

Glass Transitions: A Chemical Kinetic/Landau Theory[†]

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Transitions among melt, glass, and crystal states are modeled phenomenologically by integrating notions from chemical kinetics with a Landau-type generalization of the concept of affinity. The model naturally captures the melt \rightarrow glass, melt \rightarrow crystal, and glass \rightarrow crystal transitions. The Landau terms in a free energy ansatz allow for the prediction of domains of various types of molecular orderings. A simple “symmetric conflict” model is considered as a concrete realization of the approach. This model explicitly demonstrates the existence of a higher lying glasslike free energy well that is kinetically favored over a deeper-lying crystal well. Quenching to the glass state and annealing to the crystal state are shown to follow naturally. The spontaneous creation of ordering domains is proposed to be a self-organizing process. The formalism may be generalized to allow for the analysis of chemically complex, multicomponent systems.

I. Qualitative Picture

Glasses result from the fast cooling of a melt; as a consequence, the formation of a large degree of long range (crystalline) microscopic order is repressed. Because of the restricted time, short (and not long) range ordering may become locked in through the existence of local free energy minima and kinetic barriers that lie above the global thermodynamic (crystal) minimum. The higher-lying energy state imparts to the system a driving force which can allow it to be sufficiently out of equilibrium to meet one of the necessary conditions for self-organization. These systems are highly nonlinear, are described by the kinetics of first-order phase transitions, and display natural and laboratory spatial patterning phenomena. The purpose of the present article is to present a new mesoscopic theory of glass kinetics that captures most of their salient features noted above.

The lowest free energy form of matter at low temperature is generally believed to be the crystalline solid. Yet rapidly cooled melts often become solids that are not well-ordered crystalline materials. The molecular building units of these noncrystalline solids are arranged in space at sites and in orientations which do not constitute a spatially periodic lattice (Elliott, 1990). As both the supercooled melt and the glass are higher free energy states than the crystalline solid, such a system is out of equilibrium with respect to melt, glass \rightarrow crystalline solid processes. In the present study, a kinetic model of these systems is developed and their potential for self-organization and other nonlinear behavior is indicated.

The properties and formation kinetics of glasses arise out of several, often conflicting tendencies. For example, consider a

collection of elongate molecules comprising a condensed phase. In the liquid state these molecules are constantly making large displacements and reorientations relative to each other. In the perfect crystal they are, on the average, located on a periodic lattice and have a well-defined preferred orientation relative to that lattice. For each molecule, crystallization from the melt consists of two processes—relocation onto a lattice site and reorientation relative to the lattice. However, things can go “wrong”. The elongate molecules may have a particular tendency (due to certain molecule–molecule binding configurations) that is not compatible with the crystal lattice. Although the perfect crystal can have the lowest free energy, these bindings can yield lower free energy than the (bond-broken) liquid. Hence the system may evolve to the intermediate free energy, highly bonded molecular configurations, and if cooled sufficiently rapidly, activation energy barriers for rotation to lattice orientational order may be frozen out for exceedingly long times. Thus, the system can be caught in a free energy well of intermediate depth and without crystalline order.

The formation of a glass is, thereby, seen to have both kinetic and free energy aspects. There can be both crystal and glass minima in the free energy. The relative speed of the kinetics of the evolution of the translation and rotational/bond-forming ordering (or that of other degrees of freedom) can occur on widely different time scales. Depending on system preparation (notably cooling rate), solidification can lead to the system being forced into a glass or crystal free energy well.

There can be a number of degrees of freedom that must be correctly aligned to attain crystalline order. Besides location at lattice sites, molecules in a perfect crystal must have the correct overall orientation and the value of internal molecular rotation or bending angles or the location and orientation of secondary and other molecules in a multicomponent system. As the number of such degrees of freedom increases, the opportunities increase for forming glasses and not crystalline solids upon cooling a melt. Indeed polymers, especially those which are complex or which can cross-link, as well as binary or more complex melts are likely examples of glass-forming systems.

There are many open questions in our understanding of glasses. Glasses are a transient stage of a system for which the transformation from fluid (gas or liquid) to crystalline solid is arduous. This transformation can take place on geological time scales. An interesting example is “snowflake obsidian”—see

[†] Dedication to John Ross. This paper is written to be one of a collection in honor of John Ross. The author has many fond memories of the very rewarding times spent with John Ross at the Massachusetts Institute of Technology. John Ross gave me many insights into the physics and chemistry of macroscopic systems; these have served to give me a rewarding career in science. I am also deeply indebted to John for the encouragement and friendship he has given me over the intervening years since my postdoc with him. The present manuscript has benefited greatly from the conversations and papers written with John in that period. In particular, I cite the use of Landau-type equations for analyzing the kinetics of first-order phase transitions. Also the formulation of dynamical problems in terms of chemical kinetic concepts followed naturally from our many discussions on the latter. These ideas and the applications to far-from-equilibrium phenomena and self-organization have been the core of much of the author's work as summarized in two monographs (Ortoleva, 1992, 1994).

