

## Discontinuous Bending Rigidity and Cosurfactant Adsorption of Amphiphile Layers

Lionel Foret and Alois Würger

*Université Bordeaux I, CPMOH,\* 351 cours de la Libération, 33405 Talence, France*

(Received 16 January 2001)

We study a simple model for an amphiphilic layer that may adsorb cosurfactant molecules from a reservoir. Upon varying the length of the cosurfactant, we obtain a discontinuous change of the adsorption rate and a corresponding discontinuity of the bending rigidity  $\kappa$ . With realistic values for the chemical potential and the interaction energy of the hydrophobic tails, our model accounts quantitatively for the measured rigidity and the discontinuity observed for the ternary system AOT/water/oil and for SDS/alcohol bilayers.

DOI: 10.1103/PhysRevLett.86.5930

PACS numbers: 68.05.Cf

Amphiphilic layers of polar or ionic molecules play an essential role in biological membranes, soap films and foams, and at the interfaces of microemulsions. The standard model for amphiphilic films is based on 2D continuous mechanics. Helfrich introduced an elastic free energy density  $\frac{1}{2}\kappa(c_1 + c_2 - 2c_0)^2 + \bar{\kappa}c_1c_2$  that depends on the two principal curvatures  $c_1 = 1/R_1$  and  $c_2 = 1/R_2$  [1]. The model parameters are the spontaneous curvature  $c_0$ , the bending rigidity  $\kappa$ , and the saddle-splay modulus  $\bar{\kappa}$ .

The elastic constant  $\kappa$  describes the stiffness of the membrane with respect to undulations, whereas  $\bar{\kappa}$  and  $c_0$  rather determine its topology and give rise to micelles, bi-continuous or lamellar phases. The origin of these quantities in terms of the underlying forces may be understood through their dependencies on temperature, salinity, and the molecular structure of the constituents; experimentally one finds that the elastic constants increase with salinity and decrease with temperature [2–4].

Comparison with available theoretical models is far from satisfying. For ionic surfactant molecules, the curvature elasticity due to the electrostatic interaction of charged bilayers has been studied in terms of Poisson-Boltzmann theory [5]. The contribution of the hydrophobic tails has been considered in two different models: In a picture of flexible polymers, the entropic repulsion of the tails has been shown to strongly enhance the elastic constants as the area per molecule decreases [6]; a similar result was obtained in a complementary approach from a model of rigid molecules with Lennard-Jones interactions [7]. From elasticity theory for thin films, one expects a variation with the cube of the molecular length  $L$ . The model of rigid rods yields a correlation of the constants  $\kappa$  and  $\bar{\kappa}$  that roughly corresponds to the observed ratio  $-\frac{1}{2} > \bar{\kappa}/\kappa > -2$  [7].

These studies take the film composition to be constant. In the present paper we consider an amphiphilic film that may adsorb cosurfactant or oil molecules from a reservoir. A similar idea has been proposed by Safran *et al.* [8], and generalized by Porte and Ligoure [9], to explain the symmetry breaking in mixed bilayers occurring at the lamellar-vesicle transition, in terms of a local layer composition that changes with curvature. In the present work we allow

for a variable cosurfactant concentration, and we calculate the penetration rate as a function of the cosurfactant or oil length, the interaction energy of the tails, and the chemical potential of the cosurfactant reservoir. At constant area per surfactant headgroup, a finite penetration rate results in a densification of the layer and, according to all microscopic theories [6,7], in an increase of the bending elastic constants.

Our study is motivated by the experimental observation of a discontinuous change of the rigidity with the cosurfactant or oil length, i.e., with their number of methylene units  $m_c$ . Kellay *et al.* determined the roughness of sodium diethylhexylsulfosuccinate (AOT) monolayers at the interfaces of the ternary mixture AOT/water/oil by ellipsometry and deduced the bending rigidity [3]. They found  $\kappa \approx 1k_B T$  for short alkanes ( $m_c < 11$ ) and  $\kappa \approx 0.1k_B T$  for longer ones ( $m_c > 11$ ) (cf. Fig. 2). Moreover, deuterated NMR measurements showed that the higher rigidity in the first case is related to quite stiff alkane chains with few conformational defects and to an alignment of the alkanes with the AOT molecules [10], as suggested in our Fig. 1. As a second example, Safinya *et al.* observed a similar behavior when adding alcohol as a cosurfactant to sodium

