



Rheological modelling of dispersions of casein micelles considered as microgel particles

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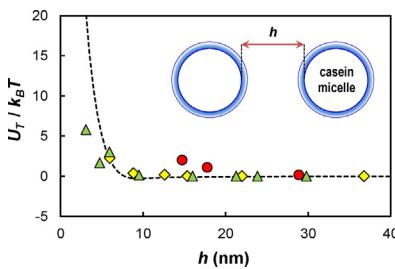
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HIGHLIGHTS

- Viscosity model for casein micelles (CM).
- Indications that CM at concentrated regime behave as soft spheres.
- Pair interaction energy between CM directly obtained from rheometric data.
- Promising methodology for studying CM dispersions as colloidal systems.
- New perspectives for studying the stability of dairy products.

GRAPHICAL ABSTRACT

Total interaction potential energy U_I normalized with the thermal energy $k_B T$ as function of surface-to-surface distance between casein micelles.



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ABSTRACT

Rheological behavior of dispersions of casein micelles (CM) was predicted through a viscosity model in which CM were considered as microgel particles. A simple structure for CM composed of a spherical core with a brush of κ -casein was considered. An explicit relationship between viscosity and shear stress allows obtaining key parameters such as the packing fractions corresponding to the shear stress limits and the critical shear stress closely related to the total interaction potential between two CM. The analysis of the model parameters fitted from experimental viscosity curves indicates that CM at concentrated regime behave as soft spheres. In addition, the model provides the pair interaction energy between CM directly from rheometric data. The values obtained agree with a DLVO-like theory previously proposed for CM. Indeed, using independent experimental data and parameters, it was possible to cross check both models. The results obtained are very promising for studying CM dispersions as colloidal systems and the stability of dairy products under different physicochemical environments.

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1. Introduction

Native casein micelles (CM) can be considered as colloidal particles formed via self-assembly of four casein proteins (α_{s1} -, α_{s2} -, β - and κ -caseins) and calcium phosphate. These spherical particles

are dispersed in a continuous phase composed of water, salt, lactose and serum proteins [1]. This fascinating microstructural organization regulates the calcium phosphate concentration of its environment by a calcium-sequestering mechanism. Thus, CM make milk supersaturated with calcium phosphate and transport the mineral calcium phosphate through the mammary gland [2].

Casein micelles in milk constitute a very stable colloidal system. This phenomenon generates great interest from the scientific and technological point of view. The knowledge of the structure and physicochemical interactions that generate the stability of CM in milk is the key for the development of new dairy products, for

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the improvement of unit operations of the dairy industry and for the application of these concepts to the synthetic polymer science. The structure of the CM has been studied for many years and it is still debated [2–5]. Various models of casein micelles have been proposed [6] such as the sub-micelle model [7], the dual-binding model [3] and the nanocluster model [8].

In spite of the internal structure of CM is still controversial, it is established that most κ -casein is present on the surface of the micelles and it forms a layer or brush extending the C-terminus portion into milk serum. This organization generates the so-called steric stabilization [1,3,5]. Tuinier and de Kruif [9] calculated the pair potential between CM, containing the essential contributions of brush repulsion, electrostatic repulsion, and van der Waals attraction. The authors demonstrated that the steric interaction is the most important stabilizing factor.

Skim milk at native pH behaves as Newtonian fluid. However, in skim milk concentrates, the distance between the CM decreases. Under these conditions, the fluid starts to behave like a shear thinning non-Newtonian fluid because CM interact more frequently with each other [10]. In fact, any macroscopic property, *inter alia*, viscosity is a consequence of the position, size, form and movement of the microscopic particles. Several authors showed that dispersions of CM can be closely described by the so-called hard sphere model [11–13]. However, at higher packing fractions the deformability of CM plays an important role in the viscous behavior. Bouchoux et al. [14] and Dahbi et al. [15] showed CM dispersion behavior at concentrated regime through rheological experiments. Clearly, Dahbi et al. [15] observed that the viscosity deviates from hard sphere behavior when CM dispersions are concentrated (volume-fraction range of 0.55–0.61). Therefore, in that concentration regime CM dispersions must be considered as deformable colloids like microgel particles [15,16].

