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Size distribution of vesicles with topological defects

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We study a diluted suspension of nearly spherical vesicles near the temperature where the in-plane orientational (hexatic) order is destroyed through an unbinding of pairs of disclinations. We focus on the size distribution of the vesicles, extending a well known theory for fluid membranes. At sufficiently low temperatures, the vesicles are in the hexatic phase, with, however, twelve extra (positive) disclinations due to a topological constraint. Above a certain temperature, additional unbound pairs of disclinations emerge. We expect an unusual vesicle size distribution with a typical vesicle size, which diverges like the hexatic correlation length just above the liquid-to-hexatic transition temperature. [S1063-651X(98)51004-5]

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We consider a system of water and a fixed volume fraction of amphiphilic molecules, like phospholipids, which assemble themselves into a secondary structure consisting of bilayers. This system will show up a tertiary structure—the conformation of the bilayers. Depending on temperature one finds vesicles, multilamellar phases, onions, and bicontinuous phases. At sufficiently high temperatures, the bilayer behaves as a two-dimensional curved fluid, well described by the Helfrich Hamiltonian (see, e.g., Ref. [1]). In this model, the energy per area of a membrane is proportional to the square of the mean curvature. Since the curvature energy is scale invariant, the tertiary structure has no preferred length scale or typical size. The distribution of the length scales is determined by logarithmic corrections mainly due to shape fluctuations.

The size distribution $n(N)$ (the numerical density of vesicles of size N) of a diluted suspension (ideal mixture) of vesicles is given by a Boltzmann factor [2],

$$n(N)=Z_N \exp(-\mu N)=\exp(-\mu N-F_N). \tag{1}$$

N is the number of amphiphilic molecules of a vesicle, μ is the Lagrange multiplier to the constrained volume fraction ϕ (V denotes the volume, v the molecular volume): $v\Sigma_N n(N)N=V\phi$ and Z_N is the partition function of the internal degrees of freedom of a single vesicle of size N, F_N the corresponding free energy. The temperature is set to one throughout the paper ($k_BT=1$).

In an exhaustive study, Morse and Milner [2] calculated the logarithmic contributions to the free energy of a nearly spherical fluid vesicle and found $\mathcal{F}\sim(7/6)\ln N$ and for the size distribution of a diluted suspension of spherical vesicles,

$$n(N)=N^{-7/6}\exp(-\mu N). \tag{2}$$

Within this theory most of the vesicles have a size near the microscopic cutoff; there are only few large vesicles. Dynamical aspects of the equilibration of a initially monodispersive ensemble are a concern of [3].

Upon lowering the temperature or varying external conditions such as salt concentration or addition of cosurfactants this picture could change, provided the membranes undergo an internal liquid to hexatic transition to a phase with quasi-long-ranged orientational order [4–11]. Near the transition, the orientational correlation length provides a typical length scale, diverging right at the transition.

Tangential orientational order on a curved manifold is frustrated and might have topological defects (disclinations). These topological defects are uniquely characterized by a chargelike quantity—the total change of the orientation while going around the defect. The sum of all charges on a manifold is constrained and depends on the topology of the manifold—it is given by $\Sigma q_i=\int dAK$, where the topological invariant $\int dAK$ is the integral over the Gaussian curvature. According to the Gauss-Bonnet theorem $\int dAK=4\pi(1-g)$ where g is the genus of the surface (number of handles).

Hexatic order on a manifold with spherical topology has an excess of 12 positive disclinations (charge $q=+\pi/3$)—recalling a soccerball. A periodic bicontinuous phase (a configuration similar to the Fermi surface of copper in k space—a plumber's nightmare) has an extensive number of (negative) excess charges proportional to the number of unit cells.

The topological defects interact through the two-dimensional Coulomb law, where the interaction grows logarithmically with distance. These interactions are screened in the presence of smaller dipoles of defects (Debye-Hückel screening) and shape fluctuations [12]. In fact, a disclination can lower its energy by a shape deformation (buckling) [7,10]. Positive defects tend to concentrate in regions with positive Gaussian curvature, while negative disclinations prefer saddle-shaped regions with negative curvature.

