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Slow Dynamics Near the Glass Transition

Abstracts

PHYS **23 [636846]: Structural signatures of vitrification in hard core fluids**
Sanat K. Kumar, Dept. of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY 12210, Shekhar Garde, Department of Chemical Engineering, Rensselaer Polytechnic Institute, Jack F. Douglas, Polymers Division, National Institute of Standards and Technology, and Francis W. Starr, Polymers Division and Center for Theoretical & Computational Materials Science, National Institute of Standards and Technology

Free volume models suggest that the glass transition of a supercooled liquid occurs when the amount of unoccupied space becomes critically small. While several methods exist for quantifying local free volume, they have found limited application in describing the glass transition. Here, computer simulations of hard spheres and disks are used to estimate the most probable cavity size, $\square_{cavity}$, and a "rattle" size, $\square_{rattle}$, over which a particle can translate holding all other particles fixed. Both of these measures appear to extrapolate to zero at the random close packed density, $\$\square_{rcp}\$$, close to the density where extrapolations of the viscosity diverge. We also identify the onset of caging by locating the density at which spontaneous void formation in the fluid is no longer a random event, but rather is localized to the immediate vicinity of existing cavities. These results suggest that vitrification can be viewed as a geometrical phenomenon, and that *local* free volume measures can identify the location of the onset of liquid-like dynamics, the complex dynamics of caged liquids, and vitrification.

PHYS **24 [644487]: Particle rearrangements due to transitions between inherent structures of a supercooled Lennard-Jones liquid**
Michael Vogel, Department of Chemical Engineering, University of Michigan, 2300 Hayward, Ann Arbor, MI 48109, mivogel@umich.edu, S. C. Glotzer, Depts. of Chemical Engineering and Materials Science and Engineering, University of Michigan, Andreas Heuer, Institute of Physical Chemistry, University of Muenster, and Burkhard Doliwa, Max Planck Institute for Polymer Research

Observing transitions between inherent structures near the mode-coupling temperature T_{MCT}, we quantify the displacements of individual particles, the localization of the rearrangements and the relevance of cooperative string-like motions. We find that all studied quantities vary smoothly through T_{MCT}. When the organization of the inherent structures into metabasins is considered, comparable features are observed for transitions inside and outside of metabasins. Constructing sequences of transitions that connect different metabasins, we find that the particle displacements during subsequent metabasin transitions are uncorrelated. To study the mechanism of the string-like motion, we consider suitable sequences inside and outside of metabasins, respectively. In both cases, most strings do not move coherently during a single transition, but subunits of the strings are active at different times. We discuss the relation between the properties of the energy landscape and the relaxation processes in supercooled liquids.

PHYS **25 [641881]: Density of states simulation of the thermodynamic and mechanical properties of glass formers. Bulk and confined systems**
Juan J de Pablo, Department of Chemical Engineering, University of Wisconsin - Madison, 1415 Engineering Drive, Madison, WI 53706, Fax: 608-262-5434, depablo@engr.wisc.edu

A novel method has been developed for simulation of glass forming systems. The method relies on a self-consistent estimate of the density of states, which is determined from knowledge of the instantaneous temperature of the system. Results for model glass formers consisting of binary mixtures of Lennard-Jones particles agree with literature results from molecular dynamics simulations. It appears, however, that the proposed method is able to sample configuration space at temperatures significantly lower than the mode-coupling temperature of the systems of interest. This new method is then used to probe the thermodynamic and mechanical properties of a variety of glassy systems. An analysis in terms of local moduli reveals that glassy materials can be mechanically inhomogeneous, and suggests that the dynamics of glasses are related to such inhomogeneities.

PHYS **26 [632966]: Equilibration and frequency dependence of the specific heat of glass forming liquids**
Clare C. Yu, Department of Physics and Astronomy, University of California, Irvine, Irvine, CA 92697-4575, Fax: 949-824-2174, cyu@uci.edu, and Hervé M. Carruzzo, Internap Network Services

We show that a glass transition, signaled by a peak in the specific heat vs. temperature, can occur because a glassy system that shows no signs of aging progresses so slowly through the energy landscape that the time needed to obtain an accurate estimate of the thermodynamic averages exceeds the observation time. We find that below the glass transition temperature of a three dimensional binary mixture of soft spheres, the specific heat increases with measurement time spans orders of magnitude longer than previously recognized equilibration times such as the alpha relaxation time and the aging time. The specific heat displays frequency dependence down to correspondingly low frequencies.

PHYS **27 [643902]: Low temperature properties of glass forming liquids from computer simulations**
Srikanth Sastry, Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560064, India, Fax: 91 80 856 6581, sastry@jncasr.ac.in

Most computer simulation studies of dynamic and thermodynamic behaviour of glass forming liquids to date have been confined to temperatures above the mode coupling temperatures because of the large relaxation times involved in simulating liquids at lower temperature. However, it is beginning to be possible to study the behaviour below the mode coupling temperature with present day computers. Results are presented concerning the dynamic and thermodynamic behaviour of model glass forming liquids near and below the mode coupling temperature, including the observed change in qualitative behaviour below the mode coupling temperature, and results pertaining to the existence of an ideal glass transition.

PHYS **28 [637278]: Understanding the dynamics of a supercooled liquid in terms of its potential energy landscape**
Andreas Heuer, Institute of Physical Chemistry, University of Muenster, Schlossplatz 4/7, 48149 Muenster, Germany, Fax: +49 251 8329159, andheuer@uni-muenster.de

The jump motion among potential energy minima of a Lennard-Jones model glass former is investigated by extensive computer simulations. From the time series of minima energies one can identify a superstructure of the energy landscape giving rise to the notion of metabasins. The long-range dynamics can be described as a random-walk among metabains. This is reminiscent of a trapping picture. The whole temperature dependence is contained in the distribution of waiting times. Furthermore it is possible to define an effective activation energy to leave a metabasin of given depth. These activation energies result (i) from a direct analysis of the dynamics and (ii) from a quantitative analysis of the relevant reaction paths. In this framework it is possible to predict the temperature dependent diffusion constant from knowledge of the distribution of metabasins (thermodynamics) and the effective activation energies. Implications and possible applications of these results are discussed.

PHYS **49 [670756]: Unified classical and quantum theory of structural glasses**
Peter G. Wolynes, Chemistry and Biochemistry, University of California,San Diego, 9500 Gilman Drive, La Jolla, CA 92093, pwolynes@ucsd.edu

The relationship of glassy dynamics to an underlying random first order transition along with its accompanying entopic droplet excitations clarifies many puzzles in the phenomenology of structural glasses. I will discuss how this framework provides a quantitative treatment first of glassy phenomena in the classical regime: the coefficients in the Vogel- Fulcher law, relaxational heterogeneity and the mesoscopic hydrodynamics of viscous liquids can be calculated without adjustable constants from thermodynamic data alone. The patterns of behavior associated with liquid "fragility" can all be traced to the magnitude of configurational heat capacity. Quantizing these droplet excitations greatly enriches the standard two level system model of low temperature glass properties. The quantum theory explains how the universal scaling of the low energy density of states with Tg arises, along with the peculiar universality of the phonon scattering mean free path in glasses. Deviations from the two level picture are predicted.

These occur a higher temperature where they connect to the Boson peak and also occur at ultra low temperature where a gap in the density of state should arise.

PHYS **50 [632616]: To move or not to move, and in what direction: The essentials of glass formers**
David Chandler, Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720, Fax: 510-643-1566, chandler@cchem.berkeley.edu, and Juan P. Garrahan, Department of Physics, University of Oxford

This lecture describes a coarse grained model for atomic glass formers. Its elements are physically motivated local microscopic rules for dynamics that are parameterized by observables. Quantitative results of the model are easily established and have been used to successfully interpret existing dynamic and thermodynamic experiments. Further testable predictions of the model will be discussed.

PHYS **51 [670741]: Dynamic heterogeneities, defects, and the non-topographic view of glass transition phenomena**
Juan P. Garrahan, and Ludovic Berthier, Department of Physics, University of Oxford, 1 Keble Road, Oxford, OX1 3NP, United Kingdom, j.garrahan1@physics.ox.ac.uk

We show that most aspects of the dynamics of glass forming systems, including the dynamics between inherent structures (or dynamical traps) and the crossovers associated with the "landscape influenced" and "landscape dominated" regimes, can be understood in purely dynamical terms, without any reference to "topographic" features of the potential energy landscape. This "non-topographic" interpretation is based instead on the existence of dynamic heterogeneities and on their statistical properties. Our view is supported by the study of dynamically facilitated models of glass formers, which realize the excitation or defect picture of glass transition phenomena. This approach allows for the formulation of quantitative theoretical predictions which are successfully compared with numerical and experimental studies of local dynamics of supercooled liquids.

PHYS **52 [631636]: Dynamics of elementary excitations in supercooled liquids: on the universality of relaxation time near the crossover temperature**
Udayan Mohanty, Department of Chemistry, Boston College, Chestut Hill, Newton, MA 02467, Fax: 617-552-2705, mohanty@bc.edu

We demonstrate a novel connection between fragility index and thermodynamic observable quantities in supercooled liquids. The predictions of the model are in good agreement with experimental data for supercooled organic and polymeric liquids. We show that recently observed universality of relaxation time near the crossover temperature is intricately governed in part by the equilibrium nature of the supercooled liquid. We then ask what these properties are and whether an elucidation of the thermodynamic route will provide insights into non-equilibrium factors. The later is based on the idea that for supercooled liquids one can introduce dynamical variables that have characteristics of "elementary" excitations. The lifetime of the "elementary" excitations is determined by a variational technique. By imposing self-consistency between the lifetime of the "elementary" excitations and hopping relaxation time on the potential energy surface, the relaxation time near the crossover temperature is estimated. The predictions are critically compared with experimental data.

PHYS **53 [644667]: Dynamic transition in glass-forming liquids and proteins**
Alexei Sokolov, Department of Polymer Science, The University of Akron, 170 University Ave., Akron, OH 44325, Fax: 330-972-5290, alexei@uakron.edu

An overview of experimental results demonstrating qualitative changes in dynamics of glass forming systems at temperatures much above conventional glass transition, Tg, is presented. These results support the idea of existence of a crossover from liquid-like to solid-like dynamics on a molecular scale at some temperature T_D~1.2-1.5 Tg. Analysis of great variety of small molecular and polymeric, ionic, hydrogen- and covalent-bonded glass-forming liquids reveals that the dynamic transition happens at some universal relaxation time $\square_{\square}\sim 10^{-7}$ sec. Possible reasons for such a universal $\square_{\square}$ are discussed.
We demonstrate that dynamics of proteins and DNA is very similar to dynamics of glass-forming liquids and also shows the dynamic transition. It is known that the dynamic transition in proteins can be shifted or completely suppressed by changing solvent. We demonstrate that the dynamic transition in proteins and DNA is controlled by

the dynamic transition in the solvent. Thus proteins and DNA are "slaves" of solvents and that opens way to control their biochemical activity.

PHYS 54 [638498]: Glassy Kinetics in Protein Folding
Jin Wang, Department of Chemistry, SUNY, Stony Brook, Stony Brook, NY 11794, jinwang@sprynet.com

Through the analysis of the kinetics of first passage time, population dynamics, and paths, the glassy nature of protein folding is explored. We found at a temperature between thermodynamic folding transition temperature and glass transition temperature, the kinetics experiences a transition from single exponential process to multiexponential process, and a power law behavior of the first passage time distribution starts to emerge from the Poisson or log-normal behavior. There is also a transition from multiple paths to discrete paths.

PHYS **76 [642024]: Phase transition of reaction dynamics in glassy environment**
Jaeyoung Sung, and Robert J. Silbey, Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Ave., Room 6-230, Cambridge, MA 02139, jaeyoung@mit.edu

We derive the exact evolution equation and the boundary condition for a reactive continuous time random walker with arbitrary waiting time distributions for transport and reaction processes. Expressions for the probability distribution function and the survival probability of the reactive continuous time random walker are also presented. The results predict a novel phase transition in the behavior of the relaxation dynamics and ultimate survival probability.

PHYS **77 [644903]: Effects of dynamical heterogeneity on translational diffusion and single-molecule studies in glass forming liquids**
YounJoon Jung, Department of Chemistry, University of California Berkeley, 35 Gilman, Berkeley, CA 94720-1460, younjoon@gold.cchem.berkely.edu, David Chandler, Department of Chemistry, University of California, Berkeley, and Juan P. Garrahan, Department of Physics, University of Oxford

Based upon the coarse-grained model, we study translational and rotational diffusions of probe molecules in glass forming liquid systems. In particular, within purely dynamical and geometrical aspects, we present novel explanations of the breakdown of the Stokes-Einstein relation that has been observed in many glass forming liquid systems near the glass transition temperature. We have also studied implications of the dynamical heterogeneities on recent single molecule experiments of glass forming liquids. We investigate the distribution of the dynamical heterogeneities probed by single probe molecules over different coarse-graining timescales through numerical simulations. Based on our simulation results, we propose a new experimental measurement involving correlations among single probe molecules that will provide informations on the distributions of dynamical heterogeneity.

PHYS **78 [638941]: Self-diffusion near Tg in single component glass formers**
Mark D. Ediger, and Stephen Swallen, Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706, Fax: 608-262-0381, ediger@chem.wisc.edu

The self-diffusion coefficient is arguably the single most important measure of mobility in a liquid. We present the first direct measurement of self-diffusion of a single-component glass-forming liquid at the glass transition temperature. Forward Recoil Spectrometry (FReS) is used to measure the concentration profiles of deuterio and protio 1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene (TNB) following annealing-induced diffusion in a vapor deposited bilayer. These experiments extend the range of measured diffusion coefficients in TNB by 6 orders of magnitude. While rotational correlation times have previously been found to track the viscosity, these new results indicate a decoupling of translational diffusion from viscosity or rotation. At Tg, D is 500 times larger than expected from the Stokes-Einstein equation. These results are qualitatively consistent with previous measurements of dye diffusion in TNB and explain the unusual temperature dependence of crystal growth rates in TNB.

PHYS **79 [642295]: Single-particle dynamics in deeply supercooled liquids**
John T. Fourkas[1], Thomas J. Kempa[2], Richard A. Farrer[2], and Robert M. Dickson[3]. (1) Department of Chemistry, Boston College, Merkert Chemistry Center, 2609 Beacon St., Chestnut Hill, MA 02467, Fax: (617) 552-6887, fourkas@bc.edu, (2) Eugene F. Merkert Chemistry Center, Boston College, (3) School of Chemistry and Biochemistry, Georgia Institute of Technology

Photoluminescence from metallic nanoparticles with nanometer diameters has been used to study orientational dynamics in a deeply supercooled liquid, 4,4'-(octahydro-4,7-methano-5H-inden-5-yliden) bisphenol dimethyl ether (ODE). We explore the dependence of the bulk orientational correlation time on the bulk ODE viscosity to show that nanoparticles can provide a useful probe of local dynamics, and we discuss single-particle orientational diffusion trajectories. We will also compare the information available from two- and three-dimensional orienational trajectories.

PHYS **80 [660384]: Quenching-in of different high T complexities of glassformers for leisurely study at lower temperatures**

C. Austen Angell[1], Yuanzheng Yue[2], Li-Min Wang[1], John R. D. Copley[3], Steve Borick[4], and Stefano Mossa[5]. (1) Department of Chemistry and Biochemistry, Arizona State Universtiy, Main Campus, P.O. Box 871604, Tempe, AZ 85287, Fax: 480-965-7972, caa@asu.edu, (2) Chemistry, University of Aalborg, (3) National Institute of Standards, (4) Scottsdale Community College, (5) Center for Statistical Mechanics and Complexity, Universita di Roma

We describe a series of experiments on glass-forming liquids that are motivated by a common idea. The idea is that of trapping in a high enthalpy, high entropy, state of the system by quenching to the glassy state at extreme rates, and then observing the way the system evolves at low temperatures during a controlled annealing procedure. In this manner, events that normally occur during change of temperature may be observed occurring during passage of time, at much lower temperatures. At these low temperatures, the smearing effects of vibrationally excited modes may be greatly reduced. For simple glassformers we study both relaxational properties and vibrational properties and find that the high fictive temperature states are characterized by short relaxation times (already known) and considerably more intense boson peaks (less well known) [1]. The thermodynamic consequences of the increased populations of these low frequency modes are examined with the help of computer simulation and normal mode calculations on model glassformers. Behavior in the vibrational DOS at constant pressure is strikingly different from that at constant volume. For glassformers that can exhibit liquid-liquid transitions, one can use the cold equilibration approach to determine the fragility of the high temperature phase, and the enthalpy of the liquid-liquid transition, see ref.2. Finally, for solutions of complex molecules with interesting internal molecular transitions, such as proteins, we can quench in the unfolded states and then, using special non-crystallizing solvents, observe the molecular reorganization to low energy states as it occurs at temperatures far below the normal folding temperature [3].
References. [1] C. A. Angell, Yuanzheng Yue, Limin Wang, John R. D. Copley, Steve Borick and Stefano Mossa. J. Phys. Cond Matt 15, , S1051-S1068 (2003) [2] M. C. Wilding, P. F. McMillan, Polyamorphic transitions in yttria-alumina liquids, J. Non-Cryst. Solids 293, 357 (2001). [3] C. A Angell and Limin Wang., in Biophys. Chem., Walter Kauzmann Festschrift, 2003 in galley).

PHYS **81 [644985]: Anatomy of a string: Correlated particle motion in simulated supercooled liquids**

Sharon C. Glotzer, Yeshitila Gebremichael, Michael Vogel, and Magnus Bergroth, Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, sglotzer@umich.edu

We present new results of a detailed investigation of correlated particle motion in model supercooled liquids studied via molecular dynamics simulation. We investigate in particular the tendency for correlated motion to occur in strings. We present a detailed analysis that elucidates how and why strings form, the degree of coherence of particle motion within strings, the lifetime of strings, and the role of strings in facilitating structural relaxation in the liquid.
[1] Y. Gebremichael, M.I. Vogel and S.C. Glotzer, "String-like correlated particle motion in a Dzugutov liquid," preprint.
[2] M. Bergroth, A. Keyes, Y. Gebremichael, M.I. Vogel and S.C. Glotzer, work in progress.
[3] M. Aichele, Y. Gebremichael, F.W. Starr, J. Baschnagel, and S.C. Glotzer, "Polymer specific effects on string-like correlated motion in a glass-forming polymer melt," preprint.
[4] M.I. Vogel, B. Doliwa, A. Heuer and S.C. Glotzer, "Particle rearrangements and transitions between inherent structures in a supercooled Lennard-Jones liquid," preprint.
[5] T.B. Schroeder, S. Sastry, J. Dyre and S. C. Glotzer, ``Crossover to Potential Energy Landscape Dominated Dynamics in a Model Glass-forming Liquid," J. Chem. Phys. 112, 9834 (2000).
[6] C. Donati, J. Douglas, W. Kob, S.J. Plimpton, P.H. Poole, and S.C. Glotzer, ``String-like Cooperative Motion in a Supercooled Liquid," Phys. Rev. Lett. 80, 2338 (1998).

PHYS **103 [638678]: Fluctuating ages in glassy dynamics**

Leticia F. Cugliandolo, Laboratoire de Physique Theorique, ENS and Jussieu Paris France, 24 rue Lhomond, 75231 paris cedex 05, France, leticia@lpt.ens.fr

Firstly, I shall summarize some of the main features of the averaged and global non-equilibrium relaxation of glassy systems, weakly sheared viscous liquids and weakly tapped granular matter, and how these results have been successfully reproduced with a mean-field-like analytic approach. Secondly, I shall explain the outcome of more refined experimental and numerical measurements that point at examining the dynamics at a mesoscopic scale. Finally, I shall discuss a theoretical approach for the local mesoscopic dynamics and how its predictions compareto numerical and experimental results.

PHYS **104 [642603]: Emergence of glassy dynamics in a lattice model with constraints**

Bulbul Chakraborty, Martin Fisher School of Physics, Brandeis University, 415 South Street, MS 057, Waltham, MA 02454, Fax: 781-736-2915, bulbul@brandeis.edu

The glass transition in supercooled liquids is heralded by non-exponential relaxations and a growth of relaxation times characterized by the Vogel-Fulcher law. We have studied the stochastic dynamics of a lattice model with locally jammed states: i.e., local rearrangements cannot change the state. We find that the constraints on the rearrangements lead to relaxation processes dominated by traps that are entropic in origin. Using results of simulations, a master equation describing the order parameter dynamics has been derived. The longest relaxation time can be calculated exactly from this master equation and exhibits a Vogel-Fulcher divergence. The origin of this divergence can be traced back to ``effective'' barriers that diverge. The nature of the order parameter relaxation can also be calculated exactly and is non-exponential. I will compare these dynamics to the landscape dynamics observed in supercooled liquids.

PHYS **105 [644067]: Slow-relaxation and non-hydrodynamic behavior**

James Witkoskie, Department of Chemistry, Massachusetts Institute of Technology, MIT, 2-121, 77 Mass. Ave, Cambridge, MA 02139, jbw@mit.edu, Jianlan Wu, Department of Chemistry, MIT, and **Jianshu Cao**, Chemistry, MIT, 77 MASS. Ave, Room 6-237A, Cambridge, MA 02139, Fax: 617-253-7030, JIANSHU@MIT.EDU

This talk discusses dynamic approaches to calculate slow relaxation and stochastic models to describe non-hydrodynamic behavior. (1) Systematic approaches are used to calculate power-law and stretched exponential relaxation of many-body systems. In the hydrodynamic regime, Gaussian factorization is applied to evaluate memory kernels and is shown to recover the mode coupling effects. (2) A central result of this analysis is the relationship between the non-Gaussian behavior of the bilinear density correlation function and the non-exponential nature of linear hydrodynamic modes. This relation reveals the nature of non-linear measurements within the validity of the mode-coupling approximation and suggests the need for new dynamic models far away the hydrodynamic limit. (3) On the phenomenological level, the motion of Brownian test particles in a solvent near the glass transition can be modeled by diffusion in a stochastic potential with spatial-temporal correlation. The one-particle diffusion and two-particle correlation exhibit signatures indicative of a glassy system. The connection of the stochastic diffusion model to other hopping models are discussed and their limitations in describing realistic liquids are examined.

PHYS **106 [643990]: L'evy distribution of single molecule line shape cumulants in glasses**

Eli J. Barkai, Department of Chemistry, Notre Dame University, 251 Nieuwland Science Hall, Notre Dame, IN 46556-5670, Fax: 574-631-6652, jbarkai@nd.edu, Yuri G Vainer, Moscow Reg. 142190, Institute of Spectroscopy, Russian Academy of Sciences, Lothar Kador, Institute of Physics and Bayreuther Institut f$\ddot{u}$r Makromolek$\ddot{u}$lforschung (BIMF), Institute of Physics and BayreuthUniversity of Bayreuth, and Robert J. Silbey, Department of Chemistry, Massachusetts Institute of Technology

Experimental advances have made it possible to measure the spectral line shape of a single dye molecule embedded in different types of glassy materials. Because each individual molecule is in a unique static and dynamic environment, the line shapes of chemically identical single molecules varies from molecule to molecule. The problem of ensemble averaging is at last removed. Using the Geva-Skinner model we examine the statistical properties of line shapes of single molecules in a low temperature glass described by the standard tunneling model.

In this model, a random distribution two level systems (TLS) interacts with the molecule via {\em long range interaction} (e.g., dipolar). We show that L\'evy statistics fully characterizes the properties of the single molecule spectral line both in the {\em fast} and {\em slow modulation limits}. Computer simulation show that the slow modulation limitis valid for certain parameter set relevant to experiment. Analyzing recent the experimental data, obtained by the groups of Vainer and Kador, we show that L\'evy statistics is compatible with the experimental data. The relation between L\'evy statistics and long range interacting systems is not limited to our model system, we discuss other long range interacting systems where this relation was overlooked. The experiment and data analysis yield: (i) direct evidence for the existence of TLSs in glasses, and (ii) proof that standard tunneling model predictions work well (a few molecules being interesting exceptions).

PHYS **107 [655452]: Nanoscale noise in glass**
Nathan Israeloff, Department of Physics, Northeastern University, 111 Dana Research Center, 110 Forsyth St., Boton, MA 02115, Israeloff@neu.edu

A number of recent experiments and simulations strongly support the idea that dynamics are spatially heterogeneous in glassy materials. Relaxation times appear to be correlated over a few nanometers, supportive of the notion of cooperatively-rearranging-regions (CRR) containing of order 100 molecules. But details of the local cooperative dynamics are still mysterious. Certain issues, such as the heterogeneity lifetime, and whether local relaxation within a CRR is exponential, remain controversial. I will describe experiments in which molecular cooperativity was directly observed near the glass transition, through nanoscale probing of dielectric relaxation, and dipolar noise in polymer glasses. The dynamics and evolution of individual CRR was studied. Surprisingly, individual CRR were found to revisit a handful (2-4) of configurations up to hundreds of times. Statistical analysis of the noise gives information about the lifetime of the CRR, the local shape and evolution of the energy landscape, and the evolution from exponential to nonexponential response within a CRR.

PHYS **108 [659300]: Dynamically selective heating in viscous liquids**
Ranko Richert[1], Ken R. Jeffrey[2], and Kalyan Duvvuri[1]. (1) Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, Fax: 480-965-2747, ranko@asu.edu, (2) Department of Physics, University of Guelph

Polar liquids are associated with dielectric loss which results in energy dissipation if exposed to a large amplitude sinusoidal electric field. We employ model calculations using the dielectric and calorimetric properties of supercooled glycerol in order to demonstrate that the effect of electric field heating is measurable under realistic conditions. In particular, the dynamically heterogeneous character of viscous liquids leads to an increase in the effective temperature of only those domains whose relaxation time matches the frequency of the electric 'burn field'. These computational results are compared with dielectric hole-burning measurements on supercooled glycerol across a large range of burn frequencies. The agreement between model and experiment demonstrates that fast and slow relaxations are independent (most likely spatially separated) and correlated with the time scale of the respective heat capacity contributions. The picture is consistent with frequency resolved heat capacity data on glycerol. It is argued that dielectric hole-burning effects can be rationalized on the basis of dynamically selective heating, where the local dipole temperature and the phonon bath temperature are only weakly coupled.

PHYS **131 [644673]: Three-dimensional single molecule rotational and translational diffusion in glassy state polymer films**
Robert M. Dickson, Andrew P Bartko, and Kewei Xu, School of Chemistry and Biochemistry, Georgia Institute of Technology, 770 State Street, Atlanta, GA 30332-0400, Fax: 404-894-7452, dickson@chemistry.gatech.edu

Measuring three-dimensional orientational motions of many individual molecules within glassy state poly(methyl methacrylate) has enabled nanoscopic probing of bulk-obscured polymer dynamics. Complementing bulk studies, the measured distributions of nanoscale barriers to rotational motion afforded by our single molecule orientational methods directly probe the spatial heterogeneity and nanoscopic alpha-relaxation dynamics deep within the glassy state. By correlating orientational and translational motion for individual molecules, signatures suggestive of the translation-rotation paradox persist well below the glass transition temperature.

PHYS **132 [644122]: Confocal microscopy and the colloidal glass transition**

Eric R Weeks, and Piotr Habdas, Physics Department, Emory University, 400 Dowman Drive, mail stop 1131/002/1AB, Atlanta, GA 30322-2430, Fax: 404-727-0873, weeks@physics.emory.edu

We study concentrated colloidal suspensions, a model system which has a glass transition. We view the motion of these colloidal particles in three dimensions by using an optical confocal microscope. This allows us to directly study the microscopic behavior responsible for the macroscopic viscosity divergence of glasses. Near the glass transition we find that particle dynamics are heterogeneous in both space and time. The particles move in cooperative clusters, and the size of these clusters increases as the glass transition is approached, possibly related to the viscosity increase. Our most recent experiments use small magnetic particles to locally "poke" on the colloidal samples. The response to these perturbations changes significantly near the glass transition.

PHYS **133 [640543]: Colloidal glass transition: beyond the mode-coupling theory**

Grzegorz Szamel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523, szamel@lamar.colostate.edu

A new theory for dynamics of concentrated colloidal suspensions and the colloidal glass transition is proposed. The starting point is the memory function representation of the time-dependent density correlation function. The memory function can be expressed in terms of a time-dependent pair-density correlation function. An exact, formal equation of motion for this correlation function is derived and a factorization approximation is applied to its evolution operator. In this way a closed set of equations for the density correlation function and the memory function is obtained. The theory predicts an ergodicity breaking transition similar to that predicted by the mode-coupling theory, but at a higher density.

PHYS **134 [639661]: Supercooled fluids under shear: A mode coupling approach**

Kunimasa Miyazaki[1], Ryoichi Yamamoto[2], and David Reichman[1]. (1) Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, Fax: 617-384-7920, miyazaki@fas.harvard.edu, (2) Department of Physics, Kyoto University

Many complex materials such as polymer solutions and granular fluids exhibit very diverse rheological behavior. Shear thinning is among the most-known phenomena. Recently, it was found by simulations that supercooled liquids near glass-transition also show strong shear-thinning behavior. Such rheological behavior is interesting in its own right, but understanding the dynamics of supercooled liquids under nonequilibrium stationary state is more important because it has possibility to shed light on another nonequilibrium phenomenon known as the aging which is still a formidable task to treat theoretically due to its non-statinoary nature. We investigated dynamics of supercooled liquids under shear theoretically, by extending the standard mode-coupling theory to the system under a nonequilibrium constraint. The results reproduce the drastic reduction of relaxation time due to shear and thus the strong shear thinning observed in simulations, including the shear-thinning exponent.

PHYS **135 [639895]: Activated hopping and the glass transition in colloidal suspensions and polymer melts**

Kenneth S. Schweizer, and Erica J. Saltzman, Departments of Materials Science and Chemistry, University of Illinois, 1304 West Green Street, Urbana, IL 61801, Fax: 217-333-2736, kschweiz@uiuc.edu

A microscopic kinetic approach has been developed to describe transient localization, free energy barriers, and activated transport which combines elements of mode coupling, density functional and activated rate theory. Quantitative applications to hard sphere suspensions reveals good agreement with experiment for the glass transition volume fraction, and magnitude and volume fraction dependence of the single particle relaxation time, diffusion constant and viscosity. The approach is generalized to polymer melts at a coarse-grained segment level within a trap model framework. Slow segmental dynamics is predicted to be primarily controlled by the compressibility, packing length and chain characteristic ratio. Free energy barriers, crossover and glass transition temperatures, dynamic fragility, nonexponential relaxation and the alpha relaxation time have been studied via model calculations and applications to specific polymer materials.

PHYS **136 [643850]: Novel characterization of the distribution of glass transition temperatures across polymer films: Impact of surfaces and polymer-substrate interactions**

John M. Torkelson, Dept. of Chemical Eng. and Dept. of Materials Science and Eng, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208-3120, j-torkelson@northwestern.edu, and Christopher J. Ellison, Department of Chemical Engineering, Northwestern University

In order to obtain a fundamental understanding of Tg in thin and ultrathin films, de Gennes has called for determination of the distribution of Tg's across a film thickness. The first measurement of such distributions has been obtained by fluorescence. The temperature dependence of pyrene fluorescence intensity quantifies the impact of nanoconfinement on Tg in polymer films. Pyrene-labeled polymers are spin-coated into 10-20 nm thick films that are placed in multi-layer films with the other layers being unlabeled polymer. A polymer-air surface can lead to a significant reduction in Tg of a 10-20 nm layer tens of nm away from the surface. Conversely, if a polymer has attractive interactions with the substrate, a significant increase in Tg occurs tens of nm from the interface. Thus, a modification in the cooperativity of segmental mobility caused by surfaces or polymer-substrate interactions impacts the average segmental mobility at distances exceeding the polymer coil radius.