

## Thermal Jamming of a Colloidal Glass

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We investigate the effect of temperature on structure and dynamics of a colloidal glass created by tethering polymers to the surface of inorganic nanoparticles. Contrary to the conventional assumption, an increase in temperature slows down glassy dynamics of the material, yet causes no change in its static structure factor. We show that these findings can be explained within the soft glassy rheology framework if the noise temperature  $X$  of the glass phase is correlated with thermodynamic temperature.

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A jamming or glass transition has been observed in a wide range of soft materials including foams, emulsions, pastes, and suspensions when the fraction of the dispersed phase exceeds a critical value. Such ubiquity has led to attempts to develop a universal description of jamming, which has culminated in several phase diagrams for jammed matter [1,2]. These phase diagrams identify density, load, and temperature as the key variables that control the thermodynamics of the jamming transition, and even the physical properties of the resultant soft glassy materials. The effect of density and load on the state of jammed matter has been studied experimentally by several groups, and the findings are generally in qualitative agreement with the proposed phase diagram, typically concluding that unjamming of a glass phase occurs with decreasing density [3,4] or increasing load [5,6].

In contrast, temperature, which plays a critical role in the equilibrium properties and dynamics of molecular systems, has received little systematic attention for colloidal glasses. This situation partially stems from the athermal nature of most granular systems. The common hypothesis hitherto has been that an increase in temperature will give rise to more fluidity and hence unjam the system, as proposed in previous jamming phase diagrams [1,2]. In this Letter we perform such a systematic study using self-suspended nanoparticles densely grafted with polymer chains as a model soft glassy material [7,8]. The absence of a solvent in the self-suspended nanoparticles studied here is attractive because it precludes any temperature-dependent enthalpic interactions between the solvent and the suspended phase. Our studies show that contrary to expectations, increasing temperature enhances jamming, and that subsequent lowering of the temperature unjams the system. We further show that the effect is captured on the continuum level through coupling of the so-called noise temperature  $X$  [9] emanating from co-operativity of elements in a soft glass with the thermodynamic temperature  $T$  originating from interactions of the system with its surroundings. The fundamental origin of the coupling between  $X$  and  $T$  appears to be that higher temperatures lead to greater interpenetration of polymer brushes tethered to neighboring particles.

The limited utility of hard sphere colloids for exploring the physics of the glass transition and the phase space of jammed systems has been noted to result from their fragile behavior [10]. This has led to the growing interest in soft colloids as models for exploring soft glasses, which are typically polymer grafted nanoparticles, star polymers solutions, and crosslinked microgels [10–13]. A plethora of interesting physics has been unraveled through the study of such soft colloids, ranging from asymmetric caging [11], molecular glasslike fragility [10], reversible thermal gelation [12], and polymer mediated melting [13].

Experiments reported in this Letter were carried out using a self-suspended suspension composed of  $10 \pm 2$  nm silica nanoparticles densely grafted (grafting density  $\approx 1.5$  chains/nm<sup>2</sup>) with a polyisoprene corona of molecular weight 5000 and polydispersity index  $M_w/M_n$  of 1.05. The volume fraction of the silica nanoparticles is 10%. Mechanical rheometry in oscillatory- and transient shear flow, using an Anton Paar MCR 501 rheometer equipped with cone and plate fixture, was used to characterize the flow behavior of the material. All measurements were performed at temperatures above the glass transition temperature of polyisoprene and samples were presheared to erase any shear history, with the waiting time after the preshearing kept long compared to the measurement time to ensure that the measurements are not affected by aging [14].

The characteristic response of a soft glass subjected to oscillatory shear flow with varying strain amplitude  $\gamma$  is illustrated in the inset of Fig. 1(a) [4,7,9,15]. At least three distinct flow regimes are observed: (i) a strain independent linear viscoelastic regime at low shear strains, wherein the storage modulus ( $G'$ ) dominates the loss modulus ( $G''$ ); (ii) a nonlinear viscoelastic regime at intermediate shear strains, in which  $G''$  increases due to breaking of cages; and (iii) a strain softening liquid regime at high strains, wherein  $G'' > G'$  and both moduli are decreasing functions of the shear strain. The telltale maximum observed in  $G''(\gamma)$  is a unique feature of jammed materials, such as soft glasses, and is not observed for polymers and other viscoelastic materials. The size of the loss maximum

relative to its linear response value is therefore indicative of the degree of jamming in the system.

