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The structure of deformable particles in applied external fields

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Abstract. — The structure of two dimensional deformable particles of low interfacial tension is studied theoretically. Closed loops in the plane are used to model droplets of one liquid in a second with surface active molecules residing at the liquid-liquid interface. The mechanical properties of the surfactant layer are represented by a bending energy contribution due to Helfrich, where the relevant parameters are rigidity and local curvature, and a surface tension. Thermal shape fluctuations and the deformational response to external fields, such as those due to confining walls or neighbouring particles, are studied by a method of functional integration in conjunction with a Monte Carlo sampling technique. Our results include particle shape distribution functions for different geometrical constraints and interfacial conditions which are relevant to bilayer lipid vesicles, microemulsion particles and emulsion droplets.

1. Introduction.

In many colloidal dispersions the constituent colloidal particles are deformable and show a wide variety of non-spherical, non-symmetric shapes. Often, dispersed drops exhibit continuous shape changes on a wide range of time scales. The deformations can be in response to static or dynamic external fields such as external walls, surrounding drops, fluid flows etc. or simply as a result of thermal fluctuations. Shape polydispersity is clearly evident in oil droplets suspended in aqueous phases (particularly so if there is some surface active material present e.g. [1]) but can also be seen in phase contrast micrographs of suspensions of bilayer lipid vesicles [2] and is frequently inferred as a significant property of oil/water/surfactant systems [3].

Shape fluctuations modify both the direct and the indirect particle-particle interactions leading to shape dependent physical properties of bulk colloidal materials. Also, a geometry dependence of interfacial properties such as permeability and transport behaviour lead to shape dependent physiochemical properties. Many experimental approaches (dispersion rheology, N.M.R. spectroscopy, static and dynamic light scattering) are able to provide direct information concerning the shapes of colloidal sized objects but variable shape complicates the interpretation of the data. The theoretical treatment of highly deformable particles is very complicated. Since many degrees of freedom are associated with individual shapes methods dealing solely with the «most probable shape» are seriously deficient by neglecting fluctuations; the function space of possible drop shapes being very large. In addition the shape dependent energy contribution is often not simple containing possibly non-Hookean elasticity terms, curvature, tilt and stretch energies and curvature dependent surface energy terms etc. Previous theoreti-
cal studies of drop deformation have dealt primarily with the two limiting cases in which the drop geometry is either nearly spherical [4, 5] or very elongated (slender) [6, 7]. Deuling and Helfrich [8] have given a catalogue of «most probable» rotationally symmetric vesicle shapes, obtained from the numerical solution of a variational problem, which show a variety of indentations, cavities and membrane-membrane contacts. The nature of their solutions precludes a statistical treatment of shape fluctuations.

Using a Monte Carlo scheme originally proposed by Ostrowsky and Peyraud [9] we will consider the full range of shapes of highly flexible two dimensional particles with small or vanishing surface tension whose major contribution to the deformation energy comes from a term quadratic in curvature i.e. a bending energy [10]. We associate this term and the existence of an ultralow surface tension with the presence of surface active material but we shall neglect possible tilting and stretching energy contributions. Thus we consider the simple model interface in which the surfactant forms a layered system where the molecules are all assumed to be oriented perpendicular to the surface. The surfactant layer is analogous to a smectic A liquid crystal and the parameter $K$ (a rigidity or curvature elastic modulus) which we shall use to characterise the resistance to curvature deformations is equivalent to the splay elastic constant. We shall impose geometrical constraints of either constant perimeter length or constant enclosed area. The analogous three dimensional structures are bilayer lipid vesicles and biological cells in the first case and microemulsion droplets, micelles and large emulsion drops in the second. We note that the imposition of constraints implies assumptions concerning the functional properties of the membrane. Firstly a constant surface area constraint must be accompanied by a mechanism, efficient on the timescale of volume changes, for transport across the membrane. Secondly a constant volume constraint used in conjunction with a small finite surface tension implies either rapid transport of membrane material to and from the interface or contact with a surfactant reservoir [11]. In the case of biological membranes such a mechanism has been proposed [12]. Also microemulsion droplets are known to coexist with large amounts of surfactant aggregated in micellar form [13] so that rapid exchange is possible [14].

