

## Mechanism for Flow-Rate Controlled Breakup in Confined Geometries: A Route to Monodisperse Emulsions

Piotr Garstecki,<sup>1,\*</sup> Howard A. Stone,<sup>2</sup> and George M. Whitesides<sup>1,†</sup>

<sup>1</sup>*Chemistry and Chemical Biology Department, Harvard University, 12 Oxford Street, Cambridge, Massachusetts, USA*

<sup>2</sup>*Division of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, Massachusetts, USA*

(Received 23 June 2004; published 27 April 2005)

This Letter describes a quasistationary breakup of an immiscible, inviscid fluid at low capillary numbers. The breakup proceeds in a coflowing, viscous liquid, in a confined geometry of a long and narrow orifice. In contrast to the capillary instability in an unbounded fluid, the collapse proceeds through a series of equilibria, each yielding the minimum interfacial energy of the fluid-fluid interface. The process is slow in comparison to typical relaxation speeds of the interface, and it is reversible. Its quasistatic character of collapse forms the basis for controlled, high-throughput generation of monodisperse fluid dispersions.

DOI: 10.1103/PhysRevLett.94.164501

PACS numbers: 47.20.-k, 47.60.+i, 68.03.Cd, 82.70.-y

The study of the breakup of fluid cylinders and other interface-driven motions began with the classic works by Plateau [1] and Lord Rayleigh [2]. Recently much attention has focused on the asymptotic dynamics of breakup [3–10]. As the diameter of a breaking fluid cylinder decreases to zero, the radial curvature increases to infinity, and it has been postulated that fluid systems may help understand the formation of singularities [3,8]. These studies consider breakup in a stationary, unbounded fluid. Under such conditions, although there is a typical size of the fluid elements formed by breakup of an immiscible cylinder, such formed drops or bubbles are not generally monodisperse.

Flow-focusing devices (FFD) [11,12] produce emulsions with a polydispersity index [13]  $\sigma < 1\%$ . In spite of the wide use of coflowing liquids to generate emulsions, the problem of breakup in a confined coflow has received little theoretical attention. In this Letter, we show that the dynamics of breakup in a confined geometry of a microfluidic FFD can be entirely controlled by the rate of supply of the continuous fluid to the region in which the breakup occurs. In contrast to the classic Rayleigh-Plateau instability, where perturbations of the shape of the interface lead to rapid and irreversible collapse, here the separation of time scales between the slow progression of collapse and the fast equilibration of the interfacial tension and hydrostatic pressure fields leads to uniform times of collapse of the thread and thus to uniform volumes of the bubbles or droplets produced in the device.

We study the breakup of a gas stream focused by two liquid streams in a microfluidic FFD. Microfluidics offers precise control over the flows of fluids at small scales [14]. Several groups have exercised this control to study the breakup of immiscible liquids. The two most commonly used geometries are the T junction [15] and FFD fabricated either with capillaries [11] or into a poly(dimethylsiloxane) (PDMS) slab [12,16]. The former method apparently exploits a shear-rupturing mechanism in which the size of the droplets is controlled by the capillary number ( $Ca = v\mu/\gamma$ , where  $v$  is the velocity of the continuous liquid,

$\mu$  its viscosity, and  $\gamma$  the interfacial tension)—that is, by the interplay of the shear stress and surface tension. We have recently shown [16] that the volume of the bubbles formed in a FFD is proportional to the pressure  $p$  applied to the gas stream and inversely proportional to the product of the flow rate  $q$  and viscosity  $\mu$  of the liquid. Here, we explain this scaling and demonstrate that the geometrical confinement can be used to stabilize the fluid-fluid interface against interfacial instabilities throughout almost the entirety of the collapse process. At low  $Ca$ , the thread advances into the orifice and restricts the flow of liquid into the outlet channel; this leads to an increase of the hydrostatic pressure upstream of and in the orifice and to “squeezing” of the immiscible thread. This process is slow in comparison to relaxation of the interfacial energy, and as a result collapse proceeds through a series of equilibrium states. Eventually the narrowing neck of the thread becomes unstable and breaks rapidly without contributing appreciably to the size of the broken-off bubbles. The

