

The Role of Interdroplet Interaction in the Physics of Highly Concentrated Emulsions¹

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Abstract—The osmotic pressure and shear modulus of highly concentrated emulsions were modelled by considering both interfacial energy and interdroplet interaction. This was performed for two- and three-dimensional cases and by optimization and approximation methods of predicting film thickness. The results show that even a small source of interaction can result in non-superimposition of scaled osmotic pressure and shear modulus by Laplace pressure for different droplet sizes, and also significant deviation from the models which consider interfacial interaction as the sole source of energy. The model was used to explain the reciprocal squared diameter dependency of elastic modulus: an interaction similar to the van der Waals type can be responsible for this observation. The model can also be used to analyze the interdroplet interactions in highly concentrated emulsions.

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1. INTRODUCTION

An emulsion is an immiscible mixture of two fluids, one of which is dispersed in the continuous phase of the other, typically made by rupturing droplets down to colloidal sizes through mixing. To inhibit recombination, or coalescence, a surfactant which concentrates at the interfaces must be added to create a short range interfacial repulsion between droplets [1, 2]. Highly concentrated emulsions, in which the dispersed phase concentration increases beyond the critical value of the closest possible packing of spherical particles, have significant technological applications. Despite comprising fluids only, emulsions consisting of highly concentrated droplets can possess a striking shear rigidity that is characteristic of a solid. The nature of this elasticity is unusual; for instance, if the osmotic pressure approaches the characteristic Laplace pressure required to deform the droplets, $2\sigma/R$ where σ is the interfacial tension and R is the undeformed droplet radius, the droplets pack together and deform, creating flat facets where neighbouring droplets touch. In fact, two droplets forced together will begin to deform before their interfaces actually touch, because of the intrinsic repulsive interaction between them. Thus, emulsions minimize their total free energy by reducing the repulsion (which may have different origins, but is usually ignored) at the expense of creating some additional surface area by deforming the droplet interfaces. Provided the droplets are compressed by an osmotic pressure, additional energy can be stored by imposing shear deformations which cre-

ate additional droplet surface area; this gives rise to the emulsion's elastic modulus.

The earliest calculations of concentration dependencies of the osmotic pressure $\Pi(\Phi)$ and shear modulus $G(\Phi)$ for emulsions and foams [3 – 11] are based on perfectly ordered crystals of droplets. In such systems, at a given volume fraction and applied shear strain, all droplets are compressed equally and deform affinely under the shear; thus all droplets have exactly the same shape. Describing the dependence of Π and G on Φ then reduces to the “simpler” problem of solving the interfacial shape of a single droplet within a unit cell. Nevertheless, calculating the exact shape and area of such a single droplet at all $\Phi > \Phi^*$ is a very difficult free-boundary problem that can only be solved analytically for simple cases [12], or numerically [12, 13]. Real emulsions, however, exhibit a disordered droplet structure, and a comparison of experimental results to these theoretical predictions may not be satisfactory. In particular, by comparing the concentration dependence of the low-frequency plateau value of the storage modulus of disordered, monodisperse emulsions with the static shear modulus predicted by these studies, some inconsistencies may be found [13].

In order to understand the effects introduced by disorder, a model for compressed emulsions, which includes a disordered structure as well as realistic droplet deformations, was developed by Lacasse et al. [13]. In this model, an anharmonic potential for the repulsion between the packed droplets was formulated, based on numerical results obtained for individual droplets when confined within regular cells [12].

Numerical results for the osmotic pressure Π and the

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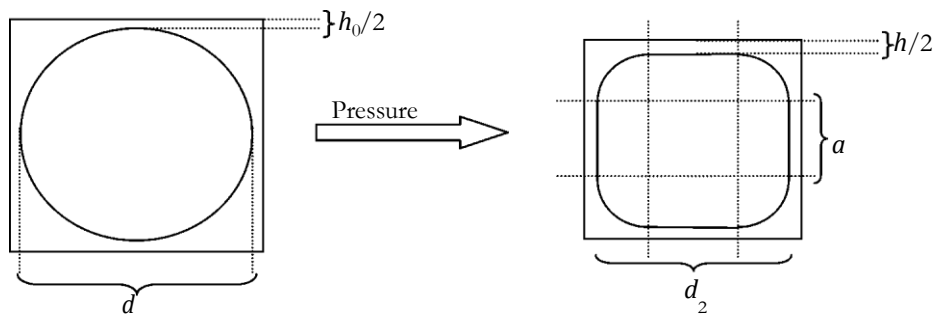


Fig. 1. Schematic representation of droplet compression.

static shear modulus G obtained from this model are in good agreement with performed experimental results, and the single droplet model can be taken as a good estimation [13].

A number of publications within the last years have described and discussed the rheological properties of highly concentrated emulsions [14 – 34]. Although the proposed models [3 – 13] predict that shear modulus and osmotic pressure are scaled with Laplace pressure, reported experimental results [14, 17 – 19, 27 – 29, 31 – 34] often show deviation from this scaling. This deviation is attributed to different parameters, e.g. neglecting continuous phase viscosity and film thickness [17], sticky surface aggregates of protein surfactant [27, 28], van der Waals interaction [32], and ignoring the film thickness [33].

In the present study, the discrepancy of the different experimental data to scale with the Laplace pressure is modified by adding the interdroplet interaction potential in terms of disjoining pressure to the existing two- and three-dimensional models. Therefore, firstly a theory section is presented in Section 2 which includes the basic relationship of modeling (Section 2.1), the two- (Section 2.2) and three-dimensional (Section 2.3) models consisting of disjoining pressure of interdroplet thin film. In the Section 3, some typical results of model will be presented. Finally in Section 4, the model is used to predict the interdroplet interaction of a highly concentrated water-in-oil emulsion which is problematic to measure by means of the existing measuring system of disjoining pressure, due to the super-saturation of the water phase with organic salts (80 wt %).

2. THEORY

2.1. Basic Relationships

The initial conception of the physics of highly concentrated emulsions was given in [3, 4, 12, 13]. In this event the osmotic pressure Π acting inside the system was assumed to be balanced by the increase of the surface energy, due to the increase of dispersed droplet area under compression, as follows:

$$\Pi = -\frac{\partial F}{\partial V}\bigg|_{V_0} = \frac{\phi^2 \partial \phi}{V_0 \partial \phi}\bigg|_{V_0}. \quad (1)$$

Parameters F , V , V_0 and ϕ are excess-free energy, droplet volume, initial droplet volume, and volume fraction of the disperse phase, respectively. This equation shows that it is necessary to express the free energy as a function of volume fraction.

The free energy is a sum of even powers of strain, Ψ , because symmetry dictates that it must be invariant with respect to the direction of the strain. If there is no compression of the material, the free energy can be written as follows [35]:

$$F = F_0 + VG \frac{\Psi^2}{2} + O[\Psi^4], \quad (2)$$

where F_0 is a constant energy of the expansion and does not play any role in the shear rheology. Hooke's law can be recovered by differentiating the free energy once with respect to Ψ :

$$\tau = \frac{1}{V} \frac{\partial F}{\partial \Psi}\bigg|_{\Psi=0}, \quad (3)$$

where the condition $\Psi \rightarrow 0$ is used to eliminate any nonlinear effects. The elastic shear modulus can be found by differentiating again with respect to Ψ :

$$G = \frac{1}{V} \frac{\partial^2 F}{\partial \Psi^2}\bigg|_{\Psi=0} = \frac{\phi}{V_0} \frac{\partial^2 F}{\partial \Psi^2}\bigg|_{\Psi=0}. \quad (4)$$

The two-dimensional layout of the compression process for a cubic arrangement of droplets can be seen schematically in Fig. 1. Here d , d_2 , h and h_0 refer to initial droplet size, compressed droplet size, variable film thickness and film thickness in a spherical maximum close-packing of droplets, respectively.

The film thickness can be either constant or have a variable function. The variation of film thickness arises from the interdroplets' interaction. This interaction has the same physical meaning as disjoining pressure, depending on the electrostatic double layer, dispersion, steric (entropic), hydrophobic and supramolecular forces in the system [36 – 39], and can affect the osmotic pressure and shear modulus of a concentrated

emulsion. In this case, the optimum film thickness and extent of droplet compression can be established through an energy minimization method. When the disjoining pressure is weak, the osmotic pressure and shear modulus are functions of increased interfacial area only; and the film thickness can be regarded as zero or a finite value due to a non-zero thickness of a neutral surfactant. This simplest model, neglecting the disjoining force, corresponds to the basic approach of Princen [3, 4] and Lacasse et al. [13].

2.2. Two-Dimensional Model

Geometrical model. In order to develop a complete two-dimensional model in this paper, some previous

ideas proposed in the basic publications were used. Therefore it is instructive to refer briefly to the main concepts of earlier works for a two-dimensional case.

According to the scheme in Fig. 1, for a compressed droplet in a cubic arrangement of droplets we have:

$$a = d_2 - 2r, \quad (5)$$

where r is the radius of curvature in the angles and a is the plateau region length. It is clear that for maximum close-packing of spherical droplets, the limiting concentration Φ_c is:

$$\Phi_c = \frac{\pi d^2}{4(d+h_0)} = \frac{\pi d^2}{4d^2} = \frac{\pi}{4} = \Phi^* \quad (6)$$

where at the critical volume fraction Φ_c , the film thickness is not zero, but for further calculation the Φ^* was introduced, which is the effective volume fraction of close-packed spherical droplets with zero film thickness.

The concentration, Φ , of compressed droplets can be expressed as:

$$\Phi = \frac{S}{(d_2+h)^2}, \quad (7)$$

where S is the area of a compressed droplet. By the droplet incompressibility assumption, $S = \frac{\pi d^2}{4}$.

