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A simple dynamical model of two-dimensional vesicles

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Abstract. Two-dimensional vesicles are modelled as pressurized, self-intersecting rings. The fluctuating motion of the bounding walls of the vesicle, when it is subjected to the random collisions of fluid molecules, is treated along the lines suggested by Rouse in his study of dilute polymer solutions. Within the model, exact solutions of the dynamical equation governing the probability distribution of shapes, when expressed in an appropriate set of normal coordinates, is obtained. Numerical simulations of the dynamical evolution of the distribution of the principal components of the square of the radius of gyration are also presented.

1. Introduction

Irregular objects formed by random processes abound in nature. Long, chain-like macromolecules, flexibile membrane surfaces, percolation and spin clusters are but a few of the examples occurring in biology, chemistry and physics. Examples can also be found in astronomy, geology and information science. Elucidating the sizes and shapes of these objects has long been a challenge to the experimentalist and theoretician. Since the early work of Kuhn (1934) on polymers (see also Solê (1977) and Rudnick and Gaspari (1987)), significant progress has been made over the past 20 years in developing a theoretical framework useful in characterizing random structures (de Gennes 1979, Nelson *et al* 1987 and references therein). Modern approaches involving computer simulations, simple scaling arguments and sophisticated analytical techniques with roots in statistical field theory have proved enormously successful in this regard.

Most investigations to date that deal with shapes have been on systems in thermodynamic equilibrium. The statistical analysis is carried out using conventional statistical mechanical ensemble theory, yielding results that pertain to static conformations only. Calculations along these lines have been performed by us for polymers (Gaspari *et al* 1987) and, more recently, on pressurized two-dimensional random walks (see Rudnick and Gaspari (1991) and the preceding paper Gaspari *et al* (1993)). The latter is a simplified version of a model of a two-dimensional vesicle acted on by osmotic pressure forces, recently formulated by Leibler and Fisher and co-workers (Liebler *et al* 1987, Camacho and Liebler 1990). These authors were the first to represent a two-dimensional vesicle as a self-avoiding random polygon walk. Their Monte Carlo simulations based on this picture provided a complete numerical description of the static shapes of these objects and their scaling properties for both positive and negative pressure differences. The two pressure regimes are called 'inflated' and 'deflated', respectively. Self-avoidance causes the theoretical study to be analytically intractable and necessitates a numerical approach such as the one they utilize. However, as has been noted by us, permitting

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walks to cross transforms the statistical theory to one that is completely solvable, leading to closed-form expressions for the probability distribution of shapes, and providing analytical formulas for various parameters describing the average shape of the walk (Rudnick and Gaspari 1991).

The two-dimensional vesicle is an extreme simplification of the actual system, but it is one that allows the intuitions of the theoretical physicist to be applied to the problem of vesicle behaviour. Because of the relationship between the statistical mechanics of the one-dimensional membrane bounding a two-dimensional vesicle and the statistical mechanics of a ring polymer, one is free to call on the body of results for the latter system. The problem of a real, three-dimensional vesicle bounded by a two-dimensional membrane is notoriously difficult. The analytical solution of this problem will require techniques transcending those developed here. However, one can imagine polymer rings confined to two-dimensional surfaces whose dynamical evolution would be asymptotically described by the methods developed here. Such rings could easily flip over, thus achieving the crossovers allowed in the model. Moreover, it is hoped that the results found for this simplified picture also have relevance to the behaviour of vesicles in higher dimensions.

This paper extends our previous research on static conformations of vesicles to include dynamic effects, where the bounding wall now deforms in time according to stochastic laws. The time evolution of the deformation can be described using both the Langevin and Smoluchowski formulations of the random process (see Chandrasekhar (1942) and Chen and Uhlenbeck (1945) for a summary of earlier work). Langevin's equations are set up and point to an appropriate set of generalized coordinates in which the motion of the bounding wall is described. In these coordinates, the desired dynamical distribution of shapes is easily determined by solving Smoluchowski's equations. The vesicle's shape can then be monitored in time from an arbitrary initial conformation to its asymptotic approach to equilibrium after considerable time has passed.