We note that our restriction to two dimensional shapes, which is motivated by computational convenience, is serious to the extent that size invariance of the curvature energy is lost. However, although limited in direct applicability, the model allows us to assess the significance of large shape fluctuations under differing constraints (for example with respect to perturbed spherical models) and is clearly an invaluable platform for an extension to a full account of solids of revolution which we have in progress.

Shape response is a central factor for the determination of stable size distributions of deformable particles. Low surface tension droplets which suffer large deformations will ultimately break up [12]. In an external field of given strength a limiting size of droplet will exist which will not rupture. Particles with a distribution of sizes below this limit may exist in a range of deformed states, whereas the larger particles will experience assorted eccentric shapes prior to fission (necks, lobes etc.). In order to find the stable particle size distribution functions produced in dispersion formation [15] it is necessary to estimate droplet stability as a function of size, field strength and interfacial properties (elastic moduli etc.).

In section two we indicate a representation for the statistical geometrical properties of deformable particles in terms of integrals over the set of possible two dimensional shape functions and a scheme for globally generating individual members of this set. We also give explicit expressions for the deformational energy in terms of a small number of parameters. In section three we give results for Monte Carlo evaluation of the integrals and in section four discuss their relevance to dispersions of deformable particles.

2. Geometry of two dimensional closed shapes.

In order to correlate particle shape information with the physical behaviour of colloidal dispersions we require a detailed knowledge of the geometry of irregular flexible shapes. For each member $\psi$ of the set $\Omega$ of particle shapes we can associate a value $p(\psi)$ with each property $p$. The statistics are then conveniently expressed in a functional integral representation. The probability distribution of $p$ is given by

$$P(p) = (1/Z) \int_{\Omega} \delta[p - p(\psi)] \times \exp(-E(\psi)/kT) \delta[G(\psi)] d\psi \quad (2.1)$$

where

$$Z = \int_{\Omega} \exp(-E(\psi)/kT) \delta[G(\psi)] d\psi \quad (2.2)$$

and similarly the mean value is

$$\bar{p} = (1/Z) \int_{\Omega} p(\psi) \exp(-E(\psi)/kT) \times \delta[G(\psi)] d\psi \quad (2.3)$$

In these integrals $G(\psi)$ represents topological constraints associated with curve closure, curve crossing etc. and $E(\psi)/kT$ is the shape dependent factor which weights the different shapes through the exponential. The details of a Monte Carlo method for evaluation of integrals (2.1)-(2.3) have been given by Ostrowsky and Peyraud [9]. We shall adopt their scheme which can be summarized as follows:
(i) Restrict the set \( \Omega \) to shapes given by a limited Fourier expansion of the tangent direction
\[
\phi(s) = \cos^{-1}(\mathbf{i} \cdot \mathbf{s}) = s + A_0 + \sum_{n=1}^{M} \times \\
(\mathbf{A}_n \cos(ms) + \mathbf{B}_n \sin(ms)) \quad s \in [0, 2\pi]
\] (2.4)
i is a unit tangent vector, \( \mathbf{s} \) is the unit vector in the x-direction and \( s \) is the normalized arc length. The set of coefficients \( A_0, A_j, B_j, j = 1, M \) define a closed curve of perimeter length \( 2\pi \).

(ii) Further restrict the shapes by choosing the \( N = 2(M - 1) \) dimensional vector of independent coefficients \( jA_j, jB_j j = 2, M \) inside an \( N \)-dimensional hypersphere of radius \( R_k \). We have consistently chosen \( R_k \) to limit the systematic error in the evaluation of (2.3) to below one percent [9]. The coefficients \( A_0, A_1, B_1 \) are defined by the topological constraints of a smooth closed curve. The functional integrals (2.1)-(2.3) are now reduced to \( N \)-dimensional multiple integrals over \( A_j, B_j j = 2, M \).

