Pis'ma v ZhETF, vol.63, iss.3, pp.203 - 208

NEARLY SPHERICAL VESICLES: SHAPE FLUCTUATIONS

E.I.Kats, V.V.Lebedev*†, A.R.Muratov‡*

**L.D.Landau Institute for Theoretical Physics, RAS*
117940 Moscow, Russia

†*Department of Physics, Weizmann Institute of Science*
76100 Rehovot, Israel

‡*Institute for Oil and Gas Research, RAS*
117917 Moscow, Russia

Submitted 11 January 1996

Isolated vesicles with "insufficient" area have a finite surface tension and spherical shapes, whereas vesicles with "excess" area are necessarily non spherical. We consider the crossover behavior between both kinds of vesicles occurring at increasing the equilibrium area. In the mean field approximation it is a second order phase transition from the spherical to a non spherical shape. We demonstrate that fluctuations smear the transition. The critical behavior of amplitudes of fluctuations and of their characteristic times is investigated.

PACS 05.20, 82.65, 68.10, 82.70.-y

A vesicle is a water droplet within a membrane of a closed shape. Vesicles are formed spontaneously in solutions of lipid molecules and these fascinating physical systems have generated considerable current interest (see e.g. the book [1] and the review [2]). In the present work we consider the role of shape fluctuations of nearly spherical vesicles.

There are two principal contributions into the energy of a vesicle. The first one is the bending energy [3]. We are interested in fluctuations which do not change the topology of the vesicle. Then we can take into account only the term with the mean curvature:

$$F_{\text{curv}} = \frac{\kappa}{2}\int dA\,\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2, \tag{1}$$

where the integral is taken over the surface of the vesicle and R_1, R_2 are its local curvature radii. The second contribution is the elastic energy [4, 5] related to variations of the surface density of molecules n_s of the membrane:

$$F_{\text{el}} = \int dA\, B\frac{(n_s - n_0)^2}{2n_0^2}, \tag{2}$$

where B is the elastic modulus of the membrane and n_0 is its equilibrium density.

The water inside the vesicle is practically incompressible and therefore the volume V of the vesicle is the conserving quantity. The next quantity which can be regarded as the conserving one is the number N of the molecules constituting the membrane. The behavior of the vesicle depends on the relation between the equilibrium area $A_0 = N/n_0$ and the area $4\pi R^2$ of the sphere with the volume V: $V = 4\pi R^3/3$. It is convenient to characterize the relation by the dimensionless parameter $x = (4\pi R^2 - A_0)/4\pi R^2$. In the case of "insufficient area" $x > 0$ the membrane is stretched and the energy (2) forces the membrane to have the spherical shape. In the case of "excess area" $x < 0$ the energy (2) forces the membrane to have the surface density $n_s = n_0$ that is to have the equilibrium area $A_0 = N/n_0$. Then the shape of the vesicle cannot be spherical. We will examine the crossover behavior between these two regimes occurring at small x.

From (2) it follows that the equilibrium condition with respect to n_s at a given number of molecules N reads $n_s = \mathrm{const}$. Substituting $n_s = N/A$ into (2) we find F_{el} as a function of A. At small x the area A is close to A_0 or to $4\pi R^2$ and we find from (2) in the main approximation

$$F_{\mathrm{el}} = 2\pi R^2 B x^2 + B x A_1 + \frac{B}{8\pi R^2} A_1^2 , \tag{3}$$

where $A_1 = A - 4\pi R^2$. Note that A_1 is a positively defined quantity since the surface area of the vesicle with the volume V cannot be less than the surface of the sphere with the volume V. Therefore the mean field analysis reproduces the above mentioned picture: the minimum of the energy (3) at $x > 0$ is achieved at $A_1 = 0$ what corresponds to a sphere while at $x < 0$ minimizing (3) gives $A_1 = 4\pi R^2 |x|$ what means that the equilibrium shape is non spherical one.

