# Modeling effective interactions of micellar aggregates of ionic surfactants with the Gauss-core potential

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Micellar aggregates of ionic surfactants are known to possess a rich variety of interesting thermodynamic as well as structural properties, which are essentially dominated by simple effective interactions between the aggregates. Because of their technological relevance enormous efforts have been invested to understand and characterize their interactions in solution with the goal of developing substances with novel material's properties. On a theoretical level several approaches have been proposed to describe their effective interactions adequately, generally based on the DLVO theory. However, these approaches do not take into account aspects of stability of the aggregates and therefore fail in the description of several important characteristics, such as, e.g., the re-entrant behavior of the apparent molal heat capacity appearing with increasing density of the micelles. In this paper we study the effective interactions of these systems by investigating the suitability of the Gauss-core model, to reproduce the relevant thermodynamic properties. To this end, we discuss the Gauss-core model in comparison to the standard DLVO model and demonstrate its aptitude to reproduce the results from calorimetric experiments of the ionic surfactant sodium decanoate in water.

**KEY WORDS:** aqueous suspensions of ionic surfactants, coarse-grained models, computer simulation

## 1.    Introduction

Micellar aggregates are formed in aqueous suspensions of amphiphilic molecules, in which the hydrophobic ends of the molecules tend to stick together and the hydrophile ends protect the resulting micelles from external influences through repulsive forces. Non-ionic surfactants typically constitute clusters of 1000 or more molecules, while ionic surfactants generally only manage to create clusters of 10–100 molecules, because their charges tend to break the particles apart. These micellar aggregates are characteristically formed in a critical

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temperature range and above a critical micellar concentration (CMC). Beside their typical spherical form in the dilute regime they can change their shape from rod- to layer-like at higher concentrations [1,2]. In addition to their aggregation tendency, another important property is their large active surface per amount of immersed material, which causes that their structural as well as thermodynamic properties are mainly influenced by effects on these surfaces and, in particular, by the effective interactions arising from them. Micellar systems are playing an important role as solvation agent in many technological applications [3–6]. In particular, they are widely used as detergents and carrier for active substances in pharmaceutics, petroleum extraction, as well as in organic synthesis.

Due to their technological relevance enormous efforts have been invested to characterize and understand their interactions in solution and to study their structural as well as thermodynamic properties. The traditional procedure is to measure their properties with experimental techniques. A very sensitive quantity is the heat capacity which results from calorimetric experiments. It is particularly sensitive to the structure, electrostatic charge, and molality of the immersed material, as well as to the external conditions imposed on the system. Knowledge of the heat capacity as a function of all these variables is necessary to optimize their material's properties and to develop new uses. The thermodynamic properties of ionic surfactants have been extensively studied at various salt concentrations, solvents and external conditions [7–11].

A difficulty of the only use of experimental methods for investigating thermodynamic properties is often the interpretation of the results. A convenient approach to remedy to this problem is to use computer simulation. Several strategies have been proposed in the past, attempting to compute micellar systems on an atomic scale. But it clearly appeared that describing them on a fully atomistic level is difficult due to their complexity and system size. To overcome this problem, several models of different degrees of sophistication and accuracy have been developed. Currently, the most accurate approach for describing systems of charged micelles is based on the so-called 2-component model [12]. In this model, the micelles as well as the surrounding counter- and salt-ions are explicitly represented by charged species, whereas the solvent is treated as a dielectric medium. Recently, extensive investigations with molecular dynamics (MD) and Monte Carlo (MC) simulation methods have been carried out to obtain accurate numerical solutions of such 2-component-model systems [12–23]. However, computer simulation of these models are often prohibited by a slow equilibration as very different length and time scales for the various ionic species are involved [24]. For this reason most simulation approaches involve some degree of coarse-graining, where the degrees of freedom of the smaller ions are traced out, while the charged micelles interact through an effective potential resulting in a coarse-grained, effective 1-component description of the suspension. A widely accepted theory to account for the effective interactions between *stable* charged micelles in aqueous electrolyte suspensions is the

Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [25–27], which has successfully been used to describe aqueous suspensions of polystyrene or silica particles [28–30]. The DLVO potential is essentially a screened Coulomb interaction and arises as a solution to the linearized Poisson–Boltzmann equation. By adding salt (or other electrolytes) to the system the effective screening can be varied and this may lead, under appropriate external conditions, to the formation of various crystal phases. This theory, however, involves several approximations which limits its scope of application. In case of aqueous suspensions of ionic surfactants a significant shortcoming is that it does not take into account the instability of the aggregates, which causes the particles at higher surfactant concentration to break apart due to strong repulsive effective interactions. As a consequence, the excess of monomers in solution further screens the interaction of the remaining micelles. This property leads, e.g., to the observation of the re-entrant behavior of the apparent molal heat capacity with increasing surfactant concentration. However, it is well-known that in studies within the DLVO theory no re-entrant behavior has been found to date [30].

In this paper we investigate the usefulness of the purely repulsive Gauss-core (G) potential to describe the *effective* interactions of aggregates of ionic surfactants in water. In particular, we investigate the influence of the inherent instability of the aggregates against an increase of the surfactant concentration. To this end, we compare the numerically evaluated heat capacities of the model with results obtained from calorimetric experiments with the standard ionic surfactant sodium decanoate (NaDec) in water.

This paper is organized as follows. In Section 2 we briefly review the characteristic features of the standard DVLO model and, subsequently, introduce the Gauss-core model. Then, in Section 3 we present and discuss the theoretical results in comparison to the data resulting from calorimetric experiments. Finally, we end the paper with a summary and the conclusions.

## 2.    Theoretical aspects and model system

In the last decades a lot effort have been invested to understand on a theoretical level the effective interactions acting between charged micelles immersed in an aqueous electrolyte suspension. They deviate from ordinary Coulombic repulsion because of the presence of a large number of very mobile simple ions (microions) in the solvent that effectively screen the interactions between the highly charged micelles (macroions). The simple ions may be the ionized monomers and their counterions, as well as the ions from an added salt. The effective interactions between the charged micelles are usually described within the framework of the DLVO theory [26, 27, 31]. Within this theory, the effective interactions between the micelles are mainly determined by the creation of electric double layers close to the charged surfaces (see figure 1). Their existence is due

to the interplay of entropic effects, which favor the homogeneous distribution of the mobile charges, and the electrostatic attraction between the charges on the surfaces and their counterions in the aqueous environment. The resulting effective interactions between the macroions adopt the form of a Yukawa-type pair potential [30, 31]

$$\Phi_D(\vec{r}) = \infty \qquad \text{for} \qquad |\vec{r}| \leqslant d,$$
$$\Phi_D(\vec{r}) = \frac{Z^2 e^2}{\epsilon} \left( \frac{\exp(\kappa d/2)}{1 + \kappa d/2} \right)^2 \frac{\exp(-\kappa|\vec{r}|)}{|\vec{r}|} \qquad \text{for} \qquad |r| > d, \qquad (1)$$

where $-Ze$ represents their respective total charge with $e$ the elementary charge. Moreover, $d$ is the diameter of the macroions and $|\vec{r}|$ is the center-to-center distance between them. The range of the potential is determined by the inverse Debye screening length $\kappa$, which depends on the temperature $T$ and the total ionic strength $I$ via

