



Connection between dynamic rheometry and pair interactions of casein micelles in concentrated skim milk

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ABSTRACT

The objective of this work was to relate dynamic rheological data to the pair interaction potential between casein micelles (CM) in concentrated systems. The elastic moduli at high frequencies (G'_{∞}) were obtained by fitting experimental data from the literature for CM dispersions at different concentrations using a Maxwell model. G'_{∞} values were also obtained using the Buscall model and the pair interaction potential (U) obtained with DLVO-type theoretical predictions proposed for CM and for sterically stabilized colloidal particles. It was observed that moduli G'_{∞} obtained from experimental data are in agreement with theoretical predictions. Therefore, this methodology allows connecting the dynamic rheometric data with pair interaction potentials of CM in concentrated skim milk dispersions and it may help to infer about the stability of milk concentrates.

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1. Introduction

Milk can be characterized as a dilute colloidal dispersion of casein micelles (CM) and fat globules. CM are dispersed in a continuous phase essentially composed by water and dissolved species such as salt, lactose, and whey proteins (Walstra, Wouters, & Geurts, 2006). CM consist of four different casein molecules (α_{s1} -, α_{s2} -, β - and κ -casein), which organize themselves into the micelle structure according to their hydrophilic/hydrophobic character. Although the internal structure of CM is still controversial, there is consensus in the literature that most of κ -casein molecules are arranged on the micelle surface, exhibiting the C-terminal protein fraction to the serum and thus, forming a polymeric brush that confers the well-known steric stabilization (Dagleish & Corredig, 2012; Dagleish, 2011; Horne, 2006, 2009).

In skim milk, CM are responsible for the macroscopic and functional properties of derived products (Liu, Dunstan, & Martin, 2012). Therefore, further research is required to better understand the colloidal behavior of CM, mainly in concentrated regimes (Bouchoux et al., 2009; Dahbi, Alexander, Trappe, Dhont, & Schurtenberger, 2010; Dagleish & Corredig, 2012; Qu, Bouchoux, & Gésan-Guiziou, 2015). The concentration of skim milk is an

important unit operation in several processes of the dairy industry. In particular, the production of skimmed milk powder requires a preliminary step in which total solids are concentrated up to 40–50%. As a consequence, it is relevant to investigate the effects of concentration on physicochemical and functional properties of milk products.

Dynamic rheometry is an essential tool to study the microstructure of colloidal suspensions as well as to control the quality of the derived products. Applying small amplitude oscillatory shear, the microstructure is slightly disturbed; hence the measured shear modulus can be related to both the interparticle potential energy and the structure. In particular, the high-frequency limit of the elastic modulus (G'_{∞}) has been theoretically described in terms of the pair interaction potential (U) for modeling colloidal systems (Berli & Quemada, 2000a). In the present work, we used the expression $G'_{\infty}(U)$ proposed by Buscall (Buscall, 1991), which has been proven to be appropriate in the case of concentrated microgel particles (Berli & Quemada, 2000b).

However, direct measurements of G'_{∞} are not trivial in conventional rheometry laboratories due to the experimental difficulties to access shear frequencies in the order of kHz or higher. A reasonable approach to this problem consists in obtaining G'_{∞} by extrapolation of data measured at relatively low frequencies, using a suitable rheological model for the elastic modulus G' . In the present work, the generalized Maxwell model was used for this purpose, which considers different relaxation times for the

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material (Bird, Armstrong, & Hassager, 1987).

Finally, the values of G'_{∞} obtained through the Maxwell model can be used in the Buscall model to predict the pair interaction potential. It is worth recalling that U helps in inferring about the stability of a colloidal dispersion (Mewis & Wagner, 2012). Additionally, the inverse path is also interesting: obtaining the interaction potential from theoretical predictions and then using it to predict G'_{∞} . To our knowledge, the described kind of connection has never been investigated for CM systems. Therefore, our objective was to relate dynamic rheological data to the pair interaction potential between casein micelles (CM) in concentrated systems.