It is convenient to introduce an "effective volume fraction" Φ_{eff} of a dispersed phase with zero film thickness defined as $\Phi_{\text{eff}} = \frac{\pi d^2}{4d_2^2}$. Then, the following relationship is valid:

$$\Phi_{\text{eff}} = \frac{\pi d^2}{4d_2^2} = \frac{d^2}{d_2^2} = \frac{\Phi^*}{\sqrt{\Phi_{\text{eff}}}} \quad (8)$$

After some geometrical calculations, we come to the following relationship:

$$r = \frac{1}{2} \sqrt{\frac{\Phi^*}{1-\Phi^*}} \sqrt{\frac{1-\Phi_{\text{eff}}}{\Phi_{\text{eff}}}}. \quad (10)$$

The free energy per unit length² as a function of volume fraction (in the absence of any interaction between surfactant covered droplets) is expressed as:

$$F = \sigma(4a + 2\pi r) \quad (11)$$

or

$$F = \pi d \sigma \left(\frac{1}{\sqrt{\Phi^* \Phi_{\text{eff}}}} - \frac{1-\Phi^*}{\sqrt{\Phi^*}} \frac{1-\Phi_{\text{eff}}}{\sqrt{\Phi_{\text{eff}}}} \right), \quad (12)$$

where σ is the interfacial tension. Based on the above written equations, the osmotic pressure is:

$$\Pi = \left. \frac{\partial F}{\partial \Phi} \right|_{V_0} = \left. \frac{\Phi^2}{V_0} \frac{\partial F}{\partial \Phi_{\text{eff}}} \frac{\partial \Phi_{\text{eff}}}{\partial \Phi} \right|_{V_0}, \quad (13)$$

where:

$$\left. \frac{\partial F}{\partial \Phi_{\text{eff}}} \right|_{V_0} = \left(\frac{1}{2\sqrt{\Phi^* \Phi_{\text{eff}}}} + \frac{1-\Phi^*}{\sqrt{\Phi^*}} \frac{1}{\sqrt{\Phi_{\text{eff}}}} \right) \quad (14)$$

$$= \pi d \sigma \left(\frac{1}{2\sqrt{\Phi^* \Phi_{\text{eff}}}} + \frac{1-\Phi^*}{\sqrt{\Phi^*}} \frac{1}{\sqrt{\Phi_{\text{eff}}}} \right).$$

And according to Eq. (9), we can write:

$$\frac{\partial \Phi_{\text{eff}}}{\partial \Phi} = \left(\frac{\Phi_{\text{eff}}}{\Phi} \right)^{\frac{3}{2}}. \quad (15)$$

Therefore, the scaled osmotic pressure by the Laplace pressure - σ/R^3 - is:

$$\frac{\Pi}{\sigma/R} = \sqrt{\frac{\Phi}{\Phi^*}} \left(\frac{1-\Phi^*}{\sqrt{1-\Phi_{\text{eff}}}} - 1 \right). \quad (16)$$

It can easily be shown that the osmotic pressure of a hexagonal arrangement of droplets follows the same function. This equation is valid only if the droplets do not interact with each other, as was assumed by different researchers [3 - 13, 30].

It should be noted that in this case, if it is assumed that the interdroplet film thickness has a constant value in all volume fractions, the osmotic pressure calculated from Eq. (16) does not scale with the reciprocity of droplet size.

For modelling the shear modulus, the strain derivation of free energy, Eq. (12), can be used. By assuming

and the real volume fraction can be written as:

$$\phi = \frac{\pi d^2}{4(d_2 + h)^2} \rightarrow \frac{1}{\phi} = \left(\frac{1}{\sqrt{\phi_{\text{eff}}}} + \frac{h/d}{\sqrt{\phi^*}} \right)^2. \quad (9)$$

²The F in the section of the two-dimensional model is free energy per unit area and its dimension is J/m.
³For the sake of simplicity, it is assumed to be half of the actual

Laplace pressure.

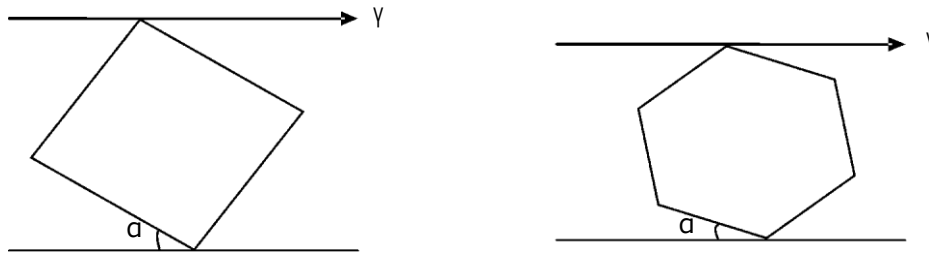


Fig. 2. Schematic representation of lattice unit orientation under shear.

the droplet incompressibility, the free energy of a deformed droplet in the cubic (equations signed with “a”) and hexagonal (equations signed with “b”) lattices under a small γ shear deformation, corresponding to the θ angle ($\tan \theta = \gamma$), with a primary orientation angle α as shown in the Fig. 2 ($0 \leq \alpha \leq \pi/4$ for cubic arrangement and $0 \leq \alpha \leq \pi/6$ for hexagonal arrangement), can be written as follows:

$$F = \sigma(4a+2\pi r) \left(\frac{x+y}{2} \right) = \sigma A \left(\frac{x+y}{2} \right), \quad (17a)$$

$$F = \sigma(6a+2\pi r) \left(\frac{x+y+z}{3} \right) = \sigma A_{\gamma=0} \left(\frac{x+y+z}{3} \right), \quad (17b)$$

where x, y and z are the change ratios of length sides of the deformed unit cell under strain. By introducing the geometrical sizes, we come to:

$$F = \frac{\sigma A_{\gamma=0}}{2} \left(\sqrt{1 + \sin^2 \left(\frac{\pi}{4} + \alpha \right) \gamma^2} - \sin \left(\frac{\pi}{2} + 2\alpha \right) \gamma \right) + \sqrt{1 + \sin^2 \left(\frac{\pi}{4} - \alpha \right) \gamma^2} + \sin \left(\frac{\pi}{2} - 2\alpha \right) \gamma \quad (18a)$$

$$F = \frac{\sigma A_{\gamma=0}}{3} \left(\sqrt{1 + \sin^2 \left(\frac{\pi}{6} + \alpha \right) \gamma^2} - \sin \left(\frac{\pi}{3} + 2\alpha \right) \gamma \right) + \sqrt{1 + \sin^2 \left(\frac{\pi}{6} - \alpha \right) \gamma^2} + \sin \left(\frac{\pi}{3} - 2\alpha \right) \gamma \quad (18b)$$

$$\frac{\partial^2 F}{\partial \gamma^2} \Big|_{\gamma=0} = \frac{\sigma A_{\gamma=0}}{2} \left(\sin^2 \left(\frac{\pi}{4} + \alpha \right) - \frac{1}{4} \sin^2 \left(\frac{\pi}{2} + 2\alpha \right) \right) + \sin^2 \left(\frac{\pi}{4} - \alpha \right) - \frac{1}{4} \sin^2 \left(\frac{\pi}{2} - 2\alpha \right) = \sigma A_{\gamma=0} \left(\frac{1}{4} - \frac{1}{2} \cos(2\alpha) \right) \quad (19a)$$

$$\frac{\partial^2 F}{\partial \gamma^2} \Big|_{\gamma=0} = \frac{\sigma A_{\gamma=0}}{3} \left(1 - \frac{1}{2} \cos(2\alpha) \right) \leq \frac{\partial^2 F}{\partial \gamma^2} \Big|_{\gamma=0} \leq \frac{\sigma A_{\gamma=0}}{2} \Big|_{\alpha=\pi/4}$$

$$\frac{\partial^2 F}{\partial \gamma^2} \Big|_{\gamma=0} = \frac{\sigma A_{\gamma=0}}{3} \left(1 + \sin^2 \left(\frac{\pi}{6} + \alpha \right) - \frac{1}{4} \sin^2 \left(\frac{\pi}{3} + 2\alpha \right) \right) + \sin^2 \left(\frac{\pi}{6} - \alpha \right) - \frac{1}{4} \sin^2 \left(\frac{\pi}{3} - 2\alpha \right) = \frac{\sigma A_{\gamma=0}}{3} \left(\frac{11}{8} + \sin^2 \alpha - \frac{1}{4} \cos^2(2\alpha) \right) \quad (19b)$$

$$\frac{9\sigma A_{\gamma=0}}{24} \Big|_{\alpha=0} \leq \frac{\partial^2 F}{\partial \gamma^2} \Big|_{\gamma=0} < \frac{25\sigma A_{\gamma=0}}{48} \Big|_{\alpha=\pi/6}$$

Therefore, it can be concluded that the second partial derivatives of free energy with respect to the strain for any type of orientation in a two-dimensional model, is proportional to $\sigma A_{\gamma=0}$ by factor varying as $1/4 \leq k_{\alpha} \leq 25/48$. Finally, the shear modulus can be expressed as:

$$G = \frac{\Phi^2}{V_0 \partial \gamma^2} \Big|_{\gamma=0} = \frac{2\sigma}{d} \frac{1 - \Phi}{\sqrt{1 - \Phi^*} \sqrt{\Phi_{eff}}} \quad (20)$$

$$= k_{\alpha} \frac{\Phi}{d} \frac{1 - \Phi}{\sqrt{\Phi^* \Phi_{eff}}} = \frac{\Phi^*}{\Phi_{eff}}$$

$$\frac{G}{\sigma/R} = \frac{1 - \sqrt{\frac{1 - \Phi_{eff}}{\Phi_{eff}}}}{1 - \sqrt{\frac{1 - \Phi^*}{\Phi^*}}} \quad (27)$$

and calculation of $\frac{\partial F}{\partial \gamma^2}$ leads to:

It is clear from the above equation that for a constant film thickness, the shear modulus normalized by

the Laplace pressure should be slightly dependent on the droplet size and film thickness similar to the osmotic pressure case. This is a more general result than obtained in earlier publications where $\frac{G}{\sigma/R}$ was invariant to the droplet size, though the difference is not big.

It should also be noticed that the dominant droplets orientation in the shear deformation of a highly concentrated emulsion can be obtained by fitting the experimental results with the obtained equations.