The main part of this paper is devoted to the detailed analysis of these ideas—we study the finite size behavior of a Sine-Gordon field theory on a sphere and the coupling between fluctuations of the hexatic order and shape fluctuations. Finally we will give arguments for an unusual size distribution with a typical length scale proportional to the correlation length of the hexatic order.

Sine-Gordon field theory. In order to model hexatic ordering on a membrane, we should consider the field of angles modulo 60°, describing the direction of the nearest neighbors

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of a lipid molecule. This orientational field can be decomposed into a smooth spin-wave part and the vortices. The latter behave as a Coulomb gas, which can be transformed, using a Hubbard–Stratonovich transformation (see, e.g., Ref. [12]), into a Sine-Gordon field theory. The above–mentioned spinwave part is exactly canceled by the transformation. We end up with a Hamiltonian consisting of the elastic energy and a covariant Sine-Gordon functional with an extra coupling of the Sine-Gordon field Φ (related to the internal electric potential of the charges) to the Gaussian curvature due to the frustration of tangential order [9,12]:

$$\mathcal{H}=\frac{1}{2K_A}\int dA g^{ij}\partial_i\Phi\partial_j\Phi - x\int dA\,\cos\left(\frac{\pi}{3}\Phi\right) + i\int dAK\Phi + 2\kappa\int dAC^2 \tag{3}$$

where K_A is the hexatic stiffness and a is a microscopic length with $a^2N=A=4\pi R^2$. g^{ij} denotes the inverse metric tensor on the manifold with indices $i,j\in\{1,2\}$ and $dA=d^2\sigma\sqrt{g}$ the surface area element. C is the mean curvature (the trace of the curvature tensor divided by two) and κ the bending rigidity. $x\equiv a^{-2}\exp(-\epsilon)$ is the fugacity of the defects, thus ϵ is the energy needed to create the core of a defect.

We will describe shape fluctuations in normal gauge

$$\delta\vec{X}(\sigma)=\eta(\sigma)\vec{N}(\sigma), \tag{4}$$

where $\vec{X}$ is the parametrization of the rigid sphere, $\vec{N}$ the corresponding normal vector, and $\eta(\sigma)$ the normal displacement.

For a geometry with constant nonzero Gaussian curvature K (like a sphere), the Sine–Gordon functional (3) has a nontrivial spatially homogeneous saddle point $\delta\mathcal{H}/\delta\Phi=0$:

$$\frac{\pi}{3}x\,\sin\left(\frac{\pi}{3}\Phi_0\right)+iK=0. \tag{5}$$

This equation has a purely imaginary [13] solution Φ_0. We expand the functional (3) around the saddle point up to the second order in $\varphi\equiv\Phi-\Phi_0$ and in the shape fluctuations η and obtain [2,14]

$$\mathcal{H}=\mathcal{F}_0+\frac{\kappa}{2}\int dA\Delta\eta(\Delta\eta+2C^2\eta) + i\int dAC(\Delta\eta+2C^2\eta)\varphi + \frac{1}{2K_A}\int dA\varphi(-\Delta\varphi)+\tau\varphi^2, \tag{6}$$

where we ignored a term $\delta\int dA\cos(\pi\Phi_0/3)$ as a contribution to the surface tension [1,2]. Δ, C, dA now refer to the rigid sphere, thus $C=-1/R$ and Δ is the spherical Laplacian, which has a spectrum $R^{-2}l(l+1), l=0,1,2,\ldots$ with multiplicity $2l+1$.

$\mathcal{F}_0$ is the value of the Hamiltonian at the saddle point:

$$\mathcal{F}_0=8\pi\kappa-\sqrt{(xA)^2+12^2}+12\,\ln[12+\sqrt{(xA)^2+12^2}] - 12\,\ln(xA), \tag{7}$$

using Eq. (5). The field φ has a mass τ with

$$\tau=K_Ax\left(\frac{\pi}{3}\right)^2\cos\left(\frac{\pi}{3}\Phi_0\right)=K_A\left(\frac{\pi}{3}\right)^2\sqrt{x^2+\left(\frac{3K}{\pi}\right)^2}. \tag{8}$$

Approaching the critical point from above, the fugacity x vanishes. For an infinite radius $K\to 0$, τ is proportional to the fugacity of the defects x. For zero fugacity, on the other hand, τ is proportional to $3K/\pi=12/(4\pi R^2)$, which is the numerical density of the excess charges. For $\kappa\to\infty$ the system has a hexatic correlation length $\xi=\tau^{-1/2}$, which grows with vanishing x until it saturates at a value of the order of the mean distance of the excess charges.

We integrate over the fields η,φ in two steps in order to obtain additional information about the effective elastic constants. Eliminating the field φ by performing a Gaussian integration we obtain a new effective action for the shape fluctuations (up to a constant):

$$\mathcal{H}_{\rm und,eff}=\frac{\kappa}{2R^2}\sum_{l,m}[l(l+1)-2]l(l+1)|\eta_{l,m}|^2 + \frac{K_A}{2R^2}\sum_{l,m}\frac{[l(l+1)-2]^2}{l(l+1)+\tau R^2}|\eta_{l,m}|^2, \tag{9}$$

where we expanded η into spherical harmonics. For modes with $l(l+1)\ll\tau R^2$, i.e., modes with a wavelength larger than the bare hexatic correlation length, the effective bending rigidity is approximately $\kappa_{\rm eff}=\kappa+K_A/(\tau R^2)$. Thus the presence of orientational order stiffens the vesicle on longer length scales.

On the other hand, if we eliminate the undulation modes first, we find an effective action (again using spherical harmonics)

$$\mathcal{H}_{\rm eff}=\frac{1}{2\kappa}\sum_{l\geqslant 2,m}\left(1-\frac{2}{l(l+1)}\right)|\varphi_{l,m}|^2 + \frac{1}{2K_A}\sum_{l,m}[l(l+1)+\tau R^2]|\varphi_{l,m}|^2+\mathcal{F}_{\rm und}+\mathcal{F}_0, \tag{10}$$

where $\mathcal{F}_{\rm und}$ is the free energy of the undulation modes of a spherical membrane, already calculated in [2] to behave like $\mathcal{F}_{\rm und}\sim(8/3)\log A$. The $\eta_{l,m}$ integration extends over the $l\geqslant 2$ modes [2] due to the translational and scale invariance of the curvature energy. A finite bending rigidity essentially shifts the mass of the φ-field $\tau_{\rm eff}=\tau+K_A/(\kappa R^2)$, which is equivalent to a reduction of the hexatic correlation length [12]. A small bending rigidity promotes the creation of defects due to buckling, thus increases the density of defects.

We yield the following free energy for a vesicle:

$$\mathcal{F}=\mathcal{F}_{\rm und}+\mathcal{F}_0+\tfrac{1}{2}\ln\left(\frac{\tau R^2}{K_A L^2}\right)+\tfrac{1}{2}\sum_{l=1}^{L-1}(2l+1)\times\ln\left[\frac{l(l+1)+\tau R^2}{K_A L^2}+\frac{1}{\kappa L^2}\left(1-\frac{2}{l(l+1)}\right)\right], \quad (11)$$

where $L=R/a\gg 1$ is a UV cutoff ($L^2\propto A$).

For $x\to 0$ the coefficient τR^2 does not depend on the vesicle size A. This allows a simple expansion of the free energy for large L. By contrast, for finite x the coefficients of the L expansion itself depend on the size A, which complicates the discussion considerably and will be postponed to the next paragraph.

We examined the free energy analytically [15] for L large and $x\to 0$, $A,K_A,\kappa=$ const and found

$$\mathcal{F}=\text{const}L^2+\mathcal{F}_{\rm und}-12\ln L^2+\left(\frac{\pi K_A/3+K_A/\kappa}{2}-\frac{1}{6}\right)\ln L^2+\cdots, \quad (12)$$

where we used the small argument behavior of Eq. (7). The term const L^2 simply shifts the chemical potential; however, this does not affect the size distribution of vesicles, since the volume fraction, not the chemical potential is held fixed.

Morse and Milner [2] reported an additional, independent contribution $\mathcal{F}_{\rm trans}\sim-(3/2)\ln L^2$ to the free energy of a single vesicle, which is the entropy of the translation modes ($l=1$). Adding $\mathcal{F}_{\rm trans}$ to $\mathcal{F}$ we finally obtain

$$\mathcal{F}_{\rm total}=\left(\frac{\pi K_A/3+K_A/\kappa}{2}+1-12\right)\ln L^2+\cdots \quad (13)$$

or for its partition function ($L^2\propto A$),

$$Z\sim A^{11-(\pi K_A/3+K_A/\kappa)/2}. \quad (14)$$

Using pertubation theory, Park and Lubensky [9] found the fixed point $x^*=0$, $K_A^*\approx 72/\pi$ and $\kappa^*=18/\pi$ for a flat geometry ($R\to\infty$). We estimate the free energy of a vesicle at the critical point by replacing the couplings by their fixed-point values. Although a single vesicle cannot become critical, the ensemble of vesicles shows critical behavior due to the presence of arbitrarily large vesicles. This yields a divergent size distribution $n(N)\sim N^{-3}$ for small sizes.

Size distribution. So far we have calculated logarithmic contributions to the free energy, responsible for the small size behavior of the size distribution. We will show now that for a small but finite fugacity of the defects x (i.e., near the critical point), the size ditribution has a maximum at $A\sim 1/x$, i.e., the typical size diverges like $A\sim\exp(\epsilon)$.

We approximate the contribution of the φ fluctuations to the free energy by an expression with the same behavior for finite x and large L:

$$\mathcal{F}_S=\frac{1}{2}\int_0^L dy(2y+1)\ln\left(\frac{y(y+1)+\tau R^2+K_A/\kappa}{K_A L^2}\right). \quad (15)$$

The integral is easily calculated for L large, $A,x,K_A,\kappa=$ const and reads (up to irrelevant terms)

$$\mathcal{F}_S=\tfrac{1}{2}(\tau R^2+K_A/\kappa)+\tfrac{1}{2}(\tau R^2+K_A/\kappa)\ln\left(\frac{L^2}{\tau R^2+K_A/\kappa}\right)+\cdots. \quad (16)$$

We have $\tau R^2=(\pi K_A/36)\sqrt{(xA)^2+12^2}$ and $L^2=xA\exp(\epsilon)/4\pi$ using the (previous) definitions $L=R/a$ and $x=a^{-2}\exp(-\epsilon)$. Approaching the critical point from above, the core energy ϵ diverges and the terms proportional to ϵ become the dominant contributions to the free energy

$$\mathcal{F}\sim\left(\frac{K_A\pi}{72}\sqrt{(xA)^2+12^2}+f_1\right)\epsilon, \quad (17)$$

where ϵf_1 consists of constant terms proportional to ϵ. We match this expression for $x\to 0$ with (13) and obtain $f_1=K_A/(2\kappa)-11$. The expression for the free energy can be written as $\mathcal{F}\sim\epsilon(R/\xi)^2+\cdots$, which is roughly the number of defects times their core energy ($\xi=\tau_{\rm eff}^{-1/2}$ is the correlation length of the hexatic order). Keeping only the dominant term, the size distribution reads $n(xA)=\exp[-f(xA)]$ with

$$f(xA)=\tilde{\epsilon}\sqrt{(xA)^2+12^2}-\mu xA+\epsilon f_1+\cdots. \quad (18)$$

where we wrote $+\mu xA$ for the Lagrange multiplier to the fixed volume fraction and denoted $\tilde{\epsilon}=(\epsilon K_A\pi)/72$. For $\tilde{\epsilon}>\mu>0$ we find a peaked size distribution. In fact f has a minimum at

