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Statistical mechanical properties of dense emulsions and microemulsions

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The impact of droplet deformability on the macroscopic properties of emulsions and microemulsions is studied. The deformation energy at the pair level is utilized in the Percus-Yevick closure for solving the Ornstein-Zernike equation. Thus the radial distribution functions and structure factors for deformable droplets are calculated and compared with the respective hard sphere results to reveal the effect of the deformation. The variation of the osmotic pressure with the droplet volume fraction for the same systems is obtained by the Percus-Yevick integral equation method. It is shown that the droplet deformability may lead to a considerable reduction of the osmotic pressure of emulsions and microemulsions. A semiempirical equation of state based on modifying the Carnahan-Starling expression is suggested and compared to the Percus-Yevick results. [S1063-651X(96)07612-X]

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I. INTRODUCTION

Emulsions and microemulsions are colloidal dispersions of liquid in liquid. They are of great industrial importance, but also present academic interest providing many fundamental problems. Experimental studies of emulsions show that in many cases the droplets may exhibit a substantial deformation when in contact with each other [1]. The deformability is usually neglected in a theoretical treatment of submicrometer emulsions (miniemulsions) and microemulsions, assuming that the small sizes of the droplets provide a sufficiently high capillary pressure which leads to a hard-sphere-type behavior. This is true for oil-water systems with high interfacial tension. It was shown recently [2–7] that in many cases the hard sphere concept is not relevant, and that the droplet deformation should be incorporated into the overall interaction energy. This energy was calculated at a pair (dilute) level, assuming that the interacting droplets obtain the shape of truncated spheres as shown in Fig. 1. This model shape allowed the derivation of an exact expression for the van der Waals interaction energy, and an approximate calculation of other long range forces, e.g. electrostatic, depletion and steric forces, as well as contributions due to surface extension and bending [3,6]. It was also shown that such an idealized model shape gives sufficiently accurate results when compared to calculations based on solving the augmented Laplace equation for the real droplet shape [5].

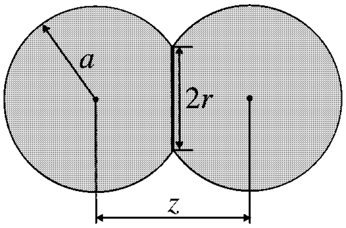

FIG. 1. Two deformed droplets. a is the droplet radius and r is the radius of the flat region.

In the present paper we extend our studies to dense miniemulsions and microemulsions. Our purpose is to relate the microscopic droplet deformability to the structure of such systems, and further to macroscopic properties as the osmotic pressure. In order to obtain these results we numerically solve the Percus-Yevick integral equation [8]. The solution allows us to obtain the radial distribution function and static structure factor for deformable droplets as well as the equation of state for the osmotic pressure vs the volume fraction of droplets. A semiempirical equation of state, based on modifying the Carnahan-Starling semiempirical expression [9] is suggested and compared to the results from the Percus-Yevick approach. In the following sections we first discuss the pair energy of the interdroplet interaction, accounting for the deformability contributions, and then we briefly present the Percus-Yevick approach. Section IV deals with the semiempirical equation of state, based on the modified Carnahan-Starling expression. Section V contains results and discussions, and Sec. VI summarizes the concluding remarks.

II. PAIR INTERACTION ENERGY

We consider a system of monodisperse fluid droplets in a suspending liquid. The pair energy of the interaction between two deformable droplets could be assumed to consist of different contributions. Expressions for these contributions were derived and analyzed in detail [3,4,6]. In this study, however, we will confine ourselves to account only for the possible effects of the surface bending and area extension energies. These two contributions have proven to be the most important for some systems of practical interest such as microemulsions and emulsions, stabilized by nonionic surfactants [7]. Below we consider two model systems: microemulsions, where only the bending energy will be taken into account, and miniemulsions, where the interaction is due to the surface extension energy.

