exc}}(\nu) = \alpha(\nu)\lambda - B\nu \quad (2)$$

considers the attenuation  $\alpha$  along wavelength  $\lambda$  that exceeds the less interesting asymptotic high-frequency term  $B\nu$ . Here  $\nu$  is the frequency of the ultrasonic field,  $\omega = 2\pi\nu$  is the angular frequency,  $A$  is an amplitude,  $B$  a parameter independent of  $\nu$ , and  $r = \ln(\tau/\hat{\tau})$ , with  $\hat{\tau}$  denoting a characteristic relaxation time. The distribution function  $G$  is normalized. Hence

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**Figure 1.** Normalized relaxation time distribution function  $G_H(\ln(\tau/\tau_H))$  for some aqueous solutions of cationic surfactants with solute concentration close to the cmc. For normalization of the surfactant concentrations the experimental characteristic concentrations  $c_c$  ( $\leq$  cmc),<sup>5</sup> as obtained from maxima in the relaxation times, are used here. The main figure shows results corresponding with *n*-hexylammonium chloride solutions ( $c_c = 1.1$  mol/L, 25 °C),<sup>18</sup> the inset such for solutions of *n*-heptylammonium chloride ( $c_c = 0.45$  mol/L, 25 °C).<sup>19</sup> The  $G_H$  data have been obtained by analytic continuation of the empirical Hill relaxation spectral function using parameters as obtained from fitting the experimental data to eq 4. Parameter  $\tau_H$  is the characteristic relaxation time of the Hill spectral function.

$$\int_{-\infty}^{\infty} G(r) dr = 1 \quad (3)$$

The distribution functions of Figure 1 have been obtained by representing the excess attenuation of the spectra by an empirical Hill relaxation function,<sup>20,21</sup> i.e., by analytically describing the experimental attenuation-per-wavelength data as

$$\alpha(\nu)\lambda = \frac{A(\omega\tau_H)^{m_H}}{[1 + (\omega\tau_H)^{2s_H}]^{(m_H+n_H)/(2s_H)}} + B\nu \quad (4)$$

In this equation,  $m_H$ ,  $n_H$ , and  $s_H$  ( $0 < m_H, n_H, s_H \leq 1$ ) control the width and the shape of the relaxation time distribution function and  $\tau_H$  is the characteristic relaxation time  $\hat{\tau}$ . With most spectra  $m_H$  has been fixed at 1, corresponding with a single-relaxation-time-type behavior at low frequencies ( $\nu \ll (2\pi\tau_H)^{-1}$ ).

Attempts to account for the broad relaxation time distribution by an extended Teubner–Kahlweit–Aniansson–Wall model of the micelle formation and disintegration kinetics have indeed exposed some important aspects.<sup>22</sup> Proceeding from reasonable assumptions on the rate constants of the isodesmic scheme of coupled reactions instead of assuming a fixed distribution of micellar and pre-micellar species clearly shows that, due to the missing minimum in the oligomer region of the size distribution, the slow and fast relaxation processes of the amphiphile systems merge near the cmc. It also provides a modest understanding of the existence of aggregate formation/disintegration processes at concentrations below the cmc. However, it does not account for the broad distribution in the corresponding ultrasonic relaxation times. This situation has prompted us to see whether the theoretical model including fluctuations of the local concentrations, as established in the first part of this paper, is capable to reasonably describe the special features in the ultrasonic spectra of the amphiphile solutions near the cmc.

## 2. THEORY

In part I of this paper,<sup>5</sup> assuming local fluctuations of the aggregation numbers  $m$  around the mean  $\bar{m}$ , and thus also of the local concentration of monomers, we have presented a relation

$$\frac{1}{u^2} = \frac{1}{u_0^2} \left[ 1 + \frac{\bar{C}_0}{C_p} \right] \quad (5)$$

between the sound velocity  $u$  of an ultrasonic field within the liquid and the heat capacity  $C_p$  at constant pressure of the amphiphile solutions. This relation can be used at any finite frequency. Here  $u_0$  is a constant and  $\bar{C}_0$  is the coupling constant of sound attenuation. It is strongly dependent upon the temperature gradient  $dc_m(T)/dT$  in the cmc  $c_m$ .<sup>5</sup> The heat capacity

$$C_p = C_{pb} + C_{pc}(\Delta c, \omega) \quad (6)$$

is composed of a background part  $C_{pb}$  and a “critical” part  $C_{pc}(\Delta c, \omega)$ , the latter being a function of the scaled amphiphile concentration  $\Delta c = c - c_m$  at  $c < c_m$ . Because of causality  $C_{pc}(\Delta c, \omega) = C_{pc}(\Delta c, i\omega)$  and, in the limit of low frequencies ( $\omega \rightarrow 0$ ),

$$C_{pc}(\Delta c) \propto (\Delta c)^{-\alpha_0} \quad (7)$$

Exponent  $\alpha_0$  is the universal critical exponent of heat capacity ( $\alpha_0 = 0.11^{23-25}$ ). It has been shown,<sup>5</sup> however, that the heat capacity does not diverge since  $\Delta c$  can not go below  $\mu^2/(4ba_0)$ , where  $\mu$ ,  $b$ , and  $a_0$  are parameters of the free energy of the system, presumed to be given by the relation

$$F = \int d^3r \left[ \frac{a}{2} m^2 + \frac{1}{2} (\vec{\nabla} m)^2 + \frac{\mu}{3} m^3 + \frac{b}{4} m^4 \right] \quad (8)$$

