# Coarse-Grained Model Simulation of Surfactant Solution in Couette Flow: Postprint

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## Abstract

This study primarily employs coarse-grained molecular dynamics methods to investigate micelle formation, velocity distribution, and rheological behavior of surfactant aqueous solutions at various concentrations in Couette flow. The results demonstrate that for surfactant solutions at identical concentrations, the time required for micelles to achieve complete dynamic equilibrium decreases with increasing shear rate. Furthermore, as surfactant molecular concentration increases, the dynamic equilibrium time also decreases, indicating progressively faster micelle formation. Regarding the relationship between shear rate and solution shear viscosity, maintaining constant surfactant molecular concentration leads to a gradual decrease in shear viscosity with increasing shear rate, exhibiting characteristic shear-thinning behavior.

## Full Text

## Preamble

### A Coarse-Grain Molecular Dynamics Simulation for Surfactant Aqueous Solution in Couette Flow

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## Abstract

This paper investigates micelle formation, velocity distribution, and rheological behavior in surfactant aqueous solutions under Couette flow using coarse-grained molecular dynamics simulations. The results demonstrate that for surfactant solutions at a given concentration, the dynamic equilibration time for micelle formation decreases with increasing shear rate. Additionally, when the shear rate is held constant, higher surfactant molecular concentrations lead to faster micelle formation and shorter equilibration times. Regarding the relationship between shear rate and solution viscosity, the simulations reveal shear-thinning behavior: at constant surfactant concentration, the shear viscosity gradually decreases as the shear rate increases.

**Keywords:** surfactant aqueous solution; coarse-grained molecular dynamics simulations; Couette flow; shear viscosity

## Introduction

As global energy demands continue to grow, the development of new energy sources and the efficient utilization of energy have become increasingly critical. Drag reduction represents an effective method for decreasing flow resistance in pipelines, thereby achieving energy savings and consumption reduction. Consequently, research on drag-reducing surfactants has emerged as a prominent area of investigation [1-4]. The microscopic structure of surfactants in solution is the key factor influencing their rheological properties, making it essential to develop a deep understanding of micelle formation and rheological characteristics in surfactant solutions.

Current research on surfactant solutions primarily focuses on experimental measurements, including macroscopic rheological measurements to infer microscopic structures or direct observation of surfactant microstructures via electron microscopy [5-7]. In terms of microscopic structure simulation, most molecular dynamics studies have addressed micelle formation, breakage, and rheology in ordinary polymers. However, simulations specifically targeting amphiphilic surfactants remain relatively scarce, with the work of N.A. Volkov and N. Arai being particularly representative. Volkov [8] conducted molecular dynamics simulations of micelle formation in sodium dodecyl sulfate (SDS) solutions, finding that NaCl addition favors the formation of larger micelles and providing detailed descriptions of micelle shape characteristics. Arai [9] employed the DPD method to investigate the rheological properties of surfactant solutions in nanoscale parallel channels under shear flow, demonstrating that hydrophobic-hydrophilic chemical modification of nanoscale channel surfaces can induce a transition from shear-thinning to shear-thickening behavior in surfactant solutions. Sambasivam [10] pioneered the use of coarse-grained molecular dynamics (CGMD) simulations to study the deformation and breakage of rod-like micelles in CTAC+NaSal solutions under shear flow, employing energy analysis methods to investigate monomer micelle length and orientation distribution in shear fields, concluding that the average CTAC micelle length is 5.4 nm over a total simulation time of 3 s. In quantitative studies of micelle formation time and size, Wataru Shinoda [11] simulated the micellization process of several surfactants, including polyoxyethylene, at air-water and oil-water interfaces, providing quantitative calculations of micelle size and formation time. Regarding rheological behavior at high shear rates, J. Castillo-Tejas [12] performed coarse-grained non-equilibrium molecular dynamics simulations of Couette and Poiseuille flows for cetyltrimethylammonium chloride (CTAC) surfactant solutions, introducing a coarse-grained model assuming one hydrophilic head group and four hydrophobic tail groups per CTAC monomer, and establishing quantitative relationships between shear velocity and shear stress as well as shear velocity and shear viscosity at various surfactant concentrations. Extending this work, E.O. Castrejón-González [13] conducted coarse-grained molecular dynamics simulations of water-surfactant-oil mixtures in Couette flow at high shear rates, observing transitions from Newtonian behavior to shear-thinning, then to shear-thickening, and finally back to Newtonian behavior as shear rate increased.