Modified 2-D Model: Introducing disjoining pressure and optimized film thickness. The experimental results presented by Mason et al. [30] show that the osmotic pressure and shear modulus scaled by Laplace pressure as functions of volume fraction do not superimpose. Those experimental results were modified by replacing the real volume fraction, Φ , with an effective

volume fraction to make them superimposed. In other words, they preferred to use some apparent concentration, without taking into account the interdroplets interaction effect – which is dependent on the surfactant characteristics – on the osmotic pressure and rheological properties. The deviation from Princen's model can be also found in different papers [27, 28, 32] and was attributed to “an additional source of elasticity [that] should be considered” [29]. This “additional source” is definitely the disjoining pressure ascribed to the interdroplet interactions which we include to build a complete model for the description of highly concentrated emulsion.

Petsev and his co-workers presented different research projects concerning the interaction energy

between droplets in emulsion systems [40 – 44]. Danov et al. [40] modelled the interaction energy between deformable droplets by using the microscopic approach of Hamaker for van der Waals interaction. Explicit expressions for the electrostatic, steric and other types of interaction were also derived on the basis of Derjaguin's approximation [40]. This work was later extended to the deformable Brownian droplets [41]. Although Petsev and Linse [42] also tried to model the properties of dense emulsions and microemulsions, their model only considers the deformation energy as dominant pair interaction energy and is limited to low concentrations.

The interaction between the surfaces of droplets named as disjoining pressure is a concept traditionally used in the field of foams and emulsions (fluid system) in colloid and interface science [36], and is completely analogous to what is commonly referred to as surface forces when considering interactions in thin films that

where these components can be found in the literature as listed in Table 1.

It should be noted that, if the electrostatic and van der Waals forces are considered as dominant interaction in the system, the resultant model will be named as DLVO theory [37, p. 246].

Besides the listed forces presenting in the interdroplet layer film, the mechanical repulsion between two soft spheres – if our surfactant covered droplets is assumed as soft spheres – can be approximated in terms of power-law, C_p/h^n , or exponential, $C_e \exp(-kh)$, functions [37, p. 112].

By adding the interaction between surfactant covered droplets, the free energy per unit length of a compressed emulsion in a two-dimensional model can be modified as:

$$F = \pi d \sigma \left(\frac{1}{\sqrt{\Phi^* \Phi_{\text{eff}}}} - \frac{\sqrt{1-\Phi^*}}{\Phi^*} \frac{\sqrt{1-\Phi_{\text{eff}}}}{\Phi_{\text{eff}}} \right) + f_{\text{inter}} \quad (23)$$

In this equation, f_{inter} is the interaction energy which is formulated by the excess surface free energy, due to disjoining pressure per unit area of a plane-parallel film of thickness as follows [45]:

$$\frac{f_{\text{inter}}}{S_{\text{cont}}} = f_{\text{dis}} = \int_h^\infty \Pi_{\text{dis}}(h) dh, \quad (24)$$

where S_{cont} is the area of contact between two neighbouring droplets. It is worth mentioning that the chemical potential of the system remains constant.

By neglecting the interaction in the plateau border region, the free energy per unit length is:

$$F = \pi d \sigma \left(\frac{1}{\sqrt{\Phi^* \Phi_{\text{eff}}}} - \frac{\sqrt{1-\Phi^*}}{\Phi^*} \frac{\sqrt{1-\Phi_{\text{eff}}}}{\Phi_{\text{eff}}} \right) + n a f_{\text{dis}}(h), \quad (25)$$

where n is the number of neighbouring droplets, being 4 for cubic and 6 for hexagonal arrangement. By replacing a with its volume fraction function, we will have:

$$F = \pi d \sigma \left[\frac{1}{\sqrt{\Phi^* \Phi_{\text{eff}}}} - \frac{\sqrt{1-\Phi^*}}{\Phi^*} \frac{\sqrt{1-\Phi_{\text{eff}}}}{\Phi_{\text{eff}}} \right] + \frac{\sigma}{\Phi_{\text{eff}}} \quad (26)$$

$$\times \left(\frac{1}{\sqrt{\Phi^* \Phi_{\text{eff}}}} - \frac{1}{\sqrt{\Phi^* (1-\Phi^*)}} \frac{\sqrt{1-\Phi_{\text{eff}}}}{\Phi_{\text{eff}}} \right)$$

separate two solid phases.

It is customary to separate the various contributions of the disjoining pressure Π_{dis} into the following

components [36 – 38]:

In order to determine the osmotic pressure of a highly concentrated emulsion, the optimum film thickness corresponding to the minimum free energy should be obtained, and then the osmotic pressure can be calculated by using Eq. (1). The procedure is as follows:

1—Definition of the h domain: The maximum film thickness in a fixed volume fraction can be obtained when the droplet is fully compressed to a

$$\Pi_{\text{dis}}(h) = \Pi_{\text{dl}} + \Pi_{\text{van}} + \Pi_{\text{steric}} + \Pi_{\text{supra}} + \dots, \quad (22)$$

Table 1. Different components of disjoining pressure

Forces	Condition	Equation	Reference
Electrostatic double layer	Constant surface potential	$\Pi_{dl} = \frac{\tau_0^2}{8\pi} \text{sech}^2(\kappa h)$	[36]
	Constant surface charge	$\Pi_{dl} = \frac{2\pi\sigma_0^2}{\epsilon} \left(\frac{1 + \text{sech}(\kappa h/2)}{\tanh(\kappa h/2)} \right)^2$	
van der Waals	Two plane-parallel surfaces ^{xx}	$\Pi_{van} = -\frac{A_H}{6\pi h^3}$	[37]
Steric (entropic)	Protrusion	$\Pi_{pro} = \frac{n\beta(h/\xi)\exp(-h/\xi)}{1 - (1 + h/\xi)e^{-h/\xi}}$	[36, 37]
	Undulation	$\Pi_{und} = \frac{(\kappa L)^2}{2K_b h^3}$	
	Peristaltic	$\Pi_{pre} = \frac{2(kT)^2}{\pi^2 K_a h^3}$	
Polymer-covered surfaces	de Gennes' s brush theory ^{zz}	$\Pi_{polym} = kT\Gamma^{3/2}[(2L/h)^{9/4} - (h/2L)^{3/4}]$ for $h < 2L$	[39]
Micellar	Semi-empirical [†]	$\Pi_{micelle} = \frac{P_0}{\left(\frac{2\pi h}{d_1}\right)^2 \left(\frac{d^3}{d_1 d_2} - \frac{h}{d_2}\right)}$ $P_{micelle}(0 < h < d) = -P_0$	[38]

^{xx} - A_H is the Hamaker constant and can be negative, which results in the repulsive van der Waals forces, e.g. in the case of polymer dissolved in organic solvent;

^{zz} - L is the brush thickness and Γ is the surface concentration of brushes.

[†] - d is the diameter of the micelles, $P_0 = nkT(1 + \phi + \phi^2 - \phi^3)/(1 - \phi)^3$ obtained from the Carnahan—Starling formula, $n = 6\phi/\pi d^3$ is the micellar number density and ϕ is the volume fraction of the micelles, while d_1 and d_2 are the period and decay length of the oscillations, defined as $d_1/d = \sqrt{2/3} + 0.237(\pi/3 \sqrt{2} - \phi) + 0.633(\pi/3 \sqrt{2} - \phi)^2$; $d_2/d = 0.4866/(\pi/3 \sqrt{2} - \phi) - 0.420$.

cube or hexagon respectively, in cubic or hexagonal lattices ($a = d_2$):

$$\phi = \frac{d_2^3}{(d_2 + h_{max})^3} \rightarrow h_{max} = d \left(\frac{1}{\sqrt{\phi}} - 1 \right). \quad (27)$$

And according to incompressibility assumption for this fully compressed case, we have:

$$h_{max} = d \sqrt{\phi} \left(\frac{1}{\sqrt{\phi}} - 1 \right). \quad (28)$$

This equation is also valid for the hexagonal arrangement of droplets. Therefore the film thickness, h , can vary between zero and h_{max} ($0 \leq h \leq h_{max}$).

2—At each volume fraction of emulsion, ϕ , by changing h , the variation of free energy is calculated, and by using Eqs. (9) and (26) and the optimized film thickness, h_{opt} , corresponding to the minimum energy, will be obtained. The interdroplet interaction energy

per unit area in Eq. (26) can be obtained experimentally by disjoining pressure measurement, or predicted from DLVO theory or any other discussed disjoining pressure contributions.

3—The osmotic pressure will be obtained through numerical derivation of free energy with respect to the volume fraction, Eq. (1).

4—The shear modulus can be obtained in a similar approach to the constant film thickness case. If it is assumed that the film thickness does not change by shearing, the free energy per unit length will be:

$$F = \left[\sigma A_{v=0} + 4a \Pi_{dis}(h_{opt}) \right] \left(\frac{x+y}{2} \right), \quad (29a)$$

$$F = \left[\sigma A_{v=0} + 6a \Pi_{dis}(h_{opt}) \right] \left(\frac{x+y+z}{3} \right). \quad (29b)$$

It can be seen that the interfacial interaction force

depending on the flattened area increases in shearing.

The shear modulus is obtained as follows:

$$G = \frac{\Phi \partial F}{V_0 \partial \gamma^2} = k_\alpha \frac{2\sigma}{d} \left[\left(\frac{1}{\sqrt{\Phi^* \Phi}} - \frac{1 - \Phi^*}{\sqrt{\Phi^*}} \frac{1 - \Phi_{eff}}{\sqrt{\Phi_{eff}}} \right) + \frac{f_{dis}(h_{opt})}{\sigma} \right] \quad (30)$$

$$\left[\frac{1}{\sqrt{\Phi^* \Phi_{eff}}} - \frac{1}{\sqrt{\Phi^* (1 - \Phi^*)}} \frac{1 - \Phi_{eff}}{\sqrt{\Phi_{eff}}} \right]$$

And modulus scaled by the Laplace pressure is calculated as:

$$\frac{G}{\sigma/R} = k_\alpha \Phi \left[\frac{1}{\sqrt{\Phi^* \Phi_{eff}}} - \frac{1 - \Phi^*}{\sqrt{\Phi^*}} \frac{1 - \Phi_{eff}}{\sqrt{\Phi_{eff}}} \right] + \frac{f_{dis}(h_{opt})}{\sigma} \left[\frac{1}{\sqrt{\Phi^* \Phi_{eff}}} - \frac{1}{\sqrt{\Phi^* (1 - \Phi^*)}} \frac{1 - \Phi_{eff}}{\sqrt{\Phi_{eff}}} \right] \quad (31)$$

where k_α changes between 1/4 and 1/2 for the cubic arrangement, and between 9/24 and 25/48 for the hexagonal arrangement of droplets. As the maximum value for the orientation coefficient in both arrangements is approximately 1/2, this value can be used for shear modulus calculations.