Since the relaxation time  $\tau$  of the fluctuations at  $c < c_m$  is a function of  $\Delta c$ ,<sup>5</sup> we can write

$$C_{pc} = C_{pc}(\tau, i\omega) \quad (9)$$

where the relaxation time follows the relation

$$\tau \propto (\Delta c)^{-2\tilde{\nu}} \quad (10)$$

with universal critical exponent  $\tilde{\nu}$  ( $= 0.63^{23,26}$ ) of the fluctuation correlation length  $\xi$ . Hence  $\tau$  is proportional to  $\xi^2$  and, in the low-frequency limit ( $\omega \rightarrow 0$ ), we have

$$C_{pc} \propto (\Delta c)^{-\alpha_0} \propto \tau^{\alpha_0/2\tilde{\nu}} \quad (11)$$

Dynamic scaling<sup>27,28</sup> yields

$$C_{pc} \propto (-i\omega)^{-\alpha_0/2\tilde{\nu}} \quad (12)$$

if  $\omega \ll \tau^{-1}$ . The general scaling relation is expected to follow the form

$$C_{pc}(\Delta c, \omega) = (-i)^{-\alpha_0/2\tilde{\nu}} f(\omega\tau) \quad (13)$$

where  $f(\omega\tau)$  is a scaling function. In the lowest order this  $C_{pc}$  is given by the function (see arguments leading to eq 125 in ref 28)

$$\Pi(\Delta c, \omega) = \int \frac{d^3p}{(2\pi)^3} \left( \frac{1}{p^2 + \kappa^2} \right)^2 \frac{1}{1 - i\omega\tau(p, \kappa)} \quad (14)$$

with  $\kappa (= \xi^{-1})$  denoting the inverse correlation length  $\xi$ . We shall revisit this formula below after introducing the connection of heat capacity with sound attenuation.

Returning to eq 5, we note that for a plane wave  $\exp[i(kx - \omega t)]$ , a complex wavenumber  $k = k_1 + ik_2$  makes the wave  $\exp[i(k_1x - \omega t)] \cdot \exp[-k_2x]$ , so that  $2k_2$  is the attenuation per unit length in the intensity of the sound field. Hence the attenuation per wavelength is given by

$$\alpha\lambda = 2k_2\lambda = 4\pi k_2/k_1 \quad (15)$$

With a frequency dependent specific heat the sound velocity in eq 5 will be complex. Using the notation  $u = u_1 + iu_2$  and considering the heat capacity composition according to eq 6, with  $C_{pc} \ll C_{pb}$ , we have

$$\begin{aligned} \left( \frac{1}{u_1 + iu_2} \right)^2 &= \frac{1}{u_0^2} \left[ 1 + \frac{\bar{C}_0}{C_{pb} + C_{pc}(\Delta c, \omega)} \right] \\ &= \frac{1}{u_0^2} \left[ 1 + \frac{\bar{C}_0}{C_{pb}} - \frac{\bar{C}_0 C_{pc}(\Delta c, \omega)}{C_{pb}^2} \right] \\ &= \frac{1}{u_0^2} \left[ 1 + \frac{\bar{C}_0}{C_{pb}} - \frac{\bar{C}_0 \text{Re}(C_{pc})}{C_{pb}^2} - i \frac{\bar{C}_0 \text{Im}(C_{pc})}{C_{pb}^2} \right] \end{aligned} \quad (16)$$

If  $u_2 \ll u_1$ , the left-hand side of this equation is approximately  $u_1^{-2}[1 - 2iu_2/u_1]$  and thus identifying  $u_1 \approx u_0$  we have

$$\frac{u_2}{u_0} = \frac{\bar{C}_0 \text{Im}(C_{pc})}{2C_{pb}^2} \approx -\frac{k_2}{k_1} \quad (17)$$