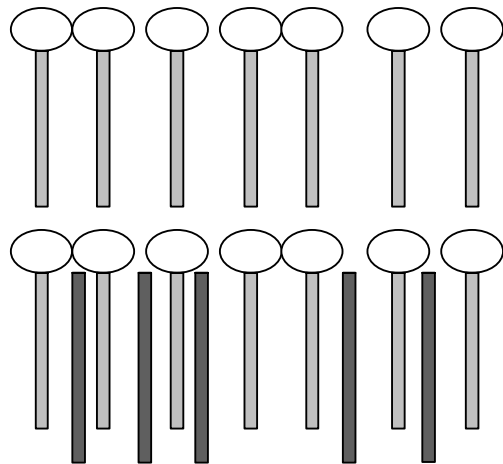


FIG. 1. Schematic representation of an amphiphilic layer and the same layer with adsorbed cosurfactant molecules.

dodecyl sulfate (SDS) bilayers in water [4]. They measured the rigidity in terms of the power law exponent of the x-ray scattering law, and report  $\kappa = 3k_B T$  for short alcohols ( $m_c < 7$ ) and  $\kappa = 13k_B T$  for longer ones ( $m_c > 7$ ) (cf. Fig. 2).

Our model consists of a two-dimensional binary liquid of  $N$  surfactant molecules and  $n$  cosurfactants.  $N$  is fixed whereas  $n$  is variable. The molecular tails are considered as rigid rods; this means that we neglect their conformational fluctuations [11]. For the system AOT/water/oil this picture of parallel rigid rods is supported by NMR measurement [7,10]. A most relevant parameter is given by the ratio of surfactant and cosurfactant lengths  $m_s$  and  $m_c$ . The equilibrium of the adsorbed cosurfactant molecules and the reservoir are determined by the chemical potential  $\mu$  whose dependence on  $m_c$  is specified below. The cosurfactant adsorption rate  $x = n/N$  is treated most conveniently in a grand canonical approach, with the thermodynamic potential

$$J(x) = U(x) - TS(x) - xN\mu, \quad (1)$$

where  $x$  varies from zero to its maximum value  $x_0 = n_{\max}/N$ . Throughout this paper we use  $x_0 = \frac{1}{2}$ . The internal energy  $U$  and the entropy  $S$  define the Helmholtz free energy  $F(x) = U - TS$  for fixed  $x$ .

For ionic surfactants, the electrostatic headgroup interactions are much stronger than those of the hydrophobic tails, and thus determine the area per surfactant molecule  $a_0$ . As a consequence,  $a_0$  does not depend on the adsorption rate  $x$ . (This seems plausible, since for most systems  $a_0$  takes values 2 or 3 times larger than the close-packing value of a hydrocarbon chain  $a_{\text{alkane}} \approx 18 \text{ \AA}^2$  [12].) Accordingly, the cosurfactants occupy the empty space between surfactant tails. Note that for constant  $a_0$ , a finite cosurfactant penetration  $x$  reduces the area per chain to  $a_0/(1+x)$  and thus densifies the hydrophobic layer. For the examples considered below, the remaining area per hydrocarbon chain at maximum adsorption,  $a_0/(1+x_0)$ , is significantly larger than the close-packing value.

The average value of the adsorption rate is determined by minimizing the grand potential (1) with respect to  $x$ . We now present our model that specifies the dependence of  $J$  on the adsorption rate, the chain lengths  $m_s$  and  $m_c$ , and the area per molecule  $a_0$ .

We start with the interaction energy of the tails,  $U$ , that comprises attractive London forces and short-range ‘‘steric’’ repulsion [12]. The potential of parallel and cylindrical rods depends only on the distance of the molecular axes  $r$  and their length  $L$ . For sufficiently long molecules  $L > r$ , the interaction energy of two neighbors  $A$  and  $B$  with  $m_A$  and  $m_B$  methylene units is proportional to the shorter length  $\min(m_A, m_B)$ , and can be written as

$$u_{AB}(r) = \begin{cases} m_A v(r) & \text{for } m_A \leq m_B, \\ m_B v(r) & \text{for } m_A > m_B. \end{cases} \quad (2)$$

The quantity  $v(r)$  gives the interaction energy per methylene unit as a function of the molecular distance  $r$ .