Thus, the system is a very dilute film of polymer-like rings being buffeted about by the liquid medium of the film while feeling the forces of an osmotic pressure differential between the inside and outside of the wall. As in the static case, we find that for a dynamical model, similar to the one first articulated by Rouse (1953) in his study of the visco-elastic properties of dilute polymer solutions, the stochastic equations yield complete analytical solutions in the dynamical case as well. While the model may be criticized, in as much as it oversimplifies the actual forces felt by the vesicles, its exact statistical description offsets this disadvantage. Moreover, there is no reason why more realistic approximate theories (Zimm (1956) or see Stockmayer (1973) for a critical review of this and other work), which have been used to successfully interpret a range of dynamical flow coefficients, cannot be brought to bear here as well. It must be borne in mind that when dealing with two-dimensional films rather than three-dimensional solutions, neglecting certain interactions may not be so severe. In any case, we view the results as a 'first cut' theory in a difficult but interesting field of study with immense technological importance. It is hoped that the work presented here will stimulate further developments in the subject (see Schwartz and Edwards (1988) and Edwards and Schwartz (1990) for a different approach).

An outline of this work is as follows. In section 2 the dynamical model is specified and the Langevin equations are solved. The probability distribution of vesicle shapes is determined in section 3. The results of numerical simulations and concluding comments are contained in section 4.

2. Langevin theory of vesicle dynamics

Case A: P = 0. The static conformations of two-dimensional vesicles are patterned as random polygonal walks of N steps (Leibler *et al* 1987) whose edges obey Gaussian statistics. For the moment, it is assumed that no osmotic forces are applied, and the vesicle is allowed to cross itself. A given shape, specified by the two-dimensional vectors $\eta_1, \eta_2, \ldots, \eta_N$, linking the $N+1$ vertices of the polygon has a probability distribution

$$P(\eta_1, \eta_2, \ldots) = \left(\frac{1}{\pi\Delta^2}\right)^N \prod_{\alpha=1}^{N} \exp(-(\eta_{\alpha x}^2 + \eta_{\alpha y}^2)/\Delta^2) \tag{1}$$

with Δ^2 being the mean square length of any link. The walk is closed; therefore the constraint of zero net displacement must be maintained by the links

$$\sum_{\alpha=1}^{N} \eta_{\alpha i} = 0. \tag{2}$$

It proves useful to express equation (1) in terms of the position vectors of the vertices, $\boldsymbol{R}_1$:

$$P(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots) = \left(\frac{1}{N\Delta^2}\right)^N \exp\left(-\sum_{\alpha=1}^{N} |\boldsymbol{R}_\alpha - \boldsymbol{R}_{\alpha+1}|^2/\Delta^2\right). \tag{3}$$

Equation (3) gives rise to the notion, at least as far as conformations are concerned, that the vesicle may be represented as a collection of mass points (i.e. beads) connected by springs, with a configurational probability given by the usual Boltzmann result

$$P(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots) = \mathrm{e}^{-\beta U}/Q \tag{4}$$

with U being the potential energy of the 'mechanical' system and Q its configurational partition function. In particular,

$$U = \frac{kT}{\Delta^2} \sum_{\alpha=1}^{N} |\boldsymbol{R}_\alpha - \boldsymbol{R}_{\alpha+1}|^2 \tag{5a}$$

and

$$Q = \int \mathrm{d}^2 R_1 \ldots \mathrm{e}^{-\beta U}. \tag{5b}$$

The dynamical motion of a solution of vesicles will then be governed by the Brownian motion of the beads. We assume that the forces can be divided into three classes: the elastic forces between the beads on the chain, a steady resistive drag and the random, collisional forces. Both of the last two forces are due to the liquid medium. To this, any externally applied forces must be added. Backflow, which leads to an indirect bead-bead interaction via the perturbed liquid medium, is neglected. The model just described was successfully utilized by Rouse (1953) in describing the motion of dilute polymer solutions. The model can be improved upon (Zimm 1956), but such corrections are omitted in our treatment for reasons mentioned in the introduction. The consequence is a local, linear theory of dynamics.

Langevin's equation for the αth bead is

$$m\frac{\partial^2 \boldsymbol{R}_\alpha}{\partial t} = -\frac{1}{\mu}\frac{\partial \boldsymbol{R}_\alpha}{\partial t} - \frac{\partial U}{\partial \boldsymbol{R}_\alpha} + \boldsymbol{f}(t). \tag{6}$$

The inertial term may be dropped when considering times long compared to the relaxation time, which is the case here. This restricts the applicability of the theory to the diffusive regime. Dropping the acceleration term reduces the equation of motion to

$$\frac{1}{\mu}\frac{\partial \boldsymbol{R}_\alpha}{\partial t} = -\frac{\partial U}{\partial \boldsymbol{R}_\alpha} + f(t) \tag{7}$$

the quantity μ being the mobility constant, while $f(t)$ is a random, impulsive, force. The fluctuations are assumed to be Markovian, and time intervals are of such a duration that the distribution of impulses can be taken to be Gaussian, which follows from the application of the central limit theorem. Both assumptions are necessary for Langevin's and Smoluchowski's approaches to be equivalent formulations. Using equation (5*b*) for U results in an equation of motion for the beads when no external forces are present. In particular, the system of equations which must be solved is

$$\frac{1}{\mu}\frac{\partial \boldsymbol{R}_\alpha}{\partial t} = -\gamma(2\boldsymbol{R}_\alpha - \boldsymbol{R}_{\alpha-1} - \boldsymbol{R}_{\alpha+1}) + f(t) \tag{8}$$

subject to

$$\langle f(t)\rangle = 0 \qquad \langle f_{\alpha i}(t) f_{\beta j}(t')\rangle = \frac{2\pi}{\mu}\delta_{\alpha\beta}\delta_{ij}\delta(t-t')$$

and the constraining equation

$$\sum_{\alpha=1}^{N} (\boldsymbol{R}_{\alpha+1} - \boldsymbol{R}_\alpha) = 0 \tag{9}$$

with $\gamma = 2kT/\Delta^2$. When the number of links is large, $N \gg 1$, no loss in generality occurs if the continuum limit is taken, e.g.

$$\boldsymbol{R}_{\alpha+1} - \boldsymbol{R}_\alpha \to \frac{\partial \boldsymbol{R}_\alpha}{\partial \alpha}.$$

Throughout the remainder of the paper, the replacement of differences by derivatives will be made whenever it proves convenient. Equation (8), when displacement or link vectors η_α are used, becomes, in the continuum limit,

$$\frac{1}{\mu}\frac{\partial \eta}{\partial t} = \gamma\frac{\partial^2 \eta_\alpha}{\partial \alpha^2} + g_\alpha(t) \qquad \sum_{\alpha=1}^{N} \eta_\alpha = 0 \tag{10}$$

where $g_\alpha(t) = f_{\alpha+1}(t) - f_\alpha(t)$ are random forces with the statistical properties

$$\langle g_\alpha\rangle = 0 \qquad \langle g_{\alpha i}(t) g_{\beta j}(t')\rangle = \frac{2kT}{\mu}\delta_{ij}\delta(t-t')\frac{\partial^2}{\partial\alpha\partial\beta}\delta(\alpha-\beta). \tag{11}$$

The above equations describing the Brownian motion of the beads need to be modified if osmotic pressure forces are acting on the wall of the vesicle. Additional force terms must be added to equation (10). We now focus on this case.

Case B: $p \neq 0$. Pressure influences the conformational probability distribution through the additional Boltzmann factor $\exp(\Delta p\, A/kT)$. The quantity A is the area enclosed by the wall of the vesicle, and $\Delta p = p_{\text{in}} - p_{\text{out}}$ is the pressure differential. Using Green's theorem, it is a straightforward exercise to express A as a function of link coordinates of the bounding polygon (Rudnick and Gaspari 1991)

$$A = \tfrac{1}{2}\sum_{\alpha\beta} \eta_{\alpha x}\eta_{\beta y}\phi(\alpha-\beta) \tag{12}$$

the function ϕ being the unit step function. The above expression for the area has a sign tagged to the path indexing, i.e. paths which are flipped change sign. The operation $\Delta p \to -\Delta p$ is equivalent to flipping all paths, with the consequence that the deflated regime becomes inaccessible. The theory discussed here applies, therefore, only to the inflated regime $\Delta p > 0$.

The potential energy, U, now contains the term ΔpA in addition to the elastic energy of the springs. We point out that the statistical analysis done here will be for constant pressure, although constant-area ensembles can be handled as well by the theory. The precise prescription for carrying out that procedure is presented in our work on vesicle statics (Gaspari *et al* 1993).

The potential energy takes on the form

$$U = \frac{\gamma}{2}\sum\left(\frac{\partial \boldsymbol{R}_\alpha}{\partial \alpha}\right)^2 - \frac{\Delta p}{2}\sum_{\alpha\beta}\frac{\partial R_{\alpha x}}{\partial \alpha}\frac{\partial R_{\beta y}}{\partial \beta}\phi(\alpha-\beta) \tag{13}$$

which gives for the force on the αth bead,

$$-\frac{\partial U}{\partial R_{\alpha x}} = \frac{\partial^2 R_{\alpha x}}{\partial \alpha^2} - \Delta p\frac{\partial R_{\alpha y}}{\partial \alpha} \qquad -\frac{\partial U}{\partial R_{\alpha y}} = \gamma\frac{\partial^2 R_{\alpha y}}{\partial \alpha^2} + \Delta p\frac{\partial R_{\alpha x}}{\partial \alpha}. \tag{14}$$

It is clear how Langevin's equation must be modified when osmotic forces are acting. For the αth link, we have

$$\frac{1}{\mu}\frac{\partial \eta_{\alpha x}}{\partial t} = \gamma\frac{\partial^2 \eta_{\alpha x}}{\partial \alpha^2} - \Delta p\frac{\partial \eta_{\alpha y}}{\partial \alpha} + g_{\alpha x}(t) \qquad \frac{1}{\mu}\frac{\partial \eta_{\alpha y}}{\partial t} = \gamma\frac{\partial^2 \eta_{\alpha y}}{\partial \alpha^2} + \Delta p\frac{\partial \eta_{\alpha x}}{\partial \alpha} + g_{\alpha y}(t). \tag{15}$$

Pressure couples the equations.

It is useful to transform to Fourier amplitudes as a first step toward decoupling the components. This is accomplished by expressing η_α as a finite Fourier series,

$$\begin{aligned}\eta_{\alpha,x} &= \sqrt{\frac{2}{N}}\sum_k (A_k\cos(k\alpha) + B_k\sin(k\alpha)) \\ \eta_{\alpha,y} &= \sqrt{\frac{2}{N}}\sum_k (A'_k\cos(k\alpha) + B'_k\sin(k\alpha))\end{aligned} \tag{16}$$

with $k = 2\pi s/N$, $s = 1, 2, \ldots$. Note that the term $k = 0$ is not present in equations (16), thereby guaranteeing that the constraint equation

$$\sum_\alpha \eta_{\alpha x} = \sum_\alpha \eta_{\alpha y} = 0$$

will be satisfied. In momentum space, then, Langevin's equations take on the form

$$\frac{1}{\mu}\frac{\mathrm{d}A_k}{\mathrm{d}t} = -\gamma k^2 A_k - k\Delta p B'_k + g^{\mathrm{c}}_{k,x} \qquad \frac{1}{\mu}\frac{\mathrm{d}B_k}{\mathrm{d}t} = -\gamma k^2 B_k + k\Delta p A'_k + g^{\mathrm{s}}_{k,x} \tag{17}$$

and similar equations for A'_k and B'_k, with $g^{\mathrm{c}}_k(g^{\mathrm{s}}_k)$ the cosine (sine) transform of $g_\alpha(t)$ satisfying the correlation equations

$$\begin{aligned}&\langle g^{\mathrm{c}}_{k,i}(t) g^{\mathrm{s}}_{k,j}(t')\rangle = 0 \\ &\langle g^{\mathrm{c}}_{k,i}(t) g^{\mathrm{c}}_q(t')\rangle = \langle g^{\mathrm{s}}_{k,i}(t) g^{\mathrm{s}}_{q,j}(t')\rangle = \frac{2kT}{\mu}\frac{2\pi}{N}q^2\delta_{ij}\delta(k-q)\delta(t-t').\end{aligned} \tag{18}$$