Taking the signs of the coupling constants into account we have

$$\alpha\lambda = 2\pi \frac{\bar{C}_0 \text{Im}(C_{pc})}{C_{pb}^2} \quad (18)$$

Now we need to use a proper scaling form for  $C_{pc}$ . The first point to be considered in this context is that, at very high frequencies ( $\omega \gg \tau^{-1}$ ),

$$\begin{aligned} C_{pc} &\propto (-i\omega)^{-\alpha_0/2\tilde{\nu}} \\ &= \omega^{-\alpha_0/2\tilde{\nu}} \exp(i\pi\alpha_0/4\tilde{\nu}) \\ &= \omega^{-\alpha_0/2\tilde{\nu}} [\cos(\pi\alpha_0/4\tilde{\nu}) - i \sin(\pi\alpha_0/4\tilde{\nu})] \end{aligned} \quad (19)$$

or

$$\text{Im}(C_{pc}) \propto \omega^{\alpha_0/2\tilde{\nu}} \quad (20)$$

Correspondingly,

$$\alpha\lambda \propto \omega^{\alpha_0/2\tilde{\nu}} \quad (21)$$

at  $\omega\tau \gg 1$ . If  $\alpha_0$  is the real critical phenomenon value ( $\alpha_0 = 0.11$ ), then this is a very slow fall off. In reality, for the transition under consideration, the true “critical” range will never be entered. Hence instead of the “true”  $\alpha_0$  of criticality one could see an effective exponent  $\alpha_{\text{eff}}$  only. With  $\tau = \tau_0/(p^2 + \kappa^2)$ , the one-loop approximation of eq 14 reads

$$\Pi(\Delta c, \omega) = \int \frac{d^3p}{(2\pi)^3} \frac{1}{p^2 + \kappa^2 - i\omega\tau_0 + p^2 + \kappa^2} \quad (22)$$

For  $\omega\tau_0 \gg 1$ , this integral has the asymptotic behavior  $\propto (-i\omega\tau_0)^{-1/2}$  and thus in this approximation  $\alpha_0 \approx 1/2$  when  $\tilde{\nu} = 1/2$ . If we are not in the truly critical region, this value of  $\alpha_0$  can be a good approximation, showing that  $\alpha_{\text{eff}}$  could lie somewhere between the asymptotic exponent 0.1 and the mean field exponent 0.5. Evaluation of the integral in eq 22 leads to

$$\Pi(\Delta c, \omega) = \frac{\Pi_0}{[(\Delta c)^{2\nu_{\text{eff}}} - i\omega\tau_0\xi^2]^{1/2} + (\Delta c)^{\tilde{\nu}}} \quad (23)$$

where  $\Pi_0$  is a constant,  $\nu_{\text{eff}}$  is an effective exponent for the correlation length, with a value between 0.5 and 0.63, and the correlation length follows power law according to

$$\xi = (\kappa^{-1}) = \xi_0(\Delta c)^{-\nu_{\text{eff}}} \quad (24)$$

As mentioned before, for  $\omega\tau_0 \gg 1$ , we have  $\Pi(\Delta c, \omega) \approx (-i\omega)^{-1/2}$  and for  $\omega \rightarrow 0$  we have  $\Pi(\Delta c, \omega) \approx (\Delta c)^{-\nu_{\text{eff}}}$ . If we define the scaled frequency as

$$\Omega = \omega\tau = \frac{\omega\tau_0\xi^2}{(\Delta c)^{2\nu_{\text{eff}}}} \quad (25)$$

we get in terms of that

$$\begin{aligned} \Pi(\Delta c, \omega) &= \frac{\Pi_0}{[-i\omega\tau_0\xi^2]^{1/2}} \frac{1}{\left(\frac{1}{-i\Omega} + 1\right)^{1/2} + \left(\frac{1}{-i\Omega}\right)^{1/2}} \\ &= \frac{\Pi'_0}{[-i\omega\tau_0]^{1/2}} \frac{(-i\Omega)^{1/2}}{1 + (1 - i\Omega)^{1/2}} \end{aligned} \quad (26)$$

Here  $\Pi'_0$  is another constant.

We compare eq 26, which is an approximation for  $C_p$ , with the description in terms of a scaling function (eq 13). If we agree on using the effective exponent  $\alpha_{\text{eff}}$  in eq 13 then we can exploit eq 26 to write

$$C_p(\Delta c, \omega) = \Pi^{\alpha_{\text{eff}}/\tilde{\nu}}(\Delta c, \omega) \quad (27)$$

where  $\alpha_{\text{eff}}/\tilde{\nu}$  will be unity in a mean field approximation and will be about 0.17<sup>23</sup> at true critical behavior. Using eq 18 it turns out that the above treatment implies the following:

$$\begin{aligned} \Pi &= \frac{\Pi'_0}{(\Delta c)^{\tilde{\nu}}} \frac{1}{1 + (1 - i\Omega)^{1/2}} \\ &= \frac{\Pi'_0}{(\Delta c)^{\tilde{\nu}}} \frac{1}{(1 + \Omega^2)^{1/4} [\cos(\Theta/2) - i \sin(\Theta/2)]} \\ &= \frac{\Pi'_0}{(\Delta c)^{\tilde{\nu}}} \frac{1 + (1 + \Omega^2)^{1/4} \cos(\Theta/2) + i(1 + \Omega^2)^{1/4} \sin(\Theta/2)}{[1 + (1 + \Omega^2)^{1/4} \cos(\Theta/2)]^2 + (1 + \Omega^2)^{1/2} \sin^2(\Theta/2)} \\ &= \frac{\Pi'_0}{(\Delta c)^{\tilde{\nu}}} \frac{\exp(i\Phi)}{\{[1 + (1 + \Omega^2)^{1/4} \cos(\Theta/2)]^2 + (1 + \Omega^2)^{1/2} \sin^2(\Theta/2)\}^{1/2}} \end{aligned} \quad (28)$$

where

$$\Theta = \arctan(\Omega) \quad (29)$$

and

$$\tan(\Phi) = \frac{(1 + \Omega^2)^{1/4} \sin(\Theta/2)}{1 + (1 + \Omega^2)^{1/4} \cos(\Theta/2)} \quad (30)$$

Equation 28 implies the form

$$\Pi^{\alpha_{\text{eff}}/\bar{\nu}} = \frac{\Pi_0^{\alpha_{\text{eff}}/\bar{\nu}}}{(\Delta c)^{\alpha_{\text{eff}}}} \frac{\exp\left(i\frac{\alpha_{\text{eff}}}{\bar{\nu}}\Phi\right)}{\{[1 + (1 + \Omega^2)^{1/4} \cos(\Theta/2)]^2 + (1 + \Omega^2)^{1/2} \sin^2(\Theta/2)\}^{\alpha_{\text{eff}}/2\bar{\nu}}} \quad (31)$$

as well as

$$\text{Im}(\Pi^{\alpha_{\text{eff}}/\bar{\nu}}) = \frac{\Pi_0^{\alpha_{\text{eff}}/\bar{\nu}}}{(\Delta c)^{\alpha_{\text{eff}}}} \frac{\sin\left(\frac{\alpha_{\text{eff}}}{\bar{\nu}}\Phi\right)}{\{[1 + (1 + \Omega^2)^{1/4} \cos(\Theta/2)]^2 + (1 + \Omega^2)^{1/2} \sin^2(\Theta/2)\}^{\alpha_{\text{eff}}/2\bar{\nu}}} \quad (32)$$

and thus

$$\alpha\lambda = \frac{\tilde{A}(\Delta c)}{(\Delta c)^{\alpha_{\text{eff}}}} \frac{\sin\left(\frac{\alpha_{\text{eff}}}{\bar{\nu}}\Phi\right)}{\{[1 + (1 + \Omega^2)^{1/4} \cos(\Theta/2)]^2 + (1 + \Omega^2)^{1/2} \sin^2(\Theta/2)\}^{\alpha_{\text{eff}}/2\bar{\nu}}} \quad (33)$$

Hence at  $c < c_m$ , where the scaled frequency  $\Omega$  is given by eq 25, we finally get

$$\alpha\lambda = \frac{\tilde{A}(\Delta c)}{(\Delta c)^{\alpha_{\text{eff}}}} F(\Omega) \quad (34)$$

with amplitude parameter  $\tilde{A}$  weakly depending upon  $\Delta c$  and with scaling function  $F(\Omega)$  to be discussed below.

Turning to concentrations larger than the cmc we have to be aware that micellar aggregates exist with finite mean value  $\bar{m}$  of their size distribution. Considering fluctuations in the aggregate sizes by writing

$$m = \bar{m} + \delta m \quad (35)$$

the specific heat correlation function becomes

$$\begin{aligned} \langle m^2(\vec{r}_1)m^2(\vec{r}_2) \rangle_{\text{cumulant}} &= \langle [(\delta m)^2 + 2\bar{m}\delta m] \\ &[(\delta m)^2 + 2\bar{m}\delta m] \rangle \\ &= 4\bar{m}^2\langle \delta m\delta m \rangle + 4\bar{m}\langle \delta m(\delta m)^2 \rangle + \langle (\delta m)^2(\delta m)^2 \rangle \end{aligned} \quad (36)$$

The last term in eq 36 is identical with the correlation function  $C_c$  of fluctuations below the cmc. Both other terms are characteristic at  $c > c_m$ . As a first approximation one may write the correlation function above the cmc,  $C_>$ , as

$$\begin{aligned} C_> &= \int 4\bar{m}^2 \langle \delta m(r_1)\delta m(r_2)d^3r_{12} \rangle \\ &+ \int \langle \delta m^2(r_1)\delta m^2(r_2)d^3r_{12} \rangle \\ &= C_>^{(1)} + C_>^{(2)} \\ &= C_>^{(1)} + C_< \end{aligned} \quad (37)$$

