

# 1 Effect of packing parameter on amphiphilic self-assembly: a Brownian dynamics study

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**Summary.** We investigate the role of packing parameter in dictating the shape and size of micelles in amphiphilic self-assembly by varying the size of the hydrophilic head for a fixed tail size using a stochastic molecular dynamics simulation.

## 1.1 Introduction

When amphiphilic molecules are dissolved into solvents, such as water, the hydrophobic nature of the hydrocarbon chains drives these molecules to self-assemble in a variety of structures where the hydrophilic heads form a surface which shields the hydrophobic tails from water. The concentration and geometric features of the amphiphiles, temperature, the salinity of the solution, *etc.*, are important in dictating the final equilibrium phases and transition among these phases. The sizes of the self-assembled aggregates (often called micelles) can be much larger than the individual amphiphilic molecules. The hydrophobic interaction that causes the self-assembly is considerably weaker than the intra-molecular covalent bonds and often entropy plays a dominant role in self-assembly. The steric and geometric effects also play important role in dictating the shape of the micelles. The shape of a micelle is characterized by the dimensionless packing parameter  $\lambda = \frac{v}{a_0 l_c}$ , where  $v$ ,  $a_0$ , and  $l_c$  are the volume, the optimal head group area, and the critical chain length of an amphiphile respectively. Spherical and non-spherical micelles, and bi-layers are formed for  $\frac{v}{a_0 l_c} < \frac{1}{3}$ ,  $\frac{1}{3} < \frac{v}{a_0 l_c} < \frac{1}{2}$ , and  $\frac{1}{2} < \frac{v}{a_0 l_c} < 1$  respectively [1]. Although there have been many analytical and numerical work [2–6] on amphiphilic self-assembly there is no systematic investigation of the role of the packing parameter for model amphiphilic systems. Here we report the preliminary results of such study in two dimensions for model amphiphilic system.

## 1.2 Model and Numerical Procedure

We model amphiphilic molecules as beads connected by springs and adopt a stochastic molecular dynamics(MD) simulation method to study the self-assembly. The MD method that we have implemented here is the same as the

one previously employed by one of us [7, 8] and very similar to the method adopted by Grest and co-workers earlier [9]. To simulate a constant temperature ensemble, the monomers are coupled to a heat bath and the equations of motion read as:

$$\ddot{\mathbf{r}}_i = -\nabla U_i - \Gamma \dot{\mathbf{r}}_i + \mathbf{W}_i(t), \quad (1.1)$$

where  $\Gamma$  is the monomer friction coefficient and  $\mathbf{W}_i(t)$  which describes the random force of the heat bath acting on each monomer is a Gaussian white noise with zero mean satisfying the fluctuation-dissipation relation:

$$\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = 6k_B T \Gamma \delta_{ij} \delta(t - t'). \quad (1.2)$$

The potential  $U_i$  consists of two parts  $U_{LJ}^{ij}$ , and  $U_{chain}$ . Here  $U_{LJ}^{ij}$  is a Lennard-Jones (LJ) potential acting between any two pair of monomers  $i$  and  $j$ :

$$U_{LJ}^{ij}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 - \left( \frac{\sigma_{ij}}{r_{ij}^c} \right)^{12} + \left( \frac{\sigma_{ij}}{r_{ij}^c} \right)^6 \right]; \quad r \leq r_{ij}^c, \quad (1.3)$$

where  $r_{ij}^c$  is the cutoff distance beyond which the LJ interaction is set to be zero,  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$  and  $\mathbf{r}_i, \mathbf{r}_j$  are the locations of the  $i$ th and  $j$ th monomers respectively. *Amphiphilicity* in this model is introduced by a repulsive cut-off distance for the head-head and head-tail ( $r_{hh}^c = 2^{1/6} \sigma_{hh}$ ,  $r_{ht}^c = 2^{1/6} \sigma_{ht}$ ), and an attractive cut-off for the tail-tail interaction ( $r_{tt}^c = 2.5 \sigma_{tt}$ ). The parameter  $\epsilon_{ij}$  is kept to unity for any pair of species. The choice of the LJ parameters are summarized in Table 1.1.  $U_{chain}$  is the Finite-Extendable Nonlinear Elas-