Berli and Quemada [17] studied the behavior of suspensions of soft spheres or microgels (particles composed of a central zone of cross-linked polymer and an external layer of polymer chains). The authors predicted the rheological behavior of concentrated microgel suspensions based on the flow-induced variation of the effective volumen fraction and the interaction energy between particles. As a paramount result, it is worth mentioning that it is possible to calculate the microscopic potential energy between particles from rheometric data of steady shear flow. In this context, CM dispersions (hairy CM assumed as microgel particles) could be studied through the model proposed by Berli and Quemada [17].

The knowledge of colloidal stability of CM dispersions at different concentrations is fundamental for practical purposes to control physical product stability. Therefore, the aim of the present work is to predict the rheological behavior of CM dispersions considered as microgel particles and to provide a relationship between CM interaction potential and macroscopic viscosity.

2. Theory

2.1. Casein micelles considered as microgel particles

A simple structure of CM as colloidal particles composed of a core of radius a with a brush of κ -casein of length H , was considered. Thus, the particle hydrodynamic radius is $a_H = a + H$ (Fig. 1). The mean surface-to-surface distance between cores h (Fig. 1) is related to the core volume fraction ϕ_p by [17]

$$h = 2a \left(\frac{\phi_m}{\phi_p} \right)^{1/3} - 2a \quad (1)$$

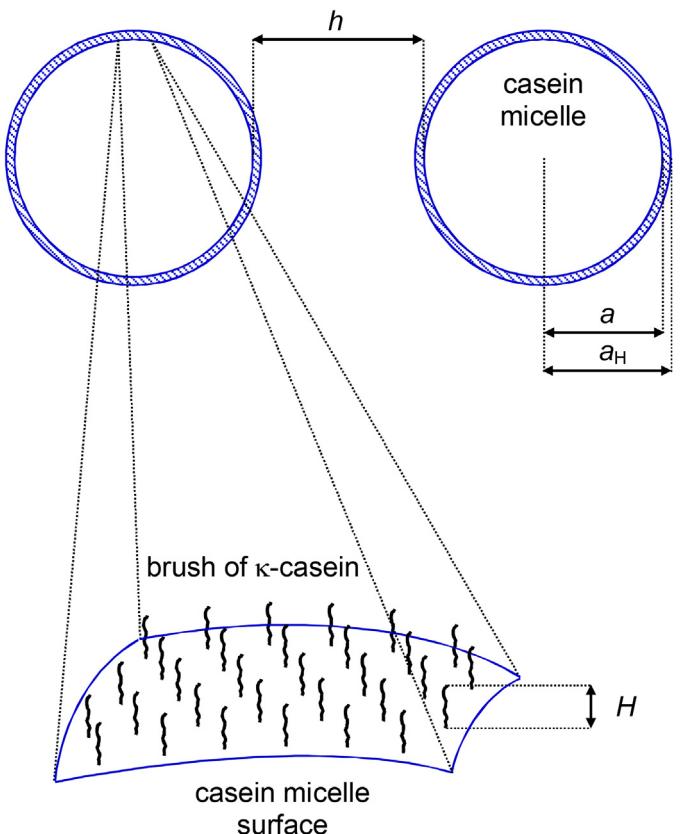


Fig. 1. Schematic representation of casein micelles considered as microgel particles.

where ϕ_m is the maximum packing fraction. In addition, CM volume fraction ϕ is [17]

$$\phi = \phi_p \left(\frac{a_H}{a} \right)^3 \quad (2)$$

Above a critical particle concentration, the polymer layers overlap and ϕ_p^* can be calculated as $\phi_p^* = \phi_{RCP}(a/a_H)^3$, where $\phi_{RCP} = 0.637$ is the random close packing volume fraction.