(iii) Generate sets of independent coefficients at random and evaluate the integrals by Monte Carlo sampling omitting all sets corresponding to curves which intersect with themselves.

The actual shapes are obtained from these shapes by scaling all distances by an appropriate factor \( R \) and moving the center of mass to the origin. Choosing a constant perimeter length \( P = 2\pi R \) gives an enclosed surface
\[
S = R^2 \int_0^{2\pi} \sin(\phi(s)) \int_0^s \cos(\phi(s')) ds' \ldots = \pi R^2. \quad (2.5)
\]
Alternatively maintaining a constant enclosed area \( S = \pi R_0^2 \) gives a length scale factor
\[
R = R_0 \left[ \pi / \int_0^{2\pi} \sin(\phi(s)) \times \\
\int_0^s \cos(\phi(s')) ds' \right]^{1/2} \geq R_0 \quad (2.6)
\]
(\( R \) and \( R_0 \) are used to choose particle size when using the constant perimeter or constant area constraints respectively). The smallest wavelength of excitation, \( M/2\pi R \), is a property of membrane structure which is taken to be invariant. Thus, in contrast to Ostrowsky and Peyraud, we link the particle size to the number of modes through \( M(R) \propto R \) and arbitrarily fix \( M(1) = 5 \). However in order to retain the efficient curve generation procedure we slightly change this choice of \( M \) when used in conjunction with equation (2.6). In this case we write \( M \propto R_0 \) with \( M(R_0) = 1 = 5 \) and when the perimeter length is such that \( R/R_0 > (M(R_0) + 1)/M(R_0) \), make an additional contribution to the Boltzmann factor in accordance with equipartition (see below). This modified scheme maintains the important contribution of the small wavelength modes to the statistical weight factor while neglecting their small effect on particle geometry.

Primarily we consider two competing shape dependent contributions to the Boltzmann factor \( E(\phi)/kT \).

Firstly a bending energy term [10] favouring smooth extended shapes and secondly an external field contribution leading to squashed and elongated shapes. (Fields of other symmetry are easily included). To compute the bending term for shape \( \psi \) we integrate \((d\phi/ds)^2\) along the curve. The result may be written
\[
B_c = (2\pi K/R) + (K\pi/R) \\
\sum_{m=-1}^{M} [(mA_m)^2 + (mB_m)^2] \quad (2.7)
\]
where \( K \) is a constant expressing the magnitude of the bending elastic modulus. By comparing the equation (2.4) with an expression in terms of independent normal displacements (i.e. a two dimensional generalization of [16]) it is possible to make an approximate identification of each value of \( m \) with two independent modes. Thus, when we invoke the constant \( S \) (variable \( R \)) constraint with \( M \propto R_0 \), we compensate equation (2.7), according to equipartition of energy, by adding unity for each mode. We write
\[
B_c \to B_c + \sum_{i=1}^{\infty} [(1/2 + 1/2) \tanh (R - R_i)/d)] \quad (2.8)
\]
where \( d \) is chosen \((\sim 1/5 M)\) to make equation (2.8) exhibit sharp steps at the transition points \( R_i \) where new modes become allowed. In practice other forms of step function could be employed and only a few steps need be included in the sum.

Each perimeter element experiences a force proportional to its distance from the y-axis and directed towards the y-axis. (i.e. the particles lie in a parabolic potential trough). The corresponding contribution to the Boltzmann factor is
\[
B_x = \alpha R^3 \int_0^{2\pi} \int_0^s \cos(\phi(s')) ds'^2 ds \quad (2.10)
\]
where \( \alpha \) expresses the field strength. This precise form of the applied field is qualitatively unimportant but could be considered to represent the squashing of a particle confined inside a thin film.

For drops with constant enclosed area we have considered a third contribution to the Boltzmann factor that is proportional to the perimeter length. We will consider small values of the « surface tension » parameter \( \gamma \), defined by
\[
B_z = \gamma R \quad (2.11)
\]
This form favours the occurrence of circular drops.
3. Results.