Modified 2-D Model: Introducing disjoining pressure and approximate film thickness. It is clear that the above-mentioned theory is extensively computer-based, and according to the example modelling result – instead of finding an optimized film thickness – it is suggested that a linear dependency of film thickness to volume fraction be assumed. In this case, the critical volume fraction Φ_c – see Eq. (6) – should be obtained experimentally, and it represents the volume fraction in which the trend of osmotic pressure and shear modulus change. Therefore the film thickness dependency will be as follows:

$$h(\Phi) = \frac{h_0 (1 - \Phi_c)}{1 - \Phi} \quad (32)$$

$$= d \sqrt{\frac{\Phi^* (1 - \Phi_c)}{1 - \Phi}} (1 - \Phi),$$

which can be put it in the Eqs. (26) and (31) to obtain the osmotic pressure and shear modulus analytically:

$$\frac{\Pi}{\sigma/R} = \left(\frac{1 - \Phi}{\sqrt{\Phi^*}} \frac{\sqrt{\Phi}}{\sqrt{1 - \Phi_{eff}}} - \frac{\sqrt{\Phi}}{\sqrt{\Phi^*}} \right) + \frac{df_{dis}(h)}{dh}$$

$$= \left[\frac{1 - \Phi_{eff}}{\sqrt{\Phi^* \Phi}} - \frac{1 - \Phi^*}{\sqrt{\Phi^*}} \frac{1 - \Phi_{eff}}{\sqrt{\Phi_{eff}}} \right] + \frac{f_{dis}(h)}{\sigma} \left[\frac{1}{\sqrt{\Phi^* \Phi_{eff}}} - \frac{1}{\sqrt{\Phi^* (1 - \Phi^*)}} \frac{1 - \Phi_{eff}}{\sqrt{\Phi_{eff}}} \right] \quad (34)$$

2.3. Three-Dimensional Model Geometrical model.

In a three-dimensional model, the number of neighbouring droplets affects the maximum close-packing of spherical droplets, while its structural and rheological properties also depend on the type of packing. In the numerical and analytical modelling performed by Lacasse et al. [13], the effect of a variable film thickness which can affect the properties was neglected; see Eq. 13 and $\frac{\partial \Phi_{eff}}{\partial \Phi}$ term in it.

In order to calculate the osmotic pressure and shear modulus of highly concentrated emulsions, the free energy, F , of a compressed droplet should be formulated. The starting point is the consideration of variations of droplet shape as a function of volume fraction.

The total surface area of a deformed droplet in a concentration higher than the maximum close-packing of spherical droplets, Φ^* , can only be determined numerically. The basic physical assumption for the deformed droplet shape is the requirement of the minimal surface area. Using Brakke's surface evolver software [46], the shape of a single droplet with a minimum surface area under the constraint of fixed droplet volume, and as a function of confinement, was calculated. In this study, the droplet was meshed with 196,610 vertices which were confined inside a polyhedral cell, particularly the rhombic doacahedron (face-centred cubic), truncated octahedron (body-centred cubic), and simple cube, all of which are space-filling polyhedrals. The total area and the flattened area (parts of droplet surface touching the polyhedral confinement) of the droplet with a unit radius were recorded as the results of this simulation.

While Lacasse et al. [12, 13] suggested the fitting of an excess surface area with power-law equation, $K(\Phi_{eff} - \Phi^*)^\alpha$, the enhanced scaling of excess surface area with $K \Phi_{eff} (\Phi_{eff} - \Phi^*)^\beta$ is observed in this work. Therefore, the total surface area, $A(\Phi)$, and the flattened surface area, $A_F(\Phi)$, of a droplet in different three-dimensional lattices were fitted respectively by the following equations:

$$\times \frac{2h_0\Phi}{\sigma} \sqrt{\frac{1-\Phi}{\Phi^*(1-\Phi^*)}} \sqrt{\frac{1-\Phi_{\text{eff}}}{1-\Phi^*}} \quad (33)$$

$$\sigma(1-\Phi_c) \left(\frac{\Phi_{\text{eff}}}{\Phi^*(1-\Phi^*)} - \sqrt{\frac{\Phi_{\text{eff}}}{\Phi^*}} \right) + \frac{f_{\text{dis}}(h)}{\sigma} \left(\frac{1}{\sqrt{\Phi^*(1-\Phi^*)}} \sqrt{\frac{\Phi}{1-\Phi_{\text{eff}}}} - \sqrt{\frac{\Phi}{\Phi^*}} \right),$$

$$\frac{A(\Phi)}{\pi d^2} = 1 + K \Phi_{\text{eff}}^{\alpha} \left(\frac{\Phi_{\text{eff}}}{1-\Phi^*} \right)^{\beta}, \quad (35)$$

$$\frac{A(\Phi)}{\pi d^2} = K' \Phi_{\text{eff}}^{\alpha'} \left(\frac{\Phi_{\text{eff}} - \Phi^*}{1-\Phi^*} \right)^{\beta'}. \quad (36)$$

Table 2. The coefficients of fittings and validity range

Type of lattice	Type of area	K	α	β	Validity (2% error)	Closest packing, ϕ^*
FCC	Total Area	$6.3E - 2$	4.52	2	96%	$\pi\sqrt{2}/6$
	Flattened Area	$7.5E - 1$	4.41	1.1	96%	
BCC	Total Area	$4.85E - 2$	2.43	2	94%	$\pi\sqrt{3}/8$
	Flattened Area	$4.35E - 1$	2.24	1.1	90%	
SC	Total Area	$1.36E - 1$	1.41	2	90%	$\pi/6$
	Flattened Area	$8.3E - 1$	1.79	1.1	92%	

The fitting parameters are summarized in Table 2. An attempt was made to fit the results with fixed exponents in both cases: $(A - A_0)/A_0 = K\phi_{\text{eff}}(\phi_{\text{eff}} - \phi^*)^{2.2}$ and $A_F/A_0 = K'\phi_{\text{eff}}(\phi_{\text{eff}} - \phi^*)^{1.3}$ equations were obtained with $K_{\text{SC}} = 1.41E - 1$, $K_{\text{BCC}} = 4.41E - 2$, $K_{\text{FCC}} = 4.28E - 2$; $K'_{\text{SC}} = 7.71E - 1$, $K'_{\text{BCC}} = 4.1E - 1$, $K'_{\text{FCC}} = 5.12E - 1$. It should be noted that the validity of these fittings with fixed exponents is up to 90 vol. % and with less than 5% error in this approximate method.

The free energy can be written as $F = \sigma A(\phi) + f_{\text{inter}}$ in order to consider the disjoining pressure effect. The results presented in Fig. 3 show that regarding the preferred arrangement of droplets, even in the presence of interdroplet interaction, up to ~0.9 of volume fraction is FCC due to the lower free energy with BCC arrangement of droplets being important in higher concentrations. Since the properties of emulsions are

mainly of interest to this study, we limit our calculations to FCC lattice.

It can easily be shown when the interdroplet interaction is negligible; osmotic pressure is analytically determined by applying Eq. (13) as follows:

$$\frac{\sigma}{R} = \frac{\alpha}{\beta} \left(\frac{\phi_{\text{eff}} - \phi^*}{1 - \phi^*} \right)^{\beta-1} \quad (37)$$

$$\phi_{\text{eff}} = \left(\frac{\phi - \phi^*}{1 - \phi^*} \right)^{1/\beta} + \phi^* \quad (38)$$

For the calculation of shear modulus, a useful method in the presence of periodic boundary conditions is to use an isochoric uniaxial compression-extension strain: an extension of $\lambda = 1 + \epsilon$ in one direction, associated with a compression of $\lambda^{-1/2}$ in the perpendicular plane. In principle, different orienta-

not lie on the cell boundary [10]. Here, the chosen orientation is along any of the three natural directions of a unit cell. The effective shear modulus G for small s is [47]:

$$u(\epsilon, \phi) - u(0, \phi) = \frac{3}{2} G \epsilon^2, \quad (39)$$

where u is the excess energy density $(F - F_0)/V$. The shear modulus is obtained by fitting the variation of excess energy density versus $(\lambda^2 + 2/\lambda - 3)/2 \approx 3\epsilon^2/2$ [12]. In the present work, the excess energy density for each volume fractions $\phi \geq \phi^*$ under different strains in the absence of interdroplet interaction was simulated and fitted successfully as presented typically for some volume fraction in Fig. 4.

The obtained shear moduli can be fitted as a function of volume fraction:

$$\sigma/R = 1.3 \phi_{\text{eff}}^2 (\phi_{\text{eff}} - \phi^*)^{0.4} + 0.105. \quad (40)$$

One can see that in the absence of interdroplet interaction, the scaling of shear modulus with the Laplace pressure is exactly valid.