Thus in the mean field approximation we deal with the continuous phase transition with x as the control parameter. Below we will study fluctuational effects which play a crucial role at small x. Note that bending fluctuations lead to the logarithmic renormalization of the modulus κ introduced by (1). The renormalization is associated with nonlinear fluctuational effects described by the same bending energy (1) and is characterized by the dimensionless parameter $T/(8\pi\kappa)$ (see for details [6], [7]). We will believe $T/(8\pi\kappa)$ to be the small parameter of the theory (it is usually equal to $10^{-2} - 10^{-3}$) and therefore we may neglect this renormalization. The main our observation is that at small x nonlinear fluctuational effects related to the elastic energy (3) are much stronger than ones associated with (1).

To describe shape fluctuations we introduce the displacement u of the vesicle from the sphere of the radius R. Then the shape of the vesicle is determined by the equation $r = R + u(\theta, \varphi)$, where r, θ, φ are spherical coordinates. At small x the shape of the vesicle is slightly deviated from the sphere. It means that $u \ll R$ and all quantities can be expanded in u. The second order term of the Helfrich energy (1) is

$$F_{\mathrm{curv}} = \frac{\kappa}{2R^2} \sum_{lm} l(l+1)(l^2 + l - 2)|u_{lm}|^2 , \tag{4}$$

where u_{lm} are coefficients of the expansion of u in the series over the spherical harmonics. The same manner one can rewrite the energy (3) using the main term of the expansion of A_1:

$$A_1 = \frac{1}{2} \sum_{l>0,m} (l^2 + l - 2)|u_{lm}|^2 . \tag{5}$$

Here and below the value of u_{00} is implied to be expressed via u_{lm} with $l > 0$ from the incompressibility condition $V = \mathrm{const}$ and is consequently excluded from the set of independent variables u_{lm}. Note that the terms with $l = 1$ in (4,5) are zero as it should be since the contributions corresponding to the first spherical harmonic are displacements of the vesicle as a whole.

From (5) it follows that the energy (3) contains the forth order term in u. It is convenient to exclude formally this anharmonic term introducing the auxiliary field ϕ. Namely, $\exp(-(F_{\rm curv}+F_{\rm el})/T) = \int_{-i\infty}^{+i\infty} d\phi/i\phi_0 \exp(-F_\phi/T)$, where $\phi_0^2 = T/(2BR^2)$ and

$$F_\phi = F_{\rm curv} - 2\pi R^2 B\phi^2 + B\phi(A_1 + 4\pi R^2 x)\,. \tag{6}$$

Correlation functions of u can now be rewritten as averages with the probability distribution function $\exp(-F_\phi/T)$ over both u_{lm} and ϕ.

Integrating the probability distribution function $\exp(-F_\phi/T)$ over u_{lm} one obtains the effective energy $F_{\rm eff}$: $\prod_{lm}\int du_{lm}\exp(-F_\phi/T) = \exp(-F_{\rm eff}/T)$, containing the full information about correlation functions. For example

$$\langle |u_{lm}|^2\rangle \simeq \int_{-i\infty}^{+i\infty} d\phi \exp(-F_{\rm eff}/T)\frac{T}{(l^2+l-2)\big(\kappa l(l+1)/R^2 + B\phi\big)}\,, \tag{7}$$

Since the energy (6) is harmonic in u the integration to find $F_{\rm eff}$ can be performed explicitly. Omitting unessential ϕ-independent terms we obtain

$$\begin{aligned} F_{\rm eff} &\to -2\pi R^2 B\phi^2 + 4\pi R^2 Bx\phi \\ &+\frac{T}{2}\sum_l (2l+1)\ln\left[l(l+1)\frac{\kappa}{BR^2}+\phi\right]\,. \end{aligned} \tag{8}$$

If $|\phi| \gg \kappa/BR^2$ then the summation over l in (8) can be substituted by integration and we find (again omitting ϕ-independent terms)

$$F_{\rm eff} \to -2\pi R^2 B\phi^2 + 4\pi R^2 Bx\phi + T\frac{BR^2}{2\kappa}\phi\ln\frac{e}{\phi}\,. \tag{9}$$