When dealing with the frequency dependent specific heat, one needs the Fourier transform of the time dependent correlation function. The second term on the right-hand side of eq 37 leads to the contribution

$$\Pi(\Delta c, \omega) = \int \frac{d^3p}{(2\pi)^2} \frac{1}{p^2 + \bar{\kappa}^2} \frac{1}{-i\omega\tau_0 + p^2 + \bar{\kappa}^2} \quad (38)$$

where, according to eq 20 of part I of this paper,<sup>5</sup>  $\bar{\kappa}^2 = b\bar{m}^2 + |a|$ . Here  $a$  and  $b$  are again parameters of the free energy as defined by eq 8. The first term  $C_>^{(1)}$  on the right-hand side of eq 37 represents the relaxation of the order parameter fluctuations at zero wavenumber. Consequently, it is an analogue of the Landau–Khalatnikov term<sup>29–31</sup> in the attenuation of sound in superfluid helium. We will call this contribution  $C_{LK}$  and we find

$$C_>^{(1)} = C_{LK} = \frac{\omega\bar{C}_0\Gamma_0\bar{\kappa}^2}{\omega^2 + (\Gamma_0\bar{\kappa}^2)^2} \quad (39)$$

where  $\Gamma_0 = \tau_0^{-1}$  and  $\bar{C}_0$  is the coupling constant defined by eq 5.

In summary, the sound attenuation due to micelle-formation-related local concentration fluctuations displays different features at amphiphile concentrations below the cmc than above the cmc. At  $c < c_m$

$$\alpha\lambda = \frac{\hat{A}}{|\Delta c|^{\alpha_{\text{eff}}}} F(\Omega) \quad (40)$$

with scaled frequency

$$\Omega = \frac{\omega}{2\Gamma_0\bar{\kappa}^2} = \frac{D_0\omega}{|\Delta c|^{2\alpha_{\text{eff}}}} \quad (41)$$

and with scaling function

$$F(\Omega) = \frac{\sin\left(\frac{\alpha_{\text{eff}}}{\bar{\nu}}\Phi\right)}{\{[1 + (1 + \Omega^2)^{1/4} \cos(\Theta/2)]^2 + (1 + \Omega^2)^{1/2} \sin^2(\Theta/2)\}^{\alpha_{\text{eff}}/2\bar{\nu}}} \quad (42)$$

In these equations,  $\hat{A}$  and  $D_0$  are parameters independent of frequency. At  $c > c_m$ , an additional relaxation term exists and the scaled frequency is different:

$$\alpha\lambda = (\alpha\lambda)_{LK} + \frac{\hat{A}}{|\Delta c|^{\alpha_{\text{eff}}}} F(\Omega') \quad (43)$$

where

$$\begin{aligned} (\alpha\lambda)_{LK} &= \frac{\tilde{A}\omega\tau_{LK}}{1 + \omega^2\tau_{LK}^2} \quad \text{and} \\ \Omega' &= \frac{\omega}{2\Gamma_0\bar{\kappa}^2} = \frac{D_0\omega}{|\Delta c| + b\bar{m}^2} \end{aligned} \quad (44)$$

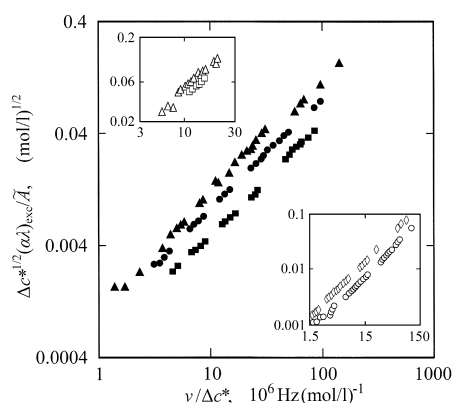
with frequency-independent amplitude  $\tilde{A}$ , relaxation time  $\tau_{LK} = 1/(\Gamma_0\bar{\kappa}^2)$ , and with  $\bar{m}$  denoting the mean aggregation number in the size distribution of micelles. In the mean field approximation,  $\alpha_{\text{eff}} = \nu_{\text{eff}} = 1/2$ .

### 3. DISCUSSION AND COMPARISON TO EXPERIMENTAL RESULTS

**3.1. Scaling Properties.** Let us first inspect the scaling form as resulting from eq 34. If the weak dependence of the amplitude parameter  $\tilde{A}$  is neglected, the sonic attenuation data should scale as  $S = (\alpha\lambda)_{\text{exc}}(\Delta c)^{\alpha_{\text{eff}}}$ . In order to take the dependence upon  $\Delta c$ , as resulting from the concentration dependence of the coupling parameter, into account,  $S$  has been divided by the amplitude  $\tilde{A}$  of the relaxation term with lowest relaxation frequency in the ultrasonic spectra. With the  $n$ -