The above system of equations is compactly written in matrix form. For that purpose we introduce a dimensionless time, τ and pressure, p:

$$\tau = \frac{t}{t_0} \qquad t_0 = \frac{\Delta^2}{2\mu kT}\frac{N^2}{4\pi^2} = \frac{1}{\gamma\mu p_c^2} \qquad p = \frac{(\Delta p)(\Delta^2)}{kT} = \frac{2\Delta p}{\gamma}.$$

We will also show that $p_c = 4\pi/N$ defines a critical value of the pressure, with the property that as $p \to p_c$ the vesicle witll no longer be able to contain the fluid inside, and, presumably, explodes. In dimensionless units, indexing with the integer s defined by $k = 2\pi s/N$, we have

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\begin{pmatrix} A_s \\ \vdots \\ B_s' \end{pmatrix} = -s^2 \begin{pmatrix} 1 & 0 & 0 & p/p_c s \\ 0 & 1 & -p/p_c s & 0 \\ 0 & -p/p_c s & 1 & 0 \\ p/p_c s & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} A_s \\ \vdots \\ B_s' \end{pmatrix}. \tag{19}$$

Fluctuation terms have been suppressed for the moment for simplicity. The coupled first-order equations are solved by standard techniques of linear algebra. The matrix has two-fold degenerate eigenvalues $\lambda_s^{\pm} = (1 \pm p/p_c s)$, with linearly independent eigenvectors. The orthogonal transformation effecting the diagonalization is

$$\begin{pmatrix} A_s \\ B_s \\ A_s \\ B_s \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & -1 & 0 & 1 \\ 1 & 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} x_s^1 \\ x_s^2 \\ x_s^3 \\ x_s^4 \end{pmatrix} \tag{20}$$

with the x_s^i obeying the equations of motion

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}\tau} x_s^i = -s^2 \lambda_s^i x_s^i + g_s^i(\tau) \\ &\langle g_s^i \rangle = 0 \qquad \langle g_s^i(\tau) g_{s'}^j(\tau') \rangle = \frac{\Delta^2 s^2}{\mu^2} \delta_{ij} \delta_{ss'} \delta(\tau - \tau') \\ &\lambda_s^i = \begin{cases} \lambda_s^+ & \text{for } i = 1, 2 \\ \lambda_s^- & \text{for } i = 3, 4. \end{cases} \end{aligned} \tag{21}$$

Now that the proper set of variables have been discovered, it is easiest to proceed directly to the probability distribution itself. The pertinent equation describing its time development is the Smoluchowski equation, which is often referred to as the Fokker-Planck equation.

3. Dynamical probability distribution

The conformational probability distribution factors into modes in the space of normal coordinates; we write

$$P(\ldots x_s^i \ldots) = \prod_{s=1}^{N} \prod_{i=1}^{4} p(x_s^i). \tag{22}$$

The Smoluchowski equation governing the time behaviour of P is separable in these coordinates and takes on a rather simple form. Using equation (22), and employing

standard arguements (Doi and Edwards 1986), leads to

$$\frac{\partial}{\partial\tau}p(x_s^i)=s^2\lambda_s^i\frac{\partial}{\partial x_s^i}(x_s^i p)+\frac{s^2\Delta^2}{2}\frac{\partial^2 p(x_s^i)}{\partial x_s'^2} \tag{23}$$

which has the well known solution

$$p(x_s^i)=\left(\frac{\lambda_s^i}{\pi\Delta^2(1-\exp(-2s^2\lambda_s^i\tau))}\right)^{1/2}\exp\left[-\frac{\lambda_s^1}{\Delta^2}\left(\frac{(x_s^i-x_{s_0}^i\exp(-s^2\lambda_s^i\tau))^2}{(1-\exp(-2s^2\lambda_s^i\tau))}\right)\right]. \tag{24}$$