**Table 1.1.** Interaction parameters for the amphiphiles

Interaction	$\frac{r_{ij}^c}{\sigma_{ij}}$	$\sigma_{ij}$	$\epsilon_{ij}$
head-head	$2^{1/6}$	$\sigma_{tt}, 2\sigma_{tt}, 3\sigma_{tt}$	1.0
head-tail	$2^{1/6}$	$\frac{\sigma_{hh} + \sigma_{tt}}{2}$	1.0
tail-tail	2.5	1.0	1.0

tic (FENE) anharmonic spring potential acting between pairs of successive monomers along a chain:

$$U_{chain}(r_{ij}) = -0.5kR_{ij} \ln \left[ 1 - \left( \frac{r_{ij}}{R_{ij}} \right)^2 \right], \quad (1.4)$$

in which  $k$  and  $R_{ij}$  are the energy and the length parameter of the potential. We have chosen  $k = 30$  and  $R_{ij} = 1.5\sigma_{ij}$  which make chain crossing practically impossible [9]. We use the reduced units throughout this study; the unit of time is  $\sigma(m/\epsilon_{tt})^{1/2}$  and the unit of temperature is  $\epsilon_{tt}/k_B$  where  $k_B$  is the Boltzmann constant. The details of the numerical expediency in choosing a fast Gaussian random number generator and a link-cell for force and energy calculation can be found in reference [7, 8]

### 1.3 Results

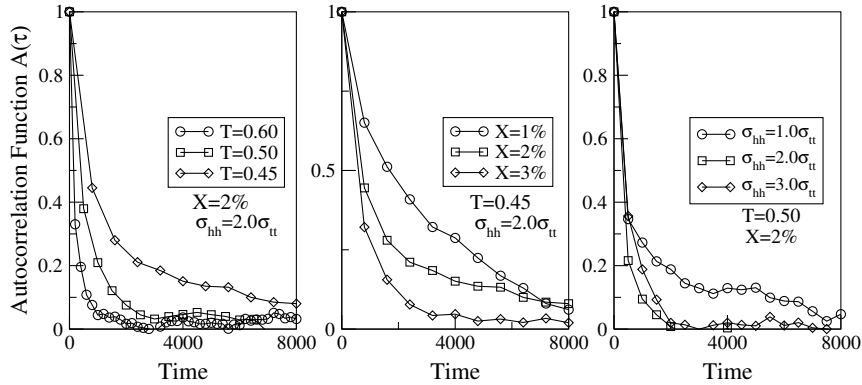
We here show the preliminary results of our two dimensional simulation. Most of the simulations are carried out in a square box of length  $100\sigma_{tt}$ . In order to study the finite size effects we have carried out simulation in a box of length  $200\sigma_{tt}$ . We consider chains consisting of one head and six tail monomers; the packing parameter is varied by choosing different head sizes,  $\sigma_{tt}$ ,  $2\sigma_{tt}$ , and  $3\sigma_{tt}$  respectively.

#### 1.3.1 Autocorrelation function $A(\tau)$

It is important to calculate the autocorrelation function  $A(t)$  [3, 4, 10] to determine how often physical quantities should be calculated for statistical averages. The quantity

$$A(\tau) = \frac{\langle N(t+\tau)N(t) \rangle - \langle N(t) \rangle^2}{\langle N^2(t) \rangle - \langle N(t) \rangle^2} \quad (1.5)$$

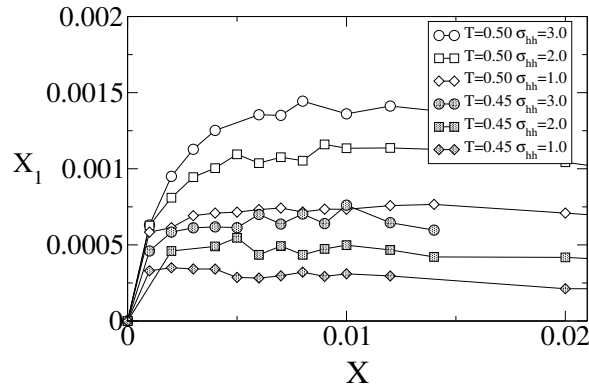
is a measure of the average life time  $\tau_c$  of a chain in a given cluster. Here  $N(t)$  is the size of the micelle where a tracer chain resides at time  $t$ . At low temperature  $\tau_c$  can be very long. Fig 1.1 shows  $A(t) \sim t$  for different  $T$ ,  $X$ , and  $\sigma_{hh}$ . We have used the correlation function to determine how often to collect data for statistical averaging purposes. Data is taken at MD time intervals bigger than  $\tau_c$ , where we define  $\tau_c$  to be the time when  $A(t)$  drops to 0.3.



**Fig. 1.1.** Behavior of  $A(\tau)$  as a function  $\tau$  for different temperature (left), amphiphilic concentration (middle), and head size (right).