One can check that the integral in (7) is determined by the narrow vicinity of the saddle point $\tilde\phi$ if $|\tilde\phi| \gg \kappa/BR^2$. Then ϕ in the denominator can be substituted by $\tilde\phi$ and we find $\langle|u_{lm}|^2\rangle = T/[(l^2+l-2)\big(\kappa l(l+1)/R^2 + B\tilde\phi\big)]$. The equation for $\tilde\phi$ is the extremum condition for the energy (9)

$$\tilde\phi = x + \frac{T}{8\pi\kappa}\ln\frac{1}{\tilde\phi}\,. \tag{10}$$

Note that the logarithmic term in the right-hand side of (10) has the same origin as the logarithmic contribution to the surface tension associated with the compressibility of the membrane discussed in [8]. If $x \gg T/(8\pi\kappa)$ then $\tilde\phi \approx x$. The value of $\tilde\phi$ diminishes with decreasing x and for $\tilde\phi \ll T/(8\pi\kappa)$ we find from (10)

$$\tilde\phi \approx \exp\left(\frac{8\pi\kappa}{T}x\right)\,, \tag{11}$$

this regime is realized at negative x. Thus in this region $\tilde\phi$ decreases fast at decreasing x. Since the expression (9) is correct at $|\phi| \gg \kappa/BR^2$ we conclude from (11) that the expression (9) can be used at $x > -x_0$ where $x_0 = (T/8\pi\kappa)\ln(BR^2/\kappa)$.

Note that $\ln(BR^2/\kappa)$ should be treated as a large parameter of the theory, in real experimental situation it is usually $15-20$.

$B\tilde{\phi}$ has the meaning of the gap in the excitation spectrum and it plays the role of the surface tension. The equation (10) coincides with one formulated by Swift [9] for the gap in the structure function of mass density fluctuations near the nematic–smectic-C phase transition. It is not an accidental coincidence since there is an analogy between the proposed theory and the weak crystallization theory developed by Brazovsky [10] (the description of the theory can be found in our review [11]). However there exists an essential difference between the considering crossover and the weak crystallization. At the crystallization the first order phase transition occurs what means that near the transition point there are two phases (symmetric and non symmetric) with close energies but separated by the potential barrier proportional to the volume of the specimen. For the vesicle the energy of the non symmetric (non spherical) phase becomes close to the energy of the symmetric (spherical) phase only for x near $-x_0$ where the potential barrier between the phases is of the order of temperature T. It means that instead of a sharp transition from the spherical to the non spherical phase one should observe a smooth crossover caused by fluctuations. At x close to $-x_0$ we cannot find explicit expressions for averages over the fluctuations but estimations are obvious, e.g. $\langle|u_{lm}|^2\rangle \sim TR^2/(\kappa l^4)$. Let us stress that smearing the phase transition is not a conventional finite size effect. Fluctuations smear the transition even in the limit $R\to\infty$ and therefore the crossover region does not shrink in this limit.

To examine the region $x<-x_0$ it is convenient to return to the representation (3). Expressing the quantity $U_2 = 2\sum_m |u_{2m}|^2$, (determining the excess area stored by u_{2m}) via A_1 from (5) one obtains

$$F_{\rm el} + F_{\rm curv} = 2\pi R^2 Bx^2 + \left(Bx + \frac{6\kappa}{R^2}\right) A_1 + \frac{B}{8\pi R^2} A_1^2 + \\ + \frac{\kappa}{2R^2} \sum_{l>2,m} (l^2+l-6)(l^2+l-2)|u_{lm}|^2 \,. \tag{12}$$

If $x<0$ the minimum of the energy is achieved at $A_1 \approx 4\pi R^2|x|$. Nevertheless at $|x|<x_0$ fluctuations of A_1 appear to be larger than $4\pi R^2|x|$ because of the condition $A_1 > U$ where $U = (1/2)\sum_{l>2,m}(l^2+l-2)|u_{lm}|^2$ determines the excess area stored by u_{lm} with $l>2$. It means that the small Boltzmann factor determining the distribution function is compensated by the large phase volume of fluctuations.