The solution for $p(x_s^i)$ has the boundary condition that as $\tau\to 0$, $p(x_s^i)\to\delta(x_s^i-x_{s_0}^i)$ corresponding to the initial configuration of the chain, whereas as $\tau\to\infty$

$$p(x_s^i)\to\sqrt{\frac{\lambda_s^i}{\Delta^2\pi}}\exp\left(-\frac{\lambda_s^i x_s^{i2}}{\Delta^2}\right)$$

demonstrating that the dynamical distribution correctly moves toward the equilibrium distribution of static conformations in time. With this, the dynamical problem, at least within the model, is solved in principle. What remains is to compute appropriate averages using it.

As an example, consider the square of the radius of gyration, $R^2(t)$. This quantity will change with time, and its average is a useful single-parameter measure of the extent of the vesicle as measured from its centre-of-mass. For a specified shape of the chain, $\boldsymbol{R}^2$ is defined to be

$$\boldsymbol{R}^2=\frac{1}{N}\sum_{\alpha=1}^{N}(\boldsymbol{R}_\alpha-\boldsymbol{R}_{\rm cm})^2 \tag{25}$$

with $\boldsymbol{R}_{\rm cm}$ being the centre-of-mass for this particular walk. To calculate the average $\boldsymbol{R}^2$ using equation (24) requires the radius of gyration to be expressed in normal coordinates. This is accomplished by realizing that $\langle\boldsymbol{R}^2\rangle$ has the expansion (Forsman and Hughes 1963)

$$\langle\boldsymbol{R}^2\rangle=\sum_{i=1}^{2}\sum_{\alpha\beta=1}^{N}a_{\alpha\beta}\langle\eta_{\alpha i}\eta_{\beta j}\rangle \tag{26}$$

where $a_{\alpha\beta}$ is a real symmetric matrix with elements

$$a_{\alpha\beta}=\begin{cases}\dfrac{1}{N+1}\alpha(N+1-\beta) & \beta>\alpha\\[2ex] \dfrac{1}{N+1}\beta(N+1-\alpha) & \alpha>\beta.\end{cases} \tag{27}$$

Fourier decomposing the ηs and, finally, transforming to normal coordinates via equation (20) leads to

$$\langle\boldsymbol{R}^2\rangle=\sum_{s=1}^{N}\frac{N}{(2\pi)^2}\frac{1}{s^2}\langle A_s^2+B_s^2+A_s'^2+B_s'^2\rangle \tag{28}$$

the averages being taken over the probability distribution just calculated. The integrals become essentially Gaussian on changing to normal coordinates. We find

$$\langle\boldsymbol{R}^2(\tau)\rangle=\sum_{s=1}^{N}\frac{1}{4\pi^2}\frac{1}{s^2}\left\{\frac{1-\exp(-2s^2\lambda_s^-\tau)}{\lambda_s^-}+\frac{1-\exp(-2s^2\lambda_s^+\tau)}{\lambda_s^+}+\sum_{i=1}^{4}(x_{s,0}^i(\tau))^2\right\}$$

with

$$x^i_{s,0}(\tau) = x^i_{s,0} \exp(-s^2 \lambda^i_s \tau).$$

Equation (28) has the expected limits for $\langle \boldsymbol{R}^2(\tau) \rangle$:

$$\begin{aligned} &\langle \boldsymbol{R}^2 \rangle \to \boldsymbol{R}^2(0) && \text{as } \tau \to 0 \\ &\langle \boldsymbol{R}^2 \rangle \to \sum \frac{N}{4\pi s^2} \left(\frac{1}{\lambda^+_s} + \frac{1}{\lambda^-_s} \right) && \text{as } \tau \to \infty \end{aligned} \tag{29}$$