Here we use the Lennard-Jones type expression obtained previously by one of us by summing the atom-atom pair potentials for all constituents of the two molecules,  $v(r) = v_0[(\sigma/r)^{12} - 2(\sigma/r)^6]$  with a minimum value  $v_0 = 0.6k_B T$  that occurs at a distance  $\sigma = 4.85 \text{ \AA}$  [13].

When taking the thermal average and summing over all pairs of molecules, we obtain the internal energy

$$U = \frac{N}{2} [m_s \varepsilon_1 + 2 \min(m_s, m_c) x \varepsilon_2 + m_c x^2 \varepsilon_2], \quad (3)$$

with the minimum length  $\min(m_s, m_c)$  defined as in (2), and the average interaction energies

$$\varepsilon_1 = \overline{v(r)}^{ss}, \quad \varepsilon_2 = \overline{v(r)}^{cs}, \quad \varepsilon_2 = \overline{v(r)}^{cc}. \quad (4)$$

In a liquid, these averages can be expressed through the corresponding density-density correlation functions  $g_{\alpha\beta}(r)$  that are different for the pairs  $\alpha\beta = ss, sc$ , and  $cc$ . In (4) we have already used the cosurfactant-surfactant and cosurfactant-cosurfactant correlation functions to show the same distance dependence, since both are determined by the hydrophobic tails. The surfactant-surfactant correlation function is different because of the headgroup repulsion that results in a bigger ‘‘correlation hole’’ (cf. Fig. 1). We choose the simplest form that is zero below a minimum distance and constant beyond, and thus have, e.g.,  $g_{ss}(r) = (1/a_0)\Theta(r - r_{ss})$  with  $\int d^2r g_{ss}(r) = N$ . According to the above discussion,  $r_{ss} > r_{sc} = r_{cc}$ . With the hard-core radius  $r_{cc} = 4.6 \text{ \AA}$  and a typical area per molecule  $a_0 = 40 \text{ \AA}^2$ , we obtain the molecular field per methylene unit  $\varepsilon_2 = -0.8k_B T$ ; these are realistic values.  $\varepsilon_1$  turns out to be irrelevant for our problem, since its contribution to the free energy is independent of  $x$ .

Now we turn to the entropic contribution to the grand potential (1). The maximum number of hydrophobic chains in the layer is given by  $(1+x_0)N$ .  $N$  of these ‘‘sites’’ are occupied by surfactants,  $n = xN$  by cosurfactants, and the remaining ones are empty. When dropping irrelevant constant terms we obtain the well-known mixing entropy of a binary system,

$$S = -Nk_B [x \ln x + (x_0 - x) \ln(x_0 - x)], \quad (5)$$

that is symmetric about  $x = \frac{1}{2}x_0$  and vanishes at  $x = 0$  and  $x = x_0$ .

Finally we consider the chemical potential of the cosurfactant molecules. Quite generally, and certainly for the two examples discussed below, we may split  $\mu$  in a constant  $\mu_0$  for the headgroup and a term for the tail that varies linearly with the number of methylene groups,

$$\mu = \mu_0 + m_c \mu_1, \quad (6)$$

where the sign and the absolute value of both terms depend on the cosurfactant and on the reservoir solvent.

Through (3)–(6) we have explicitated the grand potential in terms of the adsorption rate  $x$  and the parameters for the interaction energy and the chemical potential,  $\varepsilon_2$ ,  $\mu_0$ , and  $\mu_1$ . The average value  $\bar{x}$  is determined by minimizing

$J(x)$ . Before applying this model to the systems mentioned in the introduction, we discuss the general behavior of the equilibrium state. The minima of  $J(x)$  are characterized by zero slope  $\partial_x J = 0$ , or

$$x m_c \varepsilon_2 + \min(m_s, m_c) \varepsilon_2 - \mu = k_B T \ln \frac{x_0 - x}{x}, \quad (7)$$

and positive curvature  $\partial_x^2 J > 0$ , or

$$m_c \varepsilon_2 + k_B T \left( \frac{1}{x} + \frac{1}{x_0 - x} \right) > 0. \quad (8)$$

The curvature of the energy,  $\partial_x^2 U = N m_c \varepsilon_2$ , is constant and negative, since  $\varepsilon_2 < 0$ . That of the entropy term is always positive; it diverges at  $x = 0$  and  $x = x_0$ , and takes the finite value  $(4/x_0) N k_B T$  at  $x = \frac{1}{2} x_0$ .