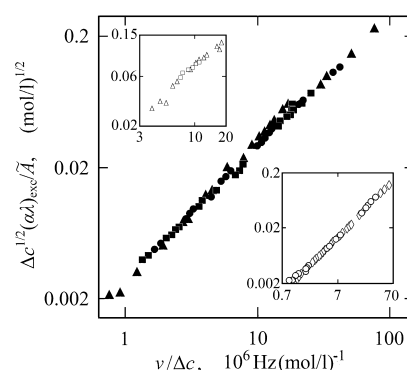
octylammonium chloride solutions, for which scaling data are presented in Figure 2, the low-frequency relaxation term is a



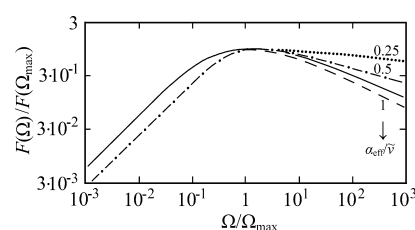
**Figure 2.** Scaling plot according to eq 34 with  $\alpha_{\text{eff}} = 1/2$  for low-frequency sound attenuation data. Experimentally determined characteristic concentrations  $c_c$  have been used to calculate the concentration distances  $\Delta c^* = c_c - c$ . Data at 25 °C are shown for aqueous solutions of *n*-pentylammonium chloride ( $\diamond$ , 1.5 mol/L;  $\circ$ , 1.7 mol/L;  $c_c = 1.9$  mol/L),<sup>5,19</sup> *n*-hexylammonium chloride ( $\blacktriangle$ , 0.7 mol/L;  $\bullet$ , 0.8 mol/L;  $c_c = 1.1$  mol/L),<sup>5,19</sup> and *n*-octylammonium chloride ( $\Delta$ , 0.22 mol/L;  $\square$ , 0.24 mol/L;  $c_c = 0.27$  mol/L).<sup>5,32</sup>

Debye term with discrete relaxation time. With the *n*-hexylammonium chloride solutions, it is a restricted Hill term with  $m_H = 1$  (eq 4), which also displays Debye-type behavior  $((\alpha\lambda)_{\text{exc}} = A\omega\tau)$  at small frequencies. The low-frequency part in the spectra of *n*-pentylammonium chloride solutions can be either described by a Debye term or by a Hill term with  $m = 0$ . Using the one-loop approximation  $\alpha_0 = 1/2$  for the effective exponent  $\alpha_{\text{eff}}$ , the  $S/\bar{A}$  data for all solutions of *n*-alkylammonium chlorides display almost the same slope. However, if the experimentally determined characteristic concentration  $c_c$  is used to calculate the concentration difference to the critical concentration, the data do not condense on one curve (Figure 2). Nonuniversal scaling is not surprising for different surfactants because the relaxation time in the scaled frequency (eq 25) will change from amphiphile to amphiphile. However, data for the same surfactant should scale. The reason for this discrepancy is likely the inadequate use of characteristic concentration  $c_c$  instead of  $c_m$ . In part I of this paper we have shown that the correlation length  $\xi$  and the relaxation time of fluctuations adopt their maximum at a concentration  $c_m - \mu^2/(4a_0b)$  smaller than the cmc, where  $\mu$ ,  $a_0$ , and  $b$  are parameters of the free energy (eq 8) with  $a_0$  denoting the amplitude in the concentration dependence  $a = a_0(c_m - c)$ . Using thus  $c_m$  values somewhat larger than the  $c_c$  values taken from the minimum in the inverse relaxation times (Figure 5 in part I), the  $S/\bar{A}$  data for each surfactant system really fall on one curve (Figure 3). Beyond verification of the scaling behavior predicted by eq 34 and thus of the disposition of our model, this result may be taken to show why cmc values derived from extrema or inflection points of different solution parameters often differ.

**3.2. Ultrasonic Attenuation Spectra.** In Figure 4 the scaling function  $F(\Omega)$  at  $c < c_m$  (eq 42) is displayed at three different  $\alpha_{\text{eff}}/\bar{\nu}$  ratios. For ease of comparison, the graphs are shown in a normalized format by relating both the scaled frequency  $\Omega$  and function  $F$  to their values at the maximum. At



**Figure 3.** Same scaling plot as Figure 2, but concentration distance  $\Delta c = c - c_m$  used instead of  $\Delta c^* = c - c_c$ . The following cmc's have been assumed: *n*-pentylammonium chloride, cmc = 2.1 mol/L; *n*-hexylammonium chloride, cmc = 1.25 mol/L; *n*-octylammonium chloride, cmc = 0.29 mol/L.