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A. Microemulsions: surface bending energy

The bending contribution to the pair interaction energy, W^C, for weakly deformed droplets $(1-z/2a\ll 1)$ is given by the following expression [3,6,7]:

$$W^C(\tilde z)=16\pi(1-\tilde z)\frac{k_C}{\tilde R_0}\left(1-\frac{\tilde R_0}{2}\right),\quad \tilde z<1$$
$$=0,\quad \tilde z>1, \tag{1}$$

where $\tilde z = z/2a$ is the distance between the droplet mass centers divided by the droplet diameter $2a$. There are two physically important parameters which control the deformation: k_C is the bending elasticity constant, and $\tilde R_0 = R_0/a$ is the radius of the spontaneous curvature divided by the droplet radius a. The greater the energy, the harder the droplets. In some practical cases, the bending contribution could be varied by changing the temperature and therefore the radius of the spontaneous curvature [7]. The bending energy could be important for larger (miniemulsion) droplets as well [6], but for clarity we will take it into account only in the microemulsion case.

B. Miniemulsions: surface area extension energy

In this case we consider the energy contribution due to the change of the droplet surface with the deformation W^S. Again for small deformations, the following expression holds [3,6,7]:

$$W^S(\tilde z)=2\pi a^2\gamma(1-\tilde z)^2,\quad \tilde z<1$$
$$=0,\quad \tilde z>1, \tag{2}$$

where γ is the interfacial tension which controls the droplet deformability. This expression could be completed with a term accounting for the Gibbs elasticity, but the latter is neglected in the present study. The greater the interfacial tension, the harder the droplets. This type of interaction energy refers to the miniemulsion case.

III. PERCUS-YEVICK APPROXIMATION FOR DEFORMABLE DROPLETS

Our purpose is to determine the radial distribution function $g(\tilde z)$, which is the probability of finding a droplet at a given distance $\tilde z$ from another one. This can be done by numerically solving the Ornstein-Zernike equation

$$h(\tilde z)=c(\tilde z)+\frac{6\Phi}{\pi}\int d\tilde{\mathbf{z}}'\,c(\tilde{\mathbf{z}}')\,h(|\tilde{\mathbf{z}}-\tilde{\mathbf{z}}'|), \tag{3}$$

where $h(\tilde z)=g(\tilde z)-1$ is the total correlation function and the unknown direct correlation function $c(\tilde z)$ is obtained by the Percus-Yevick closure [8]

$$c(\tilde z)=\left[1-\exp\left(\frac{W(\tilde z)}{kT}\right)\right]g(\tilde z), \tag{4}$$

where kT denotes the thermal energy. Equations (3) and (4), together with the expression for the potential $W(\tilde z)$ [Eqs. (1) or (2)], allow us to determine the radial distribution function $g(\tilde z)$ as well as the dependence of the osmotic pressure, P_{OS}, on the volume fraction of the droplets, Φ, from the relationship [8]

$$\frac{P_{\mathrm{OS}}}{nkT}=1-\frac{\Phi}{\pi kT}\int d\tilde z\,\frac{dW(\tilde z)}{dz}\,g(\tilde z), \tag{5}$$

where n is the particle number density.

Another measurable quantity is the structure factor of the emulsion or microemulsion which is [8]

$$S(\tilde q)=1+24\Phi\int d\tilde z\;\tilde z^2\left(\frac{\sin\tilde q\,\tilde z}{\tilde q\,\tilde z}\right)[1-g(\tilde z)]. \tag{6}$$

With q we denote the wave vector and $\tilde q = 2qa$. The structure factor may be obtained by light scattering experiments [10].

Hence we may adopt the following algorithm: the pair energy, which depends on the interfacial bending [Eq. (1)] or surface area extension [Eq. (2)], is introduced in the Percus-Yevick closure expression (4). Combining Eq. (4) with the Ornstein-Zernike equation (3) one may solve the radial distribution function. Knowing this quantity, all thermodynamic functions could be obtained [8].

IV. CARNAHAN-STARLING EXPRESSION FOR DEFORMABLE DROPLETS

For systems consisting of hard spherical particles, the most accurate equation of state is given by the Carnahan-Starling semiempirical expression [8,9]

$$\frac{P_{\mathrm{OS}}}{nkT}=\frac{1+\Phi+\Phi^2-\Phi^3}{(1-\Phi)^3}. \tag{7}$$

It is tempting, therefore, to apply this expression to deformable fluid particles as well. One possible way to incorporate other than hard sphere interactions in the Carnahan-Starling expression is based on the use of perturbation methods [8]. Such an approach was used by Brout to account for weak attractive interaction [11]. It seems quite natural to apply the perturbation method for weakly deformable spheres. However, the perturbation term, added to the pure hard sphere part — Eq. (7)—is presented by an integral over the perturbation energy multiplied by the *hard sphere* radial distribution function. Since the deformability manifests itself for distances smaller than the droplet diameter, such a term will be always zero. Therefore, the conventional perturbation theory is not relevant to the case of interacting deformable droplets. As an alternative we offer the following approach. We define an effective volume fraction