We now present in a systematic way results for the geometrical properties of two dimensional deformable particles whose shapes are controlled by a curvature elastic energy. The results are size dependent directly through $R$ in equations (2.5), (2.6) etc. and indirectly through the associated increase in the number of modes. Particles up to $M = 15$ have been considered. The other independent parameters are $K$, $\gamma$ and $\alpha$ for which an appropriate scaling corresponds to a temperature variation.

Although a mean radius could consistently be used to quantify deviations from circular geometry its definition is ambiguous for non-starshaped particles. We therefore consider $\bar{S}$, the normalized mean enclosed surface, and $\bar{P}$, the normalized mean perimeter length, as appropriate deformation measures for constant $R$ and constant $S$ particles respectively. For $\alpha = \gamma = 0$ results are shown in figures 1-3. In general large particles with smaller $K$ exhibit wider ranges of increasingly deformed shapes. Figure one shows a steadily falling rate of decrease of $\bar{S}$ with $R$ which we associate with the increased influence of the « hard core » cross-over restrictions in highly flexible particles (i.e. as particles become larger and more flexible the introduction of additional modes is more likely to cause curve crossing and less efficient at reducing $S$). This behaviour is not as clear in an analogous plot of $\bar{P}$ against $R$ for $R > 3$ which remains approximately linear with $\bar{P} = 1.4$ for $R = 2$, $K = 0.3$. Two curves in figure two ($K = 0.3$, $R = 3$; $K = 0.1$, $R = 1$) illustrate the importance of increasing the number of modes with particle size. For $M(R) =$ constant these two curves would be identical (cf. [9]).

![Fig. 1.](image1.png)

Fig. 1. — Mean enclosed surface plotted against particle size for constant perimeter particles ($\alpha = 0$). The solid lines correspond to the results for a perturbed circular model.

![Fig. 2.](image2.png)

Fig. 2. — Probability distribution functions for enclosed surface area of constant perimeter particles ($\alpha = 0$).

![Fig. 3.](image3.png)

Fig. 3. — Probability distribution functions for perimeter length of constant area particles with $K = 0.3$, $\alpha = 0$.

Deformation is aided by increasing $M$. We note that although the range in figure two is strictly finite this is not so for figure three and examples of curves with $\bar{P} > 3$ were produced by the generation scheme with very small weights.

The most significant effect of non-zero external fields is to remove the average circular geometry. (This effect is imperceptible from viewing individual shapes even...
for the highest fields considered). Figures 4-6 show average shapes for $K = 0.3$, $\gamma = 0$. (Average shapes are constructed from average coefficients $A_2$, ..., $B_M$ in the usual way). Figures 4, 5 have constant perimeter and $R = 1, 2$ respectively and figure six has constant $S$ with $R = 1$. In each case the field is stepped as $\alpha = 0.0, 0.5, 1.0, 3.0$. Clearly larger shapes show an increased average response to squashing. The constant volume constraint leads to reduced eccentricity for high external fields. We note that as the average shape becomes increasingly elongated the Monte Carlo scheme is inefficient (since a priori curves are on average circular) and it may be preferable to use reduced displacements between sets of coefficients $A_2$, ..., $A_M$, $B_2$, ..., $B_M$ [17].

Fig. 4. — Average shapes for constant perimeter particles of $K = 0.3$, $R = 1.0$ with applied fields $\alpha = 0.0, 0.5, 1.0, 3.0$.

Fig. 5. — Average shapes for constant perimeter particles of $K = 0.3$, $R = 2.0$ with applied fields $\alpha = 0.0, 0.5, 1.0, 3.0$.

Fig. 6. — Average shapes for constant area particles of $K = 0.3$, $R = 1.0$ with applied fields $\alpha = 0.0, 0.5, 1.0, 3.0$.