Thus energy and chemical potential favor one of the limiting values,  $x = 0$  or  $x = x_0$ , whereas the entropy term  $-TS$  is minimum at half occupation. For weak interaction,  $-m_c \varepsilon_2 < (4/x_0) k_B T$ , the entropic term prevails, and  $J$  has a single minimum that is determined by the ratio of the linear terms in  $U$  and  $\mu$ . The adsorption rate corresponding to this minimum changes smoothly with the parameters. (Since the real systems considered in the present paper do not satisfy the weak-interaction condition, we discard this case here but intend to discuss it elsewhere [14].)

Here we focus on the opposite case of strong interaction,  $-m_c \varepsilon_2 > (4/x_0) k_B T$ , where the curvature (8) is negative in the vicinity of  $x = \frac{1}{2} x_0$  and positive elsewhere. Thus  $J(x)$  may show two minima, depending on the linear coefficients  $\min(m_s, m_c) \varepsilon_2$  and  $\mu$ . Since  $-\varepsilon_2$  is of the order of  $kT$ , most amphiphilic layers satisfy the limit of strong interaction, where the entropic term  $-TS$  is rather irrelevant. In the remainder of this paper we study the two minima that may occur at  $x \approx 0$  and  $x \approx x_0$  and how one or the other becomes stable upon changing the cosurfactant length  $m_c$ . In physical terms, this transition corresponds to a discontinuous change of the adsorption rate  $x$ .

In order to relate this discontinuity to that observed for the bending rigidity  $\kappa$ , we need to calculate  $\kappa$  as a function of  $x$ . This is achieved in terms of the model of Ref. [7], where the rigidity  $\kappa = \kappa_a + \kappa_v$  consists of an entropic term  $\kappa_a$  and a second one,  $\kappa_v$ , that arises from the London forces. In the simplest picture, the molecular entropy varies with the area per molecule  $a = a_0/(1 + \bar{x})$  as  $s = k_B \ln a$ , and thus contributes to the bending rigidity, the term

$$\kappa_a = \frac{kT}{a_0} [L_s^2 + \bar{x} \min(L_s^2, L_c^2)] \quad (9)$$

that increases with the adsorption rate  $\bar{x}$ . Here  $L_s = m_s d$  denotes the surfactant length, with  $d = 1.27 \text{ \AA}$ .

The energetic contribution arises from the finite curvature of the Lennard-Jones potential  $v(r)$  of neighbor molecules in the layer. It increases with the density of the hydrophobic layer. For a mixed film, one finds

$$\kappa_v = \frac{1}{8a_0^2 d} [A_1 L_s^3 + 2A_2 \bar{x} \min(L_s^3, L_c^3) + A_2 \bar{x}^2 L_c^3], \quad (10)$$

where the averages are defined in terms of the different pair correlation functions discussed below (4),

$$A_1 = \frac{1}{2} \overline{r^2 v''(r)^{ss}}, \quad A_2 = \frac{1}{2} \overline{r^2 v''(r)^{sc}}, \quad (11)$$

where  $v''$  denotes the second derivative with respect to the distance  $r$ . This second derivative varies strongly with  $r$  and is negative for  $r > (13/7)^{1/6} \sigma$ . Thus our fits depend crucially on the cutoff radii of the pair correlation functions; cf. the discussion below (4). (Note that the rigidity of a SDS bilayer is twice that of a monolayer [9].) The fits of Fig. 2 have been obtained with the values  $r_{ss} = 4.63 \text{ \AA}$  and  $r_{cs} = 4.6 \text{ \AA}$  that yield negative  $A_1 = -11kT$  and positive  $A_2 = 5kT$ . As a consequence, the bending rigidity strongly increases with the adsorption rate  $\bar{x}$ . (Such a behavior is expected from any of the available microscopic models [6,7]. Both the present work and the rigidity calculation of Ref. [7] are based on rigid rods with London forces; thus with this latter model a consistent and almost quantitative comparison can be achieved.)