$$\Phi^{\mathrm{EFF}}=\frac{B_2}{B_2^{\mathrm{HS}}}\Phi, \tag{8}$$

with B_2 being the second osmotic virial coefficient,

$$B_2=12\int d\tilde z\left[1-\exp\left(\frac{W(\tilde z)}{kT}\right)\right]\tilde z^{\,2}, \tag{9}$$

and $W(\tilde z)$ is given by Eqs. (1) or (2). $B_2^{\mathrm{HS}}=4$ is the virial coefficient for hard spheres. Introducing the effective volume fraction, defined by Eq. (8) in the Carnahan-Starling expression (7) we obtain a formula relating the osmotic pressure of

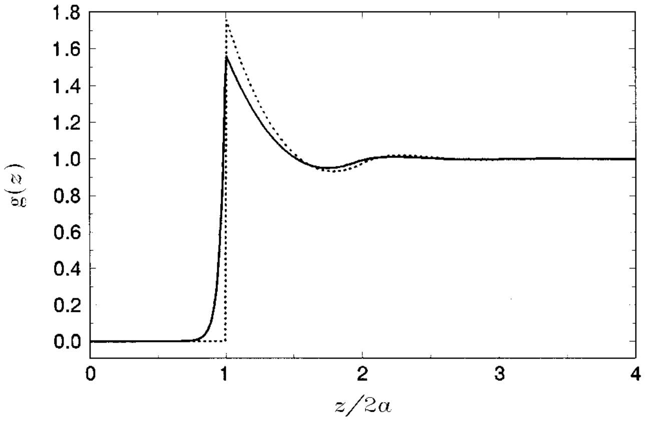

FIG. 2. Radial distribution function for microemulsion droplets (solid curve) compared with hard spheres (dotted curve). Parameters: $k_C = kT$, $\tilde{R}_0 = 1$, and $\Phi = 0.21$.

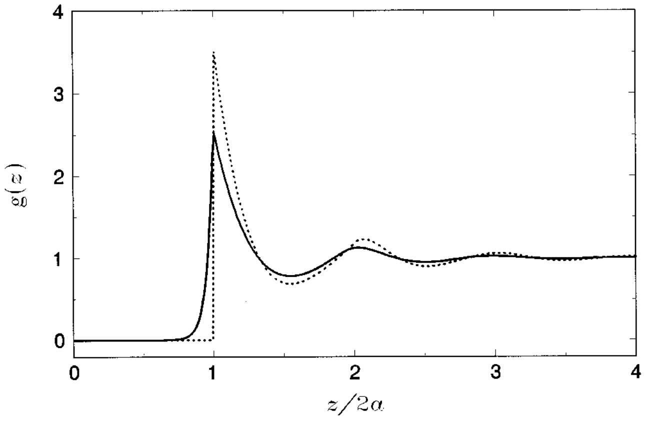

FIG. 4. Radial distribution function for microemulsion droplets (solid curve) compared with hard spheres (dotted curve). Parameters: $k_C = kT$, $\tilde{R}_0 = 1$, and $\Phi = 0.42$.

the emulsion or microemulsion to the volume fraction of droplets and their interfacial properties (surface area extension and bending). Such an approach is less rigorous than that, based on solving the Ornstein-Zernike equation (3), but is much simpler and faster. As we show below, the results seem to be quite reasonable.

V. RESULTS AND DISCUSSION

A. Radial distribution function

Figure 2 depicts a comparison between the radial distribution functions for deformable microemulsion droplets (solid curve) and hard spheres with the same radius (dotted curve), obtained from Eqs. (3) and (4). The pair energy of interaction in this case is given by Eq. (1). The parameters used in the calculation are $k_C = kT$, $\tilde{R}_0 = 1$, and $\Phi = 0.21$. The influence of the deformability is clearly seen in the figure. The radial distribution function for the microemulsion droplets is not zero for $\tilde{z} < 1$, due to the fact that the softness of the fluid particles allows them to approach at distances smaller than their diameter. Figure 3 shows the respective structure factor of the microemulsion (solid curve) and hard spheres (dotted curve) — see Eq. (6). Although some difference is present it is probably too small to be detected by a light scattering experiment.