The effect of temperature on  $G''(\gamma)$  is shown in Fig. 1(a). The figure shows an increase in the relative size of the loss maximum as temperature is increased, implying that a higher temperature leads to enhanced jamming in the system. Figure 1(b) shows the corresponding loss tangent,  $\tan\delta(\gamma) \equiv G''(\gamma)/G'(\gamma)$  at different temperatures. It is apparent that in the linear regime, the material becomes more solidlike (lower  $\tan\delta$ ) or more jammed as its temperature is increased. These effects are completely reversible and are observed over a wide range of shear

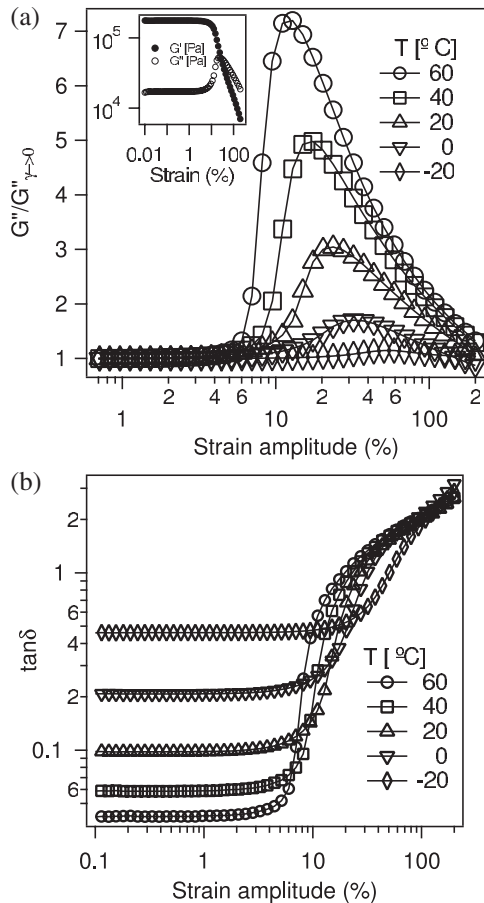


FIG. 1. (a) Results from oscillatory shear amplitude-sweep measurements at different temperatures and at a fixed angular frequency,  $\omega = 10$  rad/s. Open symbols represent  $G''(\gamma)$  normalized by its linear response value. The lines are added as a guide to the eye. The relative height of the maxima in  $G''$  is seen to increase with temperature, implying that the system is more jammed at a higher temperature. The inset shows typical features of  $G'$  and  $G''$  vs strain amplitude for our soft glassy materials. (b) Loss tangent  $\tan\delta$  versus strain amplitude at varying temperatures. At low shear strains,  $\tan\delta$  decreases with temperature implying a more solidlike response at a higher temperature. A waiting time of 5000 s was allowed after preshearing for measurements at each temperature.

frequencies and waiting times, ruling out temperature-dependent aging as the governing mechanism [16,17,19].

To investigate the effect of temperature on the interparticle structure, we have performed small angle x-ray scattering (SAXS) measurements on the materials over the same range of temperatures investigated in the rheological studies. These experiments were carried out using an Anton Paar SAXSess instrument with a line collimation setting using Cu  $K\text{-}\alpha$  radiation with a wavelength of 0.15 nm. As shown in Fig. 2(a), neither the  $q$ -dependent scattered intensity, nor the interparticle structure factor (inset) extracted from the intensity curves change in a systematic way with temperature. These results exclude the possibility that the temperature-dependent rheology is originating from the change in interparticle spacing due to a change in temperature, implying that the thermal jamming originates from the tethered polymer chains.