2.2. Interaction potential energy between casein micelles

The interaction potential (U) between CM was calculated as proposed by Tuinier and de Kruif [9]. The types of interaction can be summarized as follows, electrostatic interaction:

$$\frac{U_{er}(h)}{k_B T} = \frac{2\pi\epsilon_0\sigma_r\psi_0^2 a}{k_B T} \ln[1 + \exp(-\kappa h)] \quad (3)$$

van der Waals interaction:

$$\frac{U_{vdW}(h)}{k_B T} = -\frac{A}{6k_B T} \left\{ \frac{2a^2}{(h+2a)^2 - 4a^2} + \frac{2a^2}{(h+2a)^2} + \ln \left[\frac{(h+2a)^2 - 4a^2}{(h+2a)^2} \right] \right\} \quad (4)$$

Steric interaction:

$$\frac{U_{brush}(h)}{k_B T} = \begin{cases} \infty & \text{for } h \leq 0 \\ \frac{16\pi a H^2 \sigma^{3/2}}{35} & \left\{ \begin{array}{l} 28 \left[\left(\frac{2H}{h} \right)^{1/4} - 1 \right] + \\ \frac{20}{11} \left[1 - \left(\frac{h}{2H} \right)^{11/4} \right] + \\ 12 \left(\frac{h}{2H} - 1 \right) \end{array} \right\} & \text{for } 0 < h < 2H \\ 0 & \text{for } h \geq 2H \end{cases} \quad (5)$$

Table 1
Data used for calculations.

Parameter	Symbol	Value [units]	Reference
Casein micelle radius	a_H	71.3 [nm]	de Kruif et al. [6]
Surface potential	ψ_0	18.9 [mV]	Estimated at pH = 6.6 from de Kruif and Tuinier [22]
Relative permittivity	ϵ_r	80	de Kruif and Tuinier [22]
Debye length	κ^{-1}	1 [nm]	Tuinier and de Kruif [9]
Hamaker constant	A	$1 k_B T [\text{J}]$	Tuinier and de Kruif [9], Ettelaie et al. [23]
Number of segments of the brush	N	15	Tuinier and de Kruif [9]
Segment length	b	0.6 [nm]	Tuinier and de Kruif [9]
Excluded volume per segment	v	0	Tuinier and de Kruif [9]
Salt volume fraction	ϕ_s	0.01	Tuinier and de Kruif [9]
Mean value of the dissociation constant	K_a	$10^{-4.9}$	Tuinier and de Kruif [9]
Brush height	H	4.9 [nm]	Calculated from Eq. (6)
Grafting density	θ	0.0021	Calculated (based on data shown in Table 2)
Grafting density/surface area occupied by a brush	σ	0.02 [nm ⁻²]	Calculated (based on data shown in Table 2)

Table 2
Data used for the estimation of θ and σ .

Parameter	Value [units]	Reference
Volume fraction of casein micelles in milk	0.12	Walstra and Jenness [24]
Concentration mass of κ -casein in milk	3.3 [kg m ⁻³]	Walstra and Jenness [24]
Molecular weight of κ -casein	19 [kg kmol ⁻¹]	Walstra and Jenness [24]
Length of an amino acid group in κ -casein brush	0.32 [nm]	Tuinier and de Kruif [9]

Table 3
Parameters obtained from the viscosity model for microgel particles applied to CM dispersions.

CM concentration (% w/v)	ϕ	ϕ_0	ϕ_∞	τ_c (Pa)
Bouchoux et al. [14]				
16.8	0.739	0.755	0.869	36.32
15.8	0.695	0.730	0.835	15.19
14.6	0.642	0.699	0.797	13.09
13.8	0.607	0.716	0.822	11.16
12.1	0.532	0.706	0.801	11.16
9.2	0.405	0.670	0.698	11.16
Dahbi et al. [15]				
17.89	0.787	0.789	0.970	76.20
17.25	0.759	0.770	0.916	30.01
16.81	0.740	0.753	0.910	45.19
15.57	0.685	0.736	0.880	12.53
13.62	0.599	0.689	0.848	11.24
12.27	0.540	0.701	0.856	11.24
11.67	0.513	0.714	0.875	11.24
10.44	0.459	0.692	0.906	11.24
Nöbel et al. [20]				
14.9	0.615	0.631	0.760	33.73
14.0	0.578	0.610	0.754	23.42
11.3	0.467	0.543	0.699	12.82