Figure 4 shows a microemulsion radial distribution function (solid curve) compared with hard spheres (dotted curve) at a higher volume fraction $\Phi = 0.42$. The other parameters are the same as in Fig. 2. The radial distribution displays enhanced structuring due to the larger volume fraction, but shows a similar trend for $\tilde{z} < 1$ as for the lower volume fraction. However, the local ordering is considerably less pronounced for deformable droplets than it is for hard spheres. The main peak is smaller as well as the other peaks, corresponding to the next neighbor shells. Hence the ordering in emulsions decays more rapidly with distance due to the droplet deformability. Figure 5 illustrates the corresponding structure factor. The difference between deformable (solid curve) and hard spheres (dotted curve) in this case is large enough to expect that it could be detected by the experiment.

Figure 6 displays the radial distribution function for the emulsion, with the volume fraction $\Phi = 0.21$. In this case the droplet deformability is controlled by the surface area extension energy through the interfacial tension according to Eq.

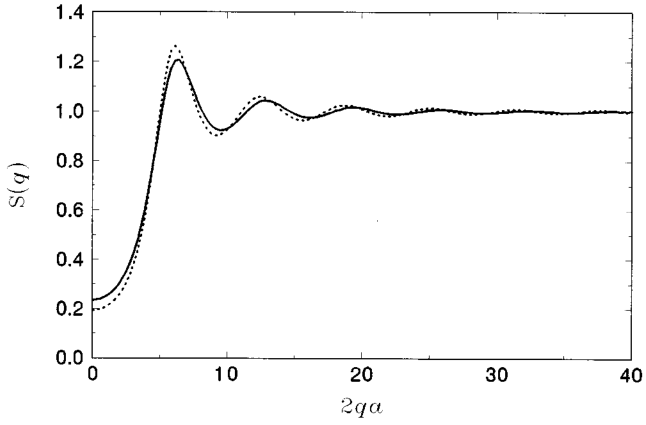

FIG. 3. Structure factor for microemulsion droplets (solid curve) and hard spheres (dotted curve). The parameters are the same as in Fig. 2.

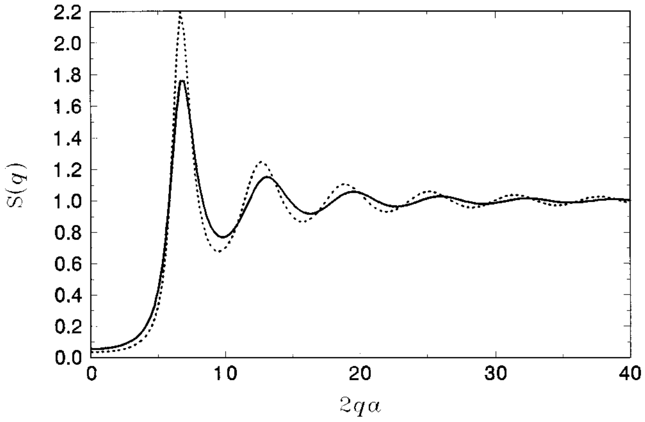

FIG. 5. Structure factor for microemulsion droplets (solid curve) and hard spheres (dotted curve). The parameters are the same as in Fig. 4.

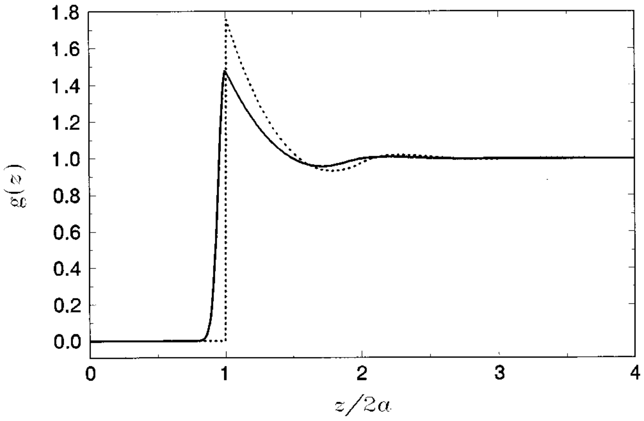

FIG. 6. Radial distribution function for emulsion droplets (solid curve) compared with hard spheres (dotted curve). The parameters used in the calculation are $\pi a^2\gamma/kT=760$ and $\Phi=0.21$.