$$\kappa^2 = \frac{4\pi e^2 I}{\epsilon k_B T}, \qquad (2)$$

where $\epsilon$ is the dielectric constant of the suspending medium. Moreover, if all the microions in the suspension are monovalent, $I$ equals the total number density
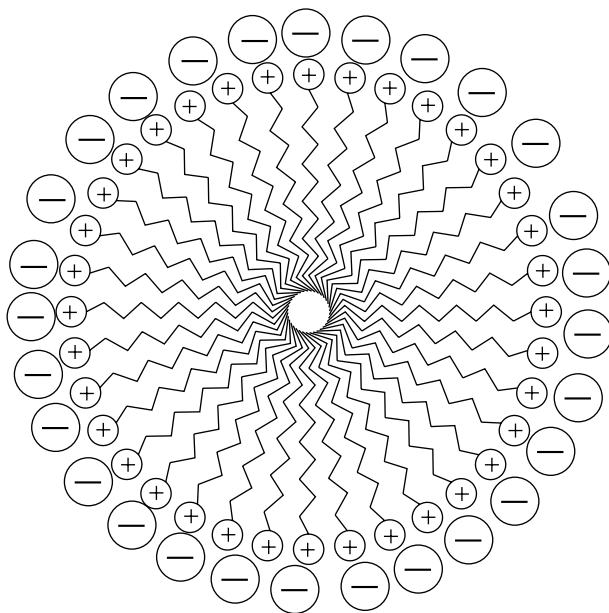


Figure 1. Double layer of ions surrounding the spherical micelle.

of microions, i.e.

$$I = Z\rho + 2\rho_s, \tag{3}$$

where $\rho$ is the density of the micelles, $Z\rho$ the counterion density and $\rho_s$ the density of pairs of added salt ions. These salt ions can either be unbounded surfactant molecules or ions of an added electrolyte. However, despite its wide application the DLVO theory involves certain approximations, which need to be considered [32]: (1) it is based on Debye–Hückel theory that involves a mean field approximation, which becomes invalid when the macroion charges or densities become large; (2) the only use of the linear term in the Taylor expansion of the exponential in the Poisson–Boltzmann equation is valid as long as the electrostatic potential is smaller than the thermal energy, which is not true at distances close to the surface of highly charged macroions; (3) the macroions are assumed to have a finite size; (4) the effect of the solvent is only considered in terms of its dielectric constant and, therefore, its structure is not taken into account, which may influence the interaction when the macroions come close together; (5) the instability of the micelles against an increase of the surfactant concentration is not taken into account, which is particularly important for aggregates formed by ionic surfactants. From these restrictions, we deduce that the DLVO theory is only applicable to a limited range of systems and parameters.

In the following we investigate the usefulness of the Gauss-core potential, which has recently successfully been used in the field of polymer research [33–35], to describe the effective interactions of aggregates formed by ionic surfactants in water. Similarly as in the DLVO model, we here only take into account the suspending medium, i.e. the microions and the solvent, as a screening agent. However, in our approach the effective interactions between the micelles are described by a potential of the Gaussian form, i.e.

$$\Phi_G(\vec{r}) = \Phi_G(0) \exp\left[-\left(\frac{\vec{r}}{\sigma}\right)^2\right], \tag{4}$$

where $\sigma$ is the length scale and $\Phi_G(0)$ the energy scale of the model. The Gauss-core potential has recently been shown to provide a very accurate description of the structural and thermodynamic properties of polymer solutions over a wide range of densities, confirming the idea that systems of polymers can be viewed as effective soft matter systems [35].

## 3. Results and discussion

In the following we show that the Gauss-core model is capable to describe the solvent-mediated effective interactions of aggregates of ionic surfactants over a broad range of densities. In particular, we demonstrate that it can reproduce

in a qualitative way their thermodynamic properties. To this end, we perform a series of canonical Metropolis Monte Carlo (NVT-MC) simulations with the Gauss-core model at different particle densities and temperatures. In the runs we consider a system of 512 particles, which is first equilibrated over 10,000 steps at a temperature of $T_G^* = 0.035$, and, then, cooled down stepwise about 30,000 steps to achieve a temperature decrease of $T_G^* = 0.005$. After the final temperature has been attained, we carry out an equilibration phase over 10,000 steps, followed by a production phase of 50,000 steps. Note that all the results presented in the following are given in reduced Gauss-core units, a system of units that is natural for the model [36]. In particular, we measure distances, energies and temperature in terms of the reduced variables $|\vec{r}_G^*| = |\vec{r}|/\sigma$, $\Phi_G^*(\vec{r}) = \Phi_G(\vec{r})/\Phi_G(0)$ and $T_G^* = k_B T/\Phi_G(0)$, respectively. The notation with an asterisk refers to the corresponding quantities in reduced units. In figure 2 we present the values obtained for the isobaric specific heat capacity per particle number as a function of the particle density at three different temperatures. The quantity is calculated using its relation to the isochoric specific heat capacity per particle number given by

