Multi-scale approach for the rheological characteristics of emulsions using molecular dynamics and lattice Boltzmann method

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An emulsion system was simulated under simple shear rates to analyze its rheological characteristics using a hierarchical multi-scale approach. The molecular dynamics (MD) simulation was used to describe the interface of droplets in an emulsion. The equations derived from the MD simulation relative to interfacial tension, temperature, and surfactant concentration were applied as input parameters within lattice Boltzmann method (LBM) calculations. In the LBM simulation, we calculated the relative viscosity of an emulsion under a simple shear rate along with changes in temperature, shear rate, and surfactant concentration. The equations from the MD simulation showed that the interfacial tension of the droplets tended to decrease with an increase in temperature and surfactant concentration. The relative viscosity from the LBM simulation decreased with an increase in temperature. The shear thinning phenomena explaining the inverse proportion between shear rate and viscosity were observed. An increase in the surfactant concentration caused an increase in the relative viscosity for a decane-in-water emulsion, because the increased deformation caused by the decreased interfacial tension significantly influenced the wall shear stress. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

The rheological characteristics of emulsions have a broad range of industrial applications in areas such as the food, medical, cosmetic, and pharmaceutical industries. An emulsion is a mixture of two or more liquids that are immiscible. Within an emulsion, the dispersed phase exists as droplets in the continuous phase. Surfactants, which are made of hydrophilic and hydrophobic segments and thus adhere to the droplet interface, are used to obtain the stability of an emulsion and to control both the size and deformability of the droplets. Surfactants on a droplet interface reduce the interfacial tension and provide the interface with rheological properties such as responses to compression and shear deformations.^{1,2} Therefore, interfacial phenomena caused by the existence of surfactants on the interface are a popular research topic. Moreover, the movement of surfactant molecules within the droplet interface needs to be described more exactly through a multi-scale approach in order to understand the rheological behaviors of emulsions.

At the micro-scale, the effects of interfacial properties on emulsions have been of high interest over a broad range of research areas.^{3–10} The effects of surface-active agents on droplet deformation in a linear extensional flow at low Reynolds numbers were analyzed. The analytical and numerical results indicated that at low capillary numbers, the presence of surfactant caused larger deformation than would occur for a droplet with a constant interfacial tension.⁷ Surfactant accumulation at the droplet pole in an extensional flow drove the interfacial tension

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to near zero, which imparted a droplet shape with highly pointed tips. Subsequently, small, surfactant-rich droplets were emitted from the termini of the tips.⁸ The surfactant had a greater effect on drop geometry for smaller viscosity ratios and the deformation increased as the transport of surfactant became more dominated by convection. The surfactant on the interface caused the droplets to align more in the direction of flow and, for both clean and surfactant-covered droplets, this alignment increased with the viscosity ratio.⁹ The film drainage of two immiscible droplets exhibited additional flow into or out of the film and this additional flow could either increase or decrease the rate of film drainage between the droplets, depending on the interfacial tension of droplets with the surrounding fluid and the interfacial tension of the two immiscible droplets.¹⁰

Many researchers have used molecular dynamics (MD) to investigate interfacial properties at the atomic-scale. MD simulation can provide clear insight into the structural characteristics of the interface. A number of types of interfaces have been studied by MD simulation including the liquid-vapor interface,^{11–14} liquid-liquid interface,^{15–18} and liquid-surfactant-liquid interfaces.^{19–21} MD results show that the structure of the interface is strongly affected by molecular interaction. The van der Waals parameter, ϵ , significantly affects the thickness of water and oil interface.¹⁶ Hydrogen bonding among molecules at the interface decides the preferred orientation of molecules which affects interfacial roughness.¹⁸ Two different surfactants showed different behaviors at the interface due to the hydrogen bonding between surfactants and orientation of the head group with respect to the tails. This difference in interfacial structure also affected the interfacial tension of the system.²⁰ MD simulation has also been used to describe rheological phenomena due to the importance of molecular interaction at the interface.²² However, MD simulation could only mimic nano-scale systems. Hence, a multi-scale approach is essential to describe the rheological problems at the micro-scale.