**Figure 4.** Graphs of the scaling function at  $c < c_m$  (eq 42) at three different exponent ratios  $\alpha_{\text{eff}}/\bar{\nu}$  shown in a frequency-normalized format. Also given by the full line is the graph of the spectral function  $R_{\text{um}}(\Omega)$  of the unifying model of non-critical concentration fluctuations (eq 47;  $\Omega = 2\pi\nu\tau_i$ ).

small frequencies ( $\Omega < \Omega_{\text{max}}$ ), the scaling function follows Debye-type relaxation behavior, in analogy with relaxation spectral functions from all other models of noncritical fluctuations in the local concentration. To accentuate this feature, the spectral function of the unifying model of noncritical fluctuations<sup>33</sup> is also presented in Figure 4. That model combines the characteristics of the Romanov–Solov'ev,<sup>34–36</sup> Montrose–Litovitz,<sup>37</sup> and Endo<sup>38</sup> theories of sound attenuation in systems with non-critical concentration fluctuations. It is based on the assumption that changes in the local concentration of the liquid may equilibrate via two parallel pathways: an elementary reaction, characterized by a discrete relaxation time  $\tau_0$ , and a diffusive process controlled by the mutual diffusion coefficient  $D$ . Hence the autocorrelation function  $\phi(\vec{r}, t)$  of the order parameter, normally the deviation  $\delta c = c(\vec{r}, t) - \bar{c}$  of the local concentration  $c(\vec{r}, t)$  at time  $t$  from the mean concentration  $\bar{c}$ , follows the differential equation

$$\partial\phi(\vec{r}, t)/\partial t = (D\nabla^2 - \tau_0^{-1})\phi(\vec{r}, t) \quad (45)$$

Focusing on isotropic liquids in which correlations depend on the distance  $r = |\vec{r}|$  only and assuming the following weight function

$$\hat{f} \propto (1 + 0.164q\xi + 0.25q^2\xi^2)^{-2} \quad (46)$$

in the  $q$  space, spectral function

$$R_{\text{um}}(\nu) = Q \int_0^\infty \hat{f}(q) q^2 \frac{\omega\tau_i}{1 + \omega^2\tau_i^2} dq \quad (47)$$

follows. In this function, amplitude factor  $Q$  is dominated by the amplitude  $Q_{\text{RS}}$  of the Romanov–Solov'ev theory, and the

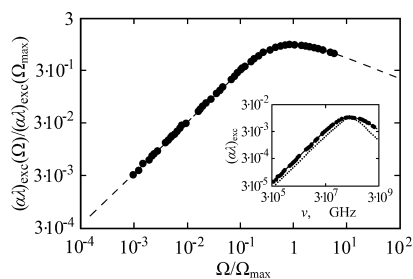
total relaxation time  $\tau_t$  corresponding with wave vector  $\vec{q}$  is given by the relation

$$\tau_t^{-1} = \tau_0^{-1} + Dq^2 \quad (48)$$

The weight function (eq 46) models short-range spatial correlations in the fluctuations ( $r < \xi$ ) by an exponential, as originally proposed by Montrose and Litovitz.<sup>37</sup> It considers long-range correlations by an Ornstein–Zernike ansatz,<sup>39</sup> as assumed by Endo.<sup>38</sup>

Toward higher frequencies, the spectral functions plotted in Figure 4 obviously deviate from one another. A flat decay with  $\Omega$  ( $>\Omega_{\max}$ ) is provided by our spectral function if  $\alpha_{\text{eff}}/\bar{\nu}$  is as small as 0.25. With increasing exponent ratio function,  $F(\Omega)$  decreases stronger at  $\Omega > \Omega_{\max}$ ; finally it declines stronger than  $R_{\text{um}}(\Omega)$ , where  $\Omega = 2\pi\nu\tau_t$ . In principle, the high-frequency wing of the ultrasonic attenuation spectra may be used to extract the  $\alpha_{\text{eff}}/\bar{\nu}$  ratio for noncritically fluctuating liquids. From an experimentalist's point of view, however, it is difficult or even impossible for several reasons. First of all, the spectra shown in Figure 4 model that attenuation-per-wavelength part only, which, due to the concentration fluctuations, exceeds the asymptotic high-frequency term  $B\nu$  in the total attenuation (eq 2). In the evaluation of the high-frequency part of attenuation spectra, different exponent ratios may thus be compensated by different  $B$  values. This is particularly true as the scaled frequency  $\Omega$  is often located near the upper limit in the experimentally available frequency range of measurements. An additional constraint in the  $\alpha_{\text{eff}}/\bar{\nu}$  determination is the fact that frequently an additional high-frequency relaxation term exists in the spectra of liquids with non-critical concentration fluctuations. This term tends to mask the high-frequency behavior of the low-frequency term under consideration.

Figure 5 shows an ultrasonic excess attenuation spectrum for an *n*-pentylammonium chloride solution with amphiphile



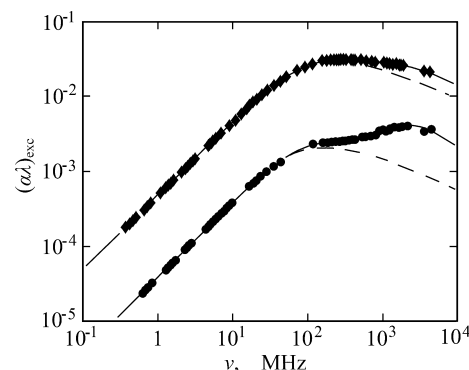
**Figure 5.** Ultrasonic excess attenuation spectrum in a normalized format for a solution of 1.7 mol/L *n*-pentylammonium chloride in water at 25 °C.<sup>18</sup> Also presented by the dashed line is the graph of the scaling function defined by eq 42 with  $\alpha_{\text{eff}}/\bar{\nu} = 1$ . In the inset the  $R_{\text{um}}(\nu)$  function (eq 47; solid line) is used to represent the experimental excess attenuation data. The dotted line shows Debye-type relaxation behavior.

concentration closely below the cmc ( $c/c_m = 0.85$ ). As revealed by the diagram, the spectrum can be well represented by our model relaxation function (eq 42) with exponents  $\alpha_{\text{eff}} = 1/2$  and  $\bar{\nu} = 1/2$ , as corresponding with the mean field approximation. With those exponents, the function can be simplified to read

$$F(\Omega) = \frac{[1 + (1 + \Omega^2)^{1/2}]^{1/2} - \sqrt{2}}{\Omega} \quad (49)$$

The inset to Figure 5 demonstrates that the same experimental spectrum can be also well represented by spectral function  $R_{\text{um}}(\nu)$  of the unifying model of concentration fluctuations. It also shows that a different  $B$  value of the asymptotic high-frequency term in the total attenuation-per-wavelength results if the model relaxation function is changed. The difference in the  $B$  values, however, is small.

The additional high-frequency sound attenuation contributions emerging in the spectra of Figure 6 are found with most



**Figure 6.** Ultrasonic excess attenuation-per-wavelength spectra for aqueous solutions of *n*-hexylammonium chloride at two concentrations<sup>18</sup> (●, 0.8 mol/L; ♦, 3 mol/L; 25 °C). Dashed lines represent the scaling function defined by eq 42 with exponent ratio  $\alpha_{\text{eff}}/\bar{\nu} = 1$ . The solid lines show the superposition of this function with a Debye term.

micelle systems. They have been assigned to the fast monomer exchange from oligomeric structures<sup>18,22</sup> in the liquids and also to structural isomerizations of the hydrocarbon chains within the micellar cores.<sup>18,40</sup> Likely, in this frequency range, the sound attenuation contains also contributions from the Landau–Khalatnikov-like relaxation, which our model (eqs 43 and 44) predicts for solute concentrations above the cmc.

#### 4. CONCLUSIONS

Proceeding from the assumption of local fluctuations in the aggregation number  $m$  of micelles around the mean  $\bar{m}$ , we have developed a theoretical model considering the effect of concentration fluctuations in the ultrasonic attenuation spectra of amphiphile solutions. The model is particularly focused on the behavior of the solutions near the cmc  $c_m$ , in which the fluctuations are large. Taking an affinity field in the free energy of the system into account, the model clearly features non-critical fluctuation behavior. Divergence of relevant parameters, such as the heat capacity at constant pressure, can not occur because, already from a concentration  $c < c_m$ , the system approaches equilibrium after a small disturbance also by a second parallel pathway, the formation of micellar or pre-micellar oligomeric structures. That concentration is given by the parameters in the free energy of the amphiphile system. The formation of aggregates at  $c < c_m$  is a fact that is well-known from a variety of ultrasonic attenuation measurements, as briefly discussed in the first part of this paper. It is also reflected by the finding of minima in the relaxation rates of fluctuations at concentrations  $c_c$  smaller than the cmc values following from scaling plots of ultrasonic attenuation data.

The scaling function in the sound attenuation predicted from our model allows for an adequate representation of experimental spectra. Above all, it features an unsymmetrical

broadening of the spectra near the cmc, in close correspondence with experimental evidence. At reasonable critical exponent ratio  $\alpha_{\text{eff}}/\bar{\nu}$  between 0.5 and 1, the scaling function from our model nicely reproduces the relaxation function of the more generally applicable unifying model of non-critical fluctuations.

At amphiphile concentration larger than  $c_m$ , the theory also predicts, by analogy with the Landau–Khalatnikov term in the sound attenuation of superfluid helium, an additional Debye-type relaxation term in the spectra of amphiphile solutions. This term represents the order parameter fluctuations at zero wavenumber. It appears in fact in the experimental spectra of amphiphile solutions with concentrations at, above and also slightly below  $c_m$ . It may, however, in addition contain contributions from the monomer exchange from oligomeric amphiphile structures and also from the rotational isomerization of the hydrocarbon chains within the micellar cores. It is therefore impossible to verify the predictions of the theory quantitatively by existing data.

## AUTHOR INFORMATION

### Notes

The authors declare no competing financial interest.

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