where k_B is the Boltzmann constant ($1.3807 \times 10^{-23} \text{ J K}^{-1}$) and T is the absolute temperature. In Eq. (3), ψ_0 is the surface potential, ϵ_0 is the permittivity in vacuum ($8.85 \times 10^{-12} \text{ F m}^{-1}$), ϵ_r is the relative permittivity and κ^{-1} is the Debye length. In Eq. (4), A is the Hamaker constant. In Eq. (5), σ is the grafting density divided by the surface area occupied by a brush. As discussed by de Kruif and Zhulina [18], κ -casein molecules can be described as charged brushes in the “salted brush” regime. In these conditions, the polyelectrolyte-type brush is quasi-neutral and the strong-stretching approximation can be used. Then, the brush height is [9],

$$H = Nb \left(\frac{8v^{\text{eff}}\theta}{\pi^2} \right)^{1/3} \quad (6)$$

where N is the number of segments of the brush and each segment has a length b . $v^{\text{eff}} = v + \alpha^2/\phi_s$ is the effective excluded volume, where v is the excluded volume per segment, and ϕ_s is the salt volume fraction. In addition, $\alpha = K_a/(K_a + [\text{H}^+])$ is the degree of dissociation where $[\text{H}^+]$ is the proton concentration ($\equiv 10^{-\text{pH}}$) and K_a

is the mean value of the dissociation constant of the carboxylic groups along the chain. θ is the grafting density, the fraction of sites occupied by the brushes at the surface of the CM.

Then, the total interaction potential between two CM is,

$$\frac{U_T(h)}{k_B T} = \frac{U_{er}(h)}{k_B T} + \frac{U_{vdW}(h)}{k_B T} + \frac{U_{brush}(h)}{k_B T} \quad (7)$$

2.3. Viscosity model for microgel particles

Berli and Quemada [17] thoroughly developed a rheological model that allows obtaining an explicit relationship between viscosity and shear stress for non-Newtonian behavior of concentrated microgel suspensions.

$$\eta_r(\tau) = \eta_{r,\infty} \left[\frac{1 + \tau/\tau_c}{(\eta_{r,\infty}/\eta_{r,0})^{1/2} + \tau/\tau_c} \right]^2 \quad (8)$$

In Eq. (8), $\eta_r = \eta/\eta_F$, where η is the dispersion viscosity and η_F is the dispersing fluid viscosity. The critical shear stress, τ_c , characterizes the shear-thinning behavior of the suspension. At high concentrations or when forces between particles are strong, particle interaction becomes important in addition to Brownian motion. Therefore, the critical shear stress is defined as,

$$\tau_c = \frac{k_B T + U_T(h)}{a_H^3} \quad (9)$$

Also, in Eq. (8), $\eta_{r,0}$ and $\eta_{r,\infty}$ are the relative limiting viscosity values corresponding to the shear stress limits $\tau \rightarrow 0$ and $\tau \rightarrow \infty$, respectively.

$$\eta_{r,0} = \left(1 - \frac{\phi}{\phi_0} \right)^{-2} \quad (10)$$

$$\eta_{r,\infty} = \left(1 - \frac{\phi}{\phi_\infty} \right)^{-2} \quad (11)$$

where ϕ_0 and ϕ_∞ are the effective maximum packing fractions corresponding to the shear stress limits $\tau \rightarrow 0$ and $\tau \rightarrow \infty$, respectively. For hard sphere dispersions, the maximum packing fractions were reported $\phi_0 = 0.63$ and $\phi_\infty = 0.71$ [19]. However, as CM contain a brush layer, the maximum packing fractions can show an additional shear stress dependence.

3. Materials and methods

3.1. Data for calculations

Data of the parameters used for the estimation of interaction potential between CM and for calculations of the viscosity model for microgel particles to CM suspensions are listed in Tables 1 and 2.