Modified 3-D Model: Introducing the disjoining pressure and optimized film thickness. Now include the disjoining pressure member in the expression for the free energy as follows:

$$F = \sigma \pi d \left[\frac{\alpha}{\beta} (\phi_{\text{eff}} - \phi^*)^\beta + 1 + K \phi_{\text{eff}} \left(\frac{\phi_{\text{eff}} - \phi^*}{1 - \phi^*} \right) + \frac{f_{\text{dis}}}{\sigma} \left(K' \phi_{\text{eff}} \left(\frac{\phi_{\text{eff}} - \phi^*}{1 - \phi^*} \right)^\beta \right) \right] \quad (41)$$

For shear modulus, the contribution of disjoining pressure is obtained by considering the area change of the flattened area, where interdroplet interaction is dominant, in the same methodology as discussed for Eq. (40) and Fig. 4. It was also assumed that interfacial and disjoining pressure contributions are addable:

$$G = \dots$$

$$\frac{\sigma}{R} [1.3 \phi_{\text{eff}} (\phi_{\text{eff}} - \phi^*)$$

$$+ (42)$$

$$0$$

$$\cdot$$

$$1$$

$$0$$

$$5$$

$$]$$

$$+ f_{\text{dis}}(h) \times 0.863 \phi_{\text{eff}}^{-8.0}$$

the extension axis would lead to effective measures of the modulus resulting from different combinations of the elastic constants. However, some orientations of the uniaxial strain involve forces that are not normal to the faces of the cell, with the result that some faces do

For a known interdroplet interaction, as discussed in preceding sections, the free energy is numerically minimized for each volume fraction in the film thick-

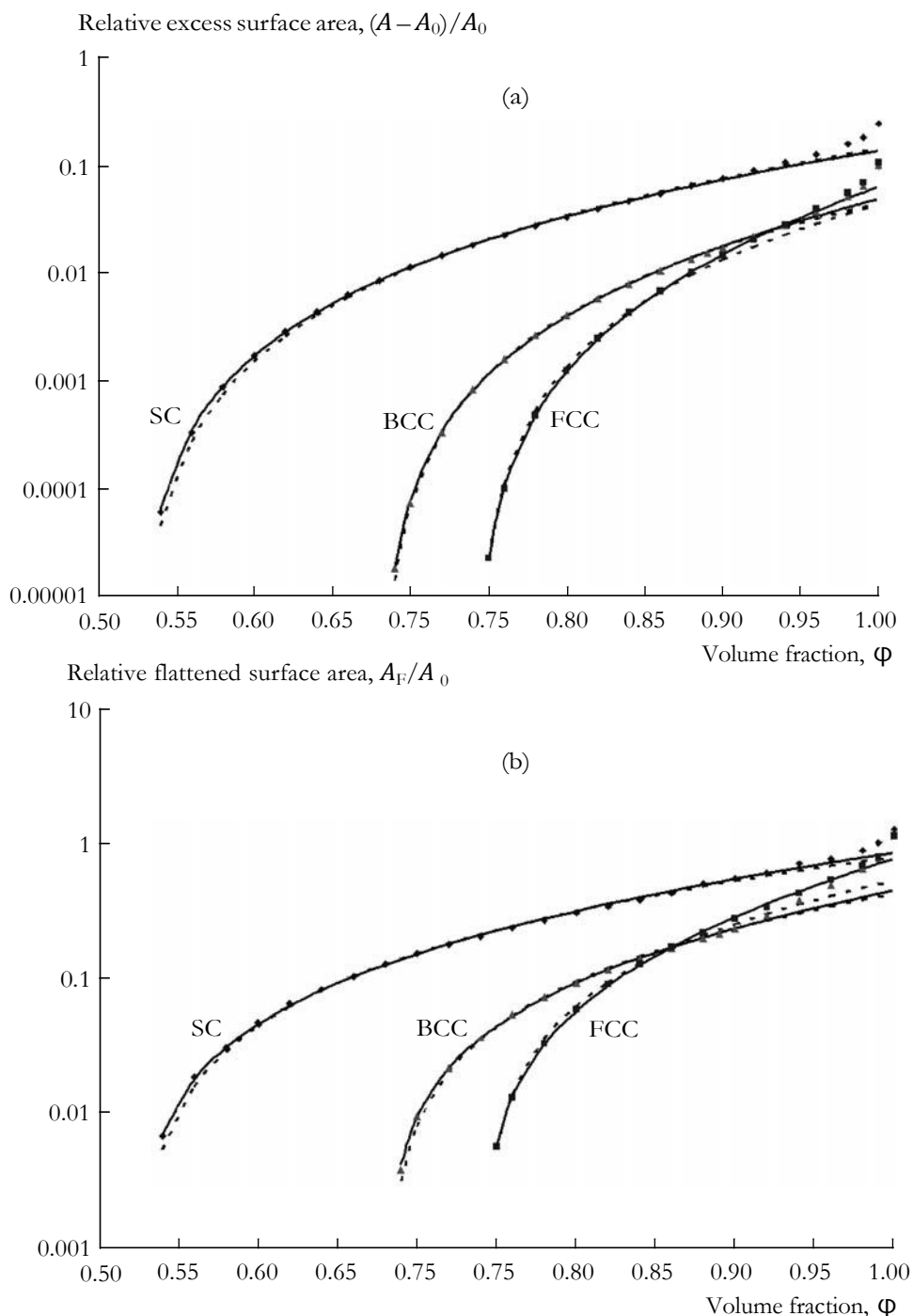


Fig. 3. The results of simulated (a) total and (b) flattened surface area for three different lattices: SC, BCC, FCC fitted by Eqs. (1) and (2) presented as continuous line or with fixed exponents (dotted line).

ness domain, $0 \leq h \leq d\Phi^{*1/3}(\Phi^{-1/3} - 1)$, followed by numerical differentiation for calculating osmotic pressure, Eq. (1), or applying the obtained optimum film thickness in Eq. (42) for the calculation of shear modulus. It is immediately clear that the results of the

present model are not scaled with Laplace pressure, due to the presence of the interaction term.

Modified 3-D Model: Introducing disjoining pressure and approximate film thickness. This model can be tackled in a similar approach to the two-dimen-

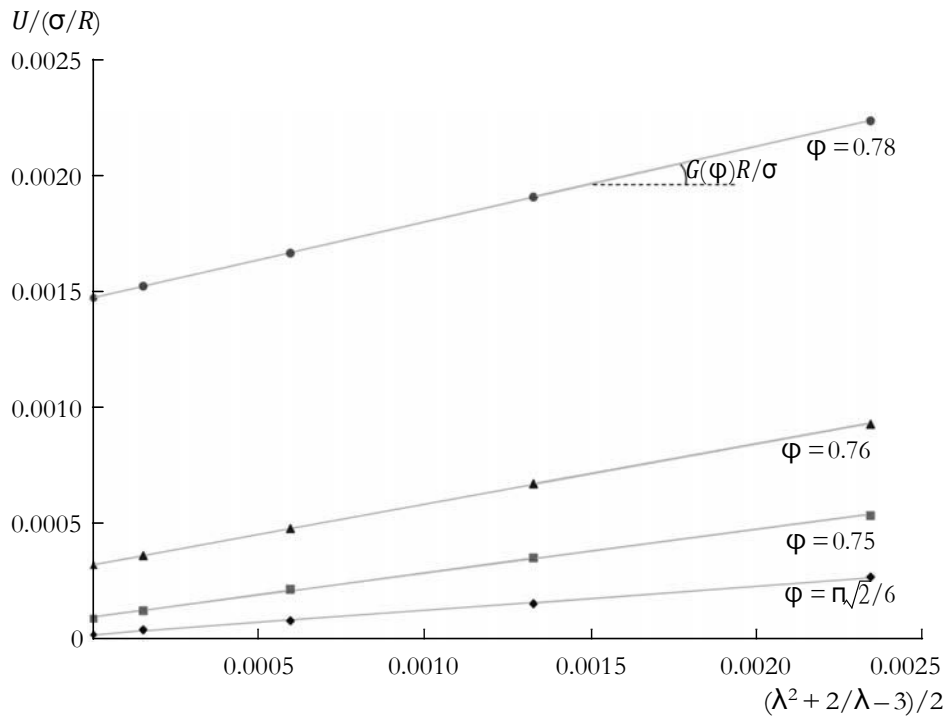


Fig. 4. The method for calculation of shear modulus from the slop of excess energy density against $(\lambda^2 + 2/\lambda - 3)/2$.

sional one, and the film thickness dependency is as follows:

$$h(\phi) = h_0 \frac{1-\phi}{1-\phi_c} \rightarrow h = d \sqrt[3]{\frac{\phi^* / \phi - 1}{1-\phi_c}} (1-\phi). \quad (43)$$

3. EXAMPLES OF THE MODEL'S PREDICTION

3.1. Effect of Disjoining Pressure

In order to show the effect of disjoining pressure on the osmotic pressure and shear modulus, an arbitrary soft repulsive force - in the form of power-law $f_{dis}(h) = A/h^2$, as discussed previously - between droplets was considered, and the osmotic pressure and shear modulus were obtained by an optimized film thickness method for a three-dimensional case with FCC arrangement. In Fig. 5, where $A = 2E-20$ and $\sigma = 0.002$ N/m, it can easily be seen that the scaled osmotic pressure and shear modulus do not superimpose for different droplet sizes. The trend of film thickness dependency versus volume fraction suggests that the film thickness increases with an increasing droplet size.

It could be interesting to see, regarding this repulsive force, how much the introduced term in the free energy equation affects the final properties in a fixed interfacial tension and droplet size (Fig. 6).

In order to evaluate the difference between adhesive and repulsive disjoining pressure, we chose the other soft repulsive potential, $f_{dis}(h) = A \exp(-kh)$. The power-law potential is not suitable in this case,

because if film thickness approaches zero, the adhesive force tends to infinity. The k was considered as $1 \mu\text{m}^{-1}$ and a negative value of A means an adhesive interaction between droplets. The results, Fig. 7, are very interesting, as the negative osmotic pressure, $A = -0.0002$, means the emulsion is not stable: the droplets will flocculate and the continuous phase drains automatically.

3.2. Comparing Different Approximations

The difference of approximations should be evaluated in order to be aware of the dependency of obtaining the models' parameters by curve fitting and/or choosing the proper model for further studies. The initial film thickness for approximate cases was chosen as the value obtained by optimized film thickness models at ϕ^* . Figure 8 demonstrates that the results of an approximate method which can be approached analytically are in good agreement with the accurate optimization method. ($A = 2E-22$ and $f_{dis}(h) = A/h^2$).

4. EXPERIMENTAL INVESTIGATION OF MODEL

4.1. Reciprocal Squared Diameter Dependency of Shear Modulus

Although the models of both Princen [3, 4] and Lacasse et al. [12, 13] predict the scaling of shear modulus with a reciprocity of droplet size diameter, in previous works [14, 33, 34] it was shown that the shear

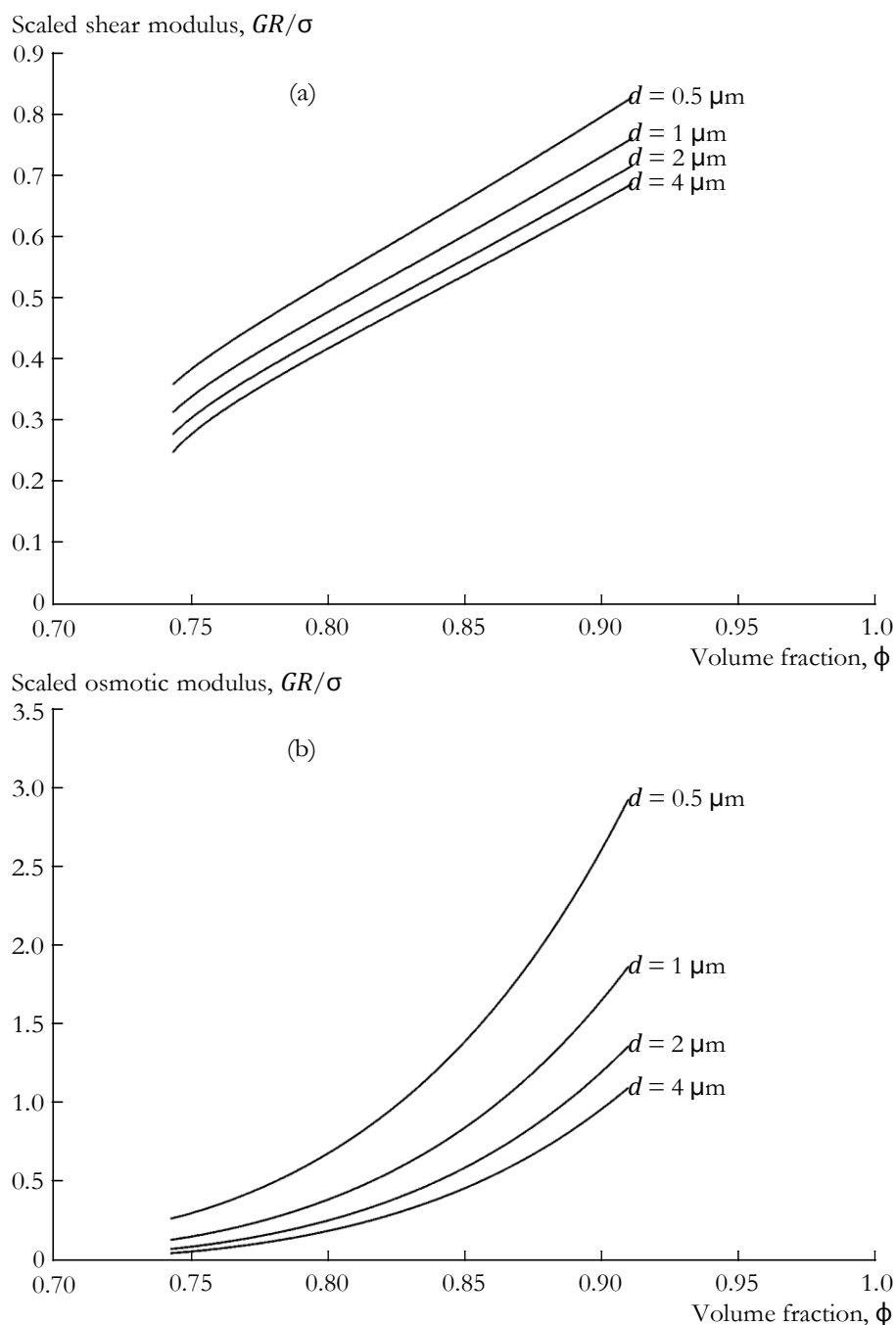


Fig. 5. The effect of droplet size on (a) the shear modulus, (b) osmotic pressure and (c) film thickness.

modulus of these highly concentrated emulsions deviate from Princen's theory, and that the shear modulus scales by the reciprocity of squared diameter rather than the reciprocity of the diameter of droplets. The same behaviour was observed by Mougel et al. [32] and Alvarez-Solano [34] for highly concentrated emulsions with a nonionic surfactant which was attributed to the van der Waals interaction between droplets.

In order to recognize the physics behind this observation, it is reasonable to rearrange Eq. (42) to express

the Gd^2 dependence, while its derivation with respect to diameter should be zero. By means of this approach, it can be shown that:

$$d \frac{\partial^2 f_{\text{dis}}(h_{\text{opt}})}{\partial d^2} + 2df_{\text{dis}}'(h_{\text{opt}}) + \sigma g(\phi) = 0, \quad (44)$$

where g is a function of compressed droplet geometry. By solving this differential equation and assuming a linear dependency of film thickness to the droplet size,

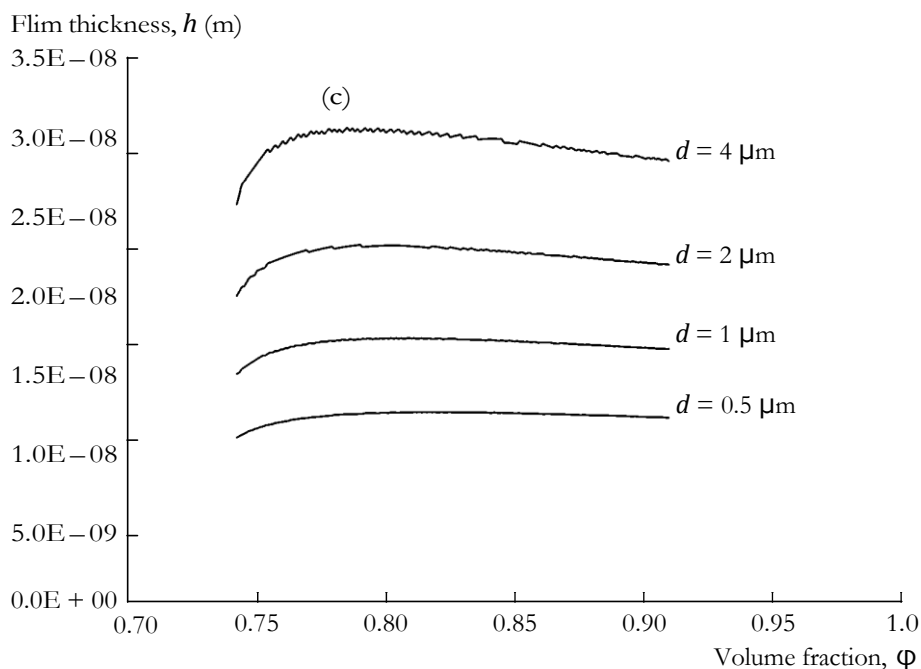


Fig. 5. Contd.

the interdroplet free energy per unit area for developing the required dependency will be as follows:

$$f_{\text{dis}}(h) = \frac{C_0}{h^2} - \frac{C_1 \log(\Phi)}{h} = \frac{C_0}{h^2} - \frac{C_1}{h} \quad (45)$$

$$\rightarrow \Pi_{\text{dis}}(h) = -\frac{2C_0}{h^3} + \frac{C_1}{h^2},$$

where C_0 is the integration constant which can be zero, negative or positive; while the second term only reflects the interfacial term; and if the interfacial tension and/or the geometrical coefficient is small (Φ slightly higher than Φ^*), the second term will be negligible. It should also be noted that because the film thickness is numerically very small, the first term will be dominant in any case. Therefore, a disjoining pressure formally similar to the van der Waals interaction⁴ results in a squared diameter dependency of shear modulus. This correlates with the results of our experimental works [14, 33], as well with publications [32, 34] where the authors used nonionic surfactant for which the main interdroplet interaction seems to be of the van der Waals type.

The interesting point in this case is that the shear modulus is not directly dependent on the interfacial tension, or in other words, shear modulus doesn't scale with interfacial tension at all. The typical model analysis in the preceding section also shows that even

a small value of C_0 results in the deviation from models being based on only geometric consideration.

4.2. Explosive Emulsions

Preparation and characterization. Highly concentrated emulsions of the explosive type were used in this part of study. These materials were described in detail in earlier publications [14, 16, 33, 35, 48 – 50]. Consequently, only some of principle features need to be repeated here. The samples are emulsions of the water-in-oil type, with a concentration of the aqueous phase up to 96 wt. %. The liquid droplets have a polygonal shape and consist in a super-cooled aqueous solution of 80 wt % ammonium nitrate which is in the state of hydrous melt where ions can move about easily [51]. These emulsions are visco-plastic materials showing a strong non-Newtonian behaviour at stresses exceeding certain limits, treated as the yield stress. The dissolution temperature of ammonium nitrate in large bulk volumes is typically higher than 50°C, while the crystallization range is 51 – 65°C. The samples were prepared through intensive milling of the components by a Hobart N50, USA, mixer at 80°C, before quickly cooling it to 20 – 25°C. Droplet size distribution of emulsions was measured using a Malvern Mastersizer-2000 instrument.

Emulsion samples were tested using a MCR300 (Paar Physica) rheometer with sandblasted plate-plate geometry. Dynamic measurements were executed in the amplitude sweep regime and the resultant plateau of storage modulus - which is also the frequency independent shear modulus - was used in this modelling

⁴ As it was mentioned before, the van der Waals interaction in the vacuum media is attractive, but using other media can result in a repulsive van der Waals interaction between two bodies [37].

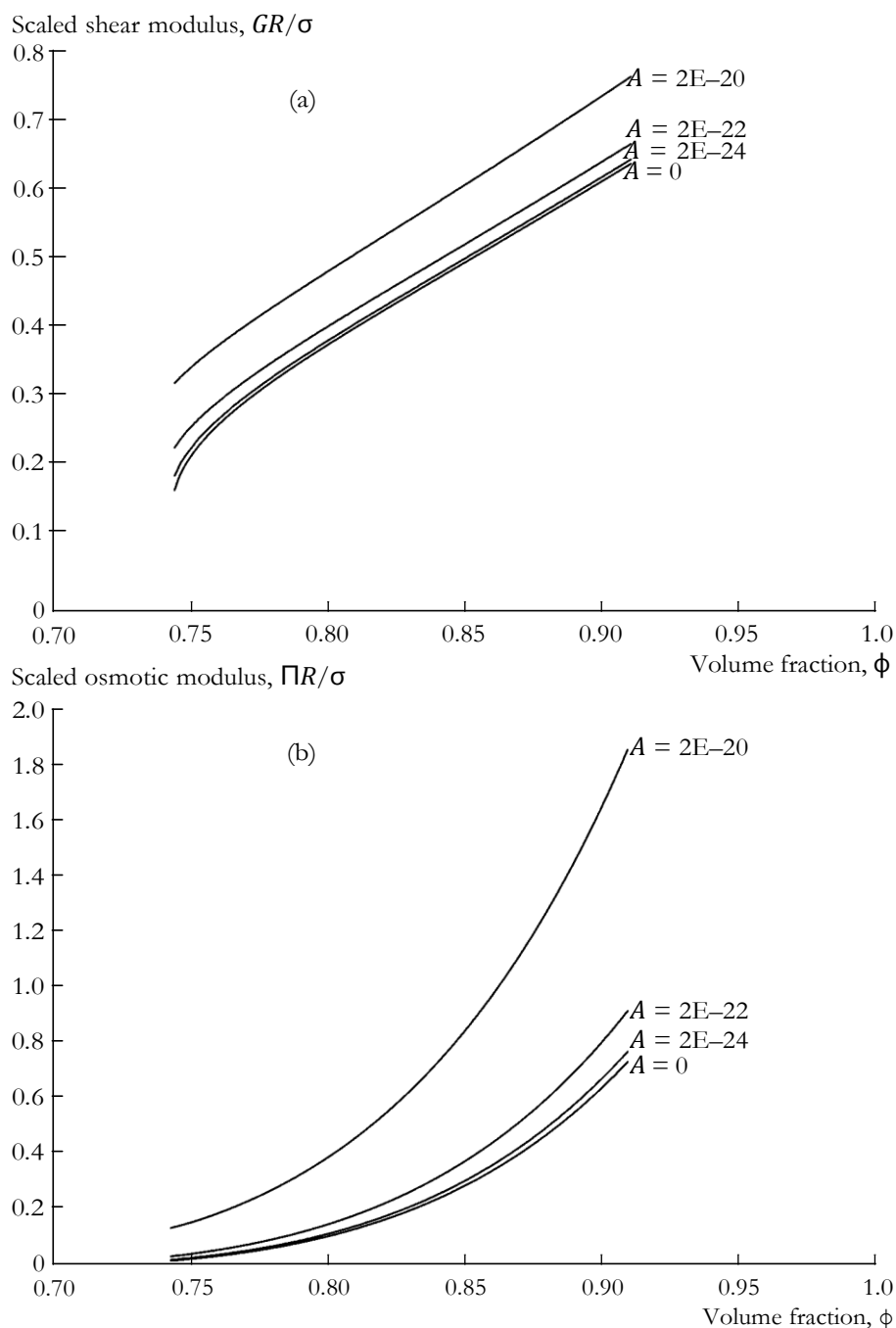


Fig. 6. The effect of interdroplet interaction gain on (a) the shear modulus, (2b) osmotic pressure and (c) film thickness ($\sigma = 0.002 \text{ N/m}$, $d = 1 \text{ }\mu\text{m}$).

study. All the experiments were carried out regularly at 30°C .

In order to demonstrate the effect of interdroplet interaction on the rheological properties of emulsion, highly concentrated water-in-oil emulsions with three different surfactants (PIBSA-MEA, PIBSA-Imide, and PIBSA-Urea supplied by Lake International Technologies, South Africa - see Fig. 9 for their chem-

ical structure) and different droplet sizes but similar droplet size distribution were prepared.

The concentration of the aqueous phase in all emulsions was 92 wt %, comprising 80 wt % ammonium nitrate, which means that the volume fraction of the dispersed phase is about 0.87. The oil phase was based on hydrocarbons containing 14 wt % dissolved surfactant. The interfacial characteristics of these sur-

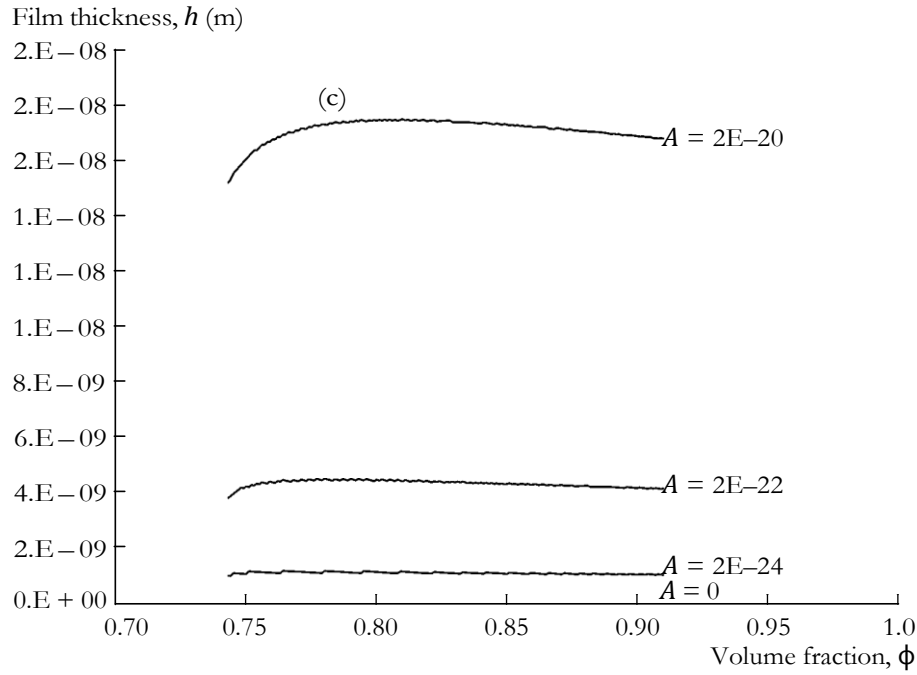


Fig. 6. Contd.

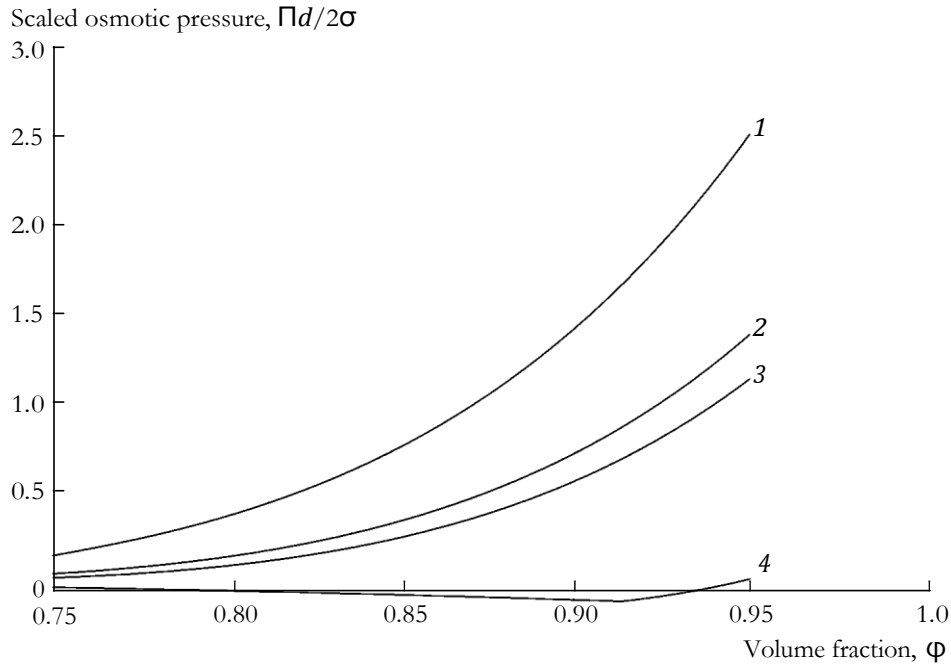


Fig. 7. Comparison of adhesive and repulsive disjoining pressure on the osmotic pressure for different A values: (1) $2E-3$, (2) $2E-4$, (3) $-2E-4$, and (4) $-2E-3$; $\sigma=0.002\text{N/m}$, $d=5\mu\text{m}$.

factants were measured by Kruss K100 and are summarised in Table 3.

Results. In Fig. 10, typical droplet size distributions of emulsions prepared by different surfactants

with equal mean droplet size are shown. The similarity of the mean droplet size and droplet size distribution means that the interfacial energy is the same, while the rheological results (Fig. 11) are different. These results

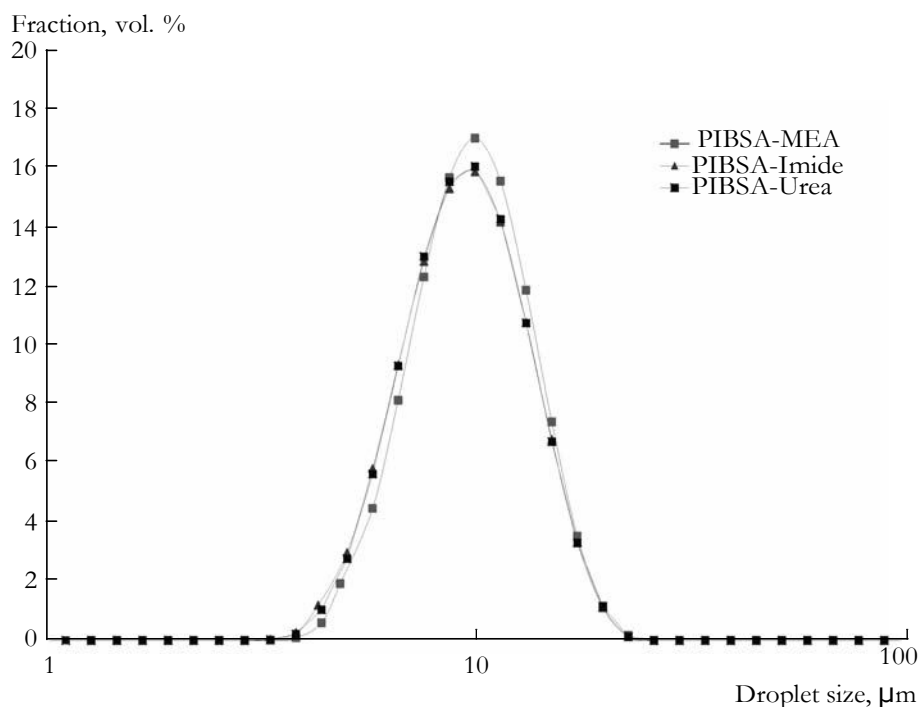


Fig. 10. Typical droplet size distributions for emulsions prepared with different surfactants and the same mean droplet size of 10 μm measured by Mastersizer.

easily checked, as shown in Fig. 11a. In this figure, the solid and dashed lines present the 3-D geometrical model (Eq. (41) and Princen's model, respectively. As the shear modulus does scale with the reciprocal squared diameter, Fig. 11b, it can be concluded that a disjoining pressure formally similar to the van der Waals one plays a significant role in these emulsions.