which is the correct average for the squared radius of gyration for the static case. In addition, $\langle \boldsymbol{R}^2(\tau) \rangle$ behaves properly when the pressure approaches its critical value. In the case $p \to p_c = 4\pi/N$ we observe that the $s = 1$ mode eigenvalue $\lambda^- \to 0$, while all other eigenvalues stay finite. The consequence is that $\langle \boldsymbol{R}^2(\tau) \rangle$ grows linearly in time. That is,

$$\begin{aligned} \langle \boldsymbol{R}^2(\tau) \rangle &= \frac{N}{4\pi^2} 2\tau + \sum_{s \neq 1} \frac{N}{4\pi s^2} \left\{ \frac{1 - \exp(-2s^2 \lambda^-_s \tau)}{\lambda^-_s} + \frac{1 - \exp(-2s^2 \lambda^+_s \tau)}{\lambda^+_s} \right\} \\ &= \frac{N}{4\pi^2} \frac{2t}{t_0} + \mathrm{O}(1) \qquad \text{as } t \to \infty. \end{aligned} \tag{30}$$

We see that the radius grows diffusively, $\langle \boldsymbol{R}^2 \rangle = 4Dt$. The diffusion constant is given by

$$D = \frac{1}{4} \frac{N}{4\pi^2} \frac{2}{t_0} = \frac{\mu k T}{2N\Delta^2}. \tag{31}$$

Similar behaviour was observed in our study of the static case. That is, as p approaches the critical pressure, p_c, the vesicle walls can no longer maintain the pressure differential, and the vesicle 'pops'. Notice that the consequences of this behaviour can also be inferred from equation (24). The probability distribution for the circular, $s = 1$, mode evolves diffusively for all times and does not relax to a Boltzmann form with finite width when $p = p_c$, which again indicates that the system becomes unstable at the critical pressure. With regard to the influence of self-avoidance in this regime, we note that a calculation in the context of the static properties of this model (Gaspari *et al* 1993) indicates that, in the immediate vicinity of the critical pressure, self-avoidance has only a perturbative effect on the properties of the inflated vesicle. This result is consistent with the intuitively appealing conclusion that when a vesicle wall is stretched to breaking point, it will not bend back on itself.

Other parameters characterizing the dynamical evolution of a vesicle's average shape can be calculated in a similar manner. However, a complete statistical description, rather than average values, is available from the joint probability distribution of the principal components, λ_1 and λ_2, of the radius of gyration tensor, $P(\lambda_1, \lambda_2)$. The gyration tensor expressed in terms of link coordinates (Forsman and Hughes 1963) is

$$T_{ij} = \sum_{\alpha\beta} a_{\alpha\beta} \eta_{\alpha i} \eta_{\beta j} \qquad R^2 = \text{Trace } \vec{T}. \tag{32}$$

In two dimensions, $\vec{T}$ is a 2×2 matrix with eigenvalues λ_1 and λ_2, the principal components of the radius of gyration. For the static conformations, we derived an exact formula for $P(\lambda_1, \lambda_2)$ (Gaspari *et al* 1993), but when the system is no longer in equilibrium these results no longer hold. However, it is a straightforward exercise to calculate the dynamical distribution function of the principal moments numerically for the equations described above.

4. Simulations and conclusions

The equations that govern the dynamical evolution of the vesicle bounding wall are readily amenable to simulation. We have generated distributions controlled by equations (22)–(24). The method by which the distributions are generated is described in the preceeding paper (Gaspari *et al* 1993). Briefly, equations (16), (19), (20), (22) and (24) are used along with a Gaussian random number generator to generate distributions of moment-of-inertia matrices at various times. From these matrices we obtain distributions of the principal components of the radius of gyration. As an initial condition, we took a vesicle with $N = 100$ that was constrained to be in a circular configuration. Thus, the initial distribution of λ's is a point. The quantities γ and Δ^2 have been set equal to 1, so lengths are normalized to the equilibruim root-mean-square distance between nodes on the closed walk. The time is expressed in units of $(2\pi/N)^2 \tau$, where τ, the normalized time, is defined below equation (18). The circumference of the initial walk is equal to the value that it would be if the distance between nodes were equal to the equilibrium RMS distance. That is, we are attempting to simulate what would happen if a two-dimensional vesicle whose wall is made up of rigid rods was placed in a zero-pressure environment after having been stretched into a circular shape. The results of these preliminary investigations are displayed as figures 1 and 2. In line with expectations, we find that as the vesicles in the ensemble fluctuate the distribution relaxes to the form predicted by equilibrium theory (Gaspari *et al* 1993). This relaxation is more or less monotonic, but there are, nevertheless, interesting features, including an intermediate spreading out of the distribution of λs during intermediate stages that is partially reversed at the end stages of relaxation. Clearly,

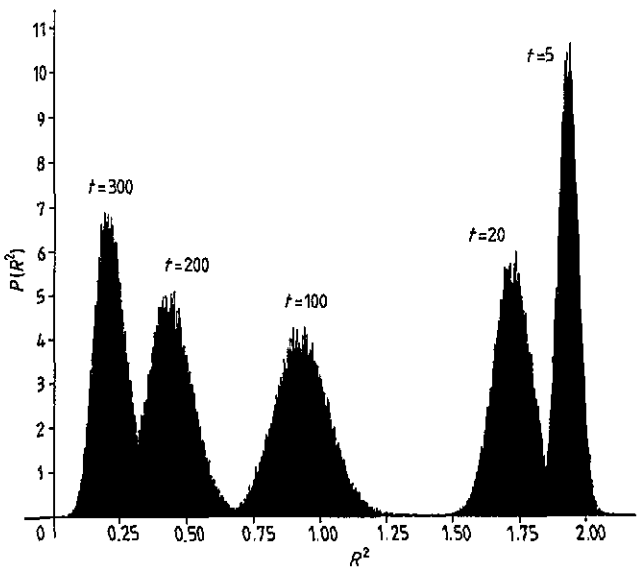

Figure 1. Histogram plot of the dynamical probability distribution function of the square of the radius of gyration, $P(R^2 = \lambda_1 + \lambda_2)$, at various times. At $t = 0$, $P(R^2)$ is a delta function spike at $\lambda_1 + \lambda_2 = 2$. The spike is not displayed. The osmotic pressure difference is taken to be zero.

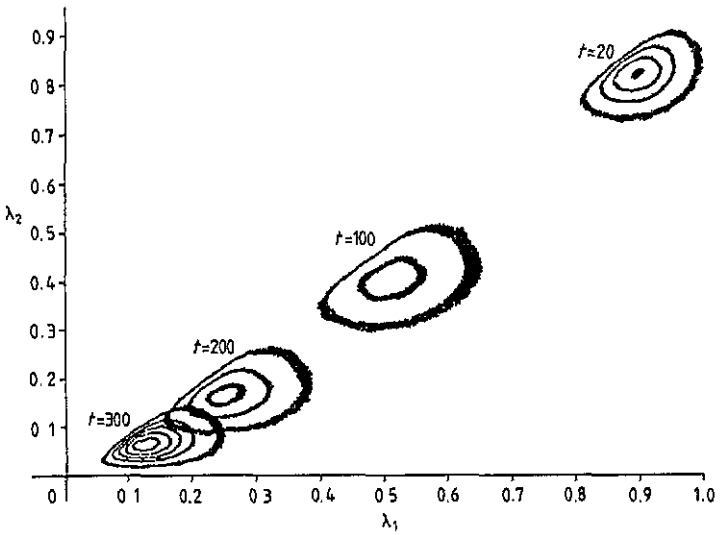

Figure 2. Time evolution of contour plots of the joint eigenvalue distribution, $P(\lambda_1, \lambda_2)$. *The quantities* λ_1 *and* λ_2 *are the principal components of the radius of gyration. As in* figure 1, the osmotic pressure difference is equal to zero. At $t = 0$, $P(\lambda_1, \lambda_2)$ is a point at $\lambda_1 = \lambda_2 = 1$. This initial distribution is not shown.

the simulations reported here do not constitute a definitive study of the dynamics of this model of two-dimensional vesicles. However, we do feel that they provide evidence that the approach to vesicle dynamics discussed in this article, and the model to which this approach is applied, will prove useful in future investigations of this important system.

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