In summary, previous studies of micelle formation time have typically employed detailed molecular models, which suffer from two major drawbacks: poor generality and enormous computational cost. This paper addresses these limitations by employing the coarse-grained molecular dynamics method, which simplifies the consideration of molecular polarity and intermolecular forces between different groups, enabling efficient determination of micelle formation times. Compared with earlier research, this study additionally considers the effects of solution concentration and temperature variables, providing qualitative analysis of surfactant rheological properties that yields conclusions consistent with current macroscopic experimental results and enhancing our understanding of surfactant solution rheology.

## 1 Numerical Methods

The simulation domain for the surfactant solution measures 30 × 20 × 15 in the x, y, and z directions, respectively (with wall regions occupying y-coordinates from -2.5 to 22.5). Each coarse-grained surfactant molecule consists of one hydrophilic head group (diameter $\sigma$) and four hydrophobic tail groups (diameter $\sigma$), with coarse-grained water molecules also having diameter $\sigma$. Interactions between surfactant head groups, surfactant head groups and water molecules, surfactant tail groups, and water molecules are all modeled using the Lennard-Jones (LJ 12-6) potential. The LJ 9-6 model is applied to represent repulsive forces between surfactant head groups and other surfactant tail groups, as well as between surfactant tail groups and coarse-grained water molecules, as illustrated in [Figure 1: see original paper].

**[Figure 1: see original paper] Surfactant and water CG molecule interaction**

Bonded interactions between adjacent surfactant head and tail groups, as well as between adjacent tail groups, are described by the Harmonic potential model. The surfactant solution employs the NVT ensemble, while solid walls utilize the NVE ensemble.

**[Figure 2: see original paper] The surfactant aqueous solution in Couette flow**

### 1.1 L-J Model

The L-J (12-6) potential is expressed as:

$$U_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], \quad r \leq r_c$$

with a cutoff radius of $r_c = 2.5\sigma$.

Repulsive potential function:

The LJ 9-6 model can be used as an approximation for repulsive interactions.

### 1.2 Harmonic Model

The Harmonic potential function is expressed as:

$$U_{harmonic} = K(r - \sigma_{ij})^2$$

where $\sigma_{ij}$ is calculated through the Lorentz-Berthelot mixing rule:

$$\sigma_{ij} = 0.5(\sigma_i + \sigma_j)$$

### 1.3 NVT and NVE Ensembles

The NVT canonical ensemble (using Nose-Hoover thermostat) is governed by:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i$$

$$\frac{d\mathbf{v}_i}{dt} = \frac{\mathbf{F}_i}{m_i} - \xi \mathbf{v}_i$$

$$\frac{d\xi}{dt} = \frac{1}{Q} \left( \sum_i \frac{m_i v_i^2}{2} - \frac{L k_B T}{2} \right)$$

where $\mathbf{r}_i$, $\mathbf{v}_i$, and $\mathbf{F}_i$ represent the position, velocity, and force of particle $i$; $T$ is the target temperature; $L$ is the number of degrees of freedom; $\xi$ is the thermodynamic friction coefficient; and $Q$ is the thermostat mass defined as $Q = \tau^2 L k_B T$, with $\tau$ being the system relaxation time.

The NVE ensemble is applied primarily at the walls, where the number of atoms, energy, and volume remain constant.

### 1.4 Additional Simulation Details

Initial configurations of coarse-grained molecules were generated using Material Studio, with the resulting coordinate information serving as initial conditions for the simulations. In these non-equilibrium molecular dynamics (NEMD) simulations, the dimensionless time step for all cases was 0.001, with each simulation run for 1.5 million steps (approximately 5.5 ns).

** Dimensionless of parameters**

## 3.1 Micelle Formation Time Analysis

Through visualization of the micelle formation process (using the open-source software OVITO, Open Visualization Tool), the time required for coarse-grained surfactant molecules to form micelles was determined for six Couette flow shear rates: 0.03, 0.06, 0.1, 0.15, 0.20, and 0.25. The typical micelle formation process generally follows four stages: initial state → small micelle cluster state → large micelle cluster state → complete dynamic equilibrium. This evolution is illustrated in [Figure 3: see original paper] for the case of surfactant molecular concentration 0.20 and shear rate 0.1.

**[Figure 3: see original paper] The dynamic equilibrium state of micelles**

**(a) Initial state (0 ns) (b) Small micelle cluster state (0.37 ns) (c) Large micelle cluster state (0.73 ns) (d) Complete dynamic equilibrium (3.28 ns)**

The relationship between shear rate and micelle formation time for surfactant concentrations of 0.05, 0.15, and 0.20 is presented in [Figure 4: see original paper].

