The T-shaped anisotropic molecule model:

a unique perspective of the glass transition and gelation

in low valence, directional, network forming liquids

Thesis by
Jennifer Elisabeth Witman

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

California Institute of Technology
Pasadena, California

2010
(Defended December 14th, 2009)

Dedication

To my Grandma-ma, Mary Elisabeth Stewart (1918-2009)

- *My admiration that she loved research, public service and teaching, may I grow to embrace this servant heart*

- *My appreciation that she travelled to family at all time, from her first trip to California to join my Grandfather as that greatest generation fought in the Pacific, to her visits to see me and encourage me in a much smaller struggle 60 years later*

- *My gratitude that she supported me in an illness that had overtaken the lives of her father, sister, and daughter. We rejoice together in modern medicine and, yes grandma-ma, I am still taking my meds.*

You have now joined all the saints before you with our Lord. Feel my hug.

Acknowledgments

I sincerely appreciate the philosophy of my advisor, Professor Zhen-Gang Wang. He views education in the broader sense of giving students freedom for personal development and discovery of vocation. His support of my decision to become a teacher and willingness to defer to an unconventional degree path means a great deal to me.

Professor David Tirrell has similarly given me the gift of exploration into a different side of scientific endeavor. Despite my short time with his group, trying my hand at laboratory research and passing along what I learned to others influenced my career decisions immensely.

The financial support of the NSF for a variety of programs has enriched my life in many ways. Starting from my high school 'Young Scholars' experience at Purdue, sending me for a field season in Antarctica, providing money for graduate work both through the CSEM and an individual fellowship and then creating wonderful material for me to use with my high school students, I hope I will prove a good return on investment.

My first professor will always have a special place in my heart. Thanks, Dad…I know you will always be there to help me with my homework. Mom, I am indebted to the many long hours of conversations, taxi driving, careful monitoring of my education experience and example of life-long inquiry. I also admire and seek to emulate your careful stewardship of your family, your lab, your home and the earth, awareness of your footsteps of all kinds.

Sisters-mine, you are my inspiration. Never stop holding me in account and reminding me of the Truth.

My gratitude to my Witman family, who has welcomed me as a daughter and sister, encouraged me unfailingly, and shares my passion for education.

The multitude people who have encouraged me and prayed with me during my work is too extensive to list. You know who you are…raise a toast for our joint accomplishment!

To my husband~ You make each day possible for me. Team Witman definitely earned this degree!

Abstract

Glass and gel formers exhibit unusual mechanical characteristics and amorphous phases which are highly dependent on their thermal history. We introduce a lattice model with T-shaped molecules that exhibits glassy and gel-like states without introducing artificial frustration. This system has a large number of degenerate energy minima separated by small barriers leading to a broad, kinetically-explored landscape. It particularly replicates valence-limited materials, which can form self-assembled materials with highly controlled physical properties. Despite its remarkable simplicity, this model reveals some of the fundamental kinetic and thermodynamic properties of the glass transition and of gel formation.

A dearth of low temperature experimental and simulation measurements has inhibited investigation in this field. We overcome this difficulty by using a modified Metropolis Monte Carlo method to quickly provide equilibrium samples. Then kinetic Monte Carlo techniques are used to explore the properties of the equilibrium system, providing a touchstone for the non-equilibrium glassy states.

Fully-dense simulation samples reveal a fragile-to-strong crossover (FSC) near the mean-field (MF) spinodal. At the FSC, the relaxation time returns to Arrhenius behavior with cooling. There is an inflection point in the configurational entropy, s_c. This behavior resolves the Kauzmann Paradox which is a result of extrapolation from above the inflection point. In constrast, we find that the s_c remains finite as $T \rightarrow 0$. We also observe different kinetics as the system is quenched below the FSC, resulting in non-equilibrium, amorphous states with high potential energy persisting for long periods of time. Simulation samples remain at non-equilibrium conditions for observation times exceeding those permitting complete equilibration slightly above the FSC. This suggests the FSC would often be

identified as the glass transition without indication that there is true arrest or a diverging length scale. Indeed, our simulations show these samples do equilibrate if sufficient time is allowed. To elucidate the complex, interdependent relation time and length scales at the FSC will require careful consideration of the spatial-dynamic heterogeneity.

Dynamic mean-field simulations at high density and in the solvated regime reveal a rich range of morphological features. They are consistent with simulated and experimental results in colloidal systems. Stability limits of decreasing length scales beneath the phase separation bimodal coincide into a single curve, which terminates at the fully-dense MF spinodal, suggesting that gelation and vitrification are the same phenomena. Our work indicates that gelation is, therefore, a result of phase separation arrested by a glass transition.

Table of Contents

List of Figures

List of Notation

The symbols and variables listed below are presented in the order of appearance. Some differences do occur between the chapters for clarity in a particular Section and ease of discussion in context of the work of others. The most prominent example is the use of T^* in chapter 1 and T in all other Sections to refer to the dimensionless temperature (the superscript was dropped due to the large number of other temperatures specified).

Some of the symbols are overloaded with several definitions, with the hope that the context will distinguish which meaning is required. We continue the convention in the field of using β not only as in its normal thermodynamic usage but also as the exponent in stretched exponential function. This unfortunate symbolic overlap was particularly problematic for me as a novice, but is so ubiquitous in the literature as to be unavoidable.

In all the work, values were reported with respect to the non-dimensional temperature (T/T_R where $T_R = \varepsilon/k = 1$). Lower case use of thermodynamic variables indicates that they are the intensive (per site or 'vertex') quantity.

Symbol	Definition (Dimensionless)	Scaling
Abstract:		
s_c	Configuration entropy per site	$(kN^2)^{-1}$
T	Temperature	
Overview:		
T_g	Glass transition temperature	
Chapter 1:		

N	Number of sites along one axis which is our fundamental length scale($N \times N$ is total number of sites)	
$-\beta\varepsilon$	Dimensionless bond association energy	
i, j	Location on lattice	(N,N)
a	State of lattice site (orientation 1,2,3,4 or vacant 5)	
$\hat{p}_a(i,j)$	Occupancy of state a at location (i, j) (either 1 or 0)	
β	$(kT)^{-1}$ where k is the Boltzmann constant	k
βH	Hamiltonian of our system	
$\beta\eta$	Strength of isotropic interaction ($\eta = 0$ in all work)	
$q_{current \to new}$	Transition probability (generic form)	
ω	Attempt frequency (this is the fundamental time unit)	
E	Energy (internal energy)	k
$\vec{i}$	Two-dimensional coordinates	(N,N)
$\langle \vec{i}, \vec{i}\,' \rangle$	Nearest neighbor sites	
$p_a(t;i,j)$	Probability of state a (used in mean-field calculation)	
$q(t;b \to a)$	Transition probability for rotation from state b to state a	
$q(t;c,\vec{i}\,' \leftrightarrow a,\vec{i})$	Transition probability for translation	
βf	Free energy per site	
ρ	Density (sum of occupied states per site)	
$\beta\mu$	Chemical potential per site	

βw	Grand potential energy per site	
$\theta(t-t_o)$	Correlation function	
τ	Relaxation time	ω^{-1}
β	Exponent in stretched exponent function	
τ_o	Vogol-Fulcher fit: characteristic relaxation	ω^{-1}
T_o	Vogol-Fulcher fit: critical temperature	
D	Volgol-Fulcher fit: fragility index	
$m(t-t_o)$	Time correlation 'order parameter' from mean-field calculations	
T_c	Critical temperature	
ν	Correlation length	N^{-1}
z	Dynamic scaling exponents	
T_k	Kauzmann Temperature	
ω	Diffusivity	
R^2	Mean-squared distance traversed during time t	$N^{-2}\omega$

Notation Changes for Sections outside of Chapter 1:

N	Total number of lattice sites
T	Dimensionless Temperature
'site'	'vertex' (we codified vertex for location vs molecule or site)

Notation Continued:

$\sigma_{\alpha}(\vec{i})$	Orientation of molecule ($\alpha = 1,2,3$ or 4)	
m	One state of the entire lattice with all orientations specified	
k	Another state of the entire lattice with all orientations specified	
$\vec{x}_{m}$	Conformation coordinate of state m on the energy landscape	
$T_{mf,critical}$	Mean-field transition temperature	
$T_{mf,spinodal}$	Mean-field stability limit	
$q_{k \rightarrow m}$	Transition probability of moving from state k to state m	
p_{m}	Probability of a given state of the entire lattice with each molecules in a specific orientation	
$\vec{x}^{*}_{m \rightarrow k}$	Transition state between state m and state k	
$E^{*}_{m \rightarrow k}$	Energy of the transition state	k
C_{v}	Heat capacity	k
s	Entropy per site	$(kN^{2})^{-1}$
T_{Cv}	Temperature at which the heat capacity is a maximum	
E_{a}	Arrhenius Fit: Activation Energy	
C	Adam-Gibbs Fit: Empirical fit constant	
J	Quadratic Fit: Empirical fit constant	
T_{a}	Quadratic Fit: Upper bound of cooperative relaxation	

regime

T_x Quadratic Fit: Lower bound of cooperative relaxation

regime

$b\left(t;\left\langle \vec{i},\vec{i}\,'\right\rangle\right)$ Bond (1 present, 0 absent) along edge connecting near-neighbor vertices $\left\langle \vec{i},\vec{i}\,'\right\rangle$ at time t (defined by orientation of molecules at sites)

$\phi_b\left(t-t_o\right)$ Bond autocorrelation function

τ_{bond} Bond relaxation time ω^{-1}

$\sigma_\alpha\left(t;\vec{i}\right)$ Molecule at vertex $\vec{i}$ is in orientation α at time t (1 if present 0 if absent)

$\phi_\sigma\left(t-t_o\right)$ Molecule-orientation autocorrelation function

τ_σ Orientation relaxation time ω^{-1}

τ_c Characteristic time ω^{-1}

β Stretching exponent

$\Gamma(z)$ Euler gamma function

$T_{\beta:fragility,\,onset}$ Highest temperature at which β is at its low temperature

plateau

$T_{\beta:FSC}$ Lowest temperature at which β is at its low temperature

plateau

γ Cooling rate ω

a,b,c,d Empirical fitting constants

T_{FSC} Fragile-to-strong crossover temperature

$T_{kMC,structure}$ Change in feature expectation value

$\tau_{first\ change}$	Time scale for the molecule to change orientation for the first time	ω^{-1}
$\tau_{exchange}$	Time scale for fast and slow molecules to exchange mobility	
μ_α	Applied aligning field to skew to one alignment	k
ε_{mn}	Bond energies when they are not all the same	k

Appendix A:

T_r	Reduced temperature	

Appendix B:

p_c	Critical probability of bond occupation for percolation	

Appendix C:

α	Order parameter indicating that either ⊣, ⊢ or ⊥, ⊤ will be dominant on the lattice	
δ	Order parameter indicating that indicates left/right or up/down orientations are dominant	

Appendix D:

ρ	Density of molecules on lattice	N
p_α	Probability that molecules are in a locally ordered domain	
p_b	Probability that molecules in an amorphous region	
βu_{random}	Internal energy per vertex of random (liquid or gas) state	kN^{-2}
βf_{random}	Free energy per vertex of random (liquid or gas) state	kN^{-2}
s_{random}	Entropy per vertex of random (liquid or gas) state	

$\beta u_{oriented}$	Internal energy per vertex of locally preferred oriented state	kN^{-2}
βf_{random}	Free energy per vertex of locally preferred oriented state	kN^{-2}
s_{random}	Entropy per vertex of locally preferred oriented state	

Appendix E:

$r_{m\rightarrow k}$	Transition rate	ω
ξ_{max}	Largest transition rate	ω
u	Random number (in this appendix only)	
n_m	Number of vertices that can change by the specific process m	

Appendix F:

A_t	Observable	
σ	Variance (Appendix F only)	

Appendix G:

E_{IS}	Inherent energy (internal energy)	k

Overview of Thesis

Amorphous materials are ubiquitous in our daily lives. As a high school teacher in the state of California, our curriculum acknowledges four states of matter: solid, liquid, gas and plasma. We give a nod to polymers and large biomolecules and move on. Inevitable when discussing materials in class, the items which catch students' eye are much more complicated. What is an LCD? Why are there different recycling codes, shouldn't we be able to mix it all together? What was that stuff they served down in the cafeteria today? It is wonderful to explain what we know and then challenge them to pursue open questions.

The center of this thesis is to develop an understanding of the characteristics and dynamics of amorphous materials. We are able to draw connections between two broad classes of glasses and physical gels by introducing a strikingly simple T-shaped molecular model on a two dimensional lattice. Having gained important insight into this relation, we then pursue more fundamental issues of the nature of the glass transition.

The focus of chapter one[1] is to identify and connect amorphous materials that are arrested on some time scale without invoking artificial frustration. The mean-field phase diagram of this model mimics those phase diagrams calculated for other systems[2] and seen in experiments[3]. Dynamic mean-field simulations demonstrate a wide variety of phases including liquid, solutions, glassy materials, foams and gels. Further evaluation demonstrated a kinetic preferred alignment and highlighted the large number of degenerate energy minima on the landscape. The calculated instabilities within the two phase region of the phase diagram converged along a line terminating in the fully-dense spinodal, suggesting a strong connection between gelation and the glass transition. Initial results of the dynamics of the simulations suggested the possibility of a return to strong behavior at the lowest

temperature. We thus were able to define gelation in this model as phase separation arrested by vitrification. As we could investigate equilibrium at low temperatures, we noticed that there was behavior consistent with the fragile-to-strong crossover.

In the time between publishing our first paper[1] (chapter 1) and now as we are finishing work leading towards a second paper (chapter 2) several powerful conclusions were drawn in other research groups. In models capturing a wide range of experimental observations, from specific DNA tetramers[3] to silicon[4], a commonality was emerging. The controlling feature in the modeled potentials was the ability to suppress the isotropic portion allowing anisotropic forces to dominate[5]. This leads to local ordering which stabilizes the overall amorphous materials inducing dynamic arrest, observed as vitrification or gelation[2]. This suggests that the overall behavior of many of these materials can be reduced to generic descriptions of their valency[6, 7].

However, as a field we are still bound by the fundamental difficulty encountered in simulation: computation time. Achieving low temperature results, particularly those which are able to avoid vitrification, will require the development of complex mechanisms to overcome difficulties in time scales in the potentials studied thus far[8]. Based on our success with this model in our initial work, we sought to overcome this difficulty. Placement of our T-shape molecules on a lattice naturally invokes the valence-limited potential with a computationally efficient Hamiltonian. We correctly postulated that using a combination of Monte Carlo simulations would allow us to investigate our system at the desirable low temperatures.

The second chapter is also formatted as an independent paper, although it includes a more extensive discussion relating to what may often be framed as future work in a dissertation.

Within this work, we concentrate on the glass transition in the fully-dense region. Our model allows us to quench the simulation samples to very low temperatures using a modified Metropolis Monte Carlo recipe. We can then apply the appropriate kinetic Monte Carlo approach to study the dynamics and structure of the equilibrium systems. This provides a backdrop against which we consider the temperature quench of simulation samples using the kinetic Monte Carlo method. Glassy states which persist for long lengths of time are documented. Overall, we see a clear signature of the fragile-to-strong crossover (FSC) at low temperatures. However, we do not observe evidence of a divergent length scale consistent with a thermodynamic critical point. We also find that the Kauzmann paradox is resolved by the change in the temperature dependence of the relaxation time at the fragile-to-strong crossover and, indeed, observe a positive configurational entropy as $T \rightarrow 0$. There is a dramatic change in the relaxation behavior at the FSC which would lead to a lower limit of the experimentally observable relaxation to equilibrium; however, this is not a fundamental kinetic arrest.

In seeking simplicity of explanation, we do not want to lose sight of the rich complexity and wide variety of glassy materials. However, with this in mind, we sally forth into an investigation of a simple model with surprisingly rich dynamics and thermodynamics.