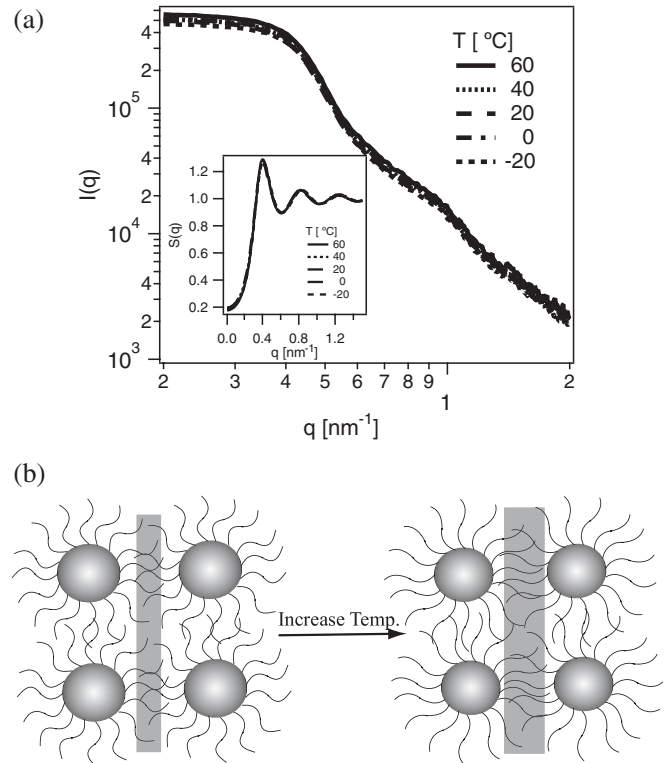


FIG. 2. (a) Intensity  $I(q)$  vs wave vector  $q$  obtained from small-angle x-ray scattering. The data show that  $I(q)$  changes negligibly over the same temperature range where large rheological changes are observed. The inset shows the structure factor  $S(q)$  vs  $q$  obtained from the  $I(q)$  vs  $q$  data.  $S(q)$  reveals no change in the interparticle spacing with temperature. (b) Schematic representation of the molecular process tentatively proposed to explain our observation of enhanced jamming at higher temperature. At higher temperature, tethered polymer chains experience a stronger driving force to uniformly fill the interparticle space, which enhances the excluded volume. For a fixed interparticle spacing, chains must therefore interpenetrate more, enhancing jamming of the particles.

Invariability of the interparticle structure with temperature points towards thermally induced changes in the conformation of tethered polymer chains as a possible mechanism for our observations. While such changes do not alter the interparticle separation, they enhance the stiffness of each tethered chain as temperature rises and might also lead to enhanced corona penetration [Fig. 2(b)]. Interestingly, this latter explanation does not comport with Flory's famous argument [18], which states that untethered polymer chains in a melt should behave like ideal chains, wherein all the interactions and hence the chain conformations are independent of temperature. However, the reversibility of the observed thermal jamming phenomena, the absence of a dependence on deformation rate or waiting time, and the lack of commensurate changes in the interparticle structure factor suggest that the changes that produce thermal jamming must be quite local and reversible, in agreement with the idea proposed in Fig. 2(b).

The soft glassy rheology (SGR) model proposed by Sollich and co-workers [9] is a widely accepted framework for theoretically predicting the rheology of soft glassy materials. In this model, a soft glass is assumed to be composed of elements which are trapped in cages formed by their neighbors, wherein each element sees an energy landscape of multiple well depth to which it can hop. A key parameter in the SGR model is the so-called noise temperature  $X$  which reflects cooperativity in the system and is indicative of the energy available for hopping out of a potential energy well in the energy landscape.  $X$  can thus be considered as the colloidal analog of temperature in molecular systems [9].  $X$  can be related to the phase lag,  $\delta$  between strain and stress by (see Supplemental Material [19]):

$$X = 1 + \frac{2}{\pi} \delta \quad (1)$$

Figure 3 reports the noise temperature  $X$  derived from the  $\tan\delta$  vs temperature data in Fig. 1(b). It is apparent from the figure that  $X$  decreases with an increase in temperature. This implies that lesser energy is available for hopping at higher temperature, supporting the aforementioned trends in Fig. 1. To the best of our knowledge, this is the first instance where  $X$  has been shown to be influenced by the thermodynamic, or measurement temperature of a glassy material. Our observation also provides a complementary method (to the widely accepted route of varying the volume fraction of particles in the suspension), for changing  $X$  in a colloidal suspension.

To verify the generality of the observations, we carried out similar experiments using self-suspended nanoparticles decorated with polymers of two other chemistries: polyethylene glycol (PEG) and polystyrene (PS). The temperature dependent rheology is qualitatively identical to observations for the polyisoprene-based material in Fig. 1. The inset in Fig. 3 compares the temperature-dependent  $X$  values obtained for materials with very