2. Materials and methods

2.1. Structure of CM

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 $a_H = a + H$ (Olivares, Achkar, & Zorrilla, 2016; Olivares, Berli, & Zorrilla, 2013). For this analysis, $a_H = 71.3$ nm and $H = 4.9$ nm were used (Tuinier & de Kruijff, 2002; de Kruijff, Huppertz, Urban, & Petukhov, 2012). The mean center-to-center distance between particles R is related to the core volume fraction ϕ_p by (Berli & Quemada, 2000b)

$$R = 2a(\phi_m/\phi_p)^{1/3} \quad (1)$$

where ϕ_m is the maximum packing fraction. In addition, CM volume fraction ϕ is (Berli & Quemada, 2000b)

$$\phi = \phi_p(a_H/a)^3 \quad (2)$$

2.2. Determination of G'_{∞} for CM dispersions from dynamic rheological data

G'_{∞} values of dispersions of CM at different volume fractions were obtained from frequency sweeps data reported in the literature (Bouchoux et al., 2009; Olivares et al., 2016) using the generalized Maxwell model. The expressions for elastic $G'(\omega_j)$ and loss $G''(\omega_j)$ moduli as function of the frequency (ω_j) used were (Bird et al., 1987):

$$G'(\omega_j) = \sum_{k=1}^N \frac{G'_{\infty,k} \lambda_k^2 \omega_j^2}{1 + (\lambda_k \omega_j)^2} \quad (3)$$

$$G''(\omega_j) = \sum_{k=1}^N \frac{G'_{\infty,k} \lambda_k \omega_j}{1 + (\lambda_k \omega_j)^2} \quad (4)$$

Experimental data of $G'_{j,\text{exp}}$ and $G''_{j,\text{exp}}$ versus ω_j were used to obtain the fitted parameter $G'_{\infty,k}$. Then, G'_{∞} results:

$$G'_{\infty} = \sum_{k=1}^N G'_{\infty,k} \quad (5)$$

λ_k are the relaxation times of the spectrum. The spacing of these was taken to be decade intervals. The longest relaxation time λ_{max} was chosen so that $\lambda_{\text{max}} \omega_{\text{min}} > 1$ where ω_{min} is the lowest frequency for which data are available. Similarly, the smallest relaxation time λ_{min} is chosen so that $\lambda_{\text{min}} \omega_{\text{max}} < 1$, where ω_{max} is the highest frequency for which data are available. The experimental data obtained by Bouchoux et al. (2009) were fitted by setting as

relaxation times $\lambda_1 = 0.1$ s, $\lambda_2 = 1$ s, $\lambda_3 = 10$ s, and $\lambda_4 = 100$ s. The experimental data obtained as described by Olivares et al. (2016) were fitted by setting as relaxation times $\lambda_1 = 1$ s, $\lambda_2 = 10$ s, and $\lambda_3 = 100$ s. The fitting of the $G'_{\infty,k}$ for each relaxation time was done by minimizing the differences between the measured ($G'_{j,\text{exp}}$, $G''_{j,\text{exp}}$) and predicted ($G'(\omega_j)_{\text{pred}}$, $G''(\omega_j)_{\text{pred}}$) moduli at N frequencies ω_j . Then, the quantity to be minimized is (Bird et al., 1987)

$$\sum_{j=1}^N \left\{ \left[\frac{G'(\omega_j)_{\text{pred}}}{G'_{j,\text{exp}}} - 1 \right]^2 + \left[\frac{G''(\omega_j)_{\text{pred}}}{G''_{j,\text{exp}}} - 1 \right]^2 \right\} \quad (6)$$