3.2. Experimental data

Experimental viscosity curves obtained from the literature [14,15,20] were used to obtain the parameters of the viscosity model. CM dispersions were prepared by dissolving native phosphocaseinate powder in a ultrafiltrated milk permeate and mixing during 15 h at 35 °C [14], by adding the milk powder to de-ionized water at 60 °C while stirring at moderate speed [15], and by weighting native casein micelle powder into ultrafiltrated milk permeate and gently stirring at 35 °C for at least 1 h [20]. These preparation conditions reported by the authors ensure that CM were maintained in their native state. The CM volume fraction ϕ was obtained by multiplying the CM concentration in g cm⁻³ by a factor q that accounts for the voluminosity of the CM. The value of q was 4.4 cm³ g⁻¹ in the case of data obtained from Bouchoux et al. [14] and Dahbi et al. [15], while q was 4.134 cm³ g⁻¹ in the case of the data obtained from Nöbel et al. [20]. Viscosity measurements were performed at 20 °C [14,20] or 22 °C [15].

3.3. Calculation procedure

Replacing Eqs. (10) and (11) in Eq. (8), the following equation is obtained:

$$1 - \eta_r^{-1/2} = \frac{\phi((1/\phi_0) + (\tau/\tau_c\phi_\infty))}{1 + (\tau/\tau_c)} \quad (12)$$

Experimental data of η_r versus τ can be used in Eq. (12) to obtain the packing fractions ϕ_0 and ϕ_∞ and the critical shear stress τ_c , as fitted parameters. It is important to take into account that in our case, values of τ_c should tend to $k_B T/a_H^3$ (scaling for colloidal suspensions of non-interacting particles) for mean distance h greater than $2H$. Therefore, in order to obtain values with physical meaning, this condition can be considered as a constraint during the fitted process. The ratio $U_T(h)/k_B T$ can be calculated from values of τ_c using Eq. (9). Values of h can be obtained from different concentrations ϕ_p using Eq. (1) and a maximum packing fraction for CM of $\phi_m = 0.68$ [20]. Note that polydispersity leads to higher values of ϕ_m in comparison with ideal monodisperse hard-spheres. Finally, ratios $U_T(h)/k_B T$ as function of h are obtained for each set of experimental data.

4. Results and discussion

Fig. 2 shows typical curves of viscosity for CM dispersions as function of shear stress. Symbols are experimental values measured by Bouchoux et al. [14], Dahbi et al. [15] and Nöbel et al. [20]. As mentioned by the authors, it is clear that the rheological behavior of suspensions is highly dependent on the concentration of CM. Full lines in Fig. 2 represent the values obtained through the viscosity model for microgel particles (Eq. (8)). The fitted values of ϕ_0 , ϕ_∞ , and τ_c are shown in Table 3. It can be observed that τ_c increases as the volume fraction of CM increases, indicating that as distance between CM decreases, repulsive forces among particles become important.

Fig. 3 shows the ratios ϕ/ϕ_0 and ϕ/ϕ_∞ as function of the core volume fraction ϕ_p . For $\tau \rightarrow 0$, the ratio ϕ/ϕ_0 grows almost linearly as ϕ_p increases and almost reaches the limit value of 1 when $\phi_p \approx 0.5$ –0.6. This behavior agrees with the packing fraction of CM