### 1.3.2 Critical Micelle concentration(CMC)

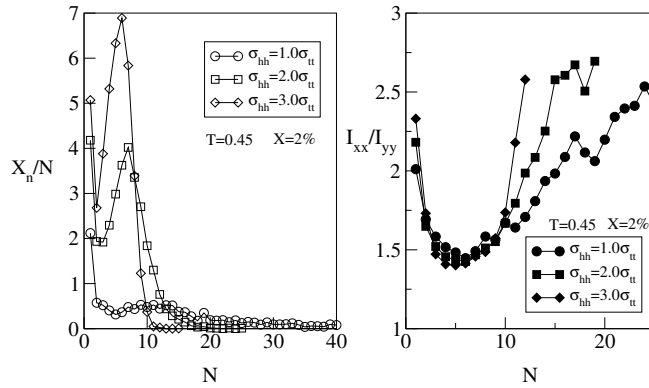
We denote  $X_n$  as the concentration of amphiphiles in an aggregate of size  $n$  so that the total concentration of amphiphiles  $X = \sum_n X_n$  and the concentration of clusters of size  $n$  is given by  $\frac{X_n}{n}$ . Typically  $X_1$  shows saturation around a certain value of  $X$ , known as the CMC, when a further increase in  $X$  results in formation of larger clusters, while  $X_1$  remains roughly the same. Fig. 1.2 shows the variation of  $X_1$  as a function  $X$  for different temperature and  $\sigma_{hh}$ . One sees that amphiphiles with larger head sizes exhibits saturation at a larger value of  $X_1$ . Fig. 1.2 also shows that the CMC increases with increasing temperature. The qualitative features are in accord studies of lattice models where a peak in the specific head has been used to characterize the CMC more accurately [11, 12].



**Fig. 1.2.** Variation of  $X_1$  as a function of  $X$  for different head group geometry and temperature.

### 1.3.3 Cluster shape and distribution

Fig. 1.3 shows the effect of the head group geometry on the cluster distribution  $\frac{X_n}{n}$  (left) and shape (right) for  $X=0.2$  and  $T=0.45$ . We have used the ratio of two principal moment of inertia  $R_{xy} = \frac{I_{xx}}{I_{yy}}$  to quantify the shape. For example, a value of  $R_{xy} = 1$  would imply the shape of the micelle to be spherical. We notice that increasing the head size has a marked impact on the distribution; the distribution becomes sharply peaked for a certain size, moreover occurrence of larger clusters become rarer. This phenomenon can be used to tailor formation of complex pattern mediated by amphiphilic self-assembly. Fig. 1.3 also shows (right) that an increase in effective head

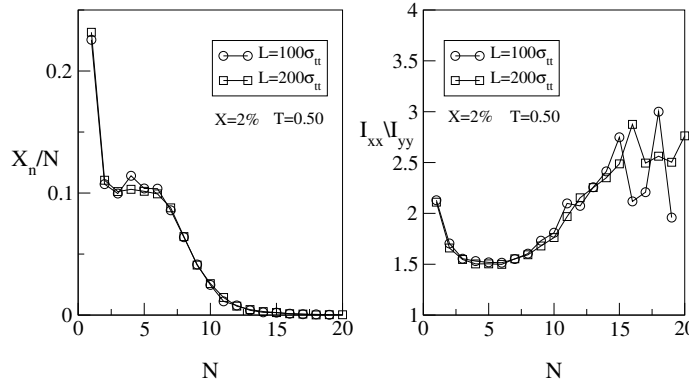


**Fig. 1.3.** Variation of cluster distribution  $\frac{X_n}{N}$  (left) and  $\frac{I_{xx}}{I_{yy}}$  (right) as a function of cluster size for different head group geometry.

size for a given concentration would produce more spherical micelles (a lower value of  $R_{xy}$  closer to unity) with a narrow cluster distribution.

### 1.3.4 The effect of the simulation box

Finally, we investigated the finite size effect of the simulation box on the cluster distribution. The largest cluster size is limited by the total number of chains and therefore it is expected that the occurrence of large clusters will be affected by the box size. Fig 1.4 shows that for cluster sizes up to 15, the size of the simulation box has hardly any effect on the distribution and shape.



**Fig. 1.4.** Finite size effect on cluster distribution (left) and shape (right). The simulations are carried out in a box of size  $100\sigma_{tt}$  with 200 chains (circles) and in a box of size  $200\sigma_{tt}$  with 800 chains (squares).

## 1.4 Conclusion

In summary, we have studied the role of the head group geometry in micellar self-assembly for a bead-spring model of flexible amphiphiles using Brownian dynamics simulation. Our studies indicate that the shape and the cluster distribution can be controlled by adjusting the head to tail ratio. This might be relevant in designing new materials using soft matter as the templating tool. A three dimensional simulation is in progress and will be reported in a separate publication.

## 1.5 Acknowledgment

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