In this paper, we studied the rheological characteristics of an emulsion by a hierarchical multi-scale approach with MD and the lattice Boltzmann method (LBM). From the MD simulation, we obtained the diffusivity of surfactant on the interface and the equations which explain

FIG. 1. Schematic diagram summarizing the objectives of the study.

FIG. 2. Initial state of the simulation system in molecular dynamics.

the relationship among interfacial tension, temperature, and surfactant concentration. These equations were then applied to an LBM simulation employed to describe the interfacial tension with respect to local changes in surfactant concentration. In the LBM simulation, the relative viscosity was calculated with several variables, such as temperature, shear rate, and interfacial tension to observe the rheological properties of the emulsion. Using this hierarchical multi-scale approach, we could study the effects of the interfacial properties on the emulsion rheology. Overall contents and objectives of this paper are shown in Fig. 1.

II. SIMULATION MODELS

A. Molecular dynamics model

In Figs. 2 and 3, the following MD simulation was performed to mimic the decane (oil)/decyl- α -glucoside (surfactant)/water interface. The two interfaces were symmetric and perpendicular to the z axis which minimized the drift of the overall system. A periodic box contained 217 molecules of decane, 1514 molecules of water, and surfactant molecules with respect to the surfactant concentrations listed in Table I. A CHARMM (Chemistry at Harvard Macromolecular Mechanics) force field²³ was used to describe inter and intra molecular interactions including covalent bonds, angle, dihedral, improper, and van der Waals bonds. For all cases, the initial strain was removed by the Polak-Ribiere version of the conjugate gradient algorithm.²⁴ Then, the pressure of the z -axis was controlled to 1 atmospheric pressure by changing the z -length of the box with a Nose-Hoover barostat.^{25,26} Total simulation time was 550 ps . After 100 ps of the pressure controlling step, 450 ps of the series of additional

FIG. 3. Decane, water, and surfactant molecules used in the simulations.

simulations were performed with the canonical ensemble to obtain equilibrium properties. The temperature of each case was controlled by a Nose-Hoover thermostat.^{25,26} All cases were performed by the parallel computing system with 32 cores of 5.0 GHz Power6 processor. Real computing time was 65 h for each case. A large-scale atomic/molecular massively parallel simulator (LAMMPS) and Visual Molecular Dynamics (VMD) were used for calculations and post processing.

1. Diffusivity

The definition of mean square displacement used to calculate the diffusivity of the surfactant molecules is shown in Eq. (1),

$$D = \lim_{t \rightarrow \infty} \frac{\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle}{t} = \lim_{t \rightarrow \infty} \frac{\langle dx^2 + dy^2 + dz^2 \rangle}{t}, \quad (1)$$

where $\mathbf{r}(t)$ represents the position vector of an atom at time t , and the brackets represent an ensemble average. dx , dy , and dz represent the magnitude of the displacement of atoms in each direction.

In the calculations, the displacement of atoms in the x , y , and z axis was considered due to the confinement of all surfactant molecules at decane/water interface during simulation. This implies that the surfactant concentration at the interface was constant during the simulation. Equilibrium diffusivity used in the LBM simulation was calculated by averaging the diffusivity of the two surfactant layers.

2. Interfacial tension

To calculate surface tension, the two interfaces were assumed to be perpendicular to the z -axis. We used the following Kirkwood-Buff equation:²⁷

TABLE I. Calculated diffusivity (m^2/s) with different concentrations at each simulation temperature. The bold numbers in the first column indicate the molarity (molar concentration) defined as the amount of the surfactant in mol divided by the volume of the simulation domain.

Concentration (M)	280 K	325 K	370 K
0.85×10^{-6}	3.49×10^{-9}	3.67×10^{-9}	1.05×10^{-8}
1.70×10^{-6}	8.78×10^{-10}	1.21×10^{-9}	1.13×10^{-8}
2.54×10^{-6}	1.07×10^{-9}	2.06×10^{-9}	5.59×10^{-9}
3.39×10^{-6}	2.33×10^{-9}	1.47×10^{-9}	1.37×10^{-8}

$$\gamma = -\frac{1}{2} \left(\frac{p_x + p_y}{2} - p_z \right) L_z, \quad (2)$$

where $p_\alpha = P_{\alpha\alpha}$ represents diagonal component of the viral pressure tensor averaged along each direction and L_z represents the box length in the z -direction.