$$c_P = c_V + \frac{VT}{N}\frac{\alpha_P^2}{\beta_T},\tag{5}$$

where $\alpha_P$ and $\beta_T$ represent the thermal expansion and isothermal compressibility, respectively. In the figure we see that all the curves possess a maximum at $\rho_G^* \approx 0.25$ and, then, smoothly converge to the same heat capacity with growing density. We also observe that the lower the temperature, the more pronounced
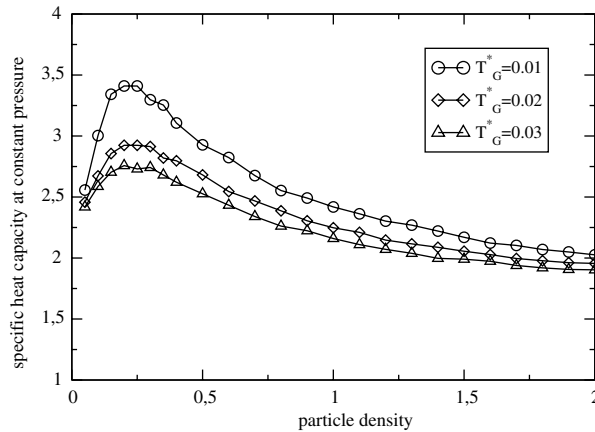


Figure 2. Specific heat capacity at constant pressure per particle number as a function of the particle density obtained from NVT-MC simulations of the Gauss-core model at different temperatures. All error bars are smaller than symbol sizes.

the shape of the peak. Next, comparing the heat capacity curves of the Gauss-core model with its melting temperature curve in figure 3, we recognize that their maxima occur at the same particle density. This clearly shows that the heat capacity is an ideal property to study the nature and strength of the effective interactions involved in the system. To further demonstrate this, we define the pair repulsion energy characterizing the importance of the repulsions at the typical particle separation $a_G^* = \rho_G^{*\,-1/3}$ [31]

$$R_G^*\left(a_G^* = \rho_G^{*\,-\frac{1}{3}}\right) = \frac{\Phi_G(a_G^*)}{\Phi_G(0)} = \exp\left[-\left(\rho_G^*\right)^{-\frac{2}{3}}\right]. \tag{6}$$

The interaction strength between the micelles is then obtained as

$$D_G^*(\rho_G^*) = \frac{\partial R_G^*(\rho_G^*)}{\partial \rho_G^*} = \frac{2}{3}\left(\rho_G^*\right)^{-\frac{5}{3}} \exp\left[-\left(\rho_G^*\right)^{-\frac{2}{3}}\right]. \tag{7}$$

In figure 4 we visualize both quantities as a function of the particle density. We see that the curve of $R_G^*$ increases monotonically with growing density, while its density derivative undergoes a maximum at $\rho_G^* \approx 0.25$. At this density the system possesses a maximum in the interaction strength, which can readily be identified to coincide with the maximum of the heat capacity and the melting temperature given in figure 2 and 3, respectively. Additionally comparing the curve of the derivative with the one of the heat capacity at the lowest temperature $T_G^* = 0.01$, we see that both curves are of similar shape. This further confirms that the heat capacity provides a sensitive measure of the strength of the micellar interactions involved in the system. At higher temperatures the particles possess a higher kinetic energy, which results in a smoothing of the respective heat capacity curves.
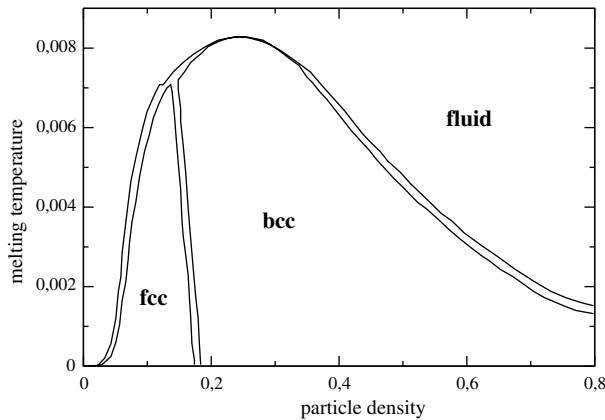


Figure 3. Melting temperature diagram of the Gauss-core model evaluated by Stillinger and Stillinger [36].