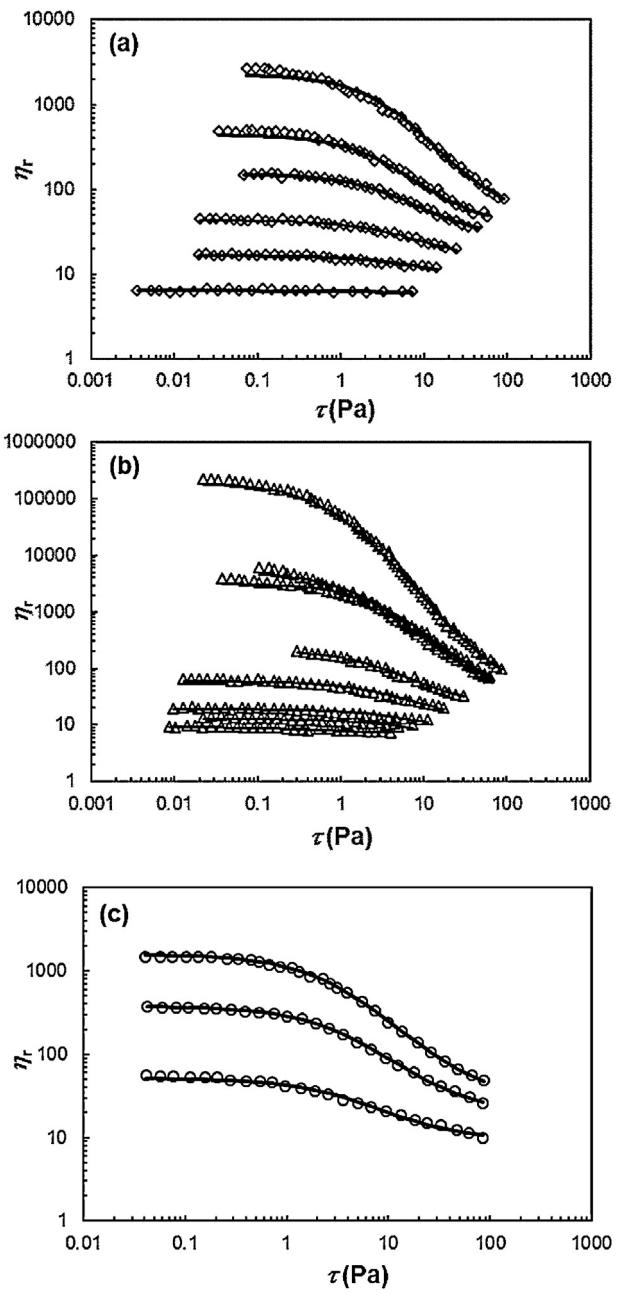


Fig. 2. Relative viscosity as function of shear stress for dispersions of CM. Symbols are experimental data and lines are the predictions from the viscosity model for microgel particles. (a) Symbols correspond from bottom to top to CM concentrations of 5.6, 9.2, 12.1, 13.8, 14.6, 15.8, 16.8% (w/v); $\eta_F = 1.2 \times 10^{-3}$ Pa s [14]. (b) Symbols correspond from bottom to top to CM concentrations of 6.84, 10.44, 11.67, 12.27, 13.62, 15.57, 16.81, 17.25, 17.89% (w/v) [15]; $\eta_F = 1.08 \times 10^{-3}$ Pa s [20]. (c) Symbols correspond from bottom to top to CM concentrations of 11.3, 14.0, 14.9% (w/v); $\eta_F = 1.14 \times 10^{-3}$ Pa s [20].

at the critical particle concentration, $\phi_p^* \approx 0.51$. It is important to emphasize that the data analyzed in this work correspond to the regime $\phi < \phi_0$ (Table 3), i.e. the shear thinning behavior without yield stress is observed [17]. For $\tau \rightarrow \infty$, the ratio ϕ/ϕ_∞ as function of ϕ_p shows a lower slope and it does not reach the limit value of 1. This behavior may be explained taking into account CM behave as soft spheres and start to deform and align along the flow direction at high shear rates. In addition, the effective radius of CM may decrease as a consequence of hydrodynamic forces on the κ-casein layer [17]. These concepts were previously suggested by Bouchoux et al. [14]. The authors concluded that at concentrations