B. Thermal lattice Boltzmann model with surfactants

1. 3-D thermal lattice Boltzmann model

The LBM has been developed to analyze the rheology of the emulsion system shown in Fig. 4. The Boltzmann kinetic equation is defined as

$$\frac{\partial f}{\partial t} + c \cdot \nabla f = \Omega(f), \quad (3)$$

where f is the density distribution function, c is the lattice velocity, and $\Omega(f)$ is the collision term. In LBM, the collision term needs to be simplified by BGK (Bhatnagar-Gross-Krook) approximation due to its complexity. The simplified equation is then discretized in nineteen specific directions for D3Q19 model shown in Fig. 5 as follows:

$$f_i(x + c_i \Delta t, t + \Delta t) - f_i(x, t) = \frac{\Delta t}{\tau} [f_i^{eq}(x, t) - f_i(x, t)], \quad (4)$$

where f_{eq} is the equilibrium distribution function which can be obtained by the following formula:

$$f_{eq} = \rho \omega_i \left[1 + \frac{3}{c^2} c_i \cdot \mathbf{u} + \frac{9}{2c^4} (c_i \cdot \mathbf{u})^2 - \frac{3}{2c^2} \mathbf{u} \cdot \mathbf{u} \right], \quad (5)$$

where ω_i is the weighting factor that determines the relative probability of a particle movement in the i th direction, and ρ and $\mathbf{u}$ are the macroscopic density and velocity which are calculated as follows:

$$\rho = \sum_{i=0}^{Q-1} f_i = \sum_{i=0}^{Q-1} f_i^{eq}, \quad (6)$$

FIG. 4. Schematic diagram for numerical domain of an emulsion system under simple shear flow.

FIG. 5. Lattice links for the D3Q19 lattice Boltzmann method used in this work.

$$\rho \mathbf{u} = \sum_{i=0}^{Q-1} c_i f_i = \sum_{i=0}^{Q-1} c_i f_i^{eq}. \quad (7)$$

The relaxation time τ of Eq. (4) is related with the kinematic viscosity as follows:

$$\nu = (\tau - 0.5)c_s^2 \Delta t, \quad (8)$$

where c_s is the lattice speed of sound and the lattice time step Δt is taken as unity. For isothermal flow, the relaxation time is fixed throughout the entire simulation time. However, if the viscosity is changed by temperature, the relaxation time should be changed locally, accordingly. In this paper, τ changes according to the local temperature change

$$\frac{\tau(T) - 0.5}{\tau_0 - 0.5} = \frac{\mu(T)}{\mu_0} = \left(\frac{T}{T_0} \right)^{-1.0868}. \quad (9)$$

Gunstensen and Rothman²⁸ simulated a two-immiscible fluid emulsion using LBM. The total distribution function is expressed by the summation of the two red-and-blue fluid distribution functions as follows:

$$f_i = r_i + b_i. \quad (10)$$

In order to make a phase field, the interfacial density between two fluids is defined

$$\rho^N = \frac{r_i - b_i}{r_i + b_i}. \quad (11)$$

Lishchuk *et al.*²⁹ employed the following macroscopic force ($F(x)$) to apply the interfacial tension force

$$F(x) = -\frac{1}{2} \alpha k \nabla \rho^N, \quad (12)$$

where α is the interfacial tension and k is the droplet curvature. The relationship between the source term in the LBM equation and the macroscopic force $F(x)$ is calculated by the method of Guo *et al.*,³⁰

$$\phi_i(x) = \omega_i \left(1 - \frac{1}{2\tau}\right) [3(e_i - u^*) + 9(e_i u^*)e_j] F(x), \quad (13)$$

$$u^* = \frac{1}{\rho} \left[\sum_{i=1}^{18} f_i e_i + \frac{1}{2} F(x) \right], \quad (14)$$

where u^* is the corrected velocity used in the calculation of the equilibrium function. The local interfacial tension affects the surface tension force, which subsequently influences the corrected velocity. After that, the fluid is separated in two parts, red and blue fluids, using the following relationship:

$$\bar{f}_i^R(x, t + \delta_t) = \frac{\rho^R}{\rho^R + \rho^B} \bar{f}_i(x, t + \delta_t) + \beta \frac{\rho^R \rho^B}{\rho^R + \rho^B} \omega_i \cos(\theta_f - \theta_i) |c_i|, \quad (15)$$

$$\bar{f}_i^B(x, t + \delta_t) = \bar{f}_i(x, t + \delta_t) - \bar{f}_i^R(x, t + \delta_t), \quad (16)$$

where $\bar{f}_i^R$ and $\bar{f}_i^B$ are the post-collision and post-segregation distribution functions of the red and blue fluids, and θ_f and θ_i are the polar angle of the color field, and the angle of the velocity link, β is the segregation parameter, and $\bar{f}_i$ is the post collision distribution function. After segregation, these two fluids are propagated separately and macroscopic properties are obtained through each distribution functions.

Many models have been developed to apply the thermal phenomena in LBM.^{31,32} Basically, the thermal phenomena of an emulsion system are governed by the following energy equation:

$$\frac{DT}{Dt} + (\nabla \cdot \mathbf{u})T - D\nabla^2 T + \Phi = 0, \quad (17)$$

where T is the local temperature, D is the thermal diffusivity and Φ is the dissipation term which is expressed as follows:

$$\Phi = \mu(T) \left\{ 2 \left[\left(\frac{\partial u_x}{\partial x} \right)^2 + \left(\frac{\partial u_y}{\partial y} \right)^2 + \left(\frac{\partial u_z}{\partial z} \right)^2 \right] + \left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right)^2 + \left(\frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \right)^2 + \left(\frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y} \right)^2 \right\} - \frac{2}{3} \mu(T) (\nabla \cdot \mathbf{u})^2, \quad (18)$$

where $\mu(T)$ is the temperature-dependent viscosity. The hopscotch explicit and unconditionally stable finite difference methods were used here to solve the energy equation. This scheme uses two consecutive sweeps through the domain, the first sweep T_{ij}^{n+1} is calculated at each grid, for which $i+j+n$ is even, by a simple explicit scheme. The second sweep T_{ij}^{n+1} is calculated at each grid point, for which $i+j+n$ is odd, by a simple implicit scheme.

2. The surfactant model

The surfactant transport on the droplet interface is governed by the following time-dependent convective-diffusion equation:³³

$$\partial_t \Gamma + \nabla_s \cdot (u_s \Gamma) + k \Gamma u_n = D_s \nabla^2 \Gamma, \quad (19)$$

where Γ is the surfactant concentration, u_s , u_n are the surface velocity and the normal velocity, k is the surface curvature, and D_s is the surfactant diffusivity, both of which were calculated from the MD simulation. In Eq. (19), $\partial_t \Gamma$ signifies the change in the local surfactant concentration as time flows, $\nabla_s \cdot (u_s \Gamma)$ is the convection term related to interfacial velocity, and $k \Gamma u_n$

shows how surface curvature affects the surfactant concentration. The right term, $D_s \nabla^2 \Gamma$, is the diffusive contribution. As in solving the energy equation, the hopscotch explicit finite difference method is used here to solve the convective-diffusion equation, and then coupled with Gunstensen LBM. More information on the solution of the convective-diffusion equation can be found in the previous work.³⁴

III. RESULTS

A. Results from the MD simulation

To analyze the effects of temperature and surfactant concentration on the diffusivity and the interfacial tension, we used three temperatures (280 K, 325 K, and 370 K) and five surfactant concentrations (0 M , $0.85 \times 10^{-6} \text{ M}$, $1.70 \times 10^{-6} \text{ M}$, $2.54 \times 10^{-6} \text{ M}$, $3.39 \times 10^{-6} \text{ M}$). The range of temperature was determined to be in between the melting point (273 K) and the boiling point (373 K) of water. A maximum surfactant concentration ($3.39 \times 10^{-6} \text{ M}$) was set in order not to exceed the critical micelle concentration (CMC). In all cases, most surfactant molecules in the simulation domain were located at the interface.

In Fig. 6, the rectangular box indicated by the dashed line represents the interface. Most surfactant molecules are located at the interface. The interfacial region can be divided into two parts based on the amphiphilic nature of the surfactant. The dotted and dashed lines at the interface show the amphiphilic nature. The head and tail groups of the surfactant molecules showed strong attractive interaction with water and decane molecules, respectively.

1. Diffusivity

In Fig. 7, a mean squared displacement (MSD), as defined in Eq. (1), is plotted. We used the linear fitting curve to clearly analyze the diffusion behavior. The slope of the MSD in the lateral direction is higher than that in the vertical direction. This result implied that surfactant molecules tended to move in the lateral direction more freely compared to the vertical direction.

FIG. 6. The final state of the simulation system at 280 K, a 2-D projection on the XZ plane. The interfacial region is divided into two parts based on the surfactant structure, head group, water interaction region and tail group, decane interaction region (see the definition of head and tail group in Fig. 3).

FIG. 7. Mean square displacement ($\text{\AA}^2$) vs. time (ps).

In Table I, the results show that the diffusivity has no dependence on surfactant concentration. The size of the empty space between surfactant molecules and the other molecules at the interface was the most important factor in determining diffusivity. However, our systems were relaxed by changing z -length to adjust the pressure of the domain to atmospheric pressure. This pressure controlling step provided water or decane molecules with enough energy to fill empty space between surfactant molecules. As a result, the size of the empty space did not change remarkably at different surfactant concentrations and the diffusivity was independent of the surfactant concentration. The results in Table I also indicate that an increase in temperature causes a significant rise in diffusivity. This is because the high temperature accelerates the Brownian motion of molecules.

2. Density profile

Density distributions of each component were calculated along with the vertical direction (z direction). Our data were averaged over the last 150 ps . Figure 8 shows the density profile with respect to a temperature of 280 K. Three different lines represent water (black squares), surfactant (red circles), and decane (blue triangles), respectively. Water and decane have bulk regions that showed a constant density. The densities of water and decane in bulk regions were almost 1 g/cm^3 and 0.7 g/cm^3 , respectively, which correspond to values in the literature.³⁴

In Fig. 8, the two interfacial regions were located between water and decane bulk regions. In these regions the densities of water and decane change drastically, and the density of the surfactant molecules had the maximum value. The overlapping regions of the density profiles indicate that components were mixed at the interface. As described in Sec. III A, the head and tail group have strong attractive interactions with water and decane molecules, respectively. Figure 8 also shows that the overlapping regions of decane and surfactant were wider than those of the water and surfactant because the chain shaped tail group is longer than the ring-shaped head group.

3. Interfacial tension

Calculated interfacial tensions are shown in Table II. In the previous experiment, the interfacial tension of water and decane is 0.050 N/m at 323.15 K .³⁵ A. R. van Buuren *et al.*¹⁶ used molecular dynamics to calculate the interfacial tension of the water and decane system. Their result was $0.037\text{--}0.083 \text{ N/m}$. In our study, the interfacial tension was 0.051 N/m at 325 K which

FIG. 8. Mass density profile and definitions of the bulk water, interface, and oil layer at 280 K.

is close to the experimental result. The interfacial tension had a decreasing trend with respect to an increase in temperature and surfactant concentration.

There have been many attempts to explain the interfacial tension-and-surfactant concentration relations.³⁶ The Langmuir equation, which is the most common model for surfactant behavior, describes the decrease of interfacial tension due to the existence of surfactants. However, the Langmuir equation has some assumptions which make an accurate analysis difficult:³⁷ (1) the interface is a perfectly flat plane with no corrugations, which means the interface is homogeneous, (2) each area on the interface can hold at most one molecule (monolayer coverage only), and (3) there are no interactions between surfactant molecules and the interfacial fluid. In order to overcome these limitations, based on our results, we derived an equation which explains the relationship between interfacial tension and surfactant concentration on the interface as the temperature changes.

Figure 9 shows the relationship among the interfacial tension, temperature and the surfactant concentration. The x - and y -axes represent the dimensionless surfactant concentration (Γ/Γ_∞) and the dimensionless interfacial tension normalized by the tension of clean droplet at 280 K. In Fig. 9(a), the equations explaining the relationship among interfacial tension, surfactant concentration, and temperature were obtained by fitting the quadratic function. The interfacial tension at low surfactant concentration was larger than that at zero surfactant concentration.

TABLE II. Calculated interfacial tension (N/m) with different concentrations at each simulation temperature.

Concentration (10^{-6} M)	280 K	325 K	370 K
0	0.061	0.051	0.050
0.47	0.056	0.057	0.053
0.85	0.056	0.054	0.056
1.31	0.055	0.058	0.048
1.70	0.054	0.057	0.048
2.17	0.054	0.047	0.045
2.54	0.047	0.047	0.045
3.01	0.045	0.033	0.031
3.39	0.038	0.041	0.035
3.76	0.037	0.030	0.021

FIG. 9. (a) Interfacial tension normalized by clean droplet interfacial tension is plotted for different dimensionless surfactant concentrations. The comparison the present model with Langmuir equation at (b) 280 K, (c) 325 K, and (d) 370 K.

We observed that there were surfactant molecules located with the direction parallel to the interface. These molecules increased the interfacial energy and interfacial tension. Hence, the interfacial tension of low surfactant concentration was larger than the case of zero surfactant concentration. Figures 9(b)–9(d) indicate that at low temperature, our results are very well matched with the Langmuir equation. However, as temperature increases, the differences become remarkable. This is because surfactant molecules become more active, consequently, the interaction between surfactant molecules becomes significant as temperature increases. The equations shown in Fig. 9(a) were used in the LBM simulation to calculate the interfacial tension depending on the surfactant concentration and temperature.

B. Emulsion viscosity calculated by LBM simulation

Various cases were simulated to study the relative viscosity of emulsions at different temperatures, shear rates, and surfactant concentration in LBM, and conditions of each are tabulated in Table III.

1. Temperature dependent viscosity

The relative viscosity ($\mu_{rel} = \mu_{eff}/\mu_{fluid}$), the ratio of the effective viscosity to fluid viscosity, was calculated as the following formula:

$$\mu_{rel} = \frac{H}{|V|W} \sum \frac{\partial u}{\partial z}, \quad (20)$$

where H and W are the height and width of domain and V is the velocity at the wall.

As shown in Fig. 10, the change in the relative viscosity of the emulsions with time was plotted at different temperatures. The relative viscosity was observed to decrease with an increase of time. This phenomenon can be explained by the concept of de-aggregation of emulsion droplets. The change of the viscosity can be divided into two phases: phase 1 for de-aggregation and phase 2 for steady state. In phase 1, the droplets in the emulsion de-aggregate

TABLE III. Temperature, concentration, and shear rate of each simulation were performed to study the relative viscosity of emulsions.

Cases	Temperature (K)	Surfactant concentration (M)	Shear rate (/s)
1	280	1.70×10^{-6}	3
2	280	1.70×10^{-6}	12
3	280	1.70×10^{-6}	48
4	280	2.54×10^{-6}	3
5	280	2.54×10^{-6}	12
6	280	2.54×10^{-6}	48
7	280	3.39×10^{-6}	3
8	280	3.39×10^{-6}	12
9	280	3.39×10^{-6}	48
10	325	1.70×10^{-6}	3
11	325	1.70×10^{-6}	12
12	325	1.70×10^{-6}	48
13	325	2.54×10^{-6}	3
14	325	2.54×10^{-6}	12
15	325	2.54×10^{-6}	48
16	325	3.39×10^{-6}	3
17	325	3.39×10^{-6}	12
18	325	3.39×10^{-6}	48
19	370	1.70×10^{-6}	3
20	370	1.70×10^{-6}	12
21	370	1.70×10^{-6}	48
22	370	2.54×10^{-6}	3
23	370	2.54×10^{-6}	12
24	370	2.54×10^{-6}	48
25	370	3.39×10^{-6}	3
26	370	3.39×10^{-6}	12
27	370	3.39×10^{-6}	48

under shear flow and thus the viscosity decreases gradually. In phase 2, the de-aggregation and deformation of the droplets reach a steady state and thus the viscosity does not undergo any further changes.

Figure 10 also shows that the relative viscosity decreases with an increase in temperature in the steady state zone, which is expected in typical emulsion rheology. The time to reach the steady state decreases as temperature increases, which means that de-aggregation is more effective at higher temperatures.

2. Shear rate dependent viscosity

For a non-Newtonian fluid, viscosity under shear flow depends on shear rates. Emulsions in particular show shear thinning phenomena which describe the inverse relationship between viscosity and shear rates. Many researchers have developed models to describe the change in emulsion viscosity with different shear rates.³⁸ One such model, the Cross model, can be defined as follows:³⁹

$$\mu_{rel} = \mu_{\infty rel} + \frac{\mu_{0rel} - \mu_{\infty rel}}{1 + (C\dot{\gamma})^q}, \quad (21)$$

where $\mu_{\infty rel}$ and μ_{0rel} are the relative viscosity for infinite and zero shear rate, C is the time constant and q is the shear thinning index which shows a good prediction when $q=0.8$. The

FIG. 10. Time evolution of relative viscosity is shown. The relative viscosity gradually decreases in the de-aggregation step and remains steady after the droplets in the emulsion reach steady state.

Cross model estimation at all three temperatures is plotted with our results which were the average values at steady state and may be found in Fig. 11. The graph shows that the relative viscosity decreases with an increase in shear rate, which is a general trend of a fluid with non-Newtonian characteristics. The graph also indicates that the shear thinning phenomenon becomes weaker as temperature increases, which means the relative viscosity changes with more sensitivity with different shear rates in low temperature conditions.

Figure 12 shows the averaged relative viscosity in the steady state zone as dependent on temperature and the shear rate. It was observed that shear rate imparted only a slight effect on the relative viscosity as temperature increased. The deformation of the droplets became bigger when the temperature increased, which meant that the droplets adapted well to shear flow at high temperature.

FIG. 11. Relative viscosity is plotted for different shear rates at different temperature and is compared with the Cross model.

FIG. 12. Relative viscosity is plotted for different temperatures and shear rates. At all three temperatures, a shear thinning phenomenon was observed and the degree of shear thinning index became weaker as the temperature increased.

3. Surfactant concentration-dependent viscosity

Under different initial surfactant concentrations, the relative viscosity showed interesting results. Figure 13 indicated that the relative viscosity increased with an increase in the surfactant concentration. From the MD simulation results, it was observed that at relatively high surfactant concentrations, the interfacial tension is inversely proportional to the surfactant concentration. Therefore, higher surfactant concentration leads to lower interfacial tension and a larger deformation of droplets under the same shear rate. If the droplets are more viscous than the continuous phase (oil-in-water emulsion), the larger interfacial area of the droplets caused

FIG. 13. Relative viscosity is plotted for different surfactant concentrations and temperature for oil-in-water emulsions (solid lines). Because the interfacial area increases as the interfacial tension decreases, the relative viscosity increases with an increase in the surfactant concentration. On the other hand, the relative viscosity of water-in-oil emulsions (dashed line) only decreases slightly with an increase in the surfactant concentration.

by large deformation at low surface tension, may result in the bigger relative viscosity because of the increase of the viscous area. As a result, the relative viscosity of the emulsion increased as the surfactant concentration increased. On the other hand, an emulsion comprised of the water droplets in oil showed a decrease in relative viscosity with an increase in the surfactant concentration because the water droplets are less viscous than the bulk fluid, as shown in Fig. 13 (dashed line).

Figure 13 also shows that the slope of the relative viscosity as the surfactant concentration changes is bigger at low temperature. At high temperature, the effect of the surfactant concentration on the relative viscosity is weak compared with the results at low temperature.

IV. CONCLUSIONS

The rheological characteristics of emulsions in terms of the interfacial properties of droplets were analyzed with a hierarchical multi-scale approach using both MD simulation and LBM simulation. From the MD simulation, the equations that explain the relationship among interfacial tension, temperature, and surfactant concentration were observed. The equations indicated that the interfacial tension had a tendency to decrease with increasing temperature and surfactant concentration. In the LBM simulation, when applying the equations to calculate the interfacial tension with regard to local change in surfactant concentration, the relative viscosity decreased with an increase in temperature and shear rate. The shear thinning phenomena found in our results were compared with those in the Cross model describing the characteristics of a non-Newtonian fluid. The relative viscosity tended to increase with an increase in surfactant concentration for the oil-in-water emulsion because the increased deformation of the more viscous droplet as the surfactant concentration increased affected the wall shear stress significantly. On the other hand, the relative viscosity decreased with an increase in surfactant concentration for water-in-oil because the droplet fluid was less viscous than the bulk fluid. Using this hierarchical multi-scale approach, the effects of interfacial properties on the rheological properties of emulsions can be studied.

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