Details of particle deformations in external fields are shown in figures 7-10. Statistical errors increase with field strength but are always below five percent for $\alpha < 2$. Small ($R = 0.5$) constant perimeter particles remain substantially unaltered by fields $\alpha < 3$ with a narrow distribution of almost circular shapes. Larger particles show a significant response to applied fields. For $R = 1.0$, $K = 0.3$ the distribution of $S$ initially broadens and shifts to smaller values as the field strength increases in contrast to the distribution of $R = 2.0$ particles which becomes sharper for $\alpha > 0$. Again we attribute this difference to the cross-over criterion which causes the distribution functions to develop sharp small $S$ cut-offs as the modal value approaches a critical value around $S = 0.3$. We note

Fig. 7. — Mean enclosed surface plotted against applied field for constant perimeter particles.
Fig. 8. — Probability distribution functions for enclosed surface area of constant perimeter particles with $K = 0.3$. From the left $R = 2.0, 2.0, 1.0, 1.0, 0.5$.

Fig. 9. — Mean perimeter length plotted against applied field for constant area particles of $K = 0.3$. $R = 1.0$ (solid line), $R = 2.0$ (dashed line).

that as $\alpha$ is increased the distributions develop significant portions with $S < 0.5$.

The curves of $P$ against $\alpha$ for particles of constant $S$ (Fig. 9) show distinct minima. It appears that the particle responds to the initial application of the field by reducing the size of the shape fluctuations and thereby reducing $P$. But as $\alpha$ increases the particle becomes elongated forcing $P$ to increase. The effect is strongest for more responsive (i.e. larger) particles. For $R = 1.0, \gamma = 0$ the distribution of $P$ shows little change for $\alpha = 0 - 3$. However for $R = 2.0$ the modal value of $P$ moves steadily to higher $P$ for $\alpha > 1.5$. Corresponding to the behaviour discussed above there is a transition region of $\alpha$, $\alpha \approx 0.5$, where the $P$ distribution may be complex.

Fig. 10. — Probability distribution functions for perimeter length of constant area particles with $K = 0.3$ and $\gamma = 0$.

Fig. 11. — Probability distribution functions for perimeter length of constant area particles with $K = 0.3$, $R = 2.0$, $e_x = 0$. 

$\alpha = 0$. 
Small non-zero surface tensions, $\gamma > 0$, reduce fluctuation amplitudes and diminish the response of drops to squashing. For $K = 0.3$ this is shown by figures 9, 11, 12. With increasing $\gamma$ the minima of figure 9 become shallower and are shifted to larger fields. Moderate surface tensions, $\gamma = 10$, are sufficient to give a substantial region of approximate field independence for small drops ($R = 1$) whereas competition between fluctuation and elongation in an external field is still evident for larger drops ($R = 2$) at $\gamma = 25$. The Monte Carlo scheme becomes inefficient at these higher parameter values. At zero external field and small $\gamma$ the normalized mean perimeter falls off more slowly than $1/\gamma$ and has explicit $R$ dependence which is associated with the relative importance of curvature elasticity (Fig. 11). As $\gamma$ is increased $P$ becomes dependent on the single variable $R/\gamma$ and otherwise is independent of particle size. The distribution functions (Fig. 12) show a transition from a broad distribution of flexible particles ($\gamma = 0$) to a distribution of fluctuating spheres ($\gamma = 10$) for $R = 2$ drops. However inspection of individual spheres confirms that this final distribution retains distinct deviations from monodisperse hard discs.

![Figure 12](image)

**Fig. 12.** Mean perimeter length plotted against $R/\gamma$ for constant area particles of $K = 0.3$ in zero external field.

4. Discussion.

Because of the restrictions inherent in a two dimensional model, we will concentrate on the qualitative particle geometry aspects of the size distributions and their stability with respect to particle deformations. Under the constraints of constant $R$ and constant $S$ the geometrical requirements for a binary fission are $S \leq 1/2$ and $R \geq \sqrt{2}$ respectively. From figures 2, 3 it can be seen that in both cases for particles with $K = 0.3$, $R = 3.0$ substantial portions of the distributions for $\alpha = 0$ correspond to geometrically unstable configurations. This is also true (but to a lesser degree, as shown above) when the flexibility is increased by lowering $K$ (i.e. $R = 1$, $K = 0.1$). Similarly figure eight illustrates the disruptive effects of applying squashing fields to smaller more rigid particles with constant $R$.