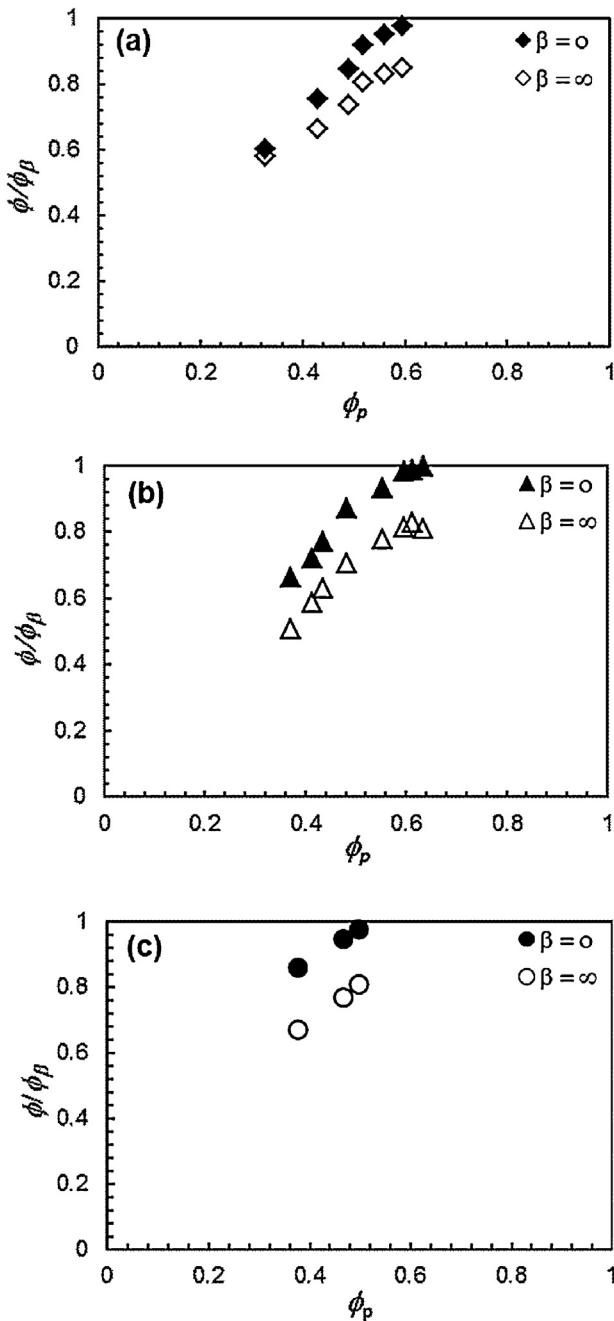


Fig. 3. Ratios ϕ/ϕ_0 and ϕ/ϕ_∞ as a function of ϕ_p obtained from the viscosity model applied to the experimental data of: (a) Bouchoux et al. [14], (b) Dahbi et al. [15], and (c) Nöbel et al. [20].

below or near the liquid-solid transition and at low shear rates, CM dispersions behave qualitatively and quantitatively as polydisperse hard-sphere fluid. At higher shear rates, a deviation from the hard-sphere fluid behavior can be observed probably caused by deformation of CM in the flow.

Fig. 4 shows the relative viscosities $\eta_{r,0}$ and $\eta_{r,\infty}$ as function of ϕ_p . For all experimental data, it can be observed that the low shear limiting viscosity grows and diverges at $\phi_p \approx 0.5\text{--}0.6$, when particles touch each other. This is a characteristic behavior of hard sphere particles in the limit $\tau \rightarrow 0$ [14,17]. However, high shear limiting viscosity increases almost linearly with concentration, indicating that when $\tau \rightarrow \infty$, CM behave as soft spheres as explained above.

Fig. 5 shows the pair interaction energy $U_T(h)/k_B T$ obtained from the viscosity model (symbols) as function of the mean distance h .