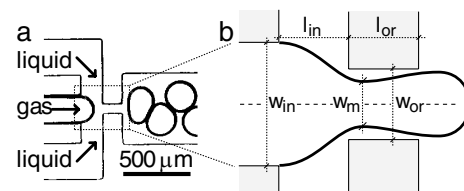


FIG. 1. (a) Optical micrograph of the FFD (top view). The channels are fabricated in PDMS and have a uniform height  $h$ . (b) Schematics of the orifice region and the gas-liquid interface. The shaded areas correspond to PDMS walls and the long-dashed line marks the center line and axis of mirror symmetry of the channel. The figure defines the dimensions of the orifice region: the width of the gas-inlet channel ( $w_{in} = 200 \mu\text{m}$ ), the distance between this inlet and the orifice ( $l_{in} = 150 \mu\text{m}$ ), and the width ( $w_{or} = 60 \mu\text{m}$ ) and length ( $l_{or}$ ) of the orifice. In our experiments we varied  $h$  (28, 36, and  $64 \mu\text{m}$ ) and  $l_{or}$  (50, 100, 150,  $250 \mu\text{m}$ ). For the analysis of breakup, we trace the evolution of the minimum width  $w_m$  of the gaseous thread and its axial curvature  $\kappa$  at this minimum.

separation of time scales for the slow progression of the collapse and fast equilibration of the interface leads to a high reproducibility of every breakup event and to very narrow size distributions of the resultant fluid elements.

Figure 1(a) illustrates the FFD; gas and liquid [17] meet upstream of the orifice at the junction of three inlet channels. The pressure drop along the axis of the device forces the tip of the gas stream into the orifice. Here the thread breaks and periodically releases bubbles into the outlet channel. Over a wide range of parameters, this system produces almost ideally monodisperse bubbles [16]. In order to identify the mechanism behind this reproducible breakup, we imaged the orifice using a high-speed camera and analyzed the shape of the collapsing gaseous thread [Fig. 1(b)]. We were interested in the evolution of the minimal width  $w_m(t)$  of the collapsing neck, and the axial curvature  $\kappa$  at the point of minimum width. We extracted  $\kappa$  by fitting the axial profile of the interface with a parabola;  $\kappa = d^2w/dz^2$ .

A single breakup process can be described by three stages (Fig. 2). First the gaseous thread enters the orifice, penetrates into the outlet channel, and starts to inflate a bubble. The width  $w_m$  of the neck stays constant, and only the portion of the thread located *upstream* of the orifice thins [Figs. 2(b) and 2(c)]. Second, a clearly visible neck develops and the thread collapses at a constant rate [Figs. 2(c)–2(f)]. In the third stage, the thread collapses rapidly, breaks [Figs. 2(f) and 2(g)], and retracts upstream of the orifice, and the whole process starts again [18]. Also, in contrast to the collapse of a gas thread in an infinite fluid, where the axial curvature remains constant [19], we observe that  $\kappa$  increases with time [Fig. 2(a)].

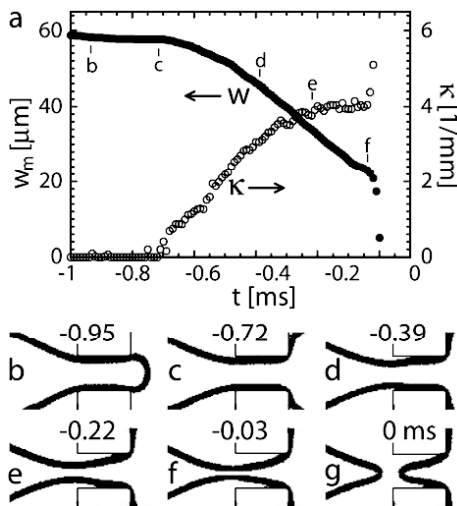


FIG. 2. (a) Evolution of the minimal width  $w_m$ , and the axial curvature  $\kappa$  of the gas-liquid interface in a typical breakup event ( $l_{or} = 100 \mu\text{m}$ ,  $h = 36 \mu\text{m}$ ,  $q = 0.56 \mu\text{L/s}$ ,  $p = 34.5 \text{ kPa}$ ,  $\mu = 0.9 \text{ mPa s}$ , and  $\gamma = 28.7 \text{ mN/m}$ ). (b)–(g) Optical micrographs of the gas-liquid interface along the breakup trajectory. The numbers give the time at which the micrographs were taken with zero set to the moment of breakup.

The qualitative features of the evolution  $w_m(t)$  shown in Fig. 2 are generic, and in order to quantify the dynamics of this process we identify the slope  $dw_m/dt$  in the second stage of the collapse [Figs. 2(c)–2(f)] as the speed of collapse. We varied the rate of flow ( $0.05 < q < 5 \mu\text{L/s}$ ) and viscosity ( $1 < \mu < 11 \text{ mPa s}$ ) [17] of the liquid, the pressure applied to the gas stream ( $5 < p < 100 \text{ kPa}$ ), and the interfacial tension ( $\gamma \approx 30$  and  $73 \text{ mN/m}$ ) [20]. For each experiment, we extracted the speed of the collapse and, rather surprisingly, we found that this speed is independent of the pressure  $p$ , viscosity  $\mu$ , and interfacial tension  $\gamma$ . Over the range of parameters tested in our experiments,  $dw_m/dt$  depends only on  $q$  and the relation between these two quantities is linear (Fig. 3).

We first compare our observations to a classic capillary instability of a gaseous thread. In an unbounded fluid, the “natural” speed of collapse  $u$  is on the order of  $u = u_{\text{VISC}} \approx \gamma/\mu$  or  $u = u_{\text{INERT}} \approx (\gamma/\rho L)^{1/2}$  depending on whether viscous or inertial terms dominate the dynamics of the system ( $L$  denotes a typical radial dimension). The transition between the two regimes is marked by the Ohnesorge number (Oh) equal to unity. For  $L = 10 \mu\text{m}$ , and water-surfactant mixture as the liquid ( $\mu \approx 1 \text{ mPa s}$  [17],  $\gamma \approx 30 \text{ mN/m}$  [20]),  $\text{Oh} = \mu/(\rho\gamma L)^{1/2} \approx 0.06$ , and  $u = u_{\text{INERT}} \approx 2 \text{ m/s}$ . For the most viscous water-glycerol-surfactant mixture we used [17]  $\mu \approx 10 \text{ mPa s}$ ,  $\text{Oh} \approx 0.6$ , and  $u = u_{\text{INERT}} \approx u_{\text{VISC}} \approx 2\text{--}3 \text{ m/s}$ . These estimates are 1 to 3 orders of magnitude larger than the collapse speeds we recorded in our experiments (Fig. 3).

Hammond showed analytically [21] for gas filaments confined to capillaries of circular cross section that, when the thickness  $w_f$  of the liquid film between the interface and the wall is much smaller than the radius  $r$  of the capillary,  $w_f \ll r$ , the speed of collapse in the viscous regime is reduced by a factor of  $(w_f/r)^4$ , and we originally associated the slow character of collapse in our system

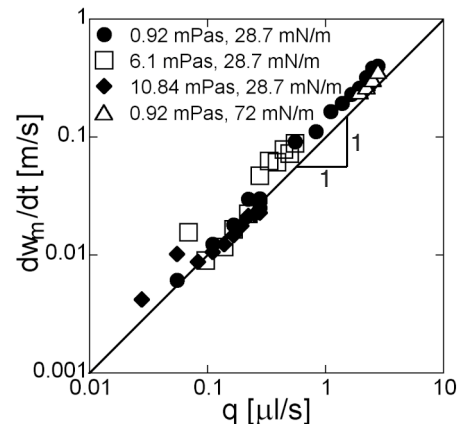


FIG. 3. A log-log plot of the speed of collapse ( $dw_m/dt$ ) plotted against the flow rate of the continuous fluid  $q$  ( $l_{or} = 150 \mu\text{m}$ ,  $h = 28 \mu\text{m}$ ). The gas pressure was set to  $p = 69 \text{ kPa}$  (10 psig). The values of viscosity and surface tension for each series are given in the figure.

with this effect. Two observations, however, contradict this association: (i) the second stage of collapse, for which we determine  $dw_m/dt$ , persists to  $w_m \approx w_{or}/2$  (half the width of the orifice  $w_{or}$ ), at which point  $w_f \approx (w_{or} - w_m)$  is *not* much smaller than  $w_{or}$ , and (ii) Hammond's results for the speed of collapse depend on the value of interfacial tension and we do not observe such dependence [22].

The observations that  $dw_m/dt$  does not depend on  $\gamma$  and that  $dw_m/dt$  is much smaller than the typical speeds of capillary waves are intriguing because the capillary number calculated for the flow of the liquid in the orifice is low:  $Ca = q\mu/(\gamma w_{or}h) \in (10^{-3}, 10^{-1})$ , where  $h$  is the height of the channel. In the following we argue that the thread is *stable* against interfacial instabilities throughout almost the entirety of the collapse, and the collapse is *not* driven by surface tension. An alternative explanation is based on the constant rate of supply of the continuous fluid from a syringe pump. As the thread enters the orifice it restricts the flow of the liquid through the orifice to thin films between the gas-liquid interface and the walls of the channel—especially at the end of the orifice, where capillary pressure forces the interface of the growing bubble to the downstream edges of the orifice. Flow in thin films is subject to an increased viscous dissipation, and, in order to sustain the fixed  $q$ , the syringe pump increases the pressure applied to the liquid streams. Increased hydrostatic pressure of the liquid leads to a displacement—or squeezing—of the interface, and this displacement has to occur at a rate proportional to  $q$ . This mechanism can explain the observed kinetics, subject to the condition that the interface is stable against the capillary instability throughout most of the collapse process.

To verify this stability we used SURFACE EVOLVER [23] to find the shape of the interface that yields the minimum of the interfacial energy. We approximate the geometry of the thread by spanning an interface on two rims of appropriate dimensions—one corresponding to the end of the gas-inlet channel, and the second corresponding to the end of the orifice—and confining the interface between two parallel plates, which correspond to the top and bottom walls of the device. We find a family of equilibrium, catenoidlike geometries parametrized by the volume  $V_{\text{thread}}$  enclosed by the interface (Fig. 4).

The shape of the  $w_m(V_{\text{thread}})$  curve (Fig. 4) is qualitatively similar to the typical evolution of the width of the thread  $w_m(t)$  [Fig. 2(a)] recorded in our experiments. In order to compare the experimental data with the equilibrium picture, we plot the experimentally measured  $w_m$  as a function of the volume of liquid pumped into the orifice region:  $w_m(tq)$ . Figure 4 shows four curves  $w_m(tq)$  illustrating the breakup dynamics over a range of rates of flow ( $q = 5.5 \times 10^{-2}$  to 2.22 mL/s), viscosities ( $\mu = 0.9$  to 10.8 mPa s), and interfacial tension ( $\gamma = 32$  to 72 mN/m). Over this whole range of parameters we observe a near perfect quantitative agreement between the observed collapse processes [ $w_m(tq)$ ] and the equilibrium shapes [ $w_m(V_{\text{thread}})$ ].

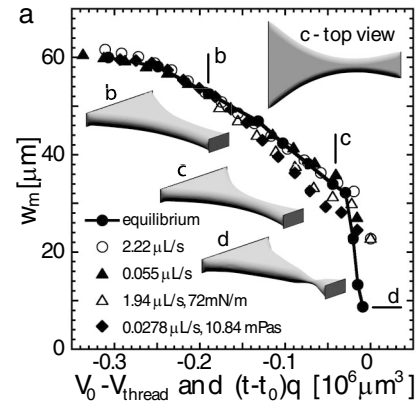


FIG. 4. (a) Comparison of the minimal width  $w_m(V_0 - V_{\text{thread}})$  of the simulated (equilibrium) interface as a function of the volume  $V_{\text{thread}}$  enclosed (solid dots connected by solid lines) and of the experimentally measured minimal widths  $w_m[(t - t_0)q]$  of collapsing threads as a function of volume of the continuous fluid pumped into the orifice (unconnected symbols). The offsets  $V_0$  and  $t_0$  used to overlap the plots are defined as follows:  $V_0$  is the volume enclosed by the gas-liquid interface at which it becomes unstable, and  $t_0$  is the time at which the thread breaks. In the experiment  $h = 28 \mu\text{m}$  and in the simulation  $h = 30 \mu\text{m}$ ; in both simulation and experiment  $l_{or} = 150 \mu\text{m}$ . The flow rate for each data series is given in the figure. Other parameters were set to the following values:  $p = 60 \text{ kPa}$ ,  $\mu = 0.9 \text{ mPa s}$ ,  $\gamma = 28.7 \text{ mN/m}$ , unless otherwise stated in the figure. (b)–(d) Rendering of the equilibrium shape of the gas-liquid interface along the trajectory leading to final breakup. Please note that the interface shown in (d) is also in equilibrium.

We conclude that the collapse proceeds through a sequence of equilibria parametrized by the volume enclosed by the gas-liquid interface. This behavior is in sharp contrast to the classic capillary instability of an inviscid thread in an unbounded fluid, where a collapsing interface can equilibrate its shape only at the speed of a capillary wave. Since this speed is the same as the velocity of the collapse, the interface travels towards the axis preserving (or “remembering” [19]) the initial, perturbed shape.

We can now identify three stages of collapse (Fig. 2). In the first stage the portion of the interface located upstream of the orifice evolves, and the width of the neck is set by the width of the orifice. In the second stage the neck gradually thins, but the interface remains in contact with the top and bottom walls (separated by a thin wetting film of the continuous fluid). In the third stage a portion of the interface detaches from the top and bottom walls and an axi-symmetric segment forms [Fig. 4(d)]. This segment thins rapidly upon further decrease of the volume enclosed by the interface and eventually becomes unstable by a Rayleigh-Plateau type of instability and breaks.

We can also understand the scaling of the volume of the bubbles [16]  $V_b \propto p/q\mu$ . This volume is proportional to the time  $\tau$  that the thread stays open ( $\tau \propto 1/q$ ) times the rate of inflow  $q_g$  of gas into the bubble:  $V_b \propto \tau q_g$ . Since the thread restricts the flow of the liquid into the outlet chan-

nel, during the process of inflation of the bubble,  $q_g$  is approximately the total rate of flow in the outlet channel and, following the Hagen-Poiseuille relation,  $q_g \propto p/\mu$ , yielding  $V_b \propto p/q\mu$ . The quasistatic character of the breakup process explains the observed narrow distribution of the sizes of bubbles generated in our device. The volume of a droplet or bubble generated in the FFD is proportional to the time interval during which the immiscible thread is open, multiplied by the rate of flow of the inner fluid through the collapsing neck. Regardless of the geometrical details of the device and of the particular flow parameters, the rate of flow into the droplet or bubble is governed by the distribution of pressure in the system. This distribution equilibrates at the speed of sound in the given media. We estimate the time scale  $\tau_s$  for the equilibration in the continuous phase to be the width of the orifice (typically 10–100  $\mu\text{m}$ ) divided by the speed of sound in water ( $\sim 10^3$  m/s); that is,  $\tau_s \approx 10^{-8}$  to  $10^{-7}$  s. This value is orders of magnitude smaller than the time it takes to close the thread, and, as a result, the size of the pinched-off fluid elements is controlled by equilibrated “macroscopic” variables, and each breakup event is virtually the same.

There are two necessary conditions for the collapse to exhibit a quasistatic character: (i) the geometry of the thread has to be stable against the capillary instability, and (ii) the rate of thinning of the thread ( $dw_m/dt$ ) has to be much slower than typical rates of relaxation of the interfacial energy ( $u_{\text{INERT}}$  or  $u_{\text{VISC}}$ ). In our system, we impose the rate of flow  $q$  of the liquid and observe that  $dw_m/dt$  is proportional to  $q$ . Keeping  $q$  constant is not, however, a prerequisite for the quasistatic character of the collapse. In fact, we do observe similar evolution of the shape of gas-liquid interface in experiments in which we control the pressure applied to the continuous phase and its rate of flow is changing during breakup. The mechanism described in this Letter should be applicable also to liquid-liquid dispersions. The presence of a liquid in the inner core introduces higher viscous stresses between the two fluids; the scaling of the size of the droplets and the shape of the interface might change, but the quasistatic character can be preserved and used to control the size distribution of droplets.

We have shown how the confinement of the orifice in the FFD can be used as a tool for controlling the dynamics of the breakup of immiscible fluids. We believe that an understanding of the influence of flow and confinement on the dynamics of immiscible threads in a coflow system is an important addition to the theoretical understanding of interfacial stability, and it might lead to applications in precise control of small fluid elements.

We thank Dr. Itai Cohen for helpful conversations. P. G. acknowledges financial support from the Foundation for Polish Science. We thank the Harvard MRSEC for the use of high-speed cameras. H. A. S. thanks Unilever for support. This work was supported by the U.S. Department of Energy (DE-FG02-00ER45852).

- \*Electronic address: pgarstecki@gmwgroup.harvard.edu  
 †Electronic address: gwhitesides@gmwgroup.harvard.edu
- [1] J. Plateau, *Statique Experimentale et Theoretique des Liquids Soumis aux Seules Forces Moleculaires* (Gautier-Villars, Paris, 1873).
  - [2] Lord Rayleigh, Proc. London Math. Soc. **10**, 4 (1879); Lord Rayleigh, Philos. Mag. **34**, 145 (1892).
  - [3] J. Eggers, Phys. Rev. Lett. **71**, 3458 (1993).
  - [4] J. Eggers, Phys. Rev. Lett. **89**, 084502 (2002); M. Moseler and U. Landman, Science **289**, 1165 (2000).
  - [5] H. A. Stone, Annu. Rev. Fluid Mech. **26**, 65 (1994).
  - [6] I. Cohen, M. P. Brenner, J. Eggers, and S. R. Nagel, Phys. Rev. Lett. **83**, 1147 (1999).
  - [7] A. Rothert, R. Richter, and I. Rehberg, Phys. Rev. Lett. **87**, 084501 (2001).
  - [8] A. U. Chen, P. K. Notz, and O. A. Basaran, Phys. Rev. Lett. **88**, 174501 (2002).
  - [9] I. Cohen and S. R. Nagel, Phys. Rev. Lett. **88**, 074501 (2002).
  - [10] D. Leppinen and J. R. Lister, Phys. Fluids **15**, 568 (2003).
  - [11] A. M. Ganan-Calvo and J. M. Gordillo, Phys. Rev. Lett. **87**, 274501 (2001).
  - [12] S. L. Anna, N. Bontoux, and H. A. Stone, Appl. Phys. Lett. **82**, 364 (2003).
  - [13] Polydispersity index defined as the standard deviation of the radius of the bubble divided by the mean radius.
  - [14] H. A. Stone, A. D. Stroock, and A. Ajdari, Annu. Rev. Fluid Mech. **36**, 381 (2004).
  - [15] T. Thorsen, R. W. Roberts, F. H. Arnold, and S. R. Quake, Phys. Rev. Lett. **86**, 4163 (2001).
  - [16] P. Garstecki, I. Gitlin, W. Diluzio, E. Kumacheva, H. A. Stone, and G. M. Whitesides, Appl. Phys. Lett. **85**, 2649 (2004).
  - [17] We have used nitrogen as the gas phase and three different aqueous solutions of glycerol [0%, 52%, and 62% (w/w)] and calculated their viscosities according to Dow-Corning tables of viscosity of water-glycerol mixtures, for 24 °C.
  - [18] See EPAPS Document No. E-PRLTAO-94-026518 for the details of the collapse process in systems with orifices of square cross section. A direct link to this document may be found in the online article’s HTML reference section. The document may also be reached via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from [ftp.aip.org](ftp://ftp.aip.org) in the directory /epaps/. See the EPAPS homepage for more information.
  - [19] P. Doshi, I. Cohen, W. W. Zhang, M. Siegel, P. Howell, O. A. Basaran, and S. R. Nagel, Science **302**, 1185 (2003).
  - [20] We have measured the interfacial tensions between the solutions and air,  $\gamma = 37$  mN/m [2% (w/w) Tween-20],  $\gamma = 31.6$  mN/m [2% (w/w) Tween-20, 52% (w/w) glycerol], and  $\gamma = 33.1$  mN/m [2% (w/w) Tween-20, 62% (w/w) glycerol]. For a clean water–nitrogen interface we assume the value for water–air interface  $\gamma = 72$  mN/m.
  - [21] P. S. Hammond, J. Fluid Mech. **137**, 363 (1983).
  - [22] Suppression of capillary instability and decrease of the speed of collapse have also been observed for immiscible threads confined between two parallel plates. These results, however, also show dependence on interfacial tension. Y. Son, N. S. Martys, J. G. Hagedorn, and K. B. Migler, Macromolecules **36**, 5825 (2003).
  - [23] Ken Brakke, <http://www.susqu.edu/facstaff/b/brakke/evolver/>.