(2). The calculations are for $\pi a^2\gamma/kT=760$. This could be, for example, the emulsion of 100-nm droplets with $\gamma=0.1$ mN/m. The behavior of the radial distribution function is similar to the case of microemulsions, with the deformability controlled by the interfacial bending. The radial distribution function again has a nonzero region for $\tilde{z}<1$. The situation at a higher volume fraction $\Phi=0.42$ (see Fig. 7) also resembles the microemulsion result. The local ordering of the deformable droplets is again suppressed in comparison with the hard sphere case, as it was for microemulsions.

B. Osmotic pressure

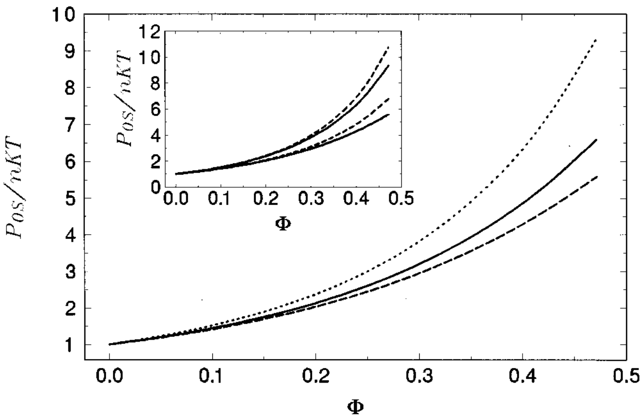

FIG. 8. Osmotic pressure calculated from the Percus-Yevick approach for microemulsion droplets with $\tilde{R}_0=1$ (solid curve), $\tilde{R}_0=1.2$ (dashed curve) and for hard spheres (dotted curve). $k_C=kT$ for all microemulsion curves. The inset presents a comparison between Percus-Yevick (solid curves) and Carnahan-Starling (dashed curves) results for hard spheres (upper pair) and microemulsion droplets with $\tilde{R}_0=1.2$ (lower pair).

The osmotic pressure is calculated both by means of the Percus-Yevick approach, using Eq. (5) or with the help of the Carnahan-Starling expression, Eq. (7), introducing the effective volume fraction—see Eq. (8). The results are plotted in Fig. 8. The main plot of Fig. 8 shows the Percus-Yevick results for deformable microemulsion droplets where the solid curve is for $\tilde{R}_0=1$, the dashed curve is for $\tilde{R}_0=1.2$, and where the dotted curve corresponds to the hard sphere case. The droplet deformability increases with the radius of spontaneous curvature, $\tilde{R}_0$ [7], and this leads to a reduced osmotic pressure. This is an expected result since the softer the droplets, the lower the pressure. The effect of the deformability on the osmotic pressure is rather substantial. The decrease in comparison with hard spheres is about 30% for $\tilde{R}_0=1$ and about 40% for $\tilde{R}_0=1.2$. The inset of Fig. 8 illustrates the comparison between Percus-Yevick (solid curves) and modified Carnahan-Starling results (dashed curves) for hard spheres (upper pair) and deformable droplets with $\tilde{R}_0=1.2$ (lower pair). For both cases the use of the Carnahan-Starling type of equation of state leads to higher

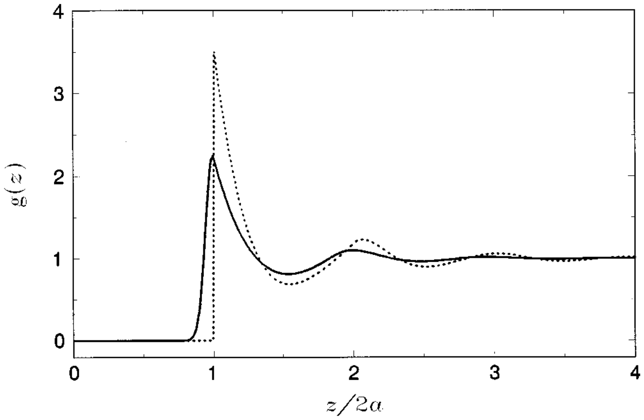

FIG. 7. Radial distribution function for emulsion droplets (solid curve) compared with hard spheres (dotted curve). The parameters used in the calculation are $\pi a^2\gamma/kT=760$ and $\Phi=0.42$.