The final distribution of particle sizes in a colloidal dispersion often evolves by repeated fragmentation (see for example [15]). The resulting functional form is dependent on the probability of breakage, $P_B$, of a given particle in a given time. (Note that when $P_B$ is « independent » or « uniform » a random fragmentation process leads asymptotically to log-normal or Weibull size distributions respectively, [18]). For two dimensional flexible drops $P_B$, established using the geometrical criterion above for $K = 0.3$, $\alpha = \gamma = 0$, is heavily weighted towards large particles and fitted accurately by the step

$$P_B(R) = 1/2(1 + \tanh (R - a)/b) \quad (4.1)$$

with $a = 2.1$, $b = 0.8$. In this case a simple analytic result for the particle size distribution cannot be obtained. Preliminary numerical results indicate that particle flexibility reduces the size of the large $R$ tail observed in Weibull size distributions.

For deformable particles in external fields figures 4-6 show that before reaching any « geometrical instability » particles may have seriously deformed average shapes ($K = 0.3$, $R = 1.0$, $\alpha = 1.0$; eccentricity = 1.2, 1.3 respectively for constant $R$ or $S$). Therefore stable distributions of « on average » non-circular shapes may occur. We also note that even in the absence of applied field a perturbed circular model is not in full agreement with our Monte Carlo calculation which includes highly deformed shapes. In figure one we have plotted

$$S = 1 - (3 R/16 K) \left(1 - (1/15 R)((20 R - 1)/(10 R - 1))\right) \quad (4.2)$$

for $K = 0.1, 0.3$. Equation (4.2) has been obtained for circular particles with independent normal surface displacements whose amplitudes are determined in accordance with the equipartition of energy and whose number is in agreement with our model (strictly analogous to the three dimensional treatment of [16]). This model underestimates fluctuations of small particles and becomes pathological as the particle size increases because of the neglect of correlations between the large numbers of modes. We conclude that in dilute dispersions of highly flexible particles or in concentrated colloidal dispersions where particles are subject to straining forces (i.e. random strains, flow fields) a circular geometry would be a poor starting point for theoretical discussion.

As pointed out by Van de Sande and Persoons [19] a knowledge of the geometry of flexible non-circular particles, given here for two dimensional shapes in
external fields, is an essential ingredient for the extraction of shape information from scattering data (which is dependent on the radius of gyration of the particles) and interpretation of shape dependent dynamics (which is dependent on the hydrodynamic radius of the particles) of three dimensional macromolecular structures. Distribution functions for these radii are ideally suited to Monte Carlo evaluation. In collections of colloidal particles, i.e. emulsions, aggregates, concentrated sediments, the individual particles will exhibit three dimensional shapes analogous to those in figures 4-6. Details of the packing and excluded volume effects of these shapes, some of which are more rod-like than circular, will therefore be necessary for studies of material rheology. To our knowledge no study of the random packing of non-circular shapes exists.

We note that in three dimensions the geometrical criterion used above may be more satisfactorily replaced by a consideration of the deformation energy contributions (readily available from the Monte Carlo treatment) and that many other properties can realistically be examined, e.g. permeability or particle transport. The method is easily extended to include positive osmotic pressure differences, which would reduce the fluctuation amplitudes, non-linear elastic terms, wave-vector dependent curvature contributions [2], and non-zero spontaneous curvatures. It has recently been suggested [20] that shape fluctuations can be driven by density fluctuations within the membrane. The Monte Carlo procedure could easily be modified to test the correlations between these two fields. An investigation of shape dependent contributions to repulsive interactions between colloidal particles is also within the range of the Monte Carlo scheme. [21].

Using a Monte Carlo method to sample a large range of two dimensional shapes we have been able to infer that circular geometries are deficient in their treatment of the shape fluctuations of flexible particles. The Monte Carlo method alleviates many of the problems associated with the theoretical treatment of highly deformable shapes and can provide reliable data on the distribution of non-spherical shapes and associated geometries under differing constraints and conditions.

References