**[Figure 4: see original paper] Shear velocity and micelle formation time**

The results indicate that for surfactant concentrations of 0.05, 0.15, and 0.20, the time required to reach complete dynamic equilibrium decreases as the upper plate shear rate in Couette flow increases (shear rates: 0.03, 0.06, 0.1, 0.15, 0.20, 0.25). Furthermore, at a constant shear rate, higher micelle concentrations lead to shorter dynamic equilibration times, meaning faster micelle formation.

## 3.2 Surfactant Concentration and Velocity Distribution

To investigate the influence of surfactant-formed micelles on the Couette flow field, velocity distributions were examined at a shear rate of 0.1 for micelle concentrations of 0, 0.05, 0.15, and 0.20. The relationship between micelle concentration and velocity distribution is shown in [Figure 5: see original paper].

**[Figure 5: see original paper] The relationship between micelle concentration and the spatial mean velocity distribution**

The velocity distribution was obtained by dividing the y-direction (velocity gradient direction) into 100 equally spaced rectangular slabs from y = 0 to y = 20, each with volume 30 × 0.2 × 15. Velocity averaging was performed over time for all coarse-grained particles (including surfactant molecules and water molecules) within each slab, calculating the mean velocity in each slab when the system reached dynamic equilibrium.

As shown in [Figure 5: see original paper], the velocity distribution for pure water solvent (surfactant concentration = 0, black line) exhibits a nearly linear increase with a slope of 1. Upon addition of coarse-grained surfactant molecules, the average velocity in the region y = 0–11 exceeds that of pure water, while velocities in the region y = 11-20 are lower than pure water. The simulation data does not support a simple correlation between lower surfactant concentration and smaller deviation from pure water velocity distribution, as the concentration 0.15 case shows greater deviation than the 0.20 case in the y = 11–20 region. Therefore, we conclude that no definitive relationship exists between surfactant concentration magnitude and the degree of modification to the Couette flow velocity profile.

## 3.3 Relationship Between Shear Rate and Shear Viscosity

Shear viscosity is calculated from shear stress and shear rate:

$$\eta = \frac{P_{xy}}{\dot{\gamma}}$$

where $\eta$ is shear viscosity, $P_{xy}$ is shear stress, and $\dot{\gamma}$ is shear rate. All quantities in this study are dimensionless.

The relationships between shear rate and shear stress, and between shear rate and shear viscosity, are presented in [Figure 6: see original paper] and [Figure 7: see original paper] for dimensionless temperature T = 1.35 and dimensionless shear rates of 0.01, 0.025, 0.05, 0.1, 0.15, 0.2, and 0.25.

**[Figure 6: see original paper] The relationship between shear rate and shear stress**

**[Figure 7: see original paper] The relationship between shear rate and shear viscosity**

[Figure 6: see original paper] reveals that shear stress increases with shear rate, and higher coarse-grained surfactant molecular concentrations yield greater shear stress. [Figure 7: see original paper] shows that except for the somewhat scattered data at shear rates of 0.01 and 0.025 (which do not exhibit shear-thinning characteristics), shear viscosity decreases with increasing shear rate, demonstrating clear shear-thinning behavior. At very low shear rates ($< 0.03$), thermal motion of coarse-grained molecules causes excessive interference, preventing fully ordered Couette flow across layers. Therefore, only the effective shear rate region of 0.05–0.25 was analyzed. Additionally, a positive correlation exists between coarse-grained surfactant molecular concentration and shear viscosity: higher surfactant concentrations produce greater shear viscosity.

## Conclusion

This study conducted non-equilibrium molecular dynamics simulations of Couette flow in surfactant solutions at various concentrations, establishing relationships between shear rate and coarse-grained surfactant micelle formation time, surfactant concentration and solution velocity distribution, and shear rate versus shear stress and viscosity. The findings indicate that both surfactant concentration and shear rate are negatively correlated with micelle formation time, while no definitive relationship exists between surfactant concentration and velocity distribution modification. At constant concentration, increasing shear rate leads to higher shear stress but lower shear viscosity, exhibiting characteristic shear-thinning behavior. Through systematic analysis of these key parameters in surfactant solutions, this work provides deeper insights into micelle formation mechanisms and the rheological properties of surfactant solutions.

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*Note: Figure translations are in progress. See original paper for figures.*