2.3. Determination of G'_{∞} for CM dispersions from a rheological model

The change of G'_{∞} with volume fraction represents the evolution of the potential with decreasing interparticle distance (Mewis & Wagner, 2012). For systems composed by electrostatically as well as sterically stabilized particles some expressions to relate G'_{∞} to the interaction potential $U(R)$ have been proposed (Berli & Quemada, 2000b; Buscall, 1991). In the present analysis, the expression derived by Buscall (1991) was used,

$$G'_{\infty} = \frac{N\phi_m}{5\pi R} \frac{\partial^2 U(R)}{\partial R^2} \quad (7)$$

where $\phi_m = 0.68$ is the maximum packing volume fraction of CM (Nöbel, Weidendorfer, & Hinrichs, 2012) and $N = 7.5$ is the number of nearest neighbors in the disordered state (Mewis & Wagner, 2012).

Therefore, G'_{∞} values were obtained from an interaction potential prediction proposed for CM, which considers the contribution of van der Waals ($U_{vdW}(R)$), electrostatic ($U_{el}(R)$) and steric ($U_{es}(R)$) interaction potentials (Olivares et al., 2013; Tuinier & de Kruijff, 2002),

$$U(R) = U_{vdW}(R) + U_{el}(R) + U_{es}(R) \quad (8)$$

In addition, G'_{∞} values were obtained from an interaction potential prediction proposed for sterically stabilized particles (Berli & Quemada, 2000b; Israelachvili, 2011),

$$U(R) = Ak_B T e^{-[\pi(R-2a)/H]} \quad (9)$$

where A is a constant related to the length H and the mean distance between the chain attachment points at the core surface (in this case, each κ -casein molecule), and $k_B T$ is the thermal Brownian energy.

3. Results and discussion

Fig. 1 shows typical frequency sweeps for dispersions of CM. Symbols are experimental values obtained by Olivares et al. (2016) and Bouchoux et al. (2009). All the dispersions analyzed presented values of G' higher than G'' , without exhibiting crossing point. Both moduli increase with increase in frequency, indicating dominant elastic properties and weak gel character. The dependence of dynamic moduli on frequency can be related to the existence of relaxation phenomena occurring even at short time scales, while the small difference between modulus values shows that a lower percentage of the stored energy is recovered (Lopes da Silva & Rao, 1999). Lines in Fig. 1 are the values obtained with the Maxwell model (Eqs. (3) and (4)). Values of G'_{∞} for the different dispersions

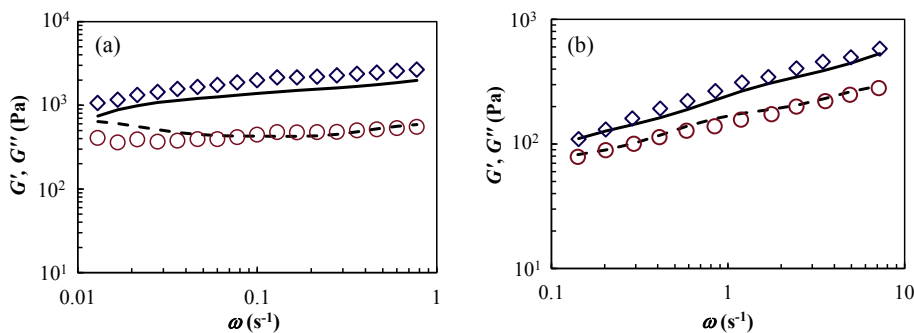


Fig. 1. Frequency sweeps of dispersions of CM: (a) Skim milk concentrate with a volume fraction of $\phi = 0.723$ (Olivares et al., 2016), (b) Dispersions of CM with a volume fraction of $\phi = 0.783$ (Bouchoux et al., 2009). Symbols are experimental values: (\diamond) G' , (\circ) G'' . Solid lines are the predictions of $G'(\omega_j)$ and dash lines are the predictions of $G''(\omega_j)$ obtained with the Maxwell model, simultaneously fitted as indicated by Eq. (6).

Table 1

Values of G'_∞ and $U/k_B T$ for the CM dispersions analyzed.