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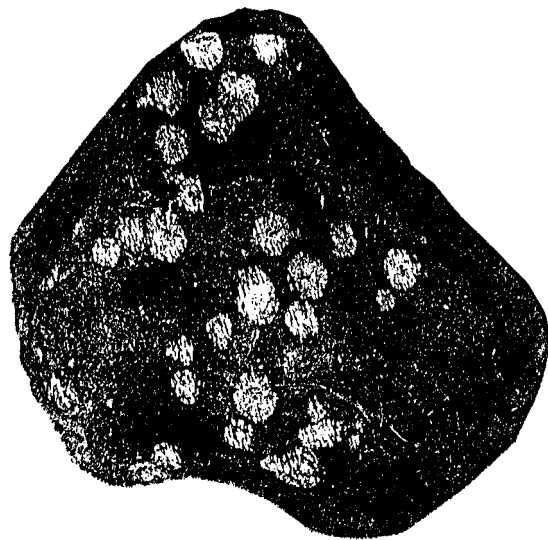


Figure 1. Snowflake obsidian, a natural glass with snowflake-like devitrification spots of recrystallized cristobalite and alkali-feldspar. Natural glasses do not survive more than a few million years. Over geological time all natural glasses appear to transform to crystalline material.

Figure 1. Over geological time, snowflake-like crystals (or crystal clusters) of one mineral nucleate and grow within the glass from components within this volcanic glass. It is challenging to determine the mechanism underlying such slow kinetic processes. Even if relatively fast experiments could be carried out at high temperatures, the predominant mechanism operating at high temperature could be quite different from that at lower temperatures. Thus, determining the relevant mechanism is the greatest challenge of geochemical kinetics.

Is it possible to have “absolute” glasses? Can there be systems for which there is such a tendency for conflict with crystalline order that the lowest free energy state at low temperature is the glass? For such systems glass would be a true equilibrium state and not a transient one. For such absolute glasses, the third law of thermodynamics is not violated. The latter simply asserts that the entropy of a perfectly crystalline material at 0 °K is zero. The third law does not assert that a crystalline state does exist at 0 °K. Furthermore, the entropy of an absolute glass at 0 °K would not be zero. Likely examples of absolute glasses are systems with many degrees of freedom or components.

The essence of the theory of glasses presented here is as follows. Two or more degrees of advancement or order parameters are introduced which, in principle, are related to coordinates characterizing the microscopic state of order. Next, a free energy is constructed from which follows entropy, specific heat, and other thermodynamic quantities. Finally, the affinities associated with the derivative of the free energy with respect to the order parameters are used to drive the dynamics of the system. In particular, the affinities can be used to obtain one kinetic equation for each order parameter. The implication of the theory presented appears to be that annealing to the crystalline state, changes of entropy across a more or less well-defined glass transition and other observations on glasses follow naturally as consequences or special limiting cases of this theory.

In further developments, the theory is extended to nonuniform systems via a Landau-type augmentation of the free energy to include gradient terms (Caginalp and Chen, 1992; Ortoleva, 1992; Caginalp and Xie, 1993; Fried and Gurtin, 1993; Grant, 1993; Sprekels and Zheng, 1993; Wang et al., 1993; Peirce, 1994, 1995). In particular, the concept of affinity is extended via a functional derivative and then used to develop an

exponential Ginzburg–Landau evolution equation. This allows for phenomena including nucleation of the crystalline state in a glass and mesoscopic alternating regions of different degrees or types of ordering. The issues of the role of quasi-molecular complexes that form from melt units are discussed as a mechanism of glass formation/crystalline solid repression. The formation of glasses associated with eutectic phenomena is briefly discussed as is the Ostwald step rule in the context of glass \rightarrow crystal transitions.

Other theories of glasses based on fundamental principles have been set forth. Mode–mode coupling theory has only met with modest success (see Zeng et al, 1994). Molecular dynamics numerical studies have shown the existence of a variety of crystal-like and amorphous states of supercooled water (Poole et al, 1992). Experiments show the existence of a dynamics of transient local ordering, not necessarily the same as long range crystalline order (Cicerone et al, 1995). Attempts to describe local clusters phenomenologically in terms of free energy as an algebraic function of cluster-size was set forth by Kivelson et al. (1994) emphasizing crystalline ordering, i.e. suggesting the notion of conflict without explicitly introducing any order parameters to express this conflict. In the present work such restrictions are surmounted using an explicit multiple order parameter theory. Furthermore, the present phenomenological theory is fully dynamical, allowing for a first such approach to the kinetics of glass formation. The present theory has a number of direct generalizations that will serve to open a new approach to glass and related phase dynamics problems.

II. Chemical Kinetic Modeling

The essence of glass kinetics and energetics as portrayed above is the interplay of a fast degree of freedom (corresponding to an associated shallow free energy well) and a slow degree of freedom associated with a deep well. Let us formulate this concept with a macroscopic kinetic model.

