University of Massachusetts Amherst
ScholarWorks@UMass Amherst

Mathematics and Statistics Department Faculty
Publication Series

Mathematics and Statistics

2003

An exploding glass?

PG Kevrekidis
University of Massachusetts - Amherst, kevrekid@math.umass.edu

et. al

Follow this and additional works at: https://scholarworks.umass.edu/math_faculty_pubs

Part of the Physical Sciences and Mathematics Commons

An exploding glass ?

P.G. Kevrekidis[1], S. K. Kumar[2] and I.G. Kevrekidis[3]

[1] *Department of Mathematics and Statistics, University of Massachusetts, Amherst, MA 01003-4515, USA*

[2] *Department of Chemical Engineering, Rensselear Polytechnic Institute, Troy, NY 12180*

[3] *Department of Chemical Engineering and PACM, Princeton University, 6 Olden Str. Princeton, NJ 08544*

(February 1, 2008)

We propose a connection between self-similar, focusing dynamics in nonlinear partial differential equations (PDEs) and macroscopic dynamic features of the glass transition. In particular, we explore the divergence of the appropriate relaxation times in the case of hard spheres as the limit of random close packing is approached. We illustrate the analogy in the critical case, and suggest a "normal form" that can capture the onset of dynamic self-similarity in both phenomena.

I. INTRODUCTION

The onset of dynamic self-similarity, *i.e.*, the emergence of solutions that blow-up (or decay) with appropriate scaling laws, has been a very widely studied topic (see e.g., [1–3] and references therein). Focusing has been extensively examined through a dynamic renormalization framework. The key idea lies in appropriately dynamically rescaling space, time and the amplitude of the solution [5], so that self-similar blowup solutions appear as steady states of the renormalized equation. A benchmark model for blowup is the nonlinear Schrödinger (NLS) equation [1], with which a large number of studies have been concerned [5–7].

In a recent study [4] we revisited NLS focusing using a template-based, dynamic renormalization approach motivated by the template-based symmetry reduction of [8]. Our procedure can be generally applied in equations that (may) possess solutions with dynamic self-similarity. Alternative such examples can be found in [9] and in the more systematic study of [10]. While essentially equivalent to other dynamic renormalization techniques, this approach provided a natural setting for studying the parametric onset of dynamic self-similarity *as a steady state bifurcation problem* for a PDAE: a PDE (in the "co-exploding" frame) coupled with an algebraic constraint. The latter imposes the instantaneous rescaling rate by comparing the evolving solution with rescaled versions of an (essentially arbitrary) template function. At steady state of the PDAE, one recovers the self-similar shape as well as the asymptotic "explosion rate" G. One also recovers -as with any correct dynamic renormalization approach- the scaling rates for time, space, and for various observables of the system as a function of (original or rescaled) time: the self-similarity exponents. The method can be applied to both types of self-similar solutions [11]; it was used in [9] to locate both the Barenblatt and the Graveleau solutions of the nonlinear diffusion equation.

The interesting twist is that, in this rescaled setting, the appearance of solutions that blow up (in the NLS setting, in finite time) becomes a steady state bifurcation problem: the bifurcation from branches of solutions with $G = 0$ to branches with nonzero G. The nature of this bifurcation was computationally explored in [4], complementing earlier analytical and numerical studies [1,5]. A good analogy to this setting could be given by the bifurcation, from a ring of stationary solutions, of nonzero-speed rotating waves in a pattern formation probem with O(2) symmetry [12].

The purpose of this note it to propose, at a phenomenological level, a connection between focusing dynamics of NLS close to criticality, on the one hand, and the onset of macroscopic glassy dynamics on the other. Our particular "glassy example" is a thought experiment involving hard-sphere jamming: it arises from modeling the continuing insertion of hard spheres in a fluid of such spheres. We will show that this non-parametric example exhibits dynamics consistent with critical blowup (i.e., with the dynamics exactly at the onset of self-similarity) in NLS. We will then go one step further in this phenomenological analogy, and consider the case of a distinguished parameter. We will speculate about the "explosion-slowdown" connection beyond criticality, motivated by a "normal form" for the parametric dependence of the NLS explosion rate. Beyond criticality, NLS solution observables explode at finite time; one might conversely think for glasses that time "blows up" at finite values of the system observables. We will conclude by a brief discussion, and outline computational experiments that might confirm or disprove the proposed analogy.

II. A CRITICAL EXAMPLE: THE SPHERE JAMMING PROBLEM

As a paradigm of glassy behavior, we examine the evolution of the density of a fluid of hard spheres in the neighborhood of the close packing limit.

We are interested in the insertion probability of an additional sphere in a fluid of hard spheres: its "materialization" is "accepted" if the new sphere does not overlap with any of the previously existing ones in the fluid.

For the hard sphere system we will consider that our thought experiment proceeds at constant volume, and the pressure increases, presumably diverging in the limit of random close packing [13].

Let us define the "density" (i.e., volume fraction), η as

$$\eta = \frac{N}{V} \frac{\pi \sigma^3}{6} \tag{1}$$

Here N is the number of spheres, each of diameter σ and V is the volume of the box. This system undergoes a crystallization transition at $\eta_m \sim 0.495$ [14–16]. The equation of state changes when one crosses this density, even though we shall be dealing with fluid phases at all times. The thermodynamics of these systems are governed by the radial distribution function at contact, i.e., $g(\sigma^+)$. For $\eta \leq \eta_m$ an excellent approximation is,

$$g(\sigma^+) = \frac{(1 - \eta/2)}{(1 - \eta)^3} \tag{2}$$

This is known as the Carnahan-Starling approximation [13,14]. For $\eta > \eta_m$, Torquato [13] has proposed the following approximation,

$$g(\sigma^+) = g_m(\sigma^+) \frac{(\eta_c - \eta_m)}{(\eta_c - \eta)} \tag{3}$$

where η_c is the random close packed density, the ultimate limit for hard spheres, and $g_m(\sigma^+)$ is the contact value of the radial distribution function at η_m. We now use that

$$A(V) - A(V = \infty) = -\int_\infty^V P dV \tag{4}$$

where A is the Helmholtz energy, P the pressure, and V the volume, and further use the identity

$$\frac{PV}{N k_B T} = 1 + 4\eta g(\sigma^+). \tag{5}$$

The probability p_{ins} for particle insertion (i.e., taking a system of N particles in volume V and adding one more particle to it) is then computed through

$$-\ln p_{ins} = A_{\text{ex}}(N + 1) - A_{\text{ex}}(N), \tag{6}$$

where $A_{\text{ex}}(N) = A(N) - A_{ID}(N)$, and $A_{ID}(N)$ is the Helmholtz energy of an ideal gas system with N particles in volume V.

Here we begin to perform a thought experiment: we attempt to add speres to the fluid at a constant attempt rate. If this attempt rate is slow compared to the relaxation of the fluid after each new addition, we can exploit thermodynamic considerations (the insertion probability based on the equilibrium radial distribution function) to extract a form of dynamics. A "kinetic" evolution of the density of spheres, based in part on our arbitrary (but slow) attempt rate, and in part on the equilibrated (for each density) radial distribution function, would then arise, in the form of the ordinary differential equation:

$$\frac{d\eta}{dt} \sim \begin{cases} \exp\left[-\frac{\eta(8 - 9\eta + 3\eta^2)}{(1-\eta)^3}\right] & \eta \leq 0.495, \\ \exp\left[-16.543 + 3.576\ln\left(\frac{0.644 - \eta}{0.644 - 0.495}\right) - 3.576\left(\frac{\eta}{0.644 - \eta} - \frac{0.495}{0.644 - 0.495}\right)\right] & 0.495 \leq \eta \leq 0.644, \end{cases} \tag{7}$$

The right hand side in Eq. (7) represents essentially the probability of insertion of an additional sphere in the fluid of spheres. This relation is meant as an equation with a non-dimensional time (rescaled by the "sphere materialization attempt rate", $\dot{N}\pi\sigma^3/(6V)$ [attempts/sec]). We repeat that these attempts are executed quasistatically, so that equilibrium ideas can be used to evaluate p_{ins}.

We examine briefly the transient behavior induced by the top line of Eq. (7). The function of the exponent $f = \eta(8 - 9\eta + 3\eta^2)/(1 - \eta)^3$ can be well-approximated by the Taylor series $f \approx 8\eta + 15\eta^2 + 24\eta^3 + 35\eta^4 + O(\eta^5)$, while the $\exp(-f)$ is practically indistinguishable (in the range of values of interest) from $\exp(-\alpha\eta - \beta\eta^2)$, with $\alpha = 8$ and $\beta = 15$. Hence a very accurate approximate solution is given by

$$\eta = \frac{-\alpha + 2\sqrt{\beta}\,\text{Erfi}^{-1}\left[\frac{2\sqrt{\beta}(t+C)\exp(\frac{\alpha^2}{4\beta})}{\sqrt{\pi}}\right]}{2\beta}, \tag{8}$$

where C is an appropriate constant chosen by the initial condition $\eta(t=0)$. Notice that already in this transient dynamics the exponential (asymptotic) behavior of the imaginary error function Erfi ($\text{Erfi}(z) \sim \exp(z^2)/z$, for large z), already preludes the logarithmic slowdown as higher densities are approached.

We now turn to the case of approach to the maximal concentration of 0.644, described by the bottom panel of Eq. (7). The latter equation can be cast in the form

$$\frac{d\eta_r}{d\tau} = -\eta_r^{a_s} \exp\left[-\frac{C_s}{\eta_r}\right], \tag{9}$$

where $\eta_r = 6.711(0.644 - \eta)$ is a rescaled measure of the density (in fact of its "distance" from the maximal density); $\tau = 2.263t$ is a rescaled time. The constants of the equation are $a_s = 3.576$, and $C_s = 15.456$.

One can straightforwardly identify Eq. (9) with the normal form equation *at criticality* of a relevant observable (the blowup rate) of the NLS equation which we will now discuss. In the following section, motivated by this analogy, we proceed to give the relevant background, examining in more detail the dynamics of focusing in the NLS setting.

III. NLS BACKGROUND: THE FOCUSING TRANSITION

As mentioned above, the nonlinear Schrödinger (NLS) equation [1] is a famous example of an envelope equation that exhibits a transition from regular to self-similarly blowing up solutions. In the NLS

$$iu_t = -u_{xx} - |u|^{2\sigma}u, \tag{10}$$

focusing phenomena (e.g., finite time blowup) are known to occur as the parameters (more specifically in the case of Eq. (10), the power σ of the nonlinearity) are varied. Here u is a complex envelope field (e.g., a slow modulation of the electric field of light) [1], while the subscripts denote partial derivatives. Notice that the one dimensional version of the equation (in space) has been used, but the problem can also be considered in d-dimensions (where the second spatial derivative is exchanged with the Laplacian). It is then found [1,4] that while solitary wave solutions exist for all values of σ in Eq. (10), for $\sigma \geq \sigma_c \equiv 2$ (and in general for $d\sigma \geq 2$), such solutions are unstable towards blowup (collapse). In the latter case, the amplitude of the solution becomes infinite (in finite time), while the "width" of the solution shrinks to 0. The two processes occur in a self-similar fashion (and with rates that are proportional to each other). These singular solutions are of the form:

$$u(x,t) = L^{-1/\sigma}e^{i\tau}v(\xi,\tau), \tag{11}$$

where $\xi = x/L(t)$ is the rescaled spatial variable and τ given by $\tau_t = 1/L^2$ is the rescaled time. $L(t) = 2G(t^\star - t)^{1/2}$ is the stretching length, and $-L_\tau/L = G$ is the blowup rate. $t^\star$ is the (finite) time at which blowup occurs. These solutions can be systematically analyzed from a dynamic renormalization point of view [1,5,4], in which they appear as (stable) steady states. Using the scaling of Eq. (11) or through the systematic procedure of deriving it [4], one obtains the renormalized PDE

$$iv_\tau = -v_{\xi\xi} - |v|^{2\sigma}v - iG(\tau)(\frac{1}{\sigma}v + \xi v_\xi). \tag{12}$$

An appropriate algebraic constraint is given by

$$\int_{-\infty}^{\infty} Re(v(\xi,\tau))T(\xi)d\xi = C, \tag{13}$$

where C is an essentially arbitrary constant and $T(\xi)$ is an arbitrary "template" function; this provides the algebraic equation that determines the instantaneous explosion rate $G(\tau)$. Other appropriate formulations of this algebraic constraint (e.g., the minimization of the distance of the evolving solution from scaled versions of the template) are equally acceptable and yield the right steady state. Essentially G plays the role of a Lagrange multiplier that enforces the conservation of the overlap integral of Eq. (13), according to:

$$G = -\frac{L_\tau}{L} = -\frac{\int_{-\infty}^{\infty}\left[W_{\xi\xi} + (U^2 + W^2)^\sigma W - W\right]T(\xi)d\xi}{\frac{C}{\sigma} + \int_{-\infty}^{\infty}\xi U_\xi T(\xi)d\xi}. \tag{14}$$

U represents the real and W the imaginary part of the solution v of Eq. (12). Then, the bifurcation of the focusing branch (with $G \neq 0$) of solutions from the (unstable for $\sigma > 2$) solitary wave one (with $G = 0$) occurs as a supercritical Hopf-like bifurcation in a new type (mixed Hamiltonian- dissipative; see e.g., [4]) of dynamical system. In the relevant bifurcation diagram shown in Fig. 1, the appearance of the new (focusing) branch occurs, as the parameter σ is varied, with an exponentially small dependence according to [1,5,4]

$$\epsilon G^{ss} \sim \exp(-\frac{C}{G^{ss}}), \tag{15}$$

where $\epsilon = (\sigma - 2)/\sigma$ and the superscript "ss" serves to denote that this equation yields the steady state value of G (i.e., the parameter-dependent, asymptotic blowup rate). We can think of G as an observable of the transient solution of the PDAE set of Eqs. (12)-(14); it is the rate by which the width of the solution must be scaled (and proportional to the rate by which the amplitude of the solution must be scaled), so that the solution appears as steady. We will return later to the parametric dependence of the asymptotic blowup rate as a function of the parameter ϵ, and even the dynamical approach of G to its steady state value in transient simulations.
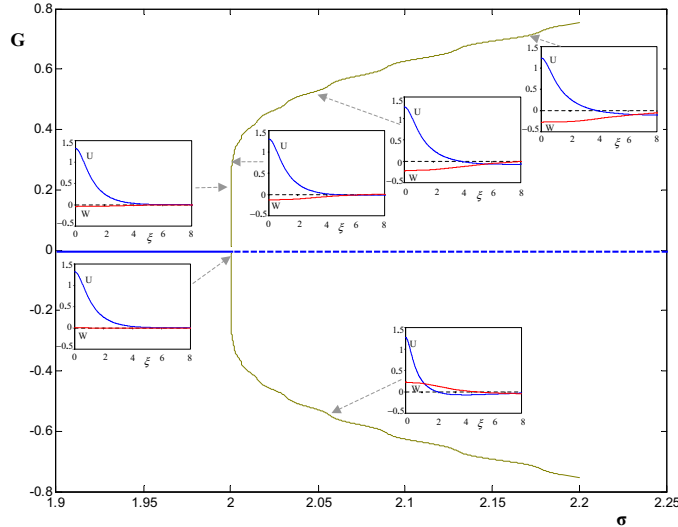

FIG. 1. The figure shows the bifurcation diagram of G vs. σ. At $\sigma_{cr} = 2$, the new branch of focusing solutions is born. The panel insets show the profile of the solution in different points along the branch.

We will now concentrate on the critical case $\sigma = 2$, where the asymptotic G is zero; indeed, at criticality, all the (appropriately) rescaled forms of the soliton are standing wave solutions of the NLS; hence, the soliton is neutral to scale perturbations. In this critical case, it is known from earlier work [1,5] that there is no solution with $G \neq 0$; if one starts close to (but not exactly on) a solution with $G = 0$, the evolution of G will follow the normal form dynamics [1,5] of

$$\frac{dG}{d\tau} = -G^a \exp\left(-\frac{C}{G}\right), \tag{16}$$

where $a = -1$, and $C \approx 3.1$.

The steady state branch results in [1,5,4] and the dynamic results for the critical case normal form of Eq. (16) can be unified [17] in a single "normal form" equation containing the salient features of the onset of dynamic self-similarity for the NLS: namely

$$\frac{dG}{d\tau} \sim \epsilon - G^a \exp\left(-\frac{C}{G}\right). \tag{17}$$

This equation encapsulates the slow (logarithmic) approach to $G = 0$ for the critical case of $\sigma = 2(\epsilon = 0)$. Setting $dG/d\tau = 0$ at supercritical σ, the equation will give the correct stable blowup solution. As a dynamic equation with

4

an equal sign, for $\sigma > 2$ it will predict the "relaxation" (in fact, reshaping) of the now unstable soliton into the stable blowup solution, and the subsequent asymptotic evolution of the latter towards infinite amplitude. The details of this normal form for the onset of dynamic self-similarity will be presented elsewhere [17]. We now turn to the connections of this normal form at criticality with our particular glassy example.

IV. FROM FOCUSING TO JAMMING: DRAWING ANALOGIES

It is interesting to draw the parallels between Eq. (9) and Eq. (16), and between the two cases more generally. In our example of glassy behavior (the sphere problem), there is no free parameter. Hence, it is natural to expect that this example is exactly on the threshold (critical point) for the onset of glassy behavior (i.e., at "$T = T_g$", or equivalently at $\sigma = 2$). Naturally then one expects that the concentration approaches the close packing limit, but with a logarithmic ("glassy") slowdown. The system "arrives" at such a limiting density in infinite time (i.e., the time explodes at finite density) but only at an extremely slow rate, as is the case for the weak collapse of NLS in the critical setting of $\sigma = 2$.

Should a natural parameter be inserted in the system, we would expect that its behavior would exhibit a transition to dynamically self-similar "glassiness" as a critical parameter value is crossed. We expect that the more general NLS "normal form" dynamics could account for the glass transition as such a bifurcation: another onset of dynamic self-similarity. This time, however, instead of explosive acceleration, a progressive slowdown of the solution observables/rates is expected.

Notice that one can further deduce, using appropriate integral asymptotic expansions [18], the asymptotics of the approach to the maximal density of 0.644. Using the transformations $\tau \to \tilde{\tau} = 1.156 \times 10^3 \tau$ and $\eta_r \to \tilde{\eta} = 15.646/\eta_r$, one obtains the asymptotic expression for the time dependence of the density

$$\tilde{\eta} \sim \ln(\tilde{\tau} - \tilde{\tau}_0) \left[1 - 1.576 \frac{\ln(\ln(\tilde{\tau} - \tilde{\tau}_0))}{\ln(\tilde{\tau} - \tilde{\tau}_0)} \right]. \tag{18}$$

A very long time evolution (for times of $O(10^6)$) of the ODE of Eq. (7) is shown in Fig. 2, verifying the prediction for logarithmic slowdown as the close packing density is approached. One might argue that, what is referred to as "the colloidal glass transition" occurs when the observed rate becomes, say, twelve orders of magnitude slower than the initial rate. Using this argument, one would "declare" a colloidal glass transition from this diagram at a density of $\eta \approx 0.566$, within the accepted range of $0.56 - 0.58$ [15]. Notice, however, that in experimental studies of the colloidal glass transition, the particles are moving even for higher concentrations, and they only freeze (and the viscosity diverges) at a density of 0.644 [19].
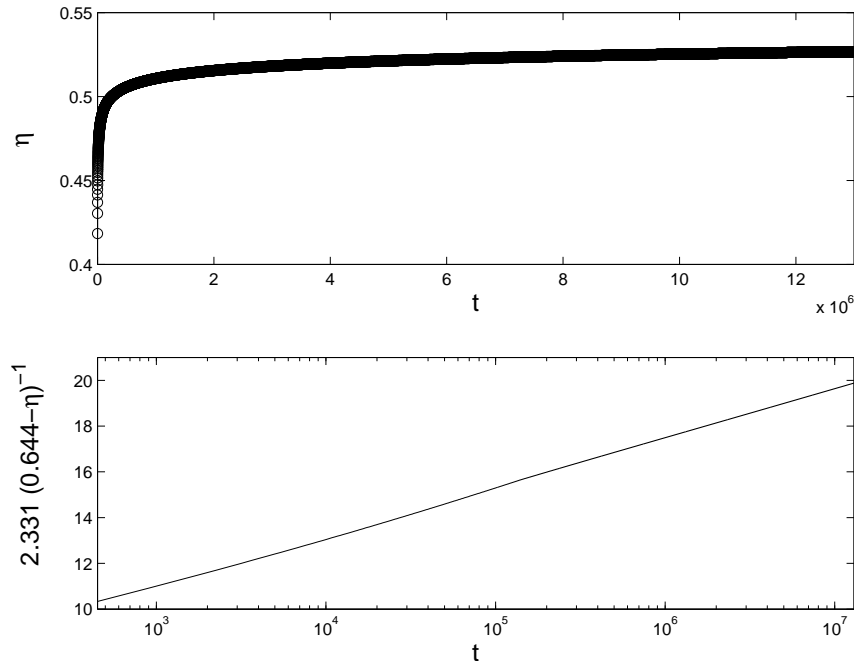
FIG. 2. The top panel shows the evolution of the density η as a function of time, from an initial condition of $\eta(0) = 0.1$. The bottom panel illustrates in a semilog plot the logarithmic nature of this dependence in plotting $\tilde{\eta}$ as a function of t. The linear best fit is yields a slope of 0.95 which is very close to the theoretically predicted slope of 1. The discrepancy can be well-justified by the asymptotic nature of the prediction as well as by the doubly logarithmic corrections of Eq. (18).

Finally, we also mention in passing that using the results of [13], one can infer the leading order spatial and temporal dependence of the conditional pair distribution function. Its amplitude will grow as $\sim 1/(\eta_c - \eta)$ i.e., logarithmically in time, while it will decay to leading order as $1/r$ in space (for large r). We will examine in more detail the spatial dependence of properties of the glass transition in a future publication.

V. DISCUSSION

The description of the glassy state has been a puzzling problem for theorists for many decades [20–22]. On the one hand, the transition to this state does not possess as clean-cut characteristics as other phase transitions [20]; on the other hand, however, it is clear that vitrification induces a significant change in the properties of a material. Furthermore, often but not always a critical (glass transition) temperature, T_g, can be identified [23].

For these reasons, the glass transition is often considered/studied as a *dynamical transition*. The relevant prism that is at present widely used [20,21] is that of mode coupling theory [24] that views the formation of the glass as a transition from ergodic to non-ergodic behavior in which structural arrest renders whole regions of phase space unavailable for microscopic configurations. In this framework, a macroscopic correlation function (in fact, the Fourier transform of the density-density correlation function) is the central object of study, and linear (or nonlinear) ordinary differential equations with delay are written for its time evolution. The existence of memory kernels in the time evolution results in the evolution towards a different "steady state" for long time asymptotics in the glassy state than in the liquid case. This dynamical transition is identified as the glass transition [20].

Motivated by the previous sections, we posit an alternative viewpoint on this transition. We showed an analogy between the logarithmic dynamics of the NLS at criticality, and the logarithmic behavior of the density in the sphere jamming problem. Based on this analogy, we argue that the non-parametric sphere-jamming problem is "critical" in its glassy dynamics. An important link in our analogy is the use (in our thought experiment) of "thermodynamic information" (an equilibrated radial distribution function) with a kinetic concept (a constant sphere addition attempt rate) to predict "glassy" dynamics. We conjecture that, when an equation corresponding to Eq. (17) becomes available, containing a distinguished parameter, dynamics analogous to the supercritical focusing NLS will emerge. While for NLS the rates of change of some observables accelerate with time (and the corresponding observables "explode" to infinity), for glasses the analogous rates will decelerate with time. When observables like density approach a finite value, the inverse of the distance of the observable from its limiting value again approaches infinity (see Eq. (18)); zeros and infinities in the two cases appear to be a matter of choice of observables.

Typical dynamic codimension-one bifurcations result in branches that are power-laws in the bifurcation parameter (see e.g., [26]). In contrast, in the NLS case, the onset of dynamic self-similarity is an exponentially small effect. We expect a similar structure in the "onset of glassiness" as a function of the distance from the corresponding critical point. One can contrast the explosion of the NLS amplitude as a function of time, to "time explosion" for the glassy case as a function of an observable such as density.

Even though qualitative, and of purely macroscopic nature, the conjecture carries a number of attractive features as an alternative viewpoint on the glass transition. A natural next step would involve the examination of the sphere model in the presence of an external tunable free parameter. Models of glassy dynamics possessing a distinguished parameter might also provide supporting evidence [27]. In [4] we computationally converged on self-similar solutions through either integration or bifurcation analysis of the dynamically renormalized equation. It is possible to extend this procedure to operate on a microscopic (e.g. molecular dynamics) simulator of a process, when we believe that macroscopic equations of the type of Eqs. (12)-(14) exist, but are not available in closed form (e.g. see [28]). In our case we were fortunate to have a single closed equation in terms of a single observable (the density); in more complicated systems the "coarse dynamics" approach can be used to search for self-similar dynamics in the evolution of several moments of an evolving particle distribution without ever writing these equations in closed form. It is conceivable that a distributed macroscopic observable (like the density-density correlation function) can be used as the object for which self-similar dynamics in space as well as in time will be sought. Another interesting direction would be to explore possible analogies between multiple interacting blowup spots in the focusing/NLS setting and the effect of heterogeneities in glassy dynamics of extended systems. Finally, it would also be relevant to examine how this view of the glass transition could be related to the explosion-collapse duality arising in some focusing problems

such as Bose-Einstein condensation [29].

[1] C. Sulem and P.L. Sulem, *The Nonlinear Schrödinger Equation*, Springer-Verlag (New York, 1999).

[2] L. Bergé, Phys. Rep. **303**, 259 (1998).

[3] J. Juul Rasmussen and K. Rypdal, Phys. Scr. **33**, 481 (1986).

[4] see e.g., C.I. Siettos, I.G. Kevrekidis and P.G. Kevrekidis, nlin.PS/0204030 and references therein.

[5] D.W. McLaughlin, G.C. Papanicolaou, C. Sulem and P.L. Sulem, Phys. Rev. A **34**, 1200 (1986); B.J. LeMesurier, G.C. Papanicolaou, C. Sulem and P.L. Sulem, Phys. D **31**, 78 (1986); *ibid.* **32D**, 210 (1988); M.J. Landman, G.C. Papanicolaou, C. Sulem and P.L. Sulem, Phys. Rev. A **38**, 3837 (1988); N. Kopell and M.J. Landman, SIAM J. Appl. Math. **55**, 1297 (1995); C. Sulem and P.L. Sulem, Nonlin. Anal. Theor. Meth. Appl. **30**, 833 (1997).

[6] M.J. Landman, G.C. Papanicolaou, C. Sulem, P.L. Sulem and X.P. Wang, Phys. D **47**, 393 (1991); W. Ren and X.P. Wang, Journal of Comp. Phys. **159**, 246 (2000).

[7] V.E. Zakharov and V.F. Shvets, JETP Lett. **47**, 275 (1988); N.E. Kosmatov, V.F. Shvets and V.E. Zakharov, Phys. D **52**, 16 (1991); S.N. Vlasov, L.V. Piskunova and V.I. Talanov, Sov. Phys. JETP **68**, 1125 (1986).

[8] C.W. Rowley and J.E. Marsden, Physica D **142**, 1 (2000).

[9] D.G. Aronson, S.I. Betelu and I.G. Kevrekidis, nlin.AO/0111055 (2001).

[10] C.W. Rowley, I. G. Kevrekidis, J. E. Marsden and K. Lust, submitted to *Nonlinearity* (2002).

[11] G.I. Barenblatt, *Scaling, Self-Similarity and Intermediate Asymptotics* (Cambridge University Press, Cambridge 1996).

[12] I.G. Kevrekidis, B. Nicolaenko and J.C. Scovel, SIAM J. Appl. Math. **50**, 760 (1990).

[13] S. Torquato, Phys. Rev. E **51**, 3170 (1995).

[14] M.D. Rintoul and S. Torquato, Phys. Rev. Lett. **77**, 4198 (1996).

[15] E.R. Weeks, J.C. Crocker, A.C. Levitt, A. Schofield and D.A. Weitz, Science **287**, 627 (2000).

[16] A. Kasper, E. Bartsch and H. Sillescu, Langmuir **14**, 5004 (1998).

[17] P.G. Kevrekidis, I.G. Kevrekidis, B. Sandstede and C.I. Siettos, preprint.

[18] A.M. Smirnov and G.M. Fraiman, Phys. D **52**, 2 (1991).

[19] Z. Cheng, J. Zhu, P.M. Chaikin, S.-E. Phan and W.B. Russel, Phys. Rev. E **65**, 041405 (2002).

[20] P.G. Debenedetti, *Metastable Liquids, Concepts and Principles*, Princeton Univ. Press (Princeton, 1996).

[21] P.G. Debenedetti and F.H. Stillinger, Nature **410**, 259 (2001).

[22] C.A. Angell *et al.*, J. Appl. Phys. **88**, 3113 (2000).

[23] W. Götze and L. Sjögren, Z. Phys. B **65**, 415 (1987).

[24] E. Leutheusser, Phys. Rev. A **29**, 2765 (1984); U. Bengtzelius, W. Götze and A. Sjölander, J. Phys. C. **17**, 5915 (1984);

[25] R. Kohlrausch, Ann. Phys. Chem. (Leipzig) **91**, 179 (1874); G. Williams and D.C. Watts, Trans. Faraday Soc. **66**, 80 (1970).

[26] J. Guckenheimer and P. Holmes, *Nonlinear Oscillations, Dynamical Systems, and Bifurcation of Vector Fields*, Springer (New York, 1983).

[27] J.P. Garrahan and D. Chandler, Phys. Rev. Lett. **89**, 035704 (2002).

[28] I. G. Kevrekidis, C. W. Gear, J. M. Hyman, P. G. Kevrekidis, O. Runborg, and C . Theodoropoulos, physics/0209043; C. W. Gear, I.G. Kevrekidis and K. Theodoropoulos, Comp. Chem. Eng. **26** 941 (2002). A. Makeev, D. Maroudas and I.G. Kevrekidis, J. Chem. Phys. **116** 10083 (2002); K. Theodoropoulos Y.-H. Qian and I.G. Kevrekidis, Proc. Natl. Acad. Sci. **97**, 9840 (2000).

[29] P.K. Ghosh, cond-mat/0109073.