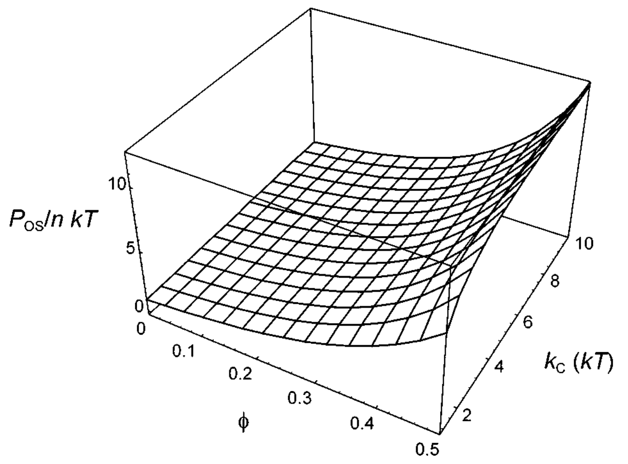

FIG. 9. Three-dimensional (3D) plot of the osmotic pressure for the microemulsion vs the volume fraction and the bending elasticity constant. $\tilde{R}_0=1.2$.

osmotic pressures than those obtained by means of the Percus-Yevick approach. It is known, however, that for hard spheres the semiempirical expression is more accurate than any integral equation result because of the closure approximations involved [8,12]. The differences between the two results are qualitatively the same for both hard and deformable spheres—the pressures calculated by the Carnahan-Starling expression are higher than those derived from the Percus-Yevick approach. One may speculate, therefore, that the simpler expression (7), together with Eqs. (8) and (9) may be even more accurate than the rigorous integral equation results. Such a speculation could be justified by appropriate experiments on osmotic pressures in emulsions and microemulsions.

Figure 9 shows a generalized picture of the osmotic pressure as a function of the volume fraction and the bending elasticity constant for the microemulsion system. Equations (7)–(9) were used for this calculation with $\tilde{R}_0 = 1.2$. Figure 10 illustrates the emulsion case for droplets with radius $a = 100$ nm. Both figures show that the effect of the droplet deformation is most substantial for droplets of low bending elasticity and/or interfacial tension, and at high volume fractions.

VI. CONCLUDING REMARKS

In the present paper we study the statistical mechanical properties of fluid Brownian particles (miniemulsions and microemulsions), taking into account the interfacial deformability of the droplets. We show that the effect of the deformability could lead to significant change in the macroscopic parameters of the system as the osmotic pressure. This is important for oil-water mixtures with low interfacial tension and bending energy as is the case for many oil-water-surfactant mixtures of practical importance [13]. Typically one should have $k_C \leqslant kT$ and $\tilde{R}_0 \geqslant 1$ for microemulsions and $\pi a^2 \gamma / kT \leqslant 10^3$ for miniemulsions in order to be able to account for deformability effects.

An important restriction of our consideration is the assumption of the monodispersity of the systems. Microemulsions are usually monodisperse since they are thermodynamically stable and their radius is fixed from thermodynamic constraints. Emulsions, conversely, are usually rather polydisperse. It was shown recently, however, that monodisperse emulsion sample could be obtained for use in model experimental studies [14].

Another assumption is the attribution of the overall interdroplet interaction to pure bending or interfacial area extension contributions. In reality there are many other possible interactions which could be present and affect the total pair energy, such as van der Waals, electrostatic, depletion, steric, etc. [3,4,6]. The incorporation of all these contributions into the present approach is straightforward. When long range interactions (like van der Waals and electrostatic) are present, additional integration is needed in order to average the pair energy with respect to all possible radii of the formed thin liquid film between the droplets [4,6],