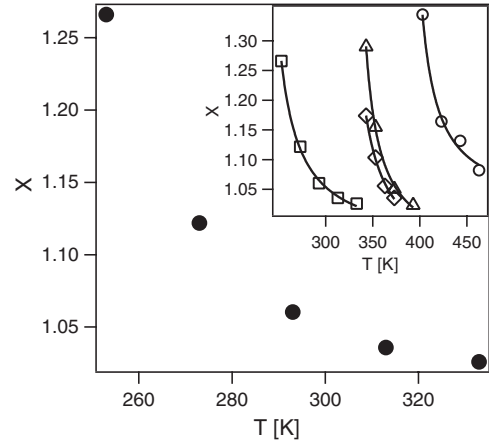


FIG. 3. The so-called noise temperature  $X$  as a function of thermodynamic temperature.  $X$  is obtained from  $\tan\delta$  at low shear strains, Fig. 1(b).  $X$  is seen to decrease with temperature, implying that less energy is available for hopping between wells in the potential energy landscape at higher temperatures. The inset shows  $X$  vs  $T$  for various tethered polymer chemistries and molecular weights. Squares: polyisoprene,  $M_w = 5000$  g/mol; diamonds: polyethylene glycol (PEG),  $M_w = 2000$  g/mol; triangles: PEG,  $M_w = 5000$  g/mol; circles: polystyrene  $M_w = 3500$  g/mol. Solid lines in the inset are fits obtained using the VFT equation described in the text; the fit parameters are provided in Table I.

different polymer chemistries. It is apparent from the figure that for all systems studied,  $X$  decreases with increase in temperature. It is also noteworthy that  $X$  vs  $T$  data for all the materials studied can be fitted to Vogel-Fulcher-Tamman (VFT) [20] dependence:

$$X = A \exp\left(\frac{B}{T - T^*}\right). \quad (2)$$

The parameters  $A$ ,  $B$ , and  $T^*$  are, respectively, the high temperature value of  $X$ , the activation energy, and Vogel temperature. Table I summarizes the VFT parameter values for all of the materials studied. Remarkably, in every case, the value of  $A$  is close to unity, indicating that the colloidal glass transition is approached at high temperature. The value of  $T^*$  is also close to the glass transition temperature for polyisoprene and polystyrene and is approximately equal to the melting temperature for PEG, indicating that the tethered polymer chains play a critical role in the observed temperature dependence of  $X$ . Interestingly, the curvature of the  $X$  vs  $T$  plot is reminiscent of that obtained

TABLE I. VFT parameters for the materials in Fig. 3.

Corona type, $M_w$	A	B	$T^*$
Polyisoprene, 5k	0.95	7.2	227
Polyethylene glycol, 2000	0.91	7.2	314
Polyethylene glycol, 5000	0.93	5.9	324
Polystyrene, 3500	1.01	5.7	382

by plotting dynamic properties, such as viscosity, against temperature in fragile glass forming liquids [10,20].

To examine the SGR model predictions under conditions similar to those studied experimentally, we performed numerical simulations of the SGR model at multiple noise temperature  $X$ . Specifically, the constitutive equation (3) proposed by Sollich *et al.* [9] has been solved numerically for the flow start-up case after the application of a constant steady shear rate,

$$\sigma(t) = \gamma(t)G_0(Z(t, 0)) - \int_0^t dt' \Gamma(t') \gamma(t') G_0(Z(t, t')), \quad (3)$$

where the hopping rate  $\Gamma(t)$  is obtained from solving the integral equation

$$1 = G_0(Z(t, 0)) + \int_0^t dt' \Gamma(t') G_0(Z(t, t')). \quad (4)$$

Here  $\sigma(t)$  is stress,  $\gamma(t)$  is strain,  $\Gamma(t)$  is the hopping rate,  $G_0(z) (= \int dE P_0(E) \exp[-z \exp(-E/x)])$  and  $G_\rho(z) (= \int dE \rho(E) \exp[-z \exp(-E/x)])$  are the surviving probabilities,  $Z(t, t') (= \int dt'' \exp[\gamma(t'') - \gamma(t')^2/2x])$  is the effective time and  $\rho(E) (= \exp(-E))$  is the probability distribution function for the yield energies. A more detailed discussion of the equations and involved parameters can be found in ref. [9].

As predicted by Sollich [9] and also observed experimentally [14,15] the shear stress in a flow start-up experiment for a soft glass goes through an overshoot before reaching its steady-state value. Although the origin of the overshoot is not clearly understood, it is believed to reflect the breaking of cages in a jammed system. Figure 4(a) summarizes the effect of  $X$  on the transient stresses, where the stress values have been normalized with the respective steady-state values at the corresponding  $X$ . The figure shows that a decrease in  $X$  results in an increase in the height of stress maximum during the flow start-up, which is qualitatively similar to the increased height of the  $G''(\gamma)$  maximum observed in oscillatory shear experiments performed at varying temperature [Fig. 1(a)].

Shear start-up experiments carried out at different temperatures using the same materials as in Fig. 1 provide a direct test of the SGR model simulations. These results show that the relative height of the shear stress overshoot increases as the temperature is increased, as reported in Fig. 4(b). This observation is consistent with the simulations results shown in Fig. 4(a) where  $X$  is varied and provides additional support for our postulate from Fig. 3 that the noise temperature is a function of the measurement temperature. Qualitative agreement between experiments and simulations is observed at different shear rates, indicating that thermal jamming of soft glasses is a general characteristic of these materials [19].

Figures 1(a) and 4(b) also provide insights into the fragility [10,20] of the glass phase with respect to strain. The maximum or overshoot in  $G''(\gamma)$  and the stress overshoot

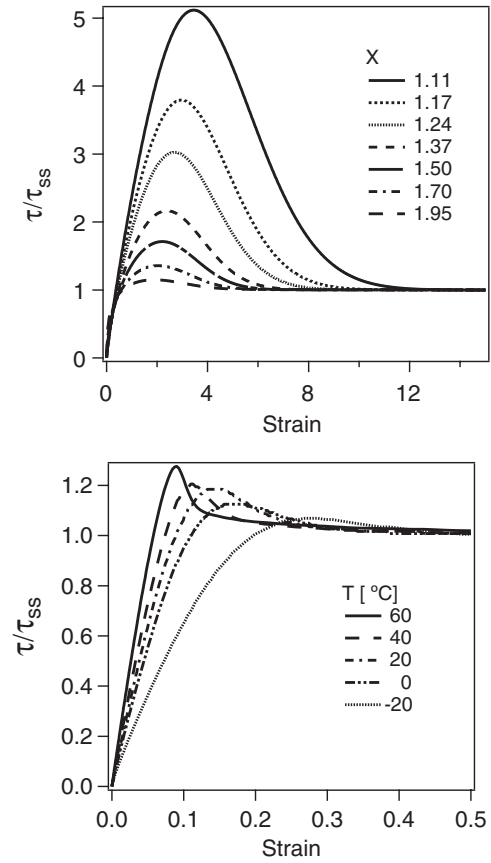


FIG. 4. (a) Simulation results obtained from the SGR model during start-up of steady shear flow at a shear rate of  $0.01 \text{ s}^{-1}$ . The data for different  $X$  values (increasing from top to bottom) show that decreasing  $X$  results in an increase in the height of the shear stress overshoot. (b) Normalized shear stress vs strain obtained from shear start-up experiments at a fixed shear rate of  $0.01 \text{ s}^{-1}$  and at variable temperature. A waiting time of 500 s was allowed after preshearing for each experiment. As in Fig. 4(a), the magnitude of the stress overshoot increases with temperature. It is also evident that the overshoots become sharper at higher temperature, implying mechanically a more fragile state.

during shear start-up are understood to reflect shear-induced breaking of cages in a soft glass. Increases in the height and narrowing of the width of the overshoot in both cases reflect a sharper transition from a solid to a liquid state, and hence are indicative of a mechanically more fragile glass phase. Therefore an increase in temperature leads to the formation of more jammed and yet mechanically more fragile glasses in this case.

The thermal jamming effect reported in this Letter bears a resemblance to the reverse thermal vitrification behavior reported in solutions of star-branched polymers and blocks copolymer micelles by Vlassopoulos and co-workers [12]. These authors found that the solution goes from a liquid to a solid state upon heating and argued that the behavior results from the formation of clusters of the stars upon heating, which gives rise to the solidlike



response observed. The primary reason for this effect was thought to be the change in solvent quality resulting from changes in temperature. This mechanism should not be applicable to the materials studied here for two reasons: first the space filling requirement on the tethered chains [8] in a one component system such as the one studied here prevents the formation of inhomogeneties and clusters; and second, the temperature-dependent enthalpic effect that gives rise to the formation of clusters is unlikely to be present in our system since the suspended and the suspending phase are one and the same.

In conclusion, we have discovered that an increase in temperature enhances jamming in a soft glassy material formed from polymer-functionalized nanoparticles. The effect is visible from linear and nonlinear oscillatory shear measurements as well as from the magnitude and shape of the stress overshoot during start-up of steady shear flow. It is qualitatively the same for polymers of a variety of chemistries and can be described within the SGR model framework by coupling the noise temperature  $X$  to the conventional thermodynamic temperature. We conjecture that this unusual behavior originates from an effective attraction force between chain segments that arises from the requirement that tethered chains in a self-suspended suspension uniformly fill the interparticle space. Such a force should lead to an excluded volume for the tethered chains that increases with temperature. Our findings underscore the need for further studies that explicitly investigate the effect of temperature on the jamming phase diagram.

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