Let us next investigate if the Gauss-core model allows us to reproduce qualitatively correctly the heat capacity curves obtained from calorimetric experiments. To this end, we consider the standard ionic surfactant NaDec in water, which finds wide technical application as detergent in soaps. In experimental investigations it is particularly convenient to determine apparent molal quantities, which are independent of the amount of solute employed in the measurements. More specifically, the apparent molal heat capacity is defined as

$$C_{P,\phi} = \frac{C_P - n^0 c_P^0}{n},$$   (8)

where $C_P$ is the heat capacity of the solution and $n$ the amount of the solute, while $n^0$ and $c_p^0$ represent the amount and the specific heat capacity of the pure solvent, respectively. The thermodynamic properties of NaDec have extensively been investigated through calorimetric experiments by De Lisi *et al.* [7]. In figure 5 we show the apparent molal heat capacity as a function of the reduced density $\rho_m^* = (m - m_c)/m_c$ at three different temperatures, where $m_c$ means the critical molality of the surfactant. For the temperature dependent CMC's we use the experimentally evaluated values given in the same reference. We can easily convince ourselves by comparing these curves with the numerically evaluated heat capacities of the Gauss-core model in figure 2 that the Gauss-core model describe qualitatively correctly the thermodynamic behavior of NaDec in water. Analogously to the theoretical curves, the experimental curves undergo a maximum at a reduced density of $\rho_m^* \approx 0.25$ and, then, join each other at a density of $\rho_m^* \approx 2.0$. In this context, it is also worth mentioning that in neutron and light scattering experiments it has been established that in the density range $0.0 < \rho_m^* \leqslant 0.8$, NaDec in water forms charged spherical micelles [1,2]. At $\rho_m^* > 0.8$
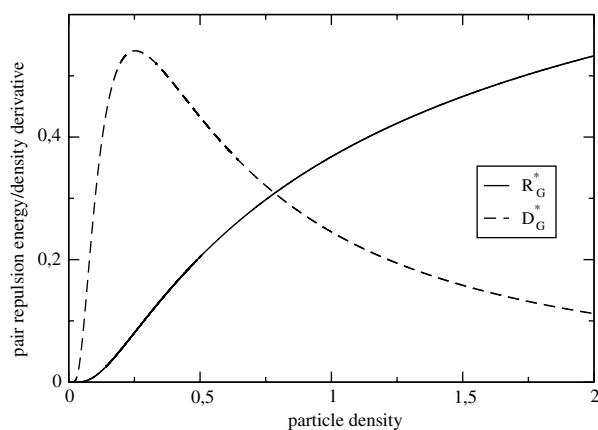


Figure 4. Pair repulsion energy of the Gauss-core model and its density derivative as a function of the particle density.

the micelles grow only slowly and maintain a spherical shape up to a density of $\rho_m^* \approx 1.6$ [2]. Based on these observations, it clearly appears that the system is a suitable example to demonstrate the usefulness of the Gauss-core model for describing effective interactions of ionic surfactants in water. Moreover, it is also worth emphasizing that several other ionic surfactants show similar behavior in their thermodynamic properties [8–10].