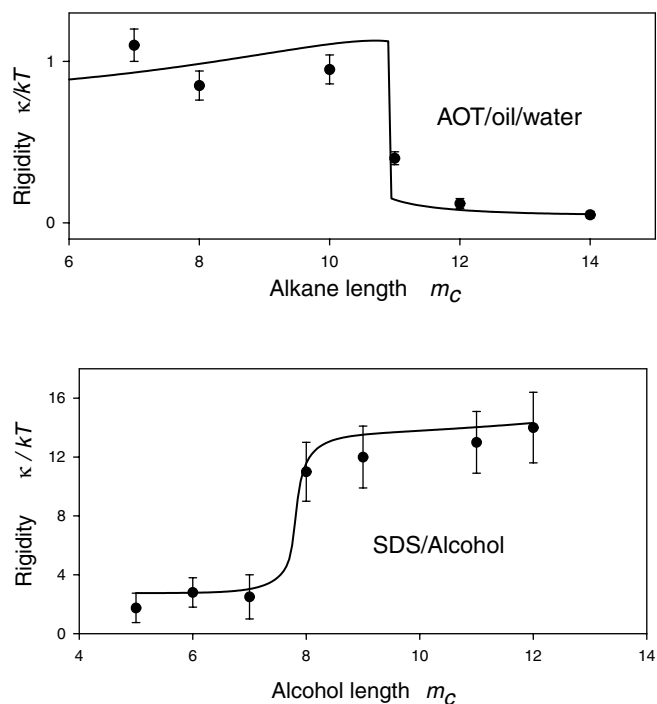


FIG. 2. Bending rigidity of an AOT layer at a water/oil interface and of a SDS layer with alcohol as cosurfactant. Black circles are experimental data taken from Refs. [3] and [4], respectively; solid lines are calculated as discussed in the text. The sudden change of the rigidity occurs where our model shows a discontinuity of the alcohol or cosurfactant adsorption rate. For both fits we used the parameters given below (11). For the area per molecule we take  $a = 35 \text{ \AA}^2$  per AOT tail and  $a = 45 \text{ \AA}^2$  per SDS molecule.

First we consider an AOT layer in a AOT/water/oil mixture. The alkanes play the role of the cosurfactant, and the excess oil phase on the top of the sample, that of the reservoir. The AOT molecule consists of a large headgroup with  $a_0 \approx 70 \text{ \AA}^2$  and two hydrophobic tails of length  $m_s = 6$ . To keep our model simple, we replace each AOT by two independent single-chain surfactants with  $a_0 = 35 \text{ \AA}^2$ . With oil being a stable liquid at room temperature, the alkane chemical potential is negative, with  $\mu_0 = 0$  and  $\mu_1 < 0$ . We focus on the case  $\mu_1 < (x_0/2)\varepsilon_2 < 0$  that presents a discontinuous transition as a function of  $m_c$ . As long as the alkane length  $m_c$  is comparable to that of AOT, the energy term prevails, resulting in strong adsorption  $x \approx x_0$ . With increasing alkane length  $m_c$ , however, the chemical potential  $-x_0 m_c \mu_1$  at some point exceeds the energy gain  $U$ . When neglecting the entropy, we find a discontinuous transition where  $U(x_0) - x_0 m_c \mu_1 = 0$  that occurs at the critical value

$$m_c^* = m_s \frac{\varepsilon_2}{\mu_1 - (x_0/2)\varepsilon_2} \quad (m_c^* > m_s). \quad (12)$$

When we identify this transition with the discontinuous change in rigidity at  $m_c = 11$  observed by Kellay *et al.*, this requires with  $m_s = 6$  the relation  $\mu_1 = \frac{35}{44}\varepsilon_2$  or, with  $\varepsilon_2 = -0.9k_B T$ , the chemical potential  $\mu_1 = -0.75k_B T$ . The fusion enthalpy for 11-alkane takes a value of  $-0.5k_B T$  per methylene unit [15]; the difference of  $-0.25k_B T$  is probably due to the conformational entropy that is significantly smaller in the adsorbed state than in the liquid. (Our model supposes rigid molecules with zero conformational entropy.)

As a second system we consider SDS bilayers in water with alcohol as a cosurfactant and its solution in water as a reservoir. Because of their polar headgroup short alcohols are well soluble in water, whereas for longer ones the hydrophobic tails strongly diminish the solubility [12]. Accordingly, the chemical potential (6) comprises a large negative constant,  $\mu_0 < 0$ , that accounts for the hydrophilic potential of the order of  $-20k_B T$ , and a positive linear term,  $\mu_1 > 0$ , for the hydrophobic interaction of about  $1k_B T$ . From these numbers it is already obvious that short alcohols will not penetrate the SDS bilayer but rather stay in the solution, whereas for longer ones the energy gain  $\mu_1 - \varepsilon_2$  per methylene unit renders the adsorbed state at maximum  $x$  more favorable. (Thus one expects a behavior opposite to that of the AOT/water/oil system.)