In order to investigate the dominant mechanism controlling the properties of explosive emulsions, we, in the following section, will try to compare the interdroplet interaction resulting from different possible sources for PIBSA-MEA surfactant, for which the micellar properties can be found in the literature [52, 53].

Interoptlet interactions. The micellar properties of the PIBSA-MEA surfactant in highly concentrated emulsions comprising a super-cooled aqueous solution of 80 wt % ammonium nitrate were measured by Reynolds et al. [52, 53]. By fitting the small angle neutron scattering results, they showed that this surfactant forms micelles in the oil phase and is also adsorbed to the interface. According to their results [53], the radius and volume fraction of micelles in an oil phase containing 14% PIBSA-MEA surfactant can be estimated respectively as 32.1 Å and 0.10, by using interpolation. The aggregation number of micelles was found to be about 13.5 – 14.6 for different surfactant concentrations [53].

The second important structural force is the interaction between polymeric surfactant adsorbed at the interface of droplets. If we assume that the oil that is

used is a theta solvent for a PIBSA-based surfactant, the interaction can be predicted by Dolan and Edwards' theory [54].

The next interdroplet interaction that should be considered is the van der Waals force between two droplets containing a hydrous melt of ammonium

nitrate [51], which means NH_4^+ and NO_3^- ions can move freely in the dispersed aqueous phase. In order to estimate the van der Waals interaction, the Hamaker constant, A_H , for the symmetric configuration of two identical phases "i" interacting across a medium "j" can be calculated from Lifshitz' theory:

$$A_H = \frac{3kT}{4} \frac{(\epsilon_i - \epsilon_j)^2}{\epsilon_i + \epsilon_j} + \frac{3h_p \nu_e (n_i^2 - n_j^2)^2}{16\sqrt{2}(n_i^2 + n_j^2)^{3/2}}, \quad (46)$$

where ϵ_i and ϵ_j are the dielectric constants of phases i and j , n_i and n_j are the respective refractive indices for visible light, h_p is the Planck constant, and ν_e is the main electronic absorption frequency [37]. The first term on the right hand side of this equation, which expresses the contribution of the orientation and induction interactions, can never exceed $3/4kT$ [38]. The second term, which accounts for the dispersion interaction, is zero for our explosive emulsion, because the refractive indices of aqueous and oil phases are the same (~ 1.445), resulting in transparent explosive emulsions.

The variation of these three interactions free energy per unit area and their total interaction for explosive

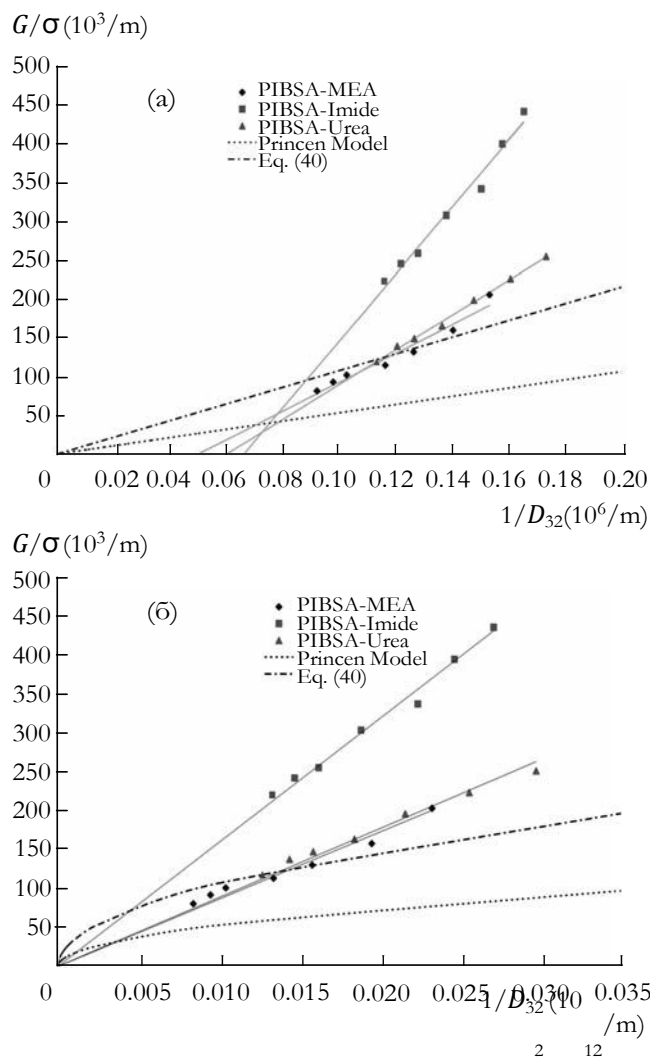


Fig. 11. The scaling study of shear modulus, (a) with reciprocal diameter, and (b) with reciprocal squared diameter.

emulsions is presented in Fig. 12. By applying the obtained total interaction energy in the model and solving it, it was found that, for our experimental range of droplet sizes, the film thickness is about 1.5 nm and the scaled shear modulus, GR/σ , increases by only 0.2%. Therefore, the higher shear elasticity of samples can be attributed to the other sources, such as the electrostatic interdroplet interaction or mechanical repulsion between droplets.

The electrostatic interaction for aqueous droplets in an oil phase has not been studied extensively. Since it was found, in the explosive emulsions, that the head-group of a surfactant forms hydrogen bonding with NH_4^+ ions of the dispersed phase [55], and therefore these ions concentrate close to the interface, electrostatic repulsion between surface layers of droplets seems to contribute to the disjoining pressure. However, for the calculation of this electrostatic interaction, the extent of ionization of ammonium nitrate in

an oil phase should be manifested or some simplifying assumptions should be made.

5. CONCLUSION

The complete model for a highly concentrated emulsion was presented. The model combines the frequently discussed effect of the increase of the surface area in so-called “compressed emulsions”, and the disjoining pressure which can be introduced by the developed optimization or approximation methods. The model quantitatively explains the reciprocal squared diameter dependency of an elastic modulus which is reported in the literature. It was shown that an interaction similar to the van der Waals type can be responsible for this observation. Finally, the model was used to explain the unusual elasticity of a highly concentrated water-in-oil explosive emulsion. It was shown that the contributions by the micellar, steric and van der Waals forces to the elasticity are negligible,

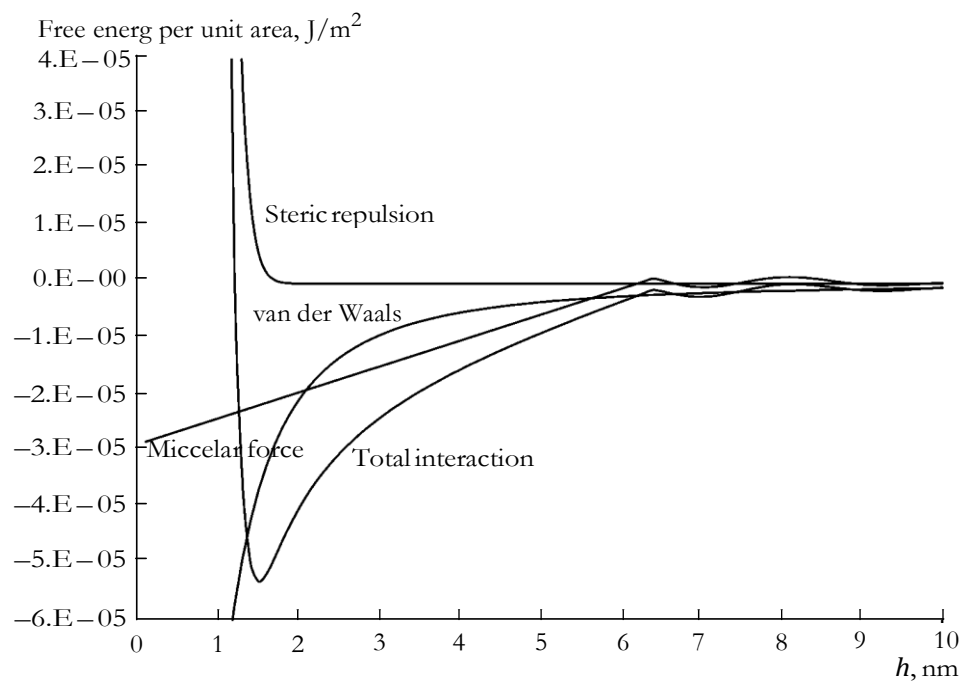


Fig. 12. The total free energy per unit area and its steric, van der Waals, and micellar components.

but an electrostatic interaction of surface layers containing adsorbed NH_4^+ ions may explain this unusual elasticity.

We thank Siphon Mudeme for his assistance in carrying out the experimental part of the work and Dr. Bernard Costello for measuring the interfacial characteristics, African Explosive Limited for their financial support of this study, and the Lake International Co. for supplying the surfactants.