Next, let us compare these results to the standard model resulting from the DLVO theory. Analogously, we compute the temperature-independent pair repulsion energy at the typical particle separation, characterizing the importance of the repulsions, namely

$$R_D^*\left(a_D^* = \rho_D^{*-\frac{1}{3}}\right) = \frac{\Phi_D(a_D^*)}{k_B T}$$

$$= Z^2 \left(\frac{\exp(\kappa_D^* d_D^*/2)}{1 + \kappa_D^* d_D^*/2}\right)^2 \left(\rho_D^*\right)^{\frac{1}{3}} \exp\left[-\kappa_D^* \left(\rho_D^*\right)^{-\frac{1}{3}}\right], \qquad (9)$$

where $\kappa_D^* = \kappa\lambda$ represents the reduced Debye screening length and $\lambda = e^2/\epsilon k_B T$ the Bjerrum length. In the following we take the Bjerrum length as the characteristic unit of length of the DLVO model, which means that the reduced density of the micelles are defined via $\rho_D^* = \rho\lambda^3$. Accordingly, the density derivative of $R_D^*(\rho_D^*)$ results in

$$D_D^*(\rho_D^*) = Z^2 \left(\frac{\exp(\kappa_D^* d_D^*/2)}{1 + \kappa_D^* d_D^*/2}\right)^2 \left[\frac{1}{3}\left(\rho_D^*\right)^{-\frac{2}{3}} + \frac{1}{3}\kappa_D^* \left(\rho_D^*\right)^{-1}\right] \exp\left[-\kappa_D^* \left(\rho_D^*\right)^{-\frac{1}{3}}\right].$$
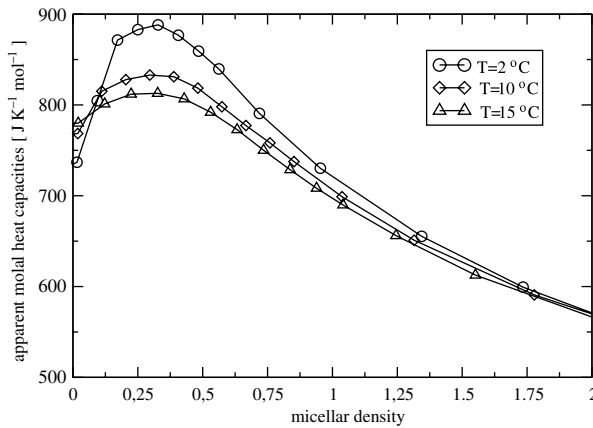
$$(10)$$



Figure 5. Heat capacity of sodium decanoate in water as a function of the reduced micellar density obtained from calorimetric experiments at different temperatures.

This quantity, which characterizes the interaction strength in the DLVO approach, possesses a maximum at a density of $\rho_{D/\max}^* = 1/2\kappa_D^{*\,3}(-5/2 + 3/2\sqrt{3})$. In figure 6 we show the pair repulsion energy and its density derivative for different particle diameters as a function of the particle density. For the calculations we use a screening parameter of $\kappa_D^* = 1.7211$ and a charge number of $Z = 1$. We recognize that the curve of the interaction strength increases strongly at low micellar densities and is maximal at $\rho_{D/\max}^* \approx 0.25$. At higher micellar densities the interaction strength decreases slightly until it reaches an upper bound, whose magnitude depends on the particle diameter. The limit is imposed by the maximum packing density, which is given by a face-centered cubic arrangement of the spherical particles. It is related to the particle diameter through the equation $\rho_{D/\text{fcc}}^* = 1.4133/d_D^{*\,3}$ [37]. Moreover, we deduce from the figure that with increasing particle diameter the decreasing part of the curves becomes smaller, which explains that in the case of the DLVO model a re-entrant behavior has only been observed in the limit of vanishing particle diameter where the DLVO potential goes over into the Yukawa potential [30]. In this context, it is also worth emphasizing that in the DLVO model the restriction on the range of densities is caused by the finite size of the *rigid* macroions [30]. This might be a valid approximation in case of aqueous suspensions of stable polystyrene spheres. In such systems each of the colloidal particles consists of a large number of polystyrene chains entangled in a coil. The chain ends are terminated with an acidic group, like for instance $-KSO_4$, dissociating in the aqueous medium. The stability of the particles is essentially due to the high entanglement of the polymeric chains, the $\pi$–$\pi$-interactions of the phenyl-rings and the strong electrostatic charges. In contrast, aggregates formed by NaDec in water are relatively unstable due to the lack of the first two stabilizing factors. Therefore, they tend with increasing effective interactions to break apart or interpenetrate by forming larger particles. Other deficiencies of the DLVO theory, already discussed in Section 2, are caused by the unreliability of several approximations involved in the DLVO theory in the regime of high micellar density [30].