At decreasing x the role of the Boltzmann factor increases and the inequality $A_1 > U$ ceases to play an essential role. Then fluctuations of the excess area A_1 can be considered on the basis of (12) without restrictions on the value of A_1. It means that A_1 is "frozen" near the value $A_1 \approx 4\pi R^2|x|$ since fluctuations of A_1 are very weak:

$$\langle(\delta A_1)^2\rangle \approx \frac{4\pi R^2 T}{B} \ll (4\pi R^2|x|)^2 \,. \tag{13}$$

In the situation where the inequality $A_1 > U$ is not relevant (12) leads to $\langle|u_{lm}|^2\rangle = TR^2/[\kappa(l^2+l-6)(l^2+l-2)]$. Using this expression we find

$$\langle U\rangle \simeq \frac{TR^2}{2\kappa}\ln\frac{BR^2}{\kappa}, \quad \langle(\delta U)^2\rangle \sim \frac{T^2R^4}{\kappa^2} \,. \tag{14}$$

The restriction $A_1 > U$ is not relevant if

$$A_1 - \langle U \rangle \gg \sqrt{\langle (\delta U)^2 \rangle}\,. \tag{15}$$

We neglected in (15) fluctuations of A_1 determined by (13) since they are smaller than fluctuations of U. Substituting (14) into (15) we find the "frozen condition": $|x| - (T/8\pi\kappa)\ln(BR^2/\kappa) \gg T/8\pi\kappa$. The condition means that at decreasing x the excess area A_1 is frozen abruptly.

The equilibrium shape of the vesicle corresponding to the minimum of (12) is described in terms of nonzero $\tilde{u}_{lm}$ (where tilde designates the average value). For small $|x|$ the term with $l = 2$ dominates what leads to

$$\sum_m |\tilde{u}_{lm}|^2 \approx 2\pi R^2 |x|\,. \tag{16}$$

The condition (16) does not fix the equilibrium shape of the vesicle, it is related to the degeneracy of (12). To find the shape one should include into consideration higher order terms of the expansion of (1) in u lifting this degeneracy. The corresponding analysis [12, 13, 14] shows that for small $|x|$ (that is for small excess area) the equilibrium shape of a vesicle is a slightly prolate uniaxial ellipsoid. As a consequence fluctuations of u_{2m} qualitatively differ from fluctuations of u_{lm} at $l > 2$. There are five modes associated with u_{2m}. Two modes describe rotations of the ellipsoid as a whole. The third mode is related to variations of U_2. Fluctuations of U_2 can be estimated using the condition A_1 = const: $\langle (\delta U_2)^2 \rangle \approx \langle (\delta U)^2 \rangle \sim T^2 R^4/\kappa^2$. We conclude that

$$\frac{\langle (\delta U_2)^2 \rangle}{U_2} \sim \left(\frac{T}{8\pi\kappa}\right)^2 \frac{R^2}{|x|}\,. \tag{17}$$

The last two modes are so called ellipsoidal "quasi-Goldstone" ones corresponding to deviations of the vesicle shape from a uniaxial ellipsoid [14]. The analysis based on the third-order term of the expansion of the energy (1) in u gives the following fluctuational amplitude for the both quasi-Goldstone modes:

$$\langle u_2^2 \rangle \sim \frac{T}{8\pi\kappa\sqrt{|x|}} R^2\,. \tag{18}$$

Comparing (18) with (17) we conclude that just the quasi-Goldstone modes determine the amplitude of shape fluctuations of the vesicle.

The estimation (18) implies that the vesicle only slightly fluctuates near its equilibrium shape what is correct if $\langle u_2^2 \rangle \ll 2\pi R^2 |x|$. This inequality is broken for small enough $|x|$, namely for $-(T/(8\pi\kappa))^{2/3} < x < -x_0$. In this region potential barriers related to the high-order term of the expansion of (1) are less than the temperature and do not play an essential role. In this case shapes of the vesicle are more or less homogeneously distributed over shapes permitted by the condition A_1 = const. It means that in this case $\langle u_2^2 \rangle \sim R^2 |x|$. Note that this behavior reminds so-called conformal fluctuations taking place for vesicles with nontrivial topology [15–17].