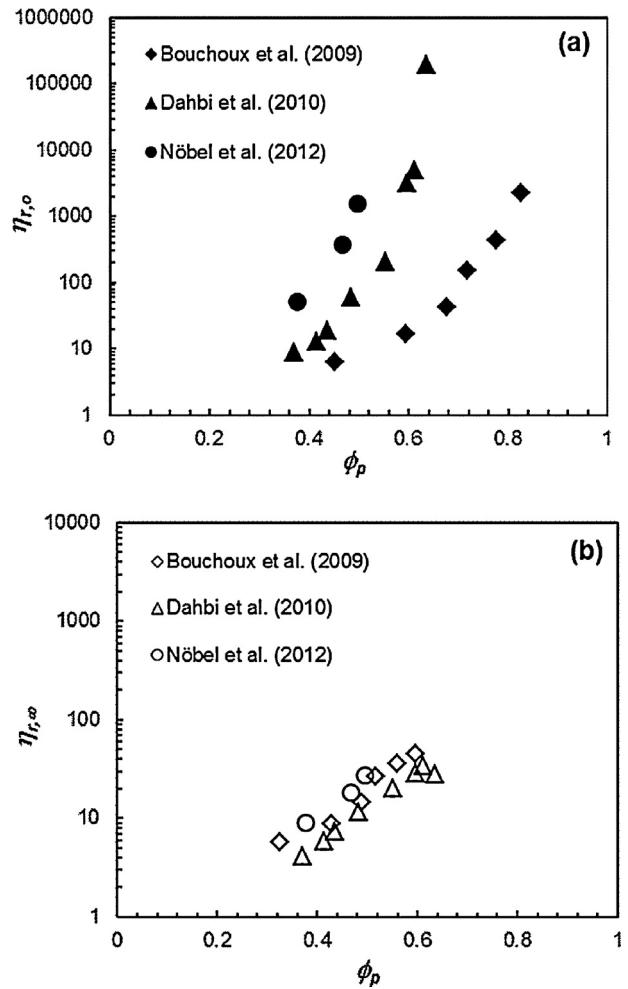


Fig. 4. Low and high shear limit of relative viscosity as a function of ϕ_p : (a) $\eta_{r,0}$ and (b) $\eta_{r,\infty}$.

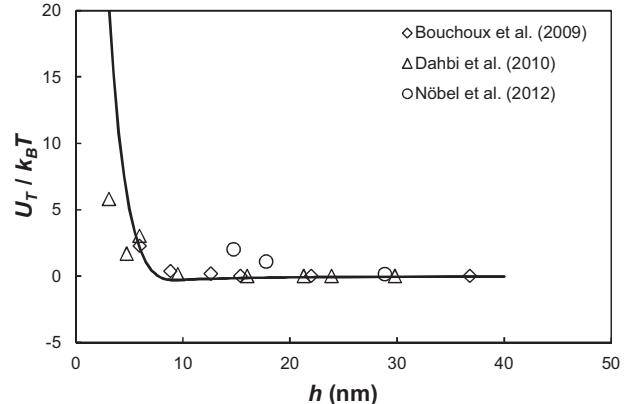


Fig. 5. Total interaction potential energy U_T normalized with the thermal energy $k_B T$ as function of surface-to-surface distance h for CM dispersions considered as microgel particles. The full line is the total interaction potential between CM due to brush and electrostatic repulsions, and van der Waals attraction. The symbols are the values obtained from the viscosity model.

The full line in Fig. 5 represents Eq. (7). It is observed that viscosity model applied to CM dispersions predicts adequately the potential interaction of CM. It is worth mentioning that the models used admit several improvements. For instance, CM basically are soft charged particles covered by a soft layer of charged polymers. The extension of the chains from the surface into the liquid

normally moves the position of the shear plane outward into the fluid. The electrical charges associated with the chains also affect the electrokinetic surface potential and the typical decaying length of the interaction [21]. However, it is important to highlight that the viscosity model appropriately describes the flow behavior of CM dispersions at different concentrations and that a quite simple DLVO-like theory allowed obtaining satisfactorily the pair potential between CM.

5. Conclusions

The parameters obtained from the viscosity model for CM dispersions applied to sets of experimental data from the literature indicate that CM, at high concentrations, behave as soft spheres that deform and align along the flow direction at high shear rates. It was hypothesized that the effective radius of CM decrease as a consequence of hydrodynamic forces on the κ -casein layer. As a confirmatory result, the pair interaction energy between CM directly obtained from rheometric data agreed satisfactorily with the values obtained with a DLVO-like theory previously proposed for CM. Indeed, using independent experimental data and parameters, it was possible to cross check both models. The results obtained are very promising for studying CM dispersions as colloidal systems and the stability of dairy products under different physicochemical environments.

Acknowledgments

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