Experimental values	ϕ	G'_∞ (Pa)	$U/k_B T$
Olivares et al. (2016)	0.689	2872	0.74
T = 298 K	0.723	4058	1.03
	0.758	9011	2.26
Bouchoux et al. (2009)	0.708	54	0.01
T = 293 K	0.783	899	0.23

analyzed are shown in Table 1. It is observed that as volume fraction of CM increases, G'_∞ values also increase, indicating that when the distance between CM decreases, the dispersions attain more elastic character.

Values of $U/k_B T$ can be calculated from G'_∞ using Eq. (7). For the sake of simplicity, values of $U/k_B T$ were obtained from G'_∞ using Eqs. (7) and (9) (Table 1). The values obtained are in the order of magnitude reported by Olivares et al. (2013).

Fig. 2 shows a cross check of the dimensionless elastic modulus at high frequency as function of the volume fraction of CM obtained from experimental data and from predictions that involve the

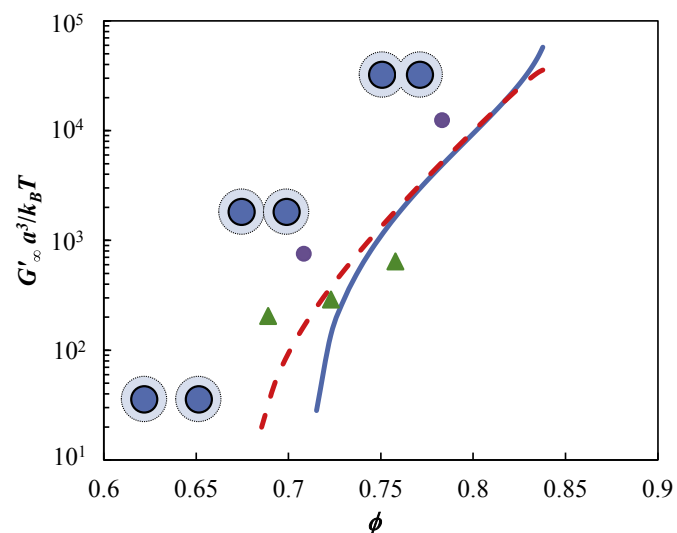


Fig. 2. Dimensionless elastic modulus at high frequencies as function of the volume fraction of CM. Symbols are experimental values (\bullet): Bouchoux et al. (2009) (\blacktriangle), Olivares et al. (2016). Solid and dash lines are the values obtained with interaction potential prediction proposed for CM (Tuinier & de Kruif, 2002) and for sterically stabilized particles (Berli & Quemada, 2000b; Israelachvili, 2011), respectively. Schematic representation of a pair of CM at different distances is shown.

calculation of interaction potentials for CM (Eqs. (8) and (9)). The differences observed between the experimental data analyzed for similar volume fractions may be explained taking into account that the samples studied by Bouchoux et al. (2009) are dispersions of native phosphocaseinate powder (NPC) dissolved in a solvent made from ultrafiltration of skimmed milk, while the samples studied by Olivares et al. (2016) are concentrated skim milk dispersions. Moreover, it is worth recalling that in both cases there are intrinsic experimental errors. The agreement of the theoretical predictions and experimental values of G'_∞ indicates that the Buscall model is appropriate for explaining the rheological behavior of concentrated systems composed by CM in experiments of dynamic rheometry. Fig. 2 also shows a schematic representation of a pair of CM at different distances to easily recall the concentration regime used in this study.

4. Conclusions

In this work, the high-frequency limit of the elastic modulus obtained from experimental data using the Maxwell model was satisfactorily compared with the theoretical values predicted from Buscall model based on the pair interaction potentials for CM. The methodology proposed allows connecting the dynamic rheometric data with pair interaction potentials of CM in concentrated skim milk dispersions and it may help to infer about the stability of milk concentrates.

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