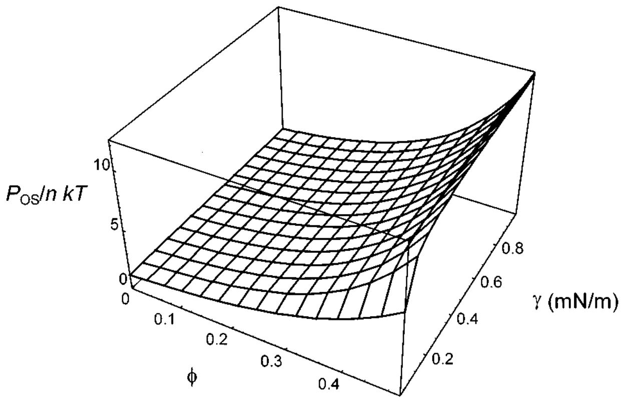

FIG. 10. 3D plot of the osmotic pressure for the emulsion vs the volume fraction and the interfacial tension. $a = 100$ nm and $T = 298$ K.

$$\overline{w(\tilde{z})} = kT \ln\left\{ \frac{4}{\Gamma(1/4)} \left(\frac{\pi a^2 \gamma}{2kT} \right)^{1/4} \int d\tilde{r} \, \exp\left[-\frac{W(\tilde{h}, \tilde{r})}{kT} \right] \right\}, \tag{10}$$

where $\tilde{h} = h/a$ and $\tilde{r} = r/a$ are the dimensionless film thickness and radius respectively. $\Gamma(x)$ is the gamma function, and $\Gamma(1/4) = 3.625609908\ldots$. In this case the pair energy, defined by Eq. (10) should be introduced into the closure (4) in order to obtain the thermodynamic parameters of the system.

Our purpose in this paper, however, was to point the importance of the droplet interfacial deformability only on the macroscopic behavior of emulsions and microemulsions. In addition, there are many cases in which these long range contributions (e.g., electrostatic and van der Waals) could be neglected without loss of accuracy [7].

The use of the Percus-Yevick closure (4) is also an approximation, necessary to solve Eq. (3). More accurate results could be obtained by numerical simulations, although they will not qualitatively change the general trends in the behavior of systems of deformable droplets. Another quantitative check of the suggested model could be a direct comparison with experimental results. One possibility is to measure the structure factor of such emulsions or microemulsions, as suggested above. Another one is to measure the osmotic pressure of such systems at different volume fractions of droplets. The latter approach seems more appropriate since the effect of the droplet deformability on the osmotic pressure is rather substantial. Therefore we believe that some efforts in these directions deserve to be performed in the future.

The consideration presented in this paper could be useful in studying the stability and equilibrium properties of emulsions and microemulsions. It could also provide a background for modeling the rheology of such systems (knowing the compressibility) which is of great industrial importance.

ACKNOWLEDGMENT

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[1] M. P. Aronson and H. Princen, Nature (London) **286**, 370 (1980); Colloids Surf. **4**, 173 (1982).

[2] N. D. Denkov, P. A. Kralchevsky, I. B. Ivanov, and C. S. Vassilieff, J. Colloid Interface Sci. **147**, 508 (1991).

[3] K. D. Danov, D. N. Petsev, and N. D. Denkov, J. Chem. Phys. **99**, 7179 (1993).

[4] N. D. Denkov, D. N. Petsev, and K. D. Danov, Phys. Rev. Lett. **71**, 3226 (1993).

[5] N. Denkov, D. N. Petsev, and K. D. Danov, J. Colloid Interface Sci. **176**, 189 (1995).

[6] D. N. Petsev, N. D. Denkov, and P. A. Kralchevsky, J. Colloid Interface Sci. **176**, 201 (1995).

[7] P. D. I. Fletcher and D. N. Petsev, J. Chem. Soc. Faraday Trans. (to be published).

[8] R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, London, 1975).

[9] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 636 (1969).

[10] J. W. Goodwin and R. H. Ottewill, J. Chem. Soc. Faraday Trans. **87**, 357 (1991).

[11] R. Brout, *Phase Transitions* (Benjamin, New York, 1965).

[12] J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).

[13] R. Aveyard, B. P. Binks, P. D. I. Fletcher, X. Ye, and J. R. Lu, in *Emulsions — A Fundamental and Practical Approach*, edited by J. Sjoblom (Kluwer, Amsterdam, 1992)

[14] J. Bibette, J. Colloid Interface Sci. **147**, 474 (1991).