Based on the above observations, we conclude that, in contrast to the DLVO model, the Gauss-core model describes qualitatively correctly the effective interactions of the micellar aggregates formed by NaDec in water. This can be explained in the following way. At a zero reduced density when the CMC is attained, first micellar aggregates are formed spontaneously and their density steeply increases with increasing surfactant concentration. The growth of the density of the micellar aggregates leads to an increase of the effective interactions between the particles. This causes that, with increasing surfactant concentration, less particles are formed or the existing ones interpenetrate by forming larger particles. As a result, an increasing amount of unbounded surfactant molecules remains dissolved in the solvent and acts as a screening agent, thereby reducing the effective interactions between the remaining aggregates. As the surfactant concentration increases, the screening effect causes first a slowing down of the
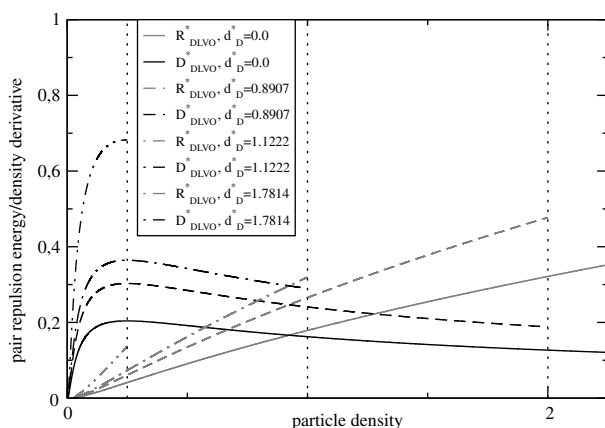
Figure 6. Pair repulsion energy of the DLVO potential and its density derivative as a function of the particle density.

growth of the interaction strength and, after passing through a maximum, to a decrease of the quantity. This behavior of the interaction strength is also clearly reflected in the heat capacity curves of NaDec in water and the curves of the Gauss-core model. Finally, we emphasize that similar behavior of the heat capacities has also been found in experiments with other systems forming micellar aggregates, such as, e.g., in case of sodium laureate or sodium palmitate in water [38,39].

## 4.    Summary and conclusions

In summary, we demonstrate in this paper that the effective interactions acting between micellar aggregates formed in aqueous suspensions of ionic surfactants are qualitatively correctly described by the Gauss-core model. To demonstrate this, we calculate and compare the heat capacities obtained with the Gauss-core model to the results obtained from calorimetric experiments with the standard ionic surfactant NaDec in water. Furthermore, we show that the behavior of the heat capacity with increasing surfactant concentration coincides with the behavior of the interaction strength between the effective particles. We explain these observations as follows. After the critical surfactant concentration has been reached, a growing amount of micellar aggregates are formed spontaneously, leading to a steep increase of the effective interactions between the micelles. This behavior is maintained until the strength of the effective interactions counteracts the formation of new micellar aggregates or induces the generation of larger ones by interparticle aggregation. As a result, a smaller amount of new particles are formed and the additional surfactant molecules prefer to stay as monomers in solution, thereby screening the effective interactions between

the remaining particles. This leads to a decrease of the interaction strength and accordingly to a decrease in magnitude of the heat capacity. By further investigating the usefulness of the Gauss-core model, we find that it gives a better qualitative description of the effective interactions in the regime of high surfactant concentration in comparison to the DLVO model. In particular, we note that in case of the DLVO model the re-entrant behavior with increasing micellar concentration has not been observed to date. In conclusion, we deduce from this study that the Gauss-core model is useful to describe the effective interactions of aggregates of ionic surfactants in water and that it reproduces the essential characteristic features of their thermodynamic properties. Moreover, it clearly appears that further investigations about the nature and role of the effective interactions are necessary for the understanding and modeling of these systems above their critical micellar concentration.

## Acknowledgments

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