It is not very difficult to obtain estimations for characteristic times of shape fluctuations. They are based on the analysis of the hydrodynamic motion near the membrane [4], [5], [18] what leads to the purely relaxational dynamics of u with the effective kinetic coefficient $\sim l/(\eta R)$, where η is the viscosity of the water. Thus we conclude that the characteristic time of the u_{lm}-fluctuations for $x > -x_0$ is $\tau \sim \eta R l^{-1}(B\tilde{\phi} + \kappa l^2/R^2)^{-1}$. If $x < -x_0$ the same estimation is valid for $l > 2$ where $\tilde{\phi} = 0$. For negative x satisfying $|x| \gg (T/(8\pi\kappa))^{2/3}$ the more interesting is the relaxational time characteristic of the quasi-Goldstone modes which is $\tau \sim \eta R^3/\sqrt{|x|}\kappa$. Note that this time is much less than the conventional rotational diffusion time $\eta R^3/T$. For $-(T/(8\pi\kappa))^{2/3} < x < -x_0$ we deal actually with the free diffusion over the configuration space, the diffusion is determined by the above kinetic coefficient. The characteristic time of the diffusion is $\tau \sim \eta R^3|x|/T$, it is the time needed for u_2 to vary on $R\sqrt{|x|}$.

The picture presented above has at least qualitative agreement with experiments. Note also that the modern experimental technique (see e.g. [19–21]) enables to obtain direct information about amplitudes and characteristic times of shape fluctuations for different regimes examined above. Thus we hope on a detail comparison of our predictions with observed data.

V. V. L. thanks E.Moses and R.Bar-Ziv for numerous helpful discussions. E.K. is also grateful to G.Volovik for valuable remarks. The research described in this publication was made possible in part by Grant INTAS 94-4078 and also by RFFR Grants.

1. S.A.Safran and N.A.Clark, Physics of Complex and Supermolecular Fluids (Wiley, New York, 1987).
2. G.Porte, J. Phys. II (Condens. Matter) **4**, 8649 (1992).
3. W.Helfrich, Z. Naturforsch **B103**, 67 (1975).
4. V.V.Lebedev and A.R.Muratov, JETP **68**, 1011 (1989).
5. E.I.Kats and V.V.Lebedev, Fluctuational Effects in the Dynamics of Liquid Crystals (Springer-Verlag, N. Y., 1993).
6. A.M.Polyakov, Nucl. Phys. B, **268**, 406 (1986).
7. H.Kleinert, Phys. Lett. A, **116**, 57 (1986).
8. F.Broshard, P.G. de Gennes, and P.Pfeuty, J. de Physique, **37**, 1099 (1976).
9. J.Swift, Phys. Rev. **A14**, 2274, 1976.
10. S.A.Brazovsky, JETP **41**, 85, 1975.
11. E.I.Kats, V.V.Lebedev and A.R.Muratov, Phys. Rep. **228**, 1, 1993.
12. M.B.Schneider, J.T.Jenkins and W.W.Webb, J.Phys. (Paris) **45**, 1457 (1984).
13. M.A.Peterson, Mol. Cryst. Liq. Cryst. **127**, 257 (1985).
14. S.T.Milner and S.A.Safran, Phys. Rev. **36 A**, 4371 (1987).
15. B.Fourcade, M.Mutz, and D. Bensimon, Phys. Rev. Lett. **68**, 2251 (1992).
16. F.Julicher, U.Seifert, and R.Lipowsky, Phys. Rev. Lett. **71**, 452 (1993)
17. E.I.Kats and V.V.Lebedev, JETP Lett., **61**, 57 (1995).
18. E.I.Kats and V.V.Lebedev, Phys. Rev. E **49**, 3003 (1994).
19. R.Bar-Ziv and E.Moses, Phys. Rev. Lett. **73**, 1392 (1994).
20. R.Bar-Ziv, R.Menes, E.Moses, and S.A.Safran, Phys. Rev. Lett. **75**, 3356 (1995).
21. R.Bar-Ziv, T.Frisch, and E.Moses, Phys. Rev. Lett. **75**, 3481 (1995).