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# Z-shaped dejamming phase diagram of colloidal gels

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#### Abstract

For physically gelled colloidal suspensions, there are two routes to transform the gel from solid to liquid. One is to raise the temperature, and the other is to increase the shear deformation. In this investigation, we found that the phase boundary of this solid-to-liquid transformation exhibits a surprising Z-shaped curve in the strain-temperature plane. This nonmonotonic feature in phase transition appears to be present in various nanoparticle-filled colloidal gels with significant differences in chemical composition, filler type, structure, particle shape, average diameter, and particle size distribution. By applying the Kraus model to the breakage and restoration of filler networks and comparing our findings to nonequilibrium glassy behavior, we found that this nonmonotonic phenomenon can be theoretically predicted by combining the glassy melting kinetics of filler networks at high temperatures with the viscosity-retarded dissociation between particles at low temperatures. © 2023 The Society of Rheology. https://doi.org/10.1122/8.0000666

# I. INTRODUCTION

Colloidal gels are soft solid materials in which an interconnected network of submicrometer-sized particles is formed and spans the entire volume of the dispersion medium [1-8]. This particle network is transient in nature and can be broken or fluidized under shear deformation or thermalization. In many cases, when shear deformation stops or the temperature decreases, the broken particle network can automatically restore its structure. If the particle concentration is high enough, the recovery of the particle network in a colloidal suspension can be achieved within minutes or even seconds [9–11]. Therefore, the formation of the particle network can be regarded as the final arrested state of the colloidal system. Many foods, medicines, cosmetics, and paintings are made with fairly stable colloidal gels. Their physical properties usually depend on the size and shape of dispersed particles, the interactions between the particles, and the spatial uniformity of the interconnected particle network [1–11].

It is noteworthy that the phenomenon of amorphous solidifications is not limited to colloidal suspensions, as it is also frequently observed in many other frustrated systems of diverse characteristic length scales, such as jammed granular materials and vitrified molecular fluids. Based on the view of jammed particles and glasses as related materials, Liu and Nagel [12] once proposed a jamming phase diagram in which the phase axes used were temperature T, load stress  $\sigma$ , and the reciprocal of particle density  $1/\phi$ . Trappe *et al.* [13] then used the data from three different colloid systems (i.e., carbon black, PMMA, and polystyrene in water) and showed that for attractive particles, the phase boundary lines are all

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monotonic concave curves, rather than the proposed convex curves. In addition, they showed that these boundary lines are symmetrical along each phase axis, diverging as the phase axis extends outward. This unique symmetry in the jamming phase diagram leads to the conclusion that glass formation, granule jamming, and colloid aggregation should a share a common ground in physics [13].

Of course, this jamming phase diagram is conceptually very helpful for understanding the physics of many frustrated systems. However, the precise characteristics of the phase boundaries, particularly the shape and location of the  $\frac{3}{4}$ solid-to-liquid transition lines in the diagram, are controversial [14–17]. One example is the study by O'Hern *et al.* [15] of jamming transition that occurs when temperature and applied stress are close to zero. They discovered that jamming transition in this limit can occur at a nonzero threshold of  $\phi_i$ , namely, the *J*-point. Their result shows that the jamming phase boundary does not diverge along the  $\phi$  -axis, so the jamming phase diagram may be partially asymmetrical. Another example is the research of Robertson and Wang [16] on the gelation behavior of mixtures of oil and silica particles. They found that although the dependence of the dejamming stress on filler volume fraction  $\phi$  is consistent with the shape of the jamming phase diagram proposed by Trappe *et al.*, the role of  $\phi$  disappears when mechanical energy input, defined as stress  $\sigma$  multiplied by strain  $\gamma$ , is used instead of stress as the critical parameter. They also found the same scenario in carbon black-filled rubber compounds [16-18]. Based on these results, they proposed a different jamming phase diagram [17] with axes of temperature T, mechanical energy  $\sigma\gamma$ , and the reciprocal of particle density  $1/\phi$ . In this case, the jamming phase diagram shows some symmetry only along the temperature axis, and the solid-to-liquid transition lines along the temperature axis are monotonically concave.

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The present study aims to further investigate the role of temperature T on the solid-to-liquid transition of colloidal suspensions under conditions of fixed particle concentration  $\phi$  but wide temperature changes. The colloidal particles tested were polyisoprene hairy nanoparticles, polystyrene nanobeads, fumed silica, and carbon black, with particle sizes ranging from 9 to 40 nm. The dispersion media used were synthetic oils with high boiling points, including squalane (which is a hydrogenation product of natural squalene), aromatic oil (which is a by-product of the petroleum refining process), and liquid polydimethylsiloxane (which is an organosilicon polymer of low molecular weight). We found that the monotonicity and symmetry along the temperature axis in the jamming phase diagram proposed in the literature are not universally valid. The phase boundaries of the colloidal systems uncovered in this paper are all partially or completely Z-shaped. Here, we report our results based on this study and intend to discuss the potential causes of this nonmonotonous phenomenon from a broad perspective.

# **II. MATERIALS AND PREPARATION**

#### A. Nanoparticles

Five nanosized colloidal particles were used in this study. The first and the second are polyisoprene hairy nanoparticles, codenamed HNP-9 and HNP-39 (see Table I), consisting of a crosslinked polystyrene (PS) core and a polyisoprene (PIP) hairy shell. They are similar in chemical composition but differ greatly in overall particle size. The average diameter of HNP-9 is 9 nm, and the average diameter of HNP-39 is about 39 nm. The third is hairless polystyrene nanobeads, codenamed NB-30, composed of crosslinked styrene, divinylbenzene, and 1-(4-vinylbenzyl) azepane. The average diameter of NB-30 is 30 nm. The fourth is commercial fumed silica, purchased from Shouguang Changtai MicroNano Chemical Plant with a product code of G-17. This material consists of white-colored SiO<sub>2</sub> particles with an average diameter of about 20 nm, which are surface modified with hexamethyldisilazane during the manufacturing process. The fifth is standard furnace N110 carbon black (or CB), purchased from Tianjin Jingiushi Chemical Co. Ltd. This material is widely used as a reinforcing agent in the tire rubber industry. The average diameter of the primary particles of N110 is 17 nm. Table I summarizes the characteristic parameters of the nanoparticles used in this study.

The polyisoprene hairy nanoparticles were synthesized by anionic polymerization in hexane solution using the method reported in the literature [19,20]. Isoprene (99% purity, Aldrich), styrene (99% purity, Aldrich), divinylbenzene (55% purity, TCI, containing isomers of divinylbenzene and ethylvinylbenzene), and hexane (99% purity, HPLC grade, Scharlau) were first treated with activated alumina to remove inhibitors and polar impurities and were then dried in a molecular sieve and in calcium hydride under nitrogen protection prior to their use. N-butyllithium/hexane solution (1.6M, Aladdin), isopropanol (Aladdin), and antioxidant butylated hydroxytoluene (or BHT) (Aldrich) were used as received. A dried 200 ml glass bottle, which previously had been sealed with an extracted septum liner and perforated crown cap under positive nitrogen protection, was used for the synthesis. In the preparation, 125 ml of hexane and 10 ml of isoprene were first charged via double-ended needles to the bottle. Polymerization was initiated by adding a predetermined amount of n-butyllithium and then by placing the bottle into a water-bath shaker that was maintained at 60 °C. After 2 h, the bottle was removed from the water bath and cooled to 23 °C. A small amount of the intermediate product was taken from the reaction bottle for analysis purposes. The bottle was then injected additionally with the same amount of n-butyllithium and followed by 8 ml of a divinylbenzene/ styrene mixture (25 wt. % of divinylbenzene). The bottle was  $\vec{a}$ then returned to the water bath shaker, which was maintained  $\frac{9}{8}$ at 60 °C for another 2 h period. After that, the active species in the bottle were terminated, and the product was released into an isopropanol solution containing 0.03% BHT. The hairy nanoparticles were precipitated from isopropanol, dried in vacuum, and then kept in a refrigerator until use. There is no difference between HNP-39 and HNP-9 in terms of preparation method or amount of monomer, except for the amount of n-butyllithium.

The molecular weights of the nanoparticles and the hair PIPs were determined using Malvern Viscotek gel permeation chromatography (GPC), equipped with a refractive index detector and a dual-light scattering detector. Tetrahydrofuran (THF) was used as the solvent. The GPC column was calibrated using polystyrene as the standard. The number of PIP hairs per particle in the shell was calculated

**TABLE I.** Characteristics of nanoparticles included in this study.

Sample	Particle diameter <sup>a</sup> (nm)	Particle mass $M_w^{b}$ (g/mol)	Polydispersity of particle $D_w/D_n$	PIP-hair $M_w^c$ (g/mol)	Core/shell ratio (v/v)	Number of hairs per particle <sup>d</sup>
HNP-9	$9 \pm 2$	$2.22 \times 10^{5}$	1.20	14070	56/44	7
HNP-39	$39 \pm 5$	$2.07 \times 10^{7}$	1.26	56330	54/46	144
NB-30	$30 \pm 15$	_	1.47	_	100/0	_
G-17	$20 \pm 10$	_	1.25	_	_	_
N110 CB	$17 \pm 7$	_	1.18	_		_

<sup>a</sup>Measured by AFM and TEM in dry state.

<sup>b</sup>Measured by GPC-light scattering in THF solution.

<sup>c</sup>Measured by GPC.

<sup>d</sup>Calculated using molecular weight and core/shell composition.

using the molecular weight of the particle, the core/shell weight ratio, and the shell PIP molecular weight. The core/ shell weight ratio was derived from the weight of isoprene monomer (or shell) and the weight of divinylbenzene-styrene mixture (or core) added during the polymerization process. The characterization of such hairy nanoparticles has been well documented in the literature [19,20]. The characteristic infrared absorptions for PIP hairs (not shown) were ascertained as trans-1,4 structure at 1385 cm<sup>-1</sup>, cis-1,4 structure at 1376 cm<sup>-1</sup>, 3,4- structure at 889 cm<sup>-1</sup>, and 1,2-vinyl structure at 909 cm<sup>-1</sup>, respectively. The 3,4-unit and *cis*-unit contents in these polymers were typically 16% and 84%, respectively. The 1,2-unit and trans-1,4 structures were less than 0.1%. The glass transition temperature  $T_g$  of the PIP hairs is in the range of -64 to -61 °C without exception, as measured by DSC at 5 °C/min.

The hairless polystyrene nanobeads (NB-30) were synthesized by microemulsion polymerization in aqueous solutions. The synthesis method was a modification of the synthesis method disclosed by Hergenrother *et al.* [21]. In the preparation, styrene (99% purity, Aldrich), 4-methylstyrene (96% purity, Aldrich), and divinylbenzene (80% purity, TCI, containing isomers of divinylbenzene and ethylvinylbenzene) were first treated with activated alumina to remove inhibitors and polar impurities and were then dried in a molecular sieve and in calcium hydride under nitrogen protection prior to the use. Sodium lauryl sulfate (99.8% purity, Aldrich), sodium bicarbonate (99.8% purity, Aladdin), potassium persulfate (99.99% purity, Aladdin), sodium chloride (99.8% purity, Aladdin), and sodium dimethyl dithiocarbamate (98% purity, Aladdin) were used as received.

A dried 200 ml glass bottle containing a magnetic stirring rod with a diameter of 8 mm and a length of 20 mm was used for the synthesis. First, to this glass bottle were added 6.4 g of sodium lauryl sulfate, 0.19 g of sodium bicarbonate, and 68 ml of oxygen-free water. Then, the bottle was sealed and purged with nitrogen for 20 min to expel the air from the bottle. After that, the bottle was placed in a 45 °C water bath, while the mixture inside the bottle was stirred slowly using the magnetic stirrer until all solids in the bottle were completely dissolved. Then, to this flask was added a mixture that contained 4.3 g of divinylbenzene, 14.79 g of styrene, 3.52 g of 4-methylstyrene, and 1.19 g of 1-(4-vinylbenzyl) azepane. The polar monomer 1-(4-vinylbenzyl) azepane was made according to the method disclosed by Rodewald et al. [22]. Adding the polar chemical to particle composition can turn the nanobeads synthesized into attractive particles. After that, the stirring speed was increased to about 300 rpm, and the temperature of the water bath was adjusted to 60 °C. After about 15 min, a milky stable emulsion was obtained. To the emulsion was then added 8 ml of a 0.037M aqueous solution of potassium persulfate to initialize polymerization. After about 7-h reaction, 0.3 ml of 3.3M sodium dimethyl dithiocarbamate aqueous solution was added to terminate the active species in the bottle. The resultant product was a translucent colloidal solution. To break the colloidal state, a saturated sodium chloride aqueous solution was added to the solution, which resulted in polystyrene particles aggregating and

precipitating. The turbid solution was then ultracentrifuged, and the lower part was collected and washed with distilled water. The obtained material was then redispersed in water, centrifuged, and washed again. This process was repeated five times in order to remove the residual surfactants inside the product. After that, the product was dried and stored for use.

The dimensions of the aforementioned nanoparticles listed in Table I were examined in the dry state using an atomic force microscopy (AFM) or a transmission electron microscope (TEM). The polymer nanoparticles in the dry state were checked using the AFM from Bruker (Multimode 8 with Nanoscope V controller). The AFM was operated in the tapping mode with an etched silicon tip. To facilitate microscopic observation, the nanoparticles to be examined were redispersed into hexane and were further diluted to about  $10^{-5}$ - $10^{-7}$  wt. %. A small drop of the diluted solution was then placed on a newly cleaved graphite surface of about  $10 \times 10$  mm size. After the solvent had completely evaporated, the dried deposit was examined under AFM. The microscopic images of core-shell hairy particles are shown in Figs. 1(a)-1(c). These particles are spherical in shape and nearly monodispersed. The microscopic image of the hairless polystyrene nanobeads NB-30 is shown in Fig. 1(d). This material contains spherical nanoparticles with diameters of approximately 30 nm. The fumed silica particles G-17 were examined with the transmission electron microscope (TEM) from Nippon Electronics (JEM-2100). The silica particles are not perfectly spherical [see Fig. 1(e)], and the primary parti- $\frac{3}{6}$ cle size of the inorganic silica is about 20 nm. The N110 CB particle size was also evaluated by the TEM. These CB particles agglomerate into branched structures of various spatial § configurations. The microscopy image is shown in Fig. 1(f). The estimated mean diameter of the primary particle of N110  $\frac{1}{10}$ is 17 nm.

The particle size was determined from the analysis of multiple microscopic images using a particle-size analysis software called NANO MEASURER (version 1.2.5). The size of each particle in these images was manually measured by drawing a line that matched the diameter of the particle. The results were then automatically collected and counted by the software. After measuring hundreds of particles and the particle size distribution becoming stable, we let the software calculate the average particle size and standard deviation [10]. In the case of AFM, the instrument comes with its own software that automatically generates particle size and distribution if the particles are well separated in a microscopic image. We also compared manual measurements with automatic measurements, and the results were basically the same. The data reported in Table I were obtained by particle size analysis software after manual measurements.

#### B. Colloidal gels

The polyisoprene hairy nanoparticles HNP-9 and HNP-39 were dispersed into squalane to form colloidal gels. Squalane is an odorless, nonvolatile and viscous liquid with good thermal and chemical stability due to the absence of double bonds. It is usually produced by hydrogenation of natural squalene using transition metal catalysts. Depending on the



FIG. 1. Microscopic images of nanoparticles used in this study: (a) AFM micrograph of hairy nanoparticles HNP-9, (b) and (c) AFM micrograph of hairy nanoparticles HMP-39, (d) AFM micrograph of PS nanobeads NB-30, (e) TEM micrograph of funed silica G-17, and (f) TEM micrograph of N110 CB.

catalyst used, commercially produced squalane may or may not be crystallizable. The squalane (98% purity) used in this study was purchased from TCI. DSC scans at 5 °C/min showed that this squalane had a glass transition temperature of about -102 to -105 °C, depending on whether the scan was heated or cooled. This squalane showed no signs of crystallization or melting at a scanning rate of 1-10 °C/min in the range from -120 to 100 °C or at a constant temperature below  $-60 \,^{\circ}\text{C}$  for more than 10 h. The boiling point of this squalane was 470 °C. In gel preparation, the hairy nanoparticles and the squalane of a predetermined ratio were first weighed into a flask on a balance with  $10^{-3}$  g accuracy. Then, to the flask, 0.1% BHT (antioxidant) equivalent was added for stabilization. After that, hexane diluent was added to the flask. The amount of hexane added was approximately nine times the amount of solids in the flask. With moderate stirring, the dispersion of hairy nanoparticles took place within 12 h. Once the solution became clear, it was poured into a flat aluminum pan to form a thin liquid film with a thickness of a few millimeters. The volatile hexane was removed in a draft hood at 23 °C. After the hexane was evaporated, the resultant material was further degassed inside a vacuum oven at 25 °C for 24 h. As the boiling point of the squalane is 470 °C, we do not need to worry about its vapor pressures near room temperature.

The NB-30 nanobeads were mixed with an aromatic oil to form colloidal gels. This aromatic oil (from PetroChina) is a liquid by-product of the petroleum refining process. It is a standard processing aid (or plasticizer) commonly used in the rubber industry. The glass transition temperature of the oil is -42 °C. The kinematic viscosity of the oil is 520 cSt at 40 °C and 20 cSt at 100 °C. The mass density of the oil is 1.01 g/cm<sup>3</sup>. According to the information provided by the manufacturer, the oil contains about 70% of aromatic rings and is a mixture of many alkane-substituted aromatic compounds of different structures and molecular weights, rather than a pure ingredient. Its atmospheric boiling range is about 350-480 °C. In the preparation of colloidal gels, the NB-30 § nanobeads and the aromatic oil in a predetermined ratio were  $\frac{\omega}{2}$ first weighed into a flask on a balance with  $10^{-3}$  g accuracy. Then, 0.1% BHT (antioxidant) was added to the flask for stabilization. After that, toluene, which was nine times the amount of solids, was added to the flask. The mixture was then stirred moderately for 12 h using a magnetic stir bar. After the solution became homogeneous, it was poured into a flat aluminum pan to form a liquid thin film with a thickness of a few millimeters. The volatile toluene was first removed in a draft hood for 6 h, and then the material was degassed in a vacuum oven at 35 °C for three days. The final sample was scraped into a glass bottle and stored in a freezer until use.

The fumed silica G-17 was dispersed into liquid polydimethylsiloxane (PDMS) to form colloidal gels. This liquid PDMS (or silicone oil) was from Shanghai Chuyijia Silicone Materials Co. Ltd, with a product code: SH-201-1000. It has a molecular weight of about 22 000 g/mol and a viscosity of 970 mPa s at 40 °C. This silicone oil has no boiling point, except that it decomposes at temperatures above 400 °C. Gels were prepared by mixing directly the fumed silica and the silicone oil at 23 °C, i.e., without adding any solvent. In the preparation, the silicone oil was first weighed into a beaker. Then, under the stirring of the homogenizer AD-25 (from Shanghai Oni Instruments) at a rate of 80 rpm, the fumed silica was slowly added to the silicone oil. The process took about 20 min. After the addition of fumed silica was completed, the mixture was further homogenized by vigorously

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stirring at a mixing speed of 750 rpm for an additional 10 min. Then, the material was scraped into a glass bottle and degassed in vacuum at 23 °C for 24 h. After that, the material was stored in a freezer until use.

The N110 CB was dispersed into squalane to form colloidal gels with the aid of a dispersant. The dispersant used is a commercial tetraethylenepentamine-terminated polyisobutylene succinimide (PIBSI), produced by Jinzhou Antai Lubricating Oil Additive Co. Ltd. The molecular weight  $M_w$ of PIBSI is 5800 g/mol, and polydispersity  $M_w/M_n$  is 2.9. Prior to use, the CB was ground into fine powders using a mini-grinder (JM10-150, SUPOR). The preparation method of colloidal gels was carried out in close accordance with that reported in the literature [23-26]. In the preparation, 1 part of carbon black and 20 parts of hexane were first added into a flask. The mixture in the flask was then placed into an ice-water bath of ultrasonication at a power of 70 W for 30 min. Then, to the flask, the dispersant PIBSI equivalent to <sup>1</sup>/<sub>4</sub> of the weight of CB was added. After that, the antioxidant BHT equivalent to 0.1% by weight of PIBSI and a predetermined amount of squalane were added to the flask. Complete homogenization took place within 24 h under moderate stirring. After the CB became well dispersed, the black solution was poured into a flat pan to form a thin liquid film of a few millimeters in thickness. The volatile hexane was first removed from a draft hood. Then, the material was degassed in a vacuum oven at 55 °C for 12 h and then at 25 °C for 24 h to remove residual hexane before being taken out for use.

#### C. Measurements

The dynamic viscoelastic properties of the aforementioned colloidal gels were measured using an Anton Paar EC Twist 302 stress-controlled rheometer with a torque ranging from  $0.02 \,\mu$ Nm to 200 mNm. This rheometer was controlled by standard RHEOPLUS 3.2 software with a waveform oscillatory test setup. At low frequencies (i.e., <10 Hz), this stress-controlled rheometer can be operated effectively in the strain-controlled mode. A cone-plate geometry was used to ensure a homogeneous strain rate field during the measurement. The plate diameter/cone angle combination used was 25 mm/0.04 radian. The cone tip was truncated by 0.25 mm to allow the virtual tip of the cone to coincide with the surface of the opposing plate without contact. The material to be tested was usually loaded on the lower plate, so that there was more material in the center of the plate than at the borders. When the upper plate was lowered, the first contact of the sample with the upper plate was in the center of the plate, thereby minimizing the possible trapping of air between the material and the plate. After the material was loaded between the cone and plate fixtures, the temperature was first set to be 10 °C above the melting temperature  $T_{\mu}$  of the material, or the temperature was set to be the temperature at which the material liquified. Then, oscillatory shear was applied at 0.5 Hz and 25% strain for about 5 min. After that, the material was set to a preselected test temperature of T. During the operation, the normal force was kept to be zero, and then the material was allowed to equilibrate at 1 Hz and 0.001% strain amplitude for 1 h before performing a strain sweep from 0.001% to 50% in logarithmic increments at 1 Hz or a temperature sweep at a fixed strain amplitude. The strain during oscillatory shearing was varied according to  $\gamma(t) = \gamma_0 \sin\omega t$ , where  $\gamma_0$  is the strain amplitude and  $\omega$  is the angular frequency. The maximum in-phase stress is given by  $\sigma = G'\gamma_0$ , where G' is the dynamical storage modulus. The squalane, aromatic oil, and silicone oil are all stable and non-volatile liquids, and we do not have to worry about their volatilization losses during the tests over a temperature range of -40 to 200 °C.

In the measurements of these colloidal gels, we restricted our experiments to a strain range that was smaller than 50%. At high strain amplitudes, complicated behaviors can occur during the tests. For instance, wall slipping could be a major problem when testing low-tackiness materials, while edge fracturing could be a main problem encountered in testing weak materials under high deformations. Although we may use sand-treated plates to avoid wall slippage to a certain extent, edge fracture can occur during the test due to the roughness of the surface. At present, there is no unified way to solve all the problems. Some of these problems are visible to the naked eye and some may require special measurements, but all of them share two warning indicators. One is that once these complex behaviors are involved, the even harmonic coefficient  $I_2/I_1$  may suddenly increase and become abnormally large. The other is that the oscillation torque may drop suddenly and display overshoot. In our case, if  $I_2/I_1$ became >4% or the oscillation torque declined sharply, we  $\vec{a}$ chose to stop the experiment. The data presented hereafter will not include these complicated scenarios.

#### **III. RESULTS AND DISCUSSION**

Let us start with a HNP-9/squalane colloidal gel containing 18 vol. % filler. The strain-dependent storage modulus G'and loss modulus G'' of this gel are shown in Fig. 2 as a function of temperature *T*. For clarity, the paired G' and G''curves in Fig. 2 are moved vertically and arbitrarily so that the curve measured at high temperature is located in the upper part of the graph and the curve determined at low temperature is located in the lower part of the graph. In addition, some pairs of G' and G'' curves have been magnified for clarity.

As shown in Fig. 2, when the test temperature  $T > 46 \,^{\circ}$ C, such as at 55  $^{\circ}$ C, the rheological response of the material exhibits typical liquid behavior, where G' < G'' over the entire strain range. This material can flow under its own weight at temperatures above 46  $^{\circ}$ C. However, when the test temperature  $T < 46 \,^{\circ}$ C, the material exhibits characteristic solid behavior with G' > G'' at the zero-strain limit and the material can support its own weight. Here, we define a characteristic temperature, i.e.,  $T_{\mu} = 46 \,^{\circ}$ C, for this liquification behavior of the material. We use the subscript " $\mu$ " instead of "m" to emphasize the fact that this type of melting is not the melting of crystals but rather the fluidization of glasslike materials.

Intriguingly, this solid behavior of the material at  $T < T_{\mu}$  exists only for small deformations. As the shear strain amplitude  $\gamma_0$  increases, the storage modulus G' of the material



**FIG. 2.** Effect of *T* on the  $\gamma_0$ -dependence of the dynamic moduli *G'* and *G''* of a colloidal gel composed of hairy nanoparticles HNP-9 and squalane, wherein the volume fraction of the nanoparticles HNP-9 is 18 vol. %. The arrow marks the onset of nonlinearity. The dashed line traces the transition loci of the material from a gel state to a fluid state. Test frequency  $\omega = 6.28$  rad/s.

starts to fall off beyond a sort of yielding strain  $\gamma_y$ , whereas the loss modulus G'' increases toward a maximum. Further increasing the strain  $\gamma_0$  results in a crossover between G' and G'' at a critical strain  $\gamma_c$ . After that, the material displays a characteristic liquid behavior with G' < G''. Therefore, the yield strain  $\gamma_y$  associated with the onset of nonlinearity and the critical strain  $\gamma_c$  associated with the crossover between G'and G'' characterize the solid-to-liquid (or dejamming) transition of this material. The temperature dependences of  $\gamma_y$  and  $\gamma_c$ , thus, outline the phase boundary of solid-to-liquid transitions.

As shown in Fig. 2, the yield strain  $\gamma_y$  with the indicated test temperature *T* exhibits a surprising Z-shaped trajectory, while the critical strain  $\gamma_c$  with the indicated temperature *T* also displays a similar Z-shaped curve. Interestingly, these two quantities  $\gamma_y$  and  $\gamma_c$  seem to have the same qualitative tendency in terms of the phase behavior of the material, and the two Z-shaped trajectories are offset equally from each other. This observation suggests that  $\gamma_y$  and  $\gamma_c$  must stem from the same ground of physics, and that both of them are



**FIG. 3.** Relationship between critical strain ( $\gamma_c$ ) and temperature (T) for a colloidal gel composed of hairy nanoparticles HNP-9 and squalane, wherein the volume fraction of the nanoparticles HNP-9 is 18 vol. %. The data are taken from the crossovers of G' and G'' shown in Fig. 2.

associated with the destruction of particle networks. The former represents the starting point of the destruction, and the latter represents the midpoint of the destruction. Here, we prefer to use the critical strain  $\gamma_c$  to describe the dejamming transition, because it is relatively easier to extract from the experimental data.

To show the dejamming transition more clearly, the criti- ₽ cal strains at various temperatures are extracted from Fig. 2 8 and replotted against the temperatures in bilinear coordinates  $\frac{3}{2}$ in Fig. 3. The region on the left side of this Z-curve represents the solid or gel state, while the region on the right side of this curve represents the liquid or fluid state. A phase transition will occur if the system traverses through the Z-shaped phase boundary. Nevertheless, this Z-shaped phase line is so far constructed based on the strain sweeps under isothermal conditions. This raises the question: if a temperature sweep with a fixed strain amplitude is deliberately chosen, such as the path shown by the dotted arrow in Fig. 3, will the system really show the three transitions predicted by the Z-shaped boundary for the solid-to-liquid, liquid-to-solid, and solid-to-liquid? The answer to this question is absolutely affirmative.

Figure 4 shows the phase behavior of the material recorded under a temperature scan of 5 °C/min, where the strain amplitude is fixed at 5%. It can be seen that at -26 °C, the material is solid because its G' > G''. As the temperature increases, the material undergoes a transition from G' > G'' solid behavior to G' < G'' liquid behavior around -20 °C. According to Robertson and Wang [16], this process should be called the "dejamming transition." As the temperature further increases, the material undergoes a reverse transition from G' < G'' liquid behavior to G' > G'' solid behavior at a temperature of about 15 °C. According to Trappe *et al.* [13], this process should be referred to as a "jamming transition." As the temperature further increases further, the formed solid reverts from the solid behavior of G' > G'' to the liquid behavior of



**FIG. 4.** Dynamic mechanical G' and G'' against temperature T at a fixed strain amplitude  $\gamma_0$  (=5%) for a colloidal gel composed of hairy nanoparticles HNP-9 and squalane, wherein the volume fraction of the nanoparticles HNP-9 is 18%. Test frequency  $\omega = 6.28$  rad/s and temperature scan rate is 5 °C/min.

G' < G'' again when the temperature reaches 45 °C. This is another "dejamming." Therefore, the material does undergo three phase transitions with continuous temperature changes. These behaviors of the material on the temperature sweep test are in perfect agreement with the prediction of the Z-shaped boundary shown in Fig. 3 on the strain sweep tests.

We also tested solid-to-liquid phase transitions using temperature sweeps at different strain amplitudes ranging from 1% to 15% and different temperature scanning rates from 1 to 5 °C/min. We did observe that varying the scanning rate affects somewhat the location of the phase boundary due to the time-dependence of gelation and melting of the colloidal gel. However, the basic shape of the dejamming phase diagram in all cases remained unchanged and very consistent with the Z-shaped boundary shown in Fig. 3. Therefore, this Z-shaped phase diagram can also be constructed by temperature scans under various isostrain conditions. Here, we choose to present the data from isothermal strain sweeps because they are relatively intuitive and easy to understand. In a later discussion, we will show a comparison between using isostrain temperature sweeps and isothermal strain sweeps in constructing this nonequilibrium phase diagram.

We notice that in the related literature [12–15], shear stress  $\sigma$  is usually selected instead of shear strain when describing the jamming phase diagram. Although the physical origin of selecting  $\sigma$  in the jamming phase diagram is not clear, recent mode-coupling theories [27] seem to suggest that including shear stress is an acceptable option. In the present study, since the maximum in-phase stress is given by  $\sigma = G' \gamma_0$ , the yielding stress  $\sigma_v$  at the onset of nonlinearity and the critical stress  $\sigma_c$  at the dejamming transition can be estimated accordingly. Figure 5 depicts the relationships between temperature T and yielding stress  $\sigma_v$  and between temperature T and critical stress  $\sigma_c$  for the colloidal gel composed of nanoparticles HNP-9 and squalane. Strikingly, these relationships are also nonmonotonic Z-shaped curves in the  $\sigma$ -T plane. This observation is inconsistent with the shape of



**FIG. 5.** Temperature *T* vs. yielding stress  $\sigma_y$  and critical stress  $\sigma_c$  for the colloidal gel composed of hairy nanoparticles HNP-9 and squalane, wherein the volume fraction of the nanoparticles HNP-9 is 18%.

reported jamming phase diagrams [12–17], where the dependence of the critical stress on *T* is predicted to be monotonic in the  $\sigma$ -*T* plane. We have also examined the total stresses as a function of temperature, and they follow the same trend. To the best of our knowledge, this is the first time that a nonmonotonic jamming phase boundary in the  $\sigma$ -*T* plane has been uncovered experimentally.

To further explore this unusual phenomenon, we studied a brown of colloidal gels composed of nanoparticles HNP-9 and squalane, but with different filler concentrations, ranging from 13 to 33 vol. %. Without exception, we found that they all showed similar Z-shaped dejamming phase diagrams. Figure 6 displays an example of a colloidal gel containing 13 vol. % of HNP-9. Comparing the result shown in Fig. 6 with that shown in Fig. 2, it can be found that reducing the particle concentration in the gel can slightly increase the yielding strain  $\gamma_y$  and the critical strain  $\gamma_c$ . At the same time, decreasing the particle concentration in the gel can also somewhat decrease the characteristic melting point  $T_{\mu}$ . However, the Z-shaped phase boundary of the gel spanning the strain-temperature plane is basically unchanged.

We also examined colloidal gels containing particles of same chemical composition but larger particle sizes, such as the particle HNP-39 as listed in Table I. The average diameter of HNP-39 is 39 nm, which is about four times the average diameter of HNP-9. The mass of HNP-39 is  $2.07 \times 10^7$  g/mol, which is about 100 times the mass of HNP-9. Figure 7 shows the rheological behavior of the colloidal gel consisting of 13 vol. % of HNP-39 and 87 vol. % of squalane. The relationship between the test temperature Tand the critical strain  $\gamma_c$  for this colloidal gel is plotted in Fig. 8. Again, we observe that the phase boundary of this gel is Z-shaped. Comparing the results shown in Fig. 8 with those shown in Fig. 6, we notice two important differences. First, the characteristic melting temperature  $T_{\mu}$  of the gel has increased from about 48 °C to about 150 °C when the particle size is increased from 9 to 39 nm. This suggests that the size

**FIG. 6.** Effect of T on the  $\gamma_0$ -dependence of the dynamic moduli G' and G'' of a colloidal gel composed of hairy nanoparticles HNP-9 and squalane, wherein the volume fraction of the nanoparticles HNP-9 is 13%. The arrow marks the onset of nonlinearity. The dashed line traces the transition loci of the material from a gel state to a fluid state. Test frequency  $\omega = 6.28$  rad/s.

and the mass of colloidal particles have significant effects on phase behavior. Second, the inflection point in the lower half of the Z-shaped curve has also increased from -15 to about 55 °C. This indicates that the lower half of the Z-shaped curve is not caused by any specific event occurring inside the dispersion medium itself, because the turning point in the lower half is neither the glass transition of the solvent nor the melting point of the solvent.

We further tested colloidal gels formed from hairless polystyrene beads (NB-30). This material, NB-30, is very similar to the one used by Trappe et al. [13], except that the particle size used here is smaller. The average diameter of NB-30 is about 30 nm (see Table I). The dispersion medium used is a highly aromatic oil. The specifications of this oil have been described in Sec. II. Figure 9 shows the rheological properties of the colloidal gel containing 22 vol. % of NB-30 as a function of temperature T and strain amplitude  $\gamma_0$ . The nonlinear responses of the material are similar to what we observed earlier. Initially, there is a strain-independent state for G' and G'' at small strains (i.e., <3%). As the test strain amplitude  $\gamma_0$  increases, the storage modulus G' and the loss

of a colloidal gel composed of hairy nanoparticles HNP-39 and squalane, wherein the volume fraction of the nanoparticles HNP-39 is 13%. The arrow marks the onset of nonlinearity. The dashed line traces the transition loci of k

modulus G'' of the gel decrease after  $\gamma_0$  passes through a sort of yielding strain  $\gamma_y$ . However, the storage modulus G' decreases faster than the loss modulus G'' does. As  $\gamma_0$ exceeds a critical strain  $\gamma_c$ , the storage modulus G' crosses with the loss modulus G''. As a result, the material changes from a solid behavior of G' > G'' to a liquid behavior of G' < G''.

The temperature dependence of the critical strain  $\gamma_c$  can be extracted from the intersection of G' and G''. Figure 10 exhibits the relationship between the test temperature and the critical strain  $\gamma_c$  in a dual linear plot. What we see here is the upper half of the Z-shaped dejamming phase diagram. The nonmonotonic feature in dejamming phase diagrams of colloidal gels is obviously more common than we initially realized. The presence of polymeric hairs on the surface of solid particles is clearly not the main cause of nonmonotonicity because the same phenomenon is observed here in the colloidal system containing hairless nanoparticles. We also tried to take measurements at lower temperatures in order to complete this phase diagram. However, we could not reliably measure the rheological properties at lower temperatures because edge fractures often occurred during the testing of





←G' at 140°C

∽-G" at 140°C

-G' at 135°C

-G" at 135℃

G' at 130°C

G" at 130°C

x200

x2(



**FIG. 8.** Relationship between critical strain ( $\gamma_c$ ) and temperature (*T*) for a colloidal gel composed of hairy nanoparticles HNP-39 and squalane, wherein the volume fraction of the nanoparticles HNP-39 is 13%. The data are taken from the intersections of *G'* and *G''* shown in Fig. 7.

this material. The relationship between the critical stress  $\sigma_c$ and temperature *T* at the de-jamming transition (not shown) for this system containing polystyrene nanobeads and aromatic oil, however, is still consistent with the isoconcentration plane of the jamming phase diagram reported by Trappe *et al.* [13] and is monotonic. Among the four colloidal systems studied, only the system containing polystyrene nanobeads displays this behavior: that is, the phase boundary line in the  $\sigma_c$ -*T* plane is monotonic. But, when the critical strain  $\gamma_c$  is used as an independent variable, the dejamming phase boundary line becomes nonmonotonic and exhibits the upper half of the Z-shaped dejamming phase diagram.

To explore the generality of this nonmonotonic feature, we further investigated colloidal gels prepared from commercial fumed silica and silicone oil, with different filler concentrations ranging from 2.8% to 15% by weight. This silica consists of nanometer-sized SiO<sub>2</sub> particles with a primary particle diameter of about 20 nm, which are aggregated into large particles with an average diameter of about 200 nm. The silicone oil is a liquid PDMS with a molecular weight of 22 000 g/mol. The prepared gels are all solids at a room temperature of 23 °C and can support their own weight without flowing. Intriguingly, when these gels are cooled to temperatures below 0 °C, they can surprisingly liquify and flow.

Figure 11 shows the rheological properties of a silica/oil gel containing 10.3% silica by weight (or 4% by volume). At 0 °C, the storage modulus G' of the material is consistently less than the loss modulus G'' over the entire test strain range, indicating that the material is completely fluid. Above 0 °C, the material is a solid because its G' > G''. However, this solid behavior of the material exists only for small deformations. As the strain amplitude increases, the storage modulus G'' displays a maximum. As the strain further increases, G' crossovers G'' and then falls below G''. The trajectory of intersections of G' and G'' at various temperatures



**FIG. 9.** Effect of *T* on the  $\gamma_0$ -dependence of the dynamic moduli *G'* and *G''* of a colloidal gel composed of nanobeads NB-30 and aromatic oil, wherein the volume fraction of the nanoparticles NB-30 is 22%. For clarity, the curves have been displaced vertically by arbitrary amounts. The arrow marks approximately the onset of nonlinearity. The dashed line traces the transition loci of the material from a gel state to a fluid state. Test frequency  $\omega = 6.28$  rad/s.



**FIG. 10.** Relationship between critical strain ( $\gamma_c$ ) and temperature (*T*) for a colloidal gel composed of hairless nanoparticles NB-30 and aromatic oil, wherein the volume fraction of the nanoparticles NB-30 is 22%. The data are taken from the crossovers of *G'* and *G''* shown in Fig. 9.



**FIG. 11.** Effect of *T* on the  $\gamma_0$ -dependence of the dynamic moduli *G'* and *G''* of a colloidal gel composed of fumed silica and PDMS liquid, wherein the volume fraction of the silica is 4 vol. %. The arrow marks the onset of nonlinearity. The dashed line traces the transition loci of the material from a gel state to a fluid state. Test frequency  $\omega = 6.28$  rad/s.

delineates the boundary of the phase behavior for this colloidal gel.

Figure 12 presents the relationship between the test temperature T and the critical strain  $\gamma_c$  at dejamming transition. Again, we observe the upper half of the Z-shaped dejamming phase diagram. The melting temperature  $T_u$  of this material increases significantly as the strain amplitude  $\gamma_c$  decreases. This phenomenon may be due to the fact that the material contains nano-sized silica particles and fused aggregates of various sizes. We have also tried to take measurements at lower temperatures to complete this dejamming phase diagram. At temperatures below -50 °C, we did observe that this material became a solid. However, the resultant solid was too brittle for us to reliably measure the rheological properties, as edge fractures often occurred when testing this material at such low temperatures. At present, we can only present the upper part of the dejamming phase diagram for this system.

The phenomenon that a colloidal suspension solidifies at high temperatures but fluidizes at low temperatures is exceptionally interesting. Over the past many years, materials with



**FIG. 12.** Relationship between critical strain ( $\gamma_c$ ) and temperature (*T*) for a colloidal gel composed of fumed silica G17 and PDMS oil, wherein the volume fraction of the silica is 4%. The data are taken from the intersections of *G'* and *G''* shown in Fig. 11.

this inverse-temperature dependence have attracted great attention [28-33] and are considered to be very useful in drug release, biopurification, engineering fluids, and artificial intelligence. In the past, most of the inverse-temperature-response materials were made from polymers with specially designed chemical structures, such as polyacrylamide and poly-Nisopropylacrylamide and their copolymers [28,29]. These polymers in aqueous solutions can shrink or expand abnormally in response to changes in temperature. Those past research studies often regarded this inverse phenomenon as a special area in  $\frac{1}{2}$ polymer science [28–33]. However, our current study suggests that this anomalous phenomenon may be prevalent in many colloidal systems. In addition to above examples, this inversetemperature dependence has recently been observed in carbon black-dispersant-lubricant ternary systems [23-26]. We believe that this anomaly stems from the Z-shaped dejamming phase diagram for attractive particles. Particularly, the upper half of the dejamming phase diagram can naturally give the inversetemperature dependence of a colloidal material.

To confirm our speculation, we prepared a CB-filled colloidal gel by mimicking the method and composition reported in the literature [23-26] but using a different dispersion medium. This gel contains 20 wt. % CB particles, 5 wt. % PIBSI, and 75 wt. % squalane. It is a solid material at 25 °C but can be surprisingly liquified at -10 °C. Figure 13 shows the temperature dependence of dynamic moduli G'and G'' for this gel at different strain amplitudes. At temperatures below -20 °C, the material is liquid. Its G'' is larger than G'. As the temperature increases, the material first experiences a transition from G' < G'' liquid behavior to G' > G''solid behavior. The transition location is a function of the strain amplitude  $\gamma_0$ . When  $\gamma_0 = 5\%$ , the jamming transition appears around -5 °C. As the temperature further increases, the material then undergoes a reverse transition, that is, from G' > G'' solid behavior to G' < G'' liquid behavior around 55 °C. Interestingly, the gap between these two transitions on the temperature axis depends on the strain amplitude and



FIG. 13. Dynamic mechanical G' and G'' against temperature T at various fixed strain amplitudes  $\gamma_0$  (= 5%, 10%, 20%, and 25%) for a colloidal gel consisting of 20 wt. % N110 CB, 5 wt. % PIBSI, and 75 wt. % squalane. Test frequency  $\omega$  is 6.28 rad/s, and the temperature scan rate is 2 °C/min. The arrow marks the transition location.

decreases as the strain amplitude increases. The two transitions eventually merge together and disappear completely when the strain amplitude is greater than 30%. As shown in Fig. 13, the dejamming phase boundary obtained using isostrain temperature sweeps, such as those marked by arrows, is clearly nonmonotonic.

The strain dependence of G' and G'' for this gel at various constant temperatures is shown in Fig. 14. At small deformations, this material displays solid characteristics at  $T \ge 0$  °C. As the shear strain amplitude  $\gamma_0$  increases, the storage modulus G' of the material falls off beyond a sort of yielding strain  $\gamma_{v}$ , whereas the loss modulus G'' increases toward a maximum. Further increasing the strain  $\gamma_0$  results in a crossover between G' and G'' at a critical strain  $\gamma_c$ . After that, the material displays a characteristic liquid behavior with G' < G''. The solid-to-liquid transition boundary of the CB-PIBSI-squalane gel, as marked by the red dashed line in Fig. 14, is also nonmonotonic. The phase boundary obtained using isothermal strain sweeps is the upper half of the Z-shaped dejamming phase diagram. Comparing the results shown in Fig. 14 with those shown in Fig. 13, one can find that the phase boundary obtained from the temperature scans is slightly shifted to a lower temperature than the phase boundary obtained by the isothermal strain sweeps. This is

0.01 0.1 10 10 Septembe  $\gamma_{\theta}$  (%) **FIG. 14.** Effect of T on the  $\gamma_0$ -dependence of the dynamic moduli G' and  $\aleph$ G" for a colloidal gel consisting of 20 wt. % N110 CB, 5 wt. % PIBSI, and 75 wt. % squalane. The arrow marks the onset of nonlinearity. The dashed line traces the transition loci of the material from a gel state to a fluid state.

understandable because there is a time-temperature effect on gelation and melting of the colloidal gel.

Test frequency  $\omega = 6.28$  rad/s.

The emergence of those partially or completely Z-shaped phase boundaries has completely changed our perception of traditional monotonic jamming phase diagrams proposed in the literature [12,13]. The nonmonotonic feature in the dejamming phase boundary is obviously much more common than we originally thought because it exists in all four systems studied (i.e., hairy nanoparticles in squalane, polystyrene nanobeads in aromatic oil, silica in silicone oil, and CB in PIBSI-squalane) that differ greatly in terms of dispersion medium, chemical composition, particle structure, average particle size, and particle size distribution. The root cause of this unusual phenomenon is very interesting and of fundamental importance.

To interpret the surprising Z-shaped dejamming phase diagram, we need to turn our attention to the fact that attractive particles in the liquid medium agglomerate and tend to form a jammed network. The filler network is transient in nature and can be broken or fluidized through shear deformations. In related literature, Kraus [34] once proposed a theoretical model in order to offer a quantitative description of the nonlinear effect based on the knowledge of breaking and



reforming of the filler network. The Kraus model still remains today one of the most widely used approaches. The Kraus expressions for the strain dependence of dynamic moduli are as follows:

$$\left(G' - G'_{\infty}\right) / \left(G'_{0} - G'_{\infty}\right) = 1 / [1 + (\gamma_{0} / \gamma_{c})^{2m}]$$
 (1)

and

$$(G'' - G''_{\infty})/(G''_{\max} - G''_{\infty}) = 2(\gamma_0/\gamma_c)^m / [1 + (\gamma_0/\gamma_c)^{2m}], \quad (2)$$

where  $G'_0$  and  $G'_{\infty}$  are linear and large strain limiting values of G', respectively.  $G''_{\text{max}}$  and G'' are the peak value and large strain limiting value of G'', respectively. The power exponent m is the model fitting parameter, usually in the range of 0.6–0.8.  $\gamma_0$  is the strain amplitude, and  $\gamma_c$  is the critical strain amplitude.

Now, let us review some details of the Kraus model, which may help us understand the mechanism by which the Z-shaped dejamming phase boundary emerges. Supposing two spherical particles of radius *a* are separated by a small distance r, Kraus showed that the attractive van der Waals potential,  $V_{attr}$ , between equal diametric spherical particles comprised of *n* molecules obeying an inverse six-power law  $(-A/r^{6})$  is approximately given by [34,35]

$$V_{attr} \cong -\pi^2 n^2 A a / 12\delta, \tag{3}$$

where  $\delta = r - 2a$  and  $\delta \ll a$ . The repulsive potential derived from an inverse twelve-power law  $(B/r^{12})$  is given by

$$V_{rep} \cong \pi^2 n^2 Ba/2520\delta^7. \tag{4}$$

By balancing the attractive and repulsive forces between the two particles, he obtained the equilibrium contact distance  $\delta_0$  between the particles and the spring constant  $K_0$  of the interparticle bond. The results are

$$\delta_0 = (B/30A)^{1/6} \tag{5}$$

and

$$K_0 = \pi^2 n^2 A a / 2\delta_0^3.$$
 (6)

From this, the energy  $w_0$  stored in the interparticle bond due to forced deformation can be simply expressed as

$$w_0 \cong K_0 x^2 / 2,\tag{7}$$

where x is the displacement of the particle from its equilibrium position and  $x \cong \gamma r$ . For  $N_0$  particle contacts, the sum of the stored energy is  $N_0 w_0$ . Assuming that the average energy stored during oscillatory shearing per cycle per unit volume is proportional to the energy stored in interparticle bonds, Kraus [34] showed that the contribution of  $N_0$  interparticle van der Waals forces to the storage modulus  $G'-G'_{\infty}$ 

can be written as

$$G_0' - G_\infty' \cong N_0 K_0 r^2. \tag{8}$$

Kraus further suggested that under a periodic sinusoidal strain at a fixed frequency,  $\gamma(t) = \gamma_0 \sin \omega t$ , the contacts between particles are constantly broken and reformed. He assumed that the rate of contact breakage,  $R_b$ , i.e., the amount of network broken, is proportional to the number of existing contacts Nand to some power of the strain amplitude  $\gamma_0$ ,

$$R_b = k_b \gamma_0^m N, \tag{9}$$

where  $k_b$  is the rate constant for breakage and m = 0.6-0.8 is the model fitting parameter. The rate of recovery of contacts,  $R_r$ , will be proportional to  $N_0 - N$  and is assumed to vary as  $\gamma_0^{-m}$ ,

$$R_r = k_r \gamma_0^{-m} (N_0 - N), \tag{10}$$

where  $k_r$  is the rate constant for recovery, and  $N_0$  is the number of contacts at zero deformation. At equilibrium, when the two rates are equal  $(R_b = R_r)$ , which gives  $N/N_0$  as

$$N/N_0 = 1/[1 + (\gamma_0/\gamma_c)^{2m}], \qquad (11)$$

where  $\gamma_c$  is the critical strain amplitude that is given by

I strain amplitude that is given by  

$$\gamma_c = (k_r/k_b)^{1/2m}$$
. (12)

From the above derivations, one can easily see that combin-  $\frac{\omega}{2}$ ing Eq. (11) for the existing contact number N with Eq. (8) for  $\frac{1}{2}$ the storage modulus G' gives the sigmoidal Eq. (1), and if the loss modulus G'' is taken to be proportional to the breakdown rate of the network, one gets Eq. (2). This theory, known as the Kraus model, is still widely used today [36–39]. Although it was originally developed for describing the nonlinear dynamic properties of particle-filled rubbers, it was later found to be also suitable for particle-filled solutions [9,18,20,39]. A reviewed article on this subject and related theoretical background is given by Heinrich and Klüppel [39].

However, the situation described above so far refers, strictly speaking, to absolute zero temperature. At any finite temperature, the particles in the particle network of the gel will experience thermal vibrations. As the temperature increases, the thermal motion of particles will become intense, which will cause the loss of particle contacts. At high temperatures, if enough contacts are lost, the particle network will be broken. Therefore, the colloid gel must "melt" at a certain high temperature  $T_{\mu}$ , after which the material will flow like a liquid. Note that this type of melting is not the melting of crystals, but the softening and fluidization of glasslike materials.

Now, let us take Eq. (12) as the starting point and analyze its variation with temperature. We first consider the possible form of the rate constant for recovery,  $k_r$ . The reaggregation of particles can be generally classified into two broad limits [40]. When the particles bond irreversibly to each other upon contact in the liquid medium, the resulting network is more

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open, with a small fractal dimension of 1.8. This is diffusionlimited cluster aggregation (or DLCA). The recovery rate constant  $k_r$  in the DLCA may be approximately modeled by a Stokes–Einstein formula,

$$k_r \cong A_r T, \tag{13}$$

where  $A_r$  is constant. A rough estimate of the constant can be made from the equation  $k_r \sim D/a^2 = k_B T/6\pi \eta a^3$ , where  $k_B$  is the Boltzmann constant.

In contrast, if multiple collisions are required owing to a repulsive barrier between particles [40], the network is more compact, with a fractal dimension of about 2.0. This is reaction-limited cluster aggregation (or RLCA). The recovery rate constant  $k_r$  in the RLCA process may be approximated as an Arrhenius formula,

$$k_r \cong A_r T \exp\left(-\frac{E_r}{RT}\right),$$
 (14)

where  $E_r$  is the energy barrier per mole for reaction-limited aggregation and R is the molar gas constant.

Next, we consider the rate constant for breakage  $k_b$ . Because of the attraction between particles, a transient network of particles will be formed; this arrested state is analogous to glass formation [1–20]. Since the relaxation time of the arrested state is inversely proportional to  $k_b$ , we may approximate the temperature dependence of the breakage rate constant  $k_b$  using the Vogel–Fulcher formula,

$$k_b = A_b \exp\left[-\frac{E_b}{R(T - T_\mu)}\right],\tag{15}$$

where  $A_b$  is constant.  $T_{\mu}$  is the characteristic melting temperature of the particulate network.  $E_b$  is associated with the activated energy per mole for the particle contact breakage.

The magnitude of  $T_{\mu}$  can be formally related to the attractive potential  $V_{attr}$ , volume fraction  $\phi$ , and particle size *a*. In the related literature, Chiew and Glandt [41] once used a dynamic percolation theory to study the gel formation of attractive spherical colloids in solutions over a wide range of concentration,  $\phi$ . They found that the relationship between the strength of attraction ( $V_{attr}/kT$ ) and volume fraction  $\phi$  at the gelation point  $T_{gel}$  can be represented by the following relation:

$$\frac{a}{6\delta_0} \exp\left(-\frac{V_{attr}}{kT_{gel}}\right) = \frac{19\phi^2 - 2\phi + 1}{12(1-\phi)^2}.$$
 (16)

Bergenholtz and Fuchs [42–44] used a dynamic selfconsistent mode-coupling theory (MCT) to treat the physical gelation of attractive colloidal particles in solutions and showed that for short-range attraction, when  $\delta_0 << a$  and  $\phi$  is low, the linkage between the attraction strength ( $V_{attr}/kT$ ) and volume fraction  $\phi$  at the gelation point  $T_{gel}$  is asymptotically given by the following expression:

$$\frac{6\delta_0}{\pi^2 a} \phi \left[ \exp\left(\frac{V_{attr}}{kT_{gel}}\right) - 1 \right]^2 = 1.42.$$
 (17)

Despite the different methods used, the outcomes of these mentioned studies are similar, that is, there is a formal relationship linking  $T_{gel}$ ,  $\phi$ , a, and  $V_{attr}$ . The characteristic melting temperature  $T_{\mu}$  for colloidal gels of attractive particles should follow the same relationship as  $T_{\mu} \cong T_{gel}$ , when the heating or cooling rate is relatively small and when the time-temperature effect is negligible. Therefore,  $T_{\mu}$  is a well-defined quantity for colloidal gels of attractive particles, which is very similar to the glass transition temperature  $T_g$  of glass-forming materials. It should be noted that a finite and nonzero  $T_{\mu}$ , arising from the attraction  $V_{attr}$  and the concentration  $\phi$  of particles, is essential for the present theory. The theoretical model described herein does not apply to  $T_{\mu} = 0$  or  $\infty$ .

Substituting Eqs. (13) and (15) into Eq. (12) yields the following result:

$$\Gamma_1 = \ln\left(\gamma_c\right)^{2m} - \ln\left(\frac{A_r T_\mu}{A_b}\right) = \ln\left(\frac{T}{T_\mu}\right) + \frac{E_b/RT_\mu}{T/T_\mu - 1},\quad(18)$$

while substituting Eqs. (14) and (15) into Eq. (12) produces a slightly different result,

$$\Gamma_{2} = \ln \left(\gamma_{c}\right)^{2m} - \ln \left(\frac{A_{r}T_{\mu}}{A_{b}}\right)$$
$$= \ln \left(\frac{T}{T_{\mu}}\right) + \frac{E_{r}}{RT_{\mu}} \cdot \left[-\frac{1}{T/T_{\mu}} + \frac{E_{b}/E_{r}}{T/T_{\mu} - 1}\right], \qquad (19)$$

where  $\Gamma_1$  and  $\Gamma_2$  are linear functions of  $\ln(\gamma_c)$ . As can be seen, when  $E_r = 0$ , Eq. (19) is simplified to formula (18).

Since  $\Gamma_1$  and  $\Gamma_2$  are simple functions of  $\ln(\gamma_c)$ , any characteristic behavior of  $ln(\gamma_c)$  in the solid-to-liquid boundary will be fully reflected in the behavior of  $\Gamma_1$  and  $\Gamma_2$  functions. Considering that the particle-contact bond is easily broken by shear and thermally melted at  $T_{\mu}$ , it would be reasonable to assume that  $E_b/RT_\mu \ll 1$ . A calculation of  $T/T_\mu$  versus  $\Gamma_1$  and  $\Gamma_2$  using Eqs. (18) and (19) with  $E_b/RT_u = 0.02$  is plotted in Fig. 15. The calculation, without losing generality, is based entirely on the use of dimensionless parameters and variables. As can be seen, this calculation has successfully predicted the upper half of the Z-shaped dejamming phase diagram. The calculated result agrees qualitatively well with that observed experimentally. Our experimental observation shows that the inflection point in the upper half of the Z-shaped curve is slightly close to the melting point  $T_{\mu}$ . Nevertheless, this agreement is remarkable considering the simplifications made in the above theoretical analysis. We also calculated the effect of  $E_b/RT_\mu$  ranging from 0.02 to 0.2 on the shape of the diagram, and the results were basically the same, only moved a little to the left in the chart.

So far, we have not considered the influence of viscosity  $\eta$  of the dispersion medium on particle movement. In reality, the viscosity will be a strong function of temperature and



**FIG. 15.** Theoretical calculation of the relationship between  $T/T_{\mu}$  and  $\Gamma_1$  or between  $T/T_{\mu}$  and  $\Gamma_2$ . The calculated results are based on Eqs. (18) and (19) using  $E_b/RT_{\mu} = 0.02$ ,  $E_r = 20E_b$ ,  $5E_b$ , and 0, respectively.

increases with decreasing temperature. The increased viscosity would have an influence on both the recovery rate and the breakage rate. On the recovery rate constant  $k_r$ , this viscosity effect is mainly reflected in the pre-exponential factor, which is minor. However, on the breakage rate constant  $k_b$ , this viscosity effect appears as in exponential form, which is a major factor and should be taken into account. According to the theory of Somogyi *et al.* [45], an increase in viscosity can significantly lower the value of the dissociation (or breakage) rate constant because the translational diffusion of particles is hindered by viscosity and the particles will recombine immediately after dissociation. The value of the observable dissociation rate constant  $k'_b$  between particles is given by the following expression [45,46]:

$$k'_b \cong k_b \exp\left(-\kappa_s \eta^2 / RT\right),\tag{20}$$

where  $\kappa_s = 18N_{av}(\pi a\delta_0)^2/M$  is a constant that depends on the equilibrium contact distance  $\delta_0$ , the particle radius *a*, the particle mass *M*, and Avogadro's constant  $N_{av}$ . Although the original theory was developed to explain the effect of viscosity on the decomposition of enzyme-ligand complexes, the revealed mechanistic picture and conclusion are applicable to particle dissociation in colloidal suspensions. Combining Eq. (20) with Eq. (15), then substituting Eq. (14) and the obtained  $k'_b$  into Eq. (12) to replace  $k_b$  results in the following relationship:

$$\Gamma_{3} = \ln (\gamma_{c})^{2m} - \ln \left(\frac{A_{r}T_{\mu}}{A_{b}}\right)$$
$$= \ln \left(\frac{T}{T_{\mu}}\right) + \frac{E_{r}}{RT_{\mu}} \cdot \left[-\frac{1}{T/T_{\mu}} + \frac{E_{b}/E_{r}}{T/T_{\mu} - 1}\right]$$
$$+ \frac{\kappa_{s}\eta^{2}/RT_{\mu}}{T/T_{u}}.$$
(21)

When  $\kappa_s = 0$ , Eq. (21) would be simplified to formula (19).

Figure 16 shows the calculation result of  $T/T_{\mu}$  versus  $\Gamma_3$ using Eq. (21). Remarkably, the Z-shape of the dejamming phase diagram can be predicted by a simple argument between the rate of breakage and the rate of recovery of the particle contacts. The deflection point in the lower half of the Z-shaped curve is a function of parameter  $\kappa_s$  and the magnitude of which is related to the viscosity-retarded effect as predicted by Somogyi et al. [45]. The calculated results agree qualitatively well with those observed experimentally. There are many details that need to be thought out, such as the temperature dependence of the pre-exponential factors and the active energy if it is driven partially by entropy. Nevertheless, these simplified calculations reveal the main fundamental principles involved in the emergence of this Z-shaped dejamming phase diagram. As shown in Fig. 16, a glasslike melting kinetics of the contact bonds between particles at high temperatures plus a viscosity-retarded dissociation of the contact bonds between particles at low temperatures can qualitatively reproduce this nonmonotonic phenomenon.

Returning to the carbon black-dispersant-lubricant ternary system, Refs. [23-26] claim that van der Waals interactions cannot explain this inverse-temperature dependence and have instead derived the temperature dependence through changes in polymeric conformations of the stabilizer. However, what we have observed here is quite the opposite. An important piece of evidence is that the same inverse-temperature dependence is present in colloidal suspensions containing hairless particles, such as fumed silica, as shown in Figs. 11 and 12. This observation clearly calls into question the interpretation and conclusions presented in Refs. [23-26]. The underlying § picture for this anomaly, according to our judgement, is the  $\frac{1}{2}$ Z-shaped dejamming phase diagram for attractive particles. Particularly, the upper half of the dejamming phase diagram can naturally give the inverse-temperature dependence of a colloidal material. By applying the Kraus model derived from van der Waals interactions to the breakage and



**FIG. 16.** Theoretical calculation of the relationship between  $T/T_{\mu}$  and  $\Gamma_3$ . Results with indicated  $\kappa_s/R$  values are calculated according to Eq. (21) using  $E_b/RT_{\mu} = 0.02$ ,  $E_r = 20E_b$ , and  $T_{\mu} = 500$  K. The viscosity of the solvent  $\eta = 10^{-8}T \exp[1639/(T-119)]$  Pa s is taken from Ref. [47] for squalane.

restoration of filler networks, we found that this anomaly can be theoretically predicted. Therefore, within the framework of van der Waals interactions, this inverse-temperature dependence of colloidal gels with attractive particles can be theoretically explained.

We used five particles in this study; strictly speaking, van der Waals potentials are only suitable for particles that are hairless or polymer stabilizer-free, such as fumed silica or polystyrene nanobeads. For hairy nanoparticles or PIBSI-stabilized carbon black, there should be an additional interaction between the particles in addition to the van der Waals potentials due to the presence of polymer hairs on the surface of particles. This additional interaction depends on spatial conformations of the hair in solution and may change with temperature [48-51]. As a result, the particle size (and therefore volume fraction), attraction, and possible osmotic effects may be temperature-dependent and may play a role here, though they only occur in certain special cases involving hairy nanoparticles or polymer-stabilized carbon black. At present, it is not clear how this additional interaction affects the nonmonotonic Z-shaped phase boundary. We hope that future theoretical development will be able to establish a sound connection between the interaction potentials and the structural properties of the filler in colloidal systems, which would completely resolve the problem.

Nevertheless, the discovery of the Z-shaped dejamming phase diagram for attractive particles is important because it implies this nonmonotonic phenomenon can occur in many colloidal systems. The question is, why has this Z-shaped diagram never been reported before? One reason may be that when the particle diameter is large, it will make thermalization difficult to debond the particles and melt the particle network. In our research, when the particle size increases from 9 to 39 nm, the melting point of colloidal gels may rise by more than a hundred degrees. Therefore, for colloidal gels made of even larger attractive particles, this melting temperature  $T_{\mu}$  may rise to several hundred to thousand degrees Celsius. Hence, conventional experimental setups will not be able to reveal this nonmonotonic phase behavior of colloidal gels made from particles of larger size and mass. In addition, many colloidal gels reported in the literature [1-15] are made from large attractive particles in aqueous solutions. A study of the influence of temperature on the phase behavior of aqueous colloidal suspensions is limited by the freezing point and vaporization point of water.

It should be pointed out that the present theory does not apply to colloidal glasses formed from hard-sphere particles. The reason is that, for jammed hard spheres,  $T_u$  can be infinite in the glass state. Therefore, the concepts and equations mentioned above have the limitation that they are only suitable for attractive particle gels, where the particle concentration  $\phi$  is not too high. The same is true when it comes to experimentation. In addition, since the formation of colloidal gels is analogous to glass formation, the shear rate and the heating (or cooling) rate should have influences on the phase behavior of colloidal gels. In our study, we did observe that different heating and cooling rates can move the phase boundary up and down, while changing the test frequency can shift the dejamming phase diagram from left to right. However, we found that the basic shape of this nonmonotonic dejamming phase diagram remained unchanged in all cases. In this report, we would like to focus on the basic shape and the potential cause of this nonmonotonic feature in the Z-shaped phase diagram because its emergence has revolutionized our perception of traditional monotonic jamming phase diagrams. As for the time-temperature effect, we will not discuss it much in this article because, first, it is expected for colloidal gels to show glass-melting kinetics, and second, the time-temperature effect is less important than the Z-shaped dejamming phase boundary. We will cover the time-temperature effect in a separate paper later. We hope that our present work will raise awareness and promote shared interests in the rheology community in furthering the understanding of the basic physics of particle-filled materials.

### **IV. CONCLUSIONS**

In this contribution, we report that the dejamming phase diagram spanning the temperature-crossover strain amplitude plane shows a surprising nonmonotonic Z-shaped dejamming phase boundary. This nonmonotonic phenomenon exists in a number of colloidal gel systems that differ vastly in their dispersion medium, chemical composition, particle structure, average particle size, particle size distribution, and interparticle interactions. In some cases, the critical stress in response to temperature changes also follows a similar Z-shaped trajectory. Interestingly, this unusual nonmonotonicity can arise from a competition between contact breakage rates of parti-g cles at low and high temperatures, with the breakage being  $\frac{3}{2}$ retarded at low temperatures because of high medium viscos- $\vec{s}_{2}$  ity while this rate accelerates at high temperatures, especially near the melting temperature. By combining the glassy E melting kinetics of the filler network at high temperatures <sup>™</sup> with the viscosity-retarded dissociation between particles at low temperatures, we show that it is theoretically possible to predict this nonmonotonic phenomenon.

# **AUTHOR DECLARATIONS**

#### **Conflict of Interest**

The authors have no conflicts to disclose.

#### REFERENCES

- Nair, S. K., S. Basu, B. Sen, M.-H. Lin, A. N. Kumar, Y. Yuan, P. J. Cullen, and D. Sarkar, "Colloidal gels with tunable mechanomorphology regulate endothelial morphogenesis," Sci. Rep. 9(1), 1072 (2019).
- [2] Lu, P. J., and D. A. Weitz, "Colloidal particles: Crystals, glasses, and gels," Annu. Rev. Condens. Matter Phys. 4(1), 217–233 (2013).
- [3] Saunders, B. R., and B. Vincent, "Microgel particles as model colloids: Theory, properties and applications," Adv. Colloid Interface Sci. 80(1), 1–25 (1999).
- [4] Lu, P. J., E. Zaccarelli, F. Ciulla, A. B. Schofield, F. Sciortino, and D. A. Weitz, "Gelation of particles with short-range attraction," Nature 453(7194), 499–503 (2008).
- [5] Joshi, Y. M., "Dynamics of colloidal glasses and gels," Annu. Rev. Chem. Biomol. Eng. