

Phys 563 Phase Transition and Renormalization groups Term paper 2010

Instructor: Prof. Nigel Goldenfeld

Title:

**Understanding glass-forming and “jamming” materials
in the context of soft colloids**

Jian Yang

Department of Materials Science and Engineering

University of Illinois, Urbana, IL 61801

Abstract

Recent experiment and simulation research on the glass forming and “jamming” materials are reviewed from the perspective of using soft colloids to establish a general picture of molecular glasses, colloids and granular materials.

PACS number: 64.70.p-, 64.70pv, 64.70Q-

I. Introduction

A. Soft colloids: Making two worlds become one

For hundreds of years, while the glass and jamming transitions are of great interest and have been widely studied extensively, scientists have established good knowledge of molecular glasses and granular materials. However, this kind of understanding is somehow independent and not under a universal picture. This helps at the very beginning of the two distinctive fields of research making one's life easier as we do not need to worry two things at the same time. However, as scientists have accumulated enough experience, puzzling questions are raised: Why do thermal liquids have distinctive behavior as approaching glass transition, some are fragile while others are strong? Is jamming transition only meaningful for granular materials? Molecular glasses and granular materials are just like two ends of the problem which seems to never overlap. Thanks to the development of colloidal science, a bridge is about to connect the two sides of the river. The particle size of colloids is large enough to make it possible to observe them with optical microscope to collect real space trajectory to study its structure correlation while it is small enough that thermal energy is still the driving force. No wonder we can achieve a lot new insights from the study of soft colloidal system whose temperature can be finely tuned.

B. Outline

The primary goal of our review is to establish how much of the rich slow dynamics of two seemingly distinctive kinds of materials: molecular glass and granular materials can be understood from the perspective of soft colloids.

In Sec. II, we review the work that relates thermal liquids and soft colloids in the context of dynamic fragility as glass transition is approached. In Sec. III, we review the work which relates granular materials and soft colloids in the context of thermal vestige of zero-temperature jamming transition. In Sec. IV, We review the work on glass melting with applied shear stress. In Sec. V, we briefly discuss the interplay of glass transition and jamming transition. Sec. VI concludes the paper.

II. Glass forming materials

A. Glass forming liquids: Molecular glasses

It has always been a crucial issue as how glass-forming liquids solidify without crystallizing as they cool. A glass-former that converts to a solid over a wide range of temperatures is often considered as an ideal system to study glass transition. And among those glass-forming liquids, some are called 'fragile' as they soften quickly upon heating; otherwise they are 'strong'. The same distinction is also applicable as to describe the behaviour of liquids under compression: fragile liquids 'jam up' very

quickly into glasses under pressure and strong ones react differently. The seemingly mysterious behavior of these molecular glasses can be understandable with the help of a work done by Mattsson *et al* [1] in a different system: soft colloids, which mimic the fragility behavior of the molecular glasses.

Mattsson *et al* [1] have studied aqueous suspensions of deformable microgel particles of varying softness. They change the particle softness and volume fraction and measure the structure relaxation time. They have constructed an equivalent “Angell Plot” [2] for thermal glass formers. They use glass transition volume fraction as when the relaxation time reaches 100 second, in analogy with the glass transition temperature to define the fragility.

Now come two questions: 1. Can we understand the change of fragility in soft colloids? 2. Can we understand the same issue in the context of molecular glasses based on what we have learnt for the prior case?

B. Glass forming colloids

Thermal liquids are composed only of molecules (or atoms or ions), which ceaselessly collide, oscillate and diffuse. [3] The fissures and gaps that form transiently in liquids are empty of matter, however, colloidal suspensions, on the opposite, consist of microscopic chunks of matter, suspended in a liquid medium. The suspended matter would settle slowly to the bottom of the colloid without the impacts it makes with the endlessly oscillating molecules of the liquid. The particles thus undergo Brownian motion, pretty much like molecules.

C. Soft colloids make strong glasses: colloids mimic molecular glasses

The behavior of athermal hard sphere colloids is remarkably similar to that of “hard-sphere fluids” which is the classical model of liquids in which the liquid particles are thought of as non-compressible spheres. The behavior of hard sphere colloids turns out to be the fragile extreme of colloidal behavior. The variation in colloidal structure relaxation times measured by Mattsson *et al.* [1] is remarkably similar to that of King *et al.*'s viscosity data [4] [5]. So, hard colloids are analogous to fragile liquids, whereas soft colloids can be compared to strong liquids. Mattsson *et al.* offer an explanation for the question: Why is soft strong? The elastic energy of colloidal particles, the energy stored when the particles are distorted determines the fragility of colloids. Since elastic energy depends particularly on particle softness, thus the fragility would also depend on softness.

D. Thermal soft colloids vs. athermal hard colloids: an effective mapping from soft to hard

Berthier *et al* [6] [7] [8] have carried out a simulation for soft repulsive colloids, where the dynamic scaling of temperature evolution of relaxation time in two distinct regimes separated by the onset of hard sphere jamming point is suggested:

$$\tau_\alpha \sqrt{T} \sim \exp\left[\frac{A}{|\phi_0 - \phi|^\delta} F_\pm\left(\frac{|\phi_0 - \phi|^{2/\mu}}{T}\right)\right]$$

Here τ_α is the structure relaxation time, T is temperature, ϕ is volume fraction, ϕ_0 is proposed as the random close packing volume fraction for hard sphere and the scaling functions $F_\pm(x)$ apply to volume fractions above/below ϕ_0 . μ is introduced as $\phi_{\text{eff}}(\phi, T) = \phi - aT^{\mu/2}$, where $\phi_{\text{eff}}(\phi, T)$ corresponds to the effective hard sphere volume fraction of a soft sphere system based on the criterion: $\tau_\alpha(\phi, T) = \tau_\alpha^{\text{HS}}(\phi_{\text{eff}})$.

One would expect that $F_+(x \rightarrow \infty) \rightarrow \infty, F_-(x \rightarrow \infty) \rightarrow 1$ to recover the hard sphere fluid limit; Moreover, continuity of τ_α at finite T and $\phi = \phi_0$ requires $F_\pm(x \rightarrow 0) \rightarrow x^{\delta\mu/2}$. Thus, one can collapse all data of relaxation time onto two curves by plotting $|\phi_0 - \phi|^\delta \log(\tau_\alpha \sqrt{T})$ versus $|\phi_0 - \phi|^{2/\mu} / T$ and using δ as a fitting parameter. They can best collapse all relaxation time data onto two curves by using $\delta = 2.2$.

The virtue of this work is that the structural relaxation time of soft repulsive colloids is now governed by a single scaling function. The interplay of temperature (softness), volume fraction can be understood in one equation.

III. Jamming materials

A. Making an analogy between traditional granular materials and molecular glasses

One of the central ideas of granular materials is jamming. The basic concepts of jamming can be easily understood from the perspective of a granular material, e.g. a bucket of sand. Generally speaking, the sand in the bucket is jammed and viewed as a solid. The reason is kind of simple, it does not flow and it supports certain amount of stress, as can be easily proven by stepping on it to support one's weight. One can tip the bucket to make the sand flow not quite different from a fluid. Here, temperature does not matter but gravity provides the shear stress that actually causes the sand to change from a solid to a fluid [9]. Another method to fluidize sand is by decreasing volume fraction as in the case of immersing the sand in a fluid. As we decreasing the

number of grains per unit volume, there will be less and less grains that eventually they will no longer be self-supporting, and thus the solid will be fluidized. However, that is all about granular materials. In analogy to molecular glasses, granular like materials can also be fluidized by changing the effective temperature if one can properly define it, e.g. gently shaking a bottle of sand to slightly suspend all the grains in the flow of air. Thus we know the two seemingly irrelevant systems can be somehow understood in a unified picture. However, the above statement about making the analogy somehow seems to be too abrupt. The problem is then, can we find a prototype model to study it? This prototype model should satisfy the following requirements: 1. Its size should be small enough so that thermal energy matters obviously; 2. Its size should also be large enough that packing volume fraction matters such that jamming is can be well defined. Zhang *et al.* [10] have provided us a very promising solution, which is using soft repulsive colloids to study them.

Zhang *et al.* [10] use aqueous suspensions of poly(Nisopropyl acrylamide) microgel colloidal particles (NIPA particles) to carry on a two-dimensional colloidal experiments probing jamming transition at non-zero temperature by tuning the packing fraction. The effective interaction between these particles they use can be tuned by changing the softness of the particle, i.e. the crosslink density. Thus, in an equivalent sense, change the temperature of the system. And they can also deform so that a very high volume fraction can be achieved (can go far beyond random close packing volume fraction).

B. Soft jamming of colloids

As one increases volume fractions, in contrast with athermal hard sphere colloids whose primary order peak of pair correlation function diverges as one approaches random close packing volume fraction, the soft colloids system will go through a maximum. This, as Zhang *et al.* [10] point out, is a thermal vestige of zero-temperature jamming transition point. The definition is consistent with the jamming point of athermal hard sphere, as they prove that the primary order peak will grow as the temperature drops and eventually recover the random close packing volume fraction.

IV. Unjamming a polymer glass

Applying stress can also make a glass flow as is seen in some softer glasses, i.e. many polymers, will yield when subjected to sufficiently large stresses. Jamming is the conceptual means of unifying glassy behavior with that of granular materials.

Lee *et al.* [11] show that the nature of shear-induced flow in molecular glasses can now be probed. By measuring the motion of small probe molecules in a polymer glass, they find fluid-like properties when the glass is sheared.

As we have stated above, any of these three approaches can take the system through the solid-to-fluid transition, and the virtue of Lee *et al.* [11] 's work is to confirm that shear does induce melting of the glass, and that the resultant flowing material has many features of a fluid.

V. Interplay of Jamming transition and glass transition: which one happens first?

Another interesting thing about Zhang *et al* [10]'s work is that since one can determine the jamming transition point structurally and glass transition in a kinetic way, one can construct a uniformed phase diagram in which the two transition curves would cross. Usually, glass transition happens first as one increase the volume fraction. However, since one can manipulate the temperature, this does not always hold. Whether this has some more significant meaning is still under discussion.

VI. Conclusions

In summary, by reviewing several recent papers on glass transition and jamming transition, a generalized picture of molecular glasses, colloids and granular materials is constructed in the context of soft colloidal particles. The relative relation can be summarized with a plot like Fig. 1:

There are three methods to fluidize amorphous solids: Applying stress, decreasing volume fraction and increasing temperature.

Soft colloids mimic thermal liquids as approaching glass transition; Soft colloids make strong glasses and hard colloids make fragile glasses;

A thermal vestige of jamming can be structurally determined as the primary ordering peak of pair correlation function goes through a maximum; Kinetic glass transition and jamming transition both exist in soft colloids and the interplay of the two affects dynamics;

The structural relaxation time can be understood based a dynamic scaling function which predicts two distinct regimes separated by the onset of hard sphere jamming point.

The comparison between a granular system and a molecular glass remains an intriguing and appealing challenge. These experiments and simulation provide strong evidence for the merit of a unified perspective, suggesting that colloids with tunable softness may provide new insights.

References:

1. Johan Mattsson, Hans M. Wyss, Alberto Fernandez-Nieves, Kunimasa Miyazaki, Zhibing Hu, David R. Reichman & David A. Weitz, *Nature*, 462(2009)
2. C.A.Angell, K.L.Ngai, G.B.McKenna, P.F.McMillan and S.W.Martin, *J.App. Phys.* **88**, 3113 (2000).
3. C. Austen Angell and Kazuhide Ueno, *Nature*, **462**, 45(2009)
4. R. L.Cook, C.A.Herbst & H.E. Jr King, *J. Phys. Chem.* **97**, 2355–2361 (1993).
5. C.A.Herbst, R.L.Cook & H.E.Jr King, *J. Non-Cryst. Solids*,172–174, 265–271 (1994).
6. L. Berthier and T. A. Witten, *EPL*, **86** (2009)
7. L. Berthier and T. A. Witten, *arXiv:0903.1934v1* (2009)
8. Ludovic Berthier, Elijah Flenner, Hugo Jacquin and Grzegorz Szamel, *PRE* **81**, 031505(2010)
9. David A. Weitz, *Nature*, **323**, 214(2009)
10. Z. Zhang, N. Xu, D. T. N. Chen, P. Yunker, A. M. Alsayed, K. B. Aptowicz, P. Habdas, A. J. Liu, S. R. Nagel & A. G. Yodh, *Nature*, 459(2009)
11. H.N. Lee, K. Paeng, S. F. Swallen, M. D. Ediger, *Science* 323, 231 (2009).

Figure Caption:

Fig. 1

Schematic representation of the connections of molecular glasses, colloids and granular materials are shown

Fig. 1