A. Free Energy Ansatz. Consider a chemical kinetic model cast in terms of two populations of “species” each corresponding to a degree of freedom with two well-defined states. Take ξ_1 to be the fraction of low-energy configurations or satisfied bonds and $1 - \xi_1$ to be the fraction in the higher energy state, both for the fast degree of freedom (denoted species 1). Similarly, ξ_2 and $1 - \xi_2$ is for the slow degree of freedom.

The free energy F of the system is taken to have a number of contributions. Let n_1 and n_2 be the maximum number of moles of satisfied one and two degrees of freedom, respectively. Then F is taken to have entropy of mixing terms $RTn_i[\xi_i \ln \xi_i + (1 - \xi_i) \ln(1 - \xi_i)]$, $i = 1, 2$. F also has a contribution $F^0(V, T, n_1, n_2)$ for the system with $\xi_1 = \xi_2 = 0$ and volume V . A direct contribution $n_i b_i \xi_i$ is for the free energy decrease ($b_i < 0$) when $n_i \xi_i$ moles of low energy i -states are created. Finally, there is assumed to be a conflict term $(cn_1 n_2 / (n_1 + n_2)) \xi_1 \xi_2$ ($c > 0$) that is introduced to account for the possible tension whereby satisfying one bond or ordering tends to make it more difficult to satisfy the other. For example, satisfying a certain molecule–molecule bond may interfere with lattice packing.

With this the model free energy takes the form

$$F = F^0 + \sum_{i=1}^2 n_i b_i \xi_i + C \xi_1 \xi_2 + RT \sum_{i=1}^2 n_i \{ \xi_i \ln \xi_i + (1 - \xi_i) \ln(1 - \xi_i) \} \quad (\text{II.A.1})$$

where $C = cn_1 n_2 / (n_1 + n_2)$. The conflict term couples the two degrees of freedom and allows for the glass-like behavior.

Without it the two degrees of freedom act “ideally” (i.e. independently). In the ideal case no multiple equilibria, i.e. glass and crystal free energy minima, are obtained.

The ideal system will evolve toward a unique free energy minimum wherein both bond or configuration type degrees of freedom are satisfied to a degree allowed by the interplay of the b_i -terms and the entropy terms for each i . Note that ξ_i acts like a degree of advancement for the i th bond type. This simple conflict model can easily be generalized by adding more nonlinear terms in ξ_1 and ξ_2 or by allowing for more degrees of freedom. The nonlinear terms could allow for coexistence between melt and solid states by inducing additional minima under conditions where, say, the crystal minimum also exists. This will not be pursued further here. Rather, the free energy expression (II.A.1) is sufficient to illustrate the kinetics and energetics of glass and crystal forming processes.

The affinity A_i for degree of freedom i is defined via

$$A_i = (\partial F / \partial \xi_i)_{V, T, n, \xi_{j \neq i}} \quad (\text{II.A.2})$$

At equilibrium A_1 and A_2 vanish and the system resides at the bottom of a free energy well.

For the above model

$$A_1 = n_1 b_1 + RT \ln \left(\frac{\xi_1}{1 - \xi_1} \right) + C \xi_2 \quad (\text{II.A.3})$$

and similarly for A_2 . If the slow degree of freedom is frozen (ξ_2 constant) then the first degree of freedom attains a ξ_2 -dependent equilibrium (local minimum in F at fixed ξ_2), i.e. $A_1 = 0$. Again, the shallower, higher lying minimum in F is taken to correspond to the glass state, while the deepest well is the crystalline state in the present model.

Setting A_1 and A_2 to zero yields

$$B_1 e^{\gamma \xi_2 \xi_1} - (1 - \xi_1) = 0 \quad (\text{II.A.4})$$

$$B_2 e^{\gamma \xi_1 \xi_2} - (1 - \xi_2) = 0 \quad (\text{II.A.5})$$

Here

$$B_i = e^{n_i b_i / RT} \quad (<1), \quad \gamma = C / RT \quad (>0) \quad (\text{II.A.6})$$

The simultaneous solution of these equations yields the position in the ξ_1, ξ_2 -plane of the extrema of F (see section III for further details).

B. Dynamics. Let us assume the dynamics of the system are similar to that of a chemical reaction. The transitions between the satisfied and unsatisfied states for the two degrees of freedom ($i = 1, 2$) are considered to be by the process

$$i(\text{unsatisfied}) \rightleftharpoons i(\text{satisfied}) \quad (\text{II.B.1})$$

For this process we adopt the rate law

$$d\xi_i / dt = \Omega_i [1 - e^{A_i / RT}] \quad (\text{II.B.2})$$

with forward rate Ω_i (>0). Using chemical kinetics arguments, one expects that Ω_i should be proportional to the fraction ($1 - \xi_i$) of unsatisfied bonds. Thus,

$$\Omega_i = k_i (1 - \xi_i) \quad (\text{II.B.3})$$

Using (II.A.3) for A_1 and a similar expression for A_2 , one has

$$d\xi_1 / dt = k_1 [(1 - \xi_1) - B_1 e^{\gamma \xi_2 \xi_1}] \equiv W_1 \quad (\text{II.B.4})$$

$$d\xi_2 / dt = k_2 [(1 - \xi_2) - B_2 e^{\gamma \xi_1 \xi_2}] \equiv W_2 \quad (\text{II.B.5})$$