$$xA^*=\frac{12\mu}{\sqrt{\tilde{\epsilon}^2-\mu^2}}. \quad (19)$$

The volume fraction of vesicles (ϕ_0 is the volume fraction of small vesicles),

$$\phi=\phi_0+v\exp(2\epsilon)\int d(xA)xA\exp[-f(xA)], \quad (20)$$

is mainly determined by the minimal value $f(xA^*)=12\sqrt{\tilde{\epsilon}^2-\mu^2}+\epsilon f_1$. Consequently we have

$$2\epsilon-12\sqrt{\tilde{\epsilon}^2-\mu^2}-\epsilon f_1=0 \quad (21)$$

to lowest order in $1/\epsilon$. Using (21) and the value for f_1 we find $\mu\approx 0.4\epsilon$ at the critical point $K_A^*=72/\pi$ and $K_A^*/\kappa^*=4$, thus

$$A^*\approx 5.23/x, \quad (22)$$

where x is proportional to the hexatic correlation length of a vesicle with infinite radius and bending rigidity. The relative width w of the peak is given by $w^2=(xA^*)^{-2}/f''(xA^*)\propto 1/\epsilon$ with $f''(xA^*)=(\tilde{\epsilon}^2-\mu^2)^{3/2}/(12\tilde{\epsilon}^2)$, i.e., the peak becomes sharp at the critical point $\epsilon\to\infty$. Moreover, the peak dominates the size distribution while small sizes are suppressed by a factor

$$\frac{\phi}{\phi_0}=\exp[f(0)-f(xA^*)]=\exp(12\tilde{\epsilon}-12\sqrt{\tilde{\epsilon}^2-\mu^2})\to\infty \quad \text{for } \epsilon\to\infty.$$

To conclude, we concentrated on the orientationally disordered phase of spherical vesicles near the hexatic-liquid transition, extending existing literature about the ordered, hexatic phase, see [11,16] and the state-of-the-art Monte Carlo simulation [17]. We considered a fluctuating, nearly spherical vesicle with orientational degrees of freedom and calculated the size dependence of its free energy, studying a saddle point approximation plus Gaussian fluctuations of a Sine-Gordon field theory in a fluctuating geometry. We calculated the logarithmical size dependence of the free energy near the critical point. The corresponding size distribution of a diluted suspension of vesicles is divergent for small sizes.

We found that, in addition to the small size divergence, the size distribution has a peak, which becomes sharp at the critical point. The typical size diverges like the inverse fugacity of the defect, which corresponds to the square of the correlation length in a flat rigid geometry.

With increasing distance to the critical point this peak should eventually disappear. However, a proof requires the numerical evaluation of the free energy (11) together with the volume fraction constraint and is beyond the scope of this article.

We hope that the anticipated diverging typical length scale and the size distribution can be unveiled experimentally by techniques used in [18] and [19]. The latter studies the freezing of tubular structures. The vesicle phase provides an excellent opportunity to literally see the hexatic-liquid transition by looking at the typical vesicle size—the vesicles would blow up while approaching the critical point from above.

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[13] One obtains other solutions by adding multiples of six to Φ_0, however, they are equivalent. We take only one of these saddle points into consideration—in fact, the integration over the zero mode of Φ in Eq. (3) is restricted to one period, otherwise the partition function would be divergent.

[14] Our calculation is similar to [12], however, avoiding some inconsistencies. To be explicit, we expand around the saddle point Φ_0 and use the variation $\delta(dAK)=dAC\Delta\eta+\mathcal{O}(\eta^2)$. Reference [12] would obtain an incorrect saddle point and mass τ.

[15] The calculation is based on the approximation

$$\sum_{l=0}^{L-1} f(l)=\int_{-1/2}^{L-1/2} f(x)dx-\tfrac{1}{24}f'(L-1/2)+\tfrac{1}{24}f'(-1/2)+\mathcal{O}(f''').$$

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