When proceeding as above and neglecting the entropic term in the grand potential  $J$ , we find a transition from weak to strong adsorption to occur at the critical length

$$m_c^* = \frac{\mu_0}{\varepsilon_2(1 + x_0/2) - \mu_1} \quad (m_c^* < m_s). \quad (13)$$

The numerical values for the parameters of the chemical potential given above yield  $m_c^* = 7$ , in agreement with the data of Safinya *et al.* [4].

Although the precise values of quantities (4) and (11) depend on the numerical values for the correlation hole,

the general behavior of the curves shown in Fig. 2 does not. Both the sign and the order of magnitude of  $\varepsilon_2$ ,  $\mu_0$ , and  $\mu_1$  can be deduced from general properties of the systems SDS/alcohol and AOT/oil/water; accordingly, the discussion of (12) and (13) is rather unambiguous. (Our results depend only weakly on  $x_0$  and  $a_0$ .)

Our simple model provides a good description of the data for both systems. The microscopic picture of cosurfactants penetrating the amphiphilic layer is strongly supported by the deuterated NMR measurements on oil in AOT layers [10]; this experiment shows an upright position of the alkanes in what we call adsorbed state. There is no such direct proof for the system SDS/alcohol. Regarding the orientation of the alcohols, one could imagine a parallel or antiparallel alignment of the polar alcohol with the SDS molecule; this latter case would amount to the formation of a double bilayer SDS/alcohol/alcohol/SDS, with interpenetration of the hydrophobic tails according to our model. (This would explain the increase of the bilayer thickness with the alcohol length reported in [4].)

In summary, we have proposed and solved a simple model for cosurfactant adsorption in an amphiphilic layer that yields, with realistic parameters, a discontinuous change of the adsorption rate with the length of the cosurfactant or oil molecule. The critical values for their length (12) and (13) depend solely on the molecular pair interaction and the chemical potential. Together with a previous theory for the elastic constants of the Helfrich free energy [7], our model shows quantitative agreement with rigidity data measured for AOT/oil/water and SDS/alcohol.

Helpful discussions with Hamid Kellay are gratefully acknowledged.

---

\*UMR CNRS 5798.

- [1] W. Helfrich, *Z. Naturforsch.* **28C**, 693 (1973).
- [2] *Micelles, Membranes, Microemulsions, and Monolayers*, edited by W.G. Gelbart, A. Ben-Shaul, and D. Roux (Springer, Berlin, 1994).
- [3] H. Kellay *et al.*, *Adv. Colloid Interface Sci.* **49**, 85 (1994).
- [4] C. R. Safinya *et al.*, *Phys. Rev. Lett.* **62**, 1134 (1989).
- [5] M. Winterhalter and W. Helfrich, *J. Phys. Chem.* **92**, 6825 (1988); **96**, 327 (1992).
- [6] I. Szleifer *et al.*, *Phys. Rev. Lett.* **60**, 1966 (1989); *J. Chem. Phys.* **92**, 6800 (1990).
- [7] A. Würger, *Phys. Rev. Lett.* **85**, 337 (2000).
- [8] S. Safran *et al.*, *Phys. Rev. A* **43**, 1071 (1991).
- [9] G. Porte and C. Ligoure, *J. Chem. Phys.* **102**, 4290 (1995).
- [10] Y. Hendrikx *et al.*, *Europhys. Lett.* **25**, 735 (1994).
- [11] P.J. Flory, *Statistical Mechanics of Chain Molecules* (Wiley, New York, 1969).
- [12] J. Israelachvili, *Intermolecular Forces and Surface Forces* (Academic Press, New York, 1992).
- [13] A. Würger, *Phys. Rev. Lett.* **83**, 4816 (1999); *J. Chem. Phys.* **112**, 3897 (2000).
- [14] L. Foret and A. Würger (to be published).
- [15] A. Marbeuf *et al.*, *Phys. Chem. Chem. Phys.* **2**, 261 (2000).