Note that $d\xi_1 / dt$ vanishes as A_1 does (and similarly for the second degree of freedom) so that the exact equilibrium is subsumed in this kinetic formulation. This kinetic model involves the rate coefficients k_1, k_2 which are assumed to have Arrhenius temperature dependence:

$$k_i = k_i^0 e^{-E_i / RT} \quad (\text{II.B.6})$$

with activation energy E_i and frequency factor k_i^0 . The B_i act like equilibrium constants. The key conflict factors $e^{\gamma \xi_2}$, $e^{\gamma \xi_1}$ act like corrections to the “ideal” model ($\gamma = 0$) wherein the degrees of freedom act independently. The present model is henceforth termed the “symmetric conflict” model.

C. Density, Order, and Other State Variables. The present model has been cast in terms of the two reaction progress variables ξ_1 and ξ_2 . One might inquire about the relation of other state variables to these order parameters. For example, a single-component glass/crystal system might be characterized in terms of the pressure p and volume V . In general, one expects a relation between p and V, ξ, n, T could be determined via

$$p(V, T, \xi, n) = - \left(\frac{\partial F}{\partial V} \right)_{T, \xi, n} \quad (\text{II.C.1})$$

Let us briefly investigate the equilibrium thermodynamics of such a system at frozen $\xi \equiv (\xi_1, \xi_2)$ and when these degrees of freedom are allowed to vary. Note $p(V, T, \xi, n)$ can be determined from experimental data and thus (II.C.1) may be used to determine the V -dependence of $F(V, T, \xi, n)$.

Next note that

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, \xi, n} \quad (\text{II.C.2})$$

This may be used with a model for F to obtain the entropy. In this way, specific heats and other thermodynamic quantities for the glass state may be defined. Kinetics experiments may then be carried out to determine the rate coefficients. This would complete the calibration of the model.

III. Glass and Crystal States for the Symmetric Conflict Model

The glass and crystal states may be viewed in the conflict model as minima in the free energy. These minima may be obtained from the simultaneous solution of the equilibrium conditions (II.A.4,5). The latter can be viewed graphically by reduction to a single equation as follows.

From (II.A.5) one obtains

$$\xi_2 = \frac{1}{1 + B_2 e^{\gamma \xi_1}} \quad (\text{III.1})$$

Putting (II.A.4) in logarithmic form and using (III.1) to eliminate ξ_2 yields

$$\ln \left(\frac{1 - \xi_1}{\xi_1} \right) - \ln B_1 = \frac{\gamma}{1 + B_2 e^{\gamma \xi_1}} \quad (\text{III.2})$$

When γ is large the right hand side of (III.2) is essentially a step function dropping rapidly from $\gamma / (1 + B_2)$ to $\gamma / (1 + B_2 e^\gamma)$ in the vicinity of $\xi_1 = -\ln B_2 / \gamma$. If this drop point is to be relevant, it must be in the interval $0 < \xi_1 < 1$. When satisfied, degree of freedom 2 has a great free energy advantage when $-\ln B_1$ is large and the conflict factor γ is large; it is seen in Figure 2

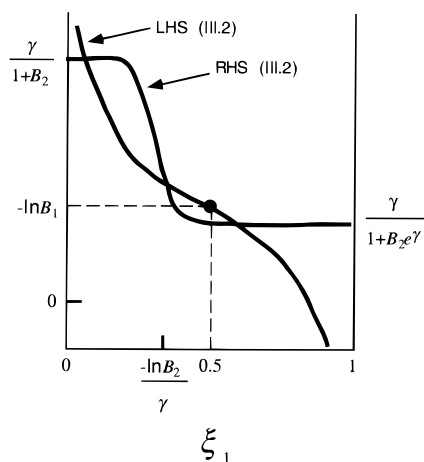


Figure 2. Graphical solution of (III.2). Curves intersect (LHS = RHS) at free energy extrema.

that there can be three solutions (free energy extrema) for the case of glass/crystal-supporting systems. The largest and smallest ξ_1 -values correspond to minima of F , while the intermediate value corresponds to an unstable state (F is a local maximum or saddle point). If $\gamma = 0$, there is no conflict and there is only one equilibrium wherein the two degrees of freedom independently minimize F . If $-\ln B_2$ is very large (the advantage to satisfy degree of freedom 2 is great), then again there is only one minimum of F . This global minimum corresponds to large ξ_2 (i.e. the deep well is at large ξ_2 , with ξ_1 taking a value compatible with degree of freedom 2 being satisfied and a value of ξ_1 that will decrease with increasing conflict γ). The topography of F is suggested in Figure 3.

In the deep two-well, strong conflicting case (the step function arising when γ and $-\ln B_2$ are large), the two equilibria are seen from Figure 2 to occur when

$$\ln\left(\frac{1 - \xi_1}{\xi_1}\right)^{xl} = \ln B_1 + \frac{\gamma}{1 + B_2} \quad (\text{III.3})$$

$$\ln\left(\frac{1 - \xi_1}{\xi_1}\right)^g = \ln B_1 + \frac{\gamma}{1 + B_2 e^\gamma} \quad (\text{III.4})$$

or

$$\xi_1^{xl} = \left[1 + B_1 \exp\left(\frac{\gamma}{1 + B_2}\right)\right]^{-1} \quad (\text{III.5})$$

$$\xi_1^g = \left[1 + B_1 \exp\left(\frac{\gamma}{1 + B_2 e^\gamma}\right)\right]^{-1} \quad (\text{III.6})$$

The state labeled “xl” is at small ξ_1 so that the first degree of freedom is typically not satisfied (bonded). From (III.1), this implies that ξ_2^{xl} is near unity (as B_2 is small). However, for the “g” state, the small B_2 factor is more than compensated by the e^γ -term; hence the exponential factor could be near unity and ξ_1^g can be 0.5 (as B_1 is near unity due to the relatively weak advantage of the 1-type bond). The xl- and g-wells are as suggested in Figure 3.

IV. Quenching and Glass vs Crystal Formation

If T is suddenly dropped from a large value ($\gg E_1/R, E_2/R$) to a value such that

$$E_2 \gg RT \cong E_1 \quad (\text{IV.1})$$

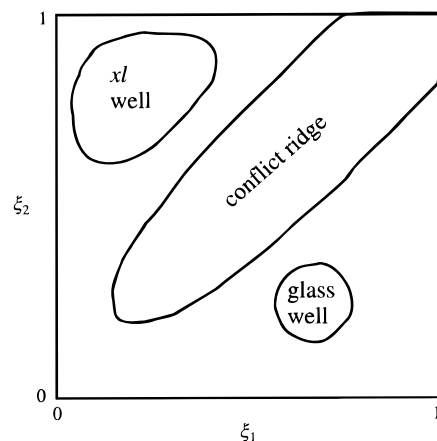


Figure 3. Topography of the free energy surface of the uniform system illustrating glass and crystal wells.

then the system will evolve at relatively constant ξ_2 (as k_2 is small). Hence the system can get fall into the glass well. If the original temperature was $\gg E_1/R, E_2/R$, and RT is much greater than any other energy in the system (i.e. b_i and c), then at equilibrium $\xi_i = 1/2, i = 1, 2$. Thus the quenched system with (II.B.4) evolves at $\xi_2 = 1/2$ to a state with the affinity $A_1 = 0$ and with $\xi_2 = 1/2$. Calling this state $\xi_1^{g,q}$ one has

$$\xi_1^{g,q} = \frac{1}{1 + B_1 e^{\gamma/2}} \quad (\text{IV.2})$$

More generally, the system dynamics are as follows. The melt is suddenly quenched to some temperature T . If the state $(\xi_1, \xi_2)^{\text{melt}}$ resided in the glass well at that lowered temperature, then the state of the quenched system will evolve to the glass state (and similarly for the crystal well). If the system is cooled sufficiently slowly, then for an appreciable time the free energy may only support the deeper crystal well, the putative shallow glass well being masked by the entropy of mixing term. Thus slow cooling (annealing) will result in a crystal, even though there is a glass well at the late-stage temperatures.

V. Self-Enhancement to the Crystal State

A. Cooperativity. A key element of the crystal state not captured in the above symmetric conflict model is the cooperative nature of the attainment of a correlated molecular orientation and location. If the neighbors of a given molecule have proper crystal orientation and site location, only then can that molecule cause free energy reduction by becoming correctly configured. With this, one expects that the term ΔF_2^{coop} in F should be replaced by the cooperative term such that, for example,

$$\Delta F_2^{\text{coop}} = n_2 b_2 \xi_2^\beta, \quad \beta > 1 \quad (\text{V.A.1})$$

where the cooperativity exponent β is greater than unity. In three dimensions β might well be 3 or greater, reflecting the number of nearest neighbors needed to support the favored configuration. This effect can make the crystal well narrower and deeper at higher T . Such effects will also allow for the simultaneous existence of melt and crystal free energy wells and thereby phenomena such as supercooled liquids and melt–crystal coexistence equilibria.

B. Landau Spatial Coupling. The cooperativity suggested above can have a longer length scale aspect. For example, gradients in ξ_1, ξ_2 can cause strains which can lead to spatial coupling terms that tend to drive a given macrovolume element of material to the crystal state if that element is near a patch of

crystalline material (see Salje, 1992, for further discussion in the context of transitions between two crystal phases). With this or other spatial coupling, one might argue that the homogeneous dynamics of ξ_2 as in (II.B.2) should somehow be augmented with a Landau-type term $\Lambda \nabla^2 \xi_2$ and similar ξ_1 -terms.

The following construction of a Landau-type augmentation suggests itself for the present chemical kinetic formulation. First, a Landau-type term is added to F of (II.A.1) in the form

$$\Delta F^{\text{Landau}} = \int_{\Omega} d^3 r \Delta f^{\text{Landau}} \quad (\text{V.B.1})$$

$$\Delta f^{\text{Landau}} = \sum_{i,j=1}^2 \frac{1}{2} \Lambda_{ij} \nabla \xi_i \cdot \nabla \xi_j \quad (\text{V.B.2})$$

$$F = \int d^3 r [f + \Delta f^{\text{Landau}}] \quad (\text{V.B.3})$$

where f is a classical free energy density given by the expression in (II.A.1) divided by the volume V ; f may be expressed in terms of intensive variables only such as $n_i/V, T, \xi$. The integral in (V.B.3) is over the domain occupied by the medium. With this the affinity A_i in the present theory is related to F through a functional derivative generalization of (II.A.2):

$$A_i = \delta F / \delta \xi_i(\vec{r}, t) \quad (\text{V.B.4})$$

For simplicity, complications arising from the functional dependence of the system domain on ξ_1, ξ_2 are ignored. It is assumed that the system is evolving in a domain constrained by the boundary stresses to be in a constant domain. With this, one adds a term $\Delta A_i^{\text{Landau}}$ to (II.A.3):

$$\Delta A_i^{\text{Landau}} = - \sum_{j=1}^2 \Lambda_{ij} \nabla^2 \xi_j \quad (\text{V.B.5})$$

It has been assumed that the Λ_{ij} are ξ -independent.

C. Exponential Landau-Type Dynamics. The above Landau-extended affinities are now used to develop a dynamical theory in analogy to that of section II.A. In that spirit, one inserts (V.B.4) and, in particular, (V.B.5), into the exponential law (II.B.2,3). With this "exponential Landau" kinetics, one obtains an augmentation to the $\gamma \xi_2$ -term in (II.B.4) such that

$$\gamma \xi_2 \rightarrow \gamma \xi_2 - \sum_{j=1}^2 \Lambda_{1j} \nabla^2 \xi_j \quad (\text{V.C1})$$

and similarly for $\gamma \xi_1$ in (II.B.5). In conclusion, the Landau augmentation arises, in this ansatz, as a correction to the equilibrium constant terms $B_1 e^{\gamma \xi_2}, B_2 e^{\gamma \xi_1}$ in (II.B.5,6), respectively. The result is an exponential dependence on gradients that is quite different from the usual Ginzburg–Landau equations wherein the kinetics depends linearly on the gradients of the order parameters.

The exponential formalism for the order parameters ξ_1, ξ_2 can be used to address questions of crystal nucleation in glass and fronts of glass \rightarrow crystal transition advancing through the system. This formalism can also provide a way of studying intermediate range order observed in glasses (Elliott, 1991). In such ordering, it appears that structures correspond to alternating zones of large and small ξ_1 and ξ_2 (in the language of the present model). Methods developed for the theory of nonlinear chemical waves should prove valuable in this analysis (see Ortoleva, 1992 and references cited).

D. Fluctuations and the Glass \rightarrow Crystal Transition. The glass \rightarrow crystal transition is very unlikely to take place uniformly when the glass well depth is much greater than RT . Rather, one expects that crystallization should be a local phenomenon starting at a heterogeneity or at the molecular level when a favorable configuration is established among a few neighboring molecules.

With this, a statistical approach to the glass \rightarrow crystal transition suggests itself. Various starting points are possible including Fokker–Planck, Chandrasekhar, cell master equation, and more fundamental statistical mechanical methods (Seeley et al., 1992; Liu and Metiu, 1993; Liu et al., 1993a,b; Zhang and Metiu, 1993; Zhang et al., 1993; Keyes, 1994). This subject is not pursued further, although it appears that the exponential Landau approach suggested here is a viable starting point. For example, the calculations as in Nitzan et al. (1974) can be employed to estimate the properties of a critical nucleus.

VI. Absolute Glasses

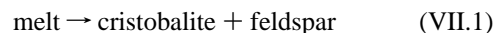
From the above model, the question arises as to the possibility of the existence of systems for which the conflict is so strong that there can be no crystalline state at even very low temperatures. Thus energetics of bond formation and that of molecular orientation and lattice formation are in such conflict that a periodic spatial structure will always have free energy higher than that for a nonperiodic one.

The analogy to toroidal dynamics suggests itself as one possibility. This could arise when an arrangement associated with bonding occurs with a periodicity that is not rational relative to that of a periodic structure that tends to minimize energy associated with molecular orientation or lattice siting. More complex chaotic arrangements also suggest themselves. Clearly the complexities and possibilities of the arrangement of molecules in three dimensions suggest that the minimum free energy state need not be one of crystalline order.

Note that whether a system is an absolute glass may depend on pressure. Thus high p may favor low volume, and hence the energy benefit of favorable spatial organization (i.e. volume minimizing organization) could become dominant over the tendency to form disruptive (conflicting) bonds above a critical pressure.

VII. Multisolid Glass

For these systems, the melt contains species which form more than one chemically distinct solid phase. A natural example is obsidian as seen in Figure 1. In that case the melt contains SiO_2 and feldspar constituents. The devitrification of obsidian leads to SiO_2 crystal (typically cristobalite) and K,Na-feldspar, the latter being a solid solution. In this system the crystallization process



can be thwarted by the relatively slow diffusive unmixing to pure SiO_2 and feldsparic regions.

For the overall process (VII.1), there can be an intermediate glass state wherein the compositional segregation has not had time to take place. Indeed, solid diffusion, the process through which segregation takes place, is very slow for temperatures that are not near that of melting. In fact, there can be a number of intermediate states; for example, even after segregation, crystalline order may not be attained.

VIII. Mesoscopic Structure and Competition among Supraunits

If units of a melt can form supraunits (quasi-molecular associations), then this may provide an impediment to the

development of crystalline order. A number of examples of this supraunit inhibition phenomenon are known. To illustrate the approach presented here to this problem, consider a system of n moles of a unit building block that can form M supraunit aggregate types, $i = 1, 2, \dots, M$. If the i th aggregate type has ν_i units, then the species are linked by

$$\nu_i X_i = X_1 \quad (\text{VIII.1})$$

where X_1 is the basic unit. Let ξ_i be the fraction of units in the i th type of aggregate. Then

$$\xi_1 + \xi_2 + \dots + \xi_M = 1 \quad (\text{VIII.2})$$

To illustrate the use of the formulation presented in the previous sections, consider the following model. Let $F_i^0(V, T)$ be the free energy of noncrystalline, pure i -solid. For simplicity, assume that a pure X_1 -solid will always rapidly revert to the crystal so that F_1^0 is the free energy of the crystal state. With this we have the conjecture

$$F = \sum_{i=1}^M n \xi_i (F_i^0 + RT \ln \xi_i) + \Delta F^{\text{int}} \quad (\text{VIII.3})$$

for the uniform system. The interaction term ΔF^{int} could express the strains caused by the mixture of aggregate types. For example, consider

$$\Delta F^{\text{int}} = \sum_{i \neq j} c_{ij} \xi_i \xi_j \quad (\text{VIII.4})$$

To complete the model, Landau-type gradient terms may also be added for nonuniform systems.

The above formalism can be used to analyze the stability of the uniform glass to the development of alternating domains of varying states of molecular aggregation. A linear stability analysis would be useful in defining the characteristic length scale of these patterns. Nonlinear methods (see Ortoleva, 1992) could also be applied.

IX. Ostwald Step Rule

Ostwald observed that precipitation of a solid from a melt or solution often takes place via a sequence of steps (Morse and Casey, 1987). First, a relatively high free energy phase forms. This then transforms to a lower free energy crystal lattice and so on through a sequence of steps terminating at the lowest free energy crystalline phase. Thus rapid precipitation from a strongly supersaturated solution can be a multistep process.

Apparently the kinetics of forming a higher free energy phase is typically faster than that for the next lower free energy phase. By analogy, the glass provides an intermediate step to crystallization in rapidly cooled systems. This suggests the sequence



could be thought of as an example of the Ostwald step rule.

The last step could summarize a further sequence of Ostwald steps. Thus the glass-crystal transition may involve a complex sequence of intermediate processes. The melt/glass/crystal system as an example of the Ostwald step rule may underlie snowflake obsidian which appears to be a snapshot in time of this process (see Figure 1).

X. Conclusions

Conflicts between local free energy minimization and long range order are conjectured to underlie the glass state. This

picture is used to develop a free energy functional that supports multiple minima. Minima are identified with the glass and the crystalline state. The free energy is augmented with Landau-type gradient terms to describe nonuniform systems.

The free energy functional is then used to define a generalized reaction affinity as a functional derivative. The latter is embedded into a classic chemical kinetics rate law to arrive at an exponential dependence on spatial gradients for the glass \rightarrow crystal transition rate. Most of the observed glass \rightarrow crystal kinetics phenomena, such as freezing into the glass state and annealing to the crystal state, are seen to be direct consequences of the large rate coefficient and shallow free energy well depth of the glass state (relative to those for the crystal). Potential applications of the theory to mesoscopic structure, the analogs of the Ostwald step rule, and other glass phenomena are pointed out. The exponential Landau methodology set forth appears to be a promising approach to the analysis of glass phenomena.

The chemical kinetic/Landau theory presented illustrates the many intriguing possibilities that are available to glass systems. Complex systems can have several order parameters. This adds to the richness of the dynamics of the transition from glass to crystalline states. These degrees of freedom may allow for multiple noncrystalline free energy wells, implying the potential for more than one distinct glass phase. In addition, multiple degree of freedom systems may display the richness of phenomena in systems maintained far from equilibrium. These phenomena include temporal oscillation, spatial self-organization, and propagating waves. Delineating the types of behavior supported by mesoscopic glass kinetic models is a rich area for future research.

The introduction of the affinity as a functional derivative could have other applications. Such a quantity and the associated nonlocal equilibrium constants could have interesting consequences for systems such as interfaces where reactions take place in regions where spatial gradients are large.

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References and Notes

- Caginalp, G.; Chen, X. *IMA Vol. Math. Appl.* **1992**, 43, 1–27.
- Caginalp, G.; Xie, W. *Phys. Rev. E* **1993**, 48, 1897–1909.
- Cicerone, M.; Blackburn, F. R.; Ediger, M. D. *J. Chem. Phys.* **1995**, 102 (1), 471–479.
- Elliott, S. R. *Physics of Amorphous Materials*, 2nd ed.; Longman: Essex, U.K., 1990.
- Elliott, S. R. *Nature* **1991**, 354, 445.
- Feeney, R.; Ortoleva, P.; Schmidt, S. L.; Strickhold, P.; Chadam, J. *J. Chem. Phys.* **1983**, 78, 1293–1311.
- Feinn, D.; Ortoleva, P. *J. Chem. Phys.* **1977**, 67, 2119–2131.
- Flicker, M. R.; Ross, J. *J. Chem. Phys.* **1974**, 60, 3458.
- Fried, E.; Gurtin, M. E. *Physica D* **1993**, 68, 326–343.
- Grant, C. P. *Comm. Part. Diff. Eqns.* **1993**, 18, 453–490.
- Kai, S.; Muller, S.; Ross, J. *J. Chem. Phys.* **1982**, 76, 1392.
- Keyes, T. *J. Chem. Phys.* **1994**, 101 (6), 5081–5092.
- Kivelson, S.; Zhao, X.; Kivelson, D.; Fischer, T.; Knobler, C. *J. Chem. Phys.* **1994**, 101 (3), 2391–2397.
- Liesegang, R. E. *Pho. Archiv.* **1896**, 21, 221.
- Liesegang, R. E. *Geologische Diffusionen*; Steinkopff: Dresden, Germany, 1913.
- Lifshitz, M.; Slyuzov, V. V. *J. Phys. Chem. Solids* **1961**, 19, 35.
- Liu, F.; Metiu, H. *Phys. Rev. B* **1993**, 48 (9), 5808–5817.
- Liu, S.; Zhang, Z.; Metiu, H. *Abstr. Am. Chem. Soc.* **1993**, 205, 250.
- Liu, S.; Zhang, Z.; Comsa, G.; Metiu, H. *Phys. Rev. Lett.* **1993**, 71 (18), 2967–2970.
- Lovett, R.; Ross, J.; Ortoleva, P. *J. Chem. Phys.* **1978**, 69, 947.
- Morse, J. W.; Casey, W. H. *Am. J. Sci.* **1987**, 288, 537–560.
- Nitzan, A.; Ortoleva, P.; Ross, J. *Nucleation in systems with multiple stationary states*. Faraday Symposium Physical Chemistry of Oscillatory Phenomena, 1974.

- Ortoleva, P. *Nonlinear Chemical Waves*; John Wiley and Sons: Chichester, U.K., 1992.
- Ortoleva, P. *Geochemical Self-Organization*; Oxford University Press: New York, 1994.
- Ortoleva, P. *Physico-Chemical Kinetics*, in preparation.
- Ostwald, W. *Kolloid-Z.* **1925**, 36, 330.
- Peirce, A. *SIAM J. Appl. Math.* **1994**, 54 (3), 708–730.
- Peirce, A. *SIAM J. Appl. Math.* **1995**, 55 (1), 136–155.
- Poole, P.; Sciortino, F.; Essmann, U.; Stanley, H. E. *Nature* **1992**, 360, 324–328.
- Salje, E. K. H. *Phys. Rep.* **1992**, 215 (2), 49–99.
- Seeley, G.; Keyes, T.; Madam, B. *J. Phys. Chem.* **1992**, 96 (10), 4074–4076.
- Sprekels, J.; Zheng, S.-M. *J. Math. Anal. Appl.* **1993**, 176, 200–223.
- Sultan, R.; Ortoleva, P.; Pasquale, F.; Tartaglia, P. *Earth Sci. Rev.* **1990**, 29, 163–174.
- Wang, S. L.; Sekerke, R. F.; Wheeler, A. A.; Murray, B. T.; Coriell, S. R.; Braun, R. J.; McFadden, G. B. *Physica D* **1993**, 69, 189–200.
- Zeng, X.; Kivelson, D.; Tarjus, G. *Phys. Rev. E* **1994**, 50 (2), 1711–1716.
- Zhang, Z.; Metiu, H. *Surface Sci.* **1993**, 292 (1–2), L781–L785.
- Zhang, Z.; Detch, J.; Metiu, H. *Phys. Rev. B* **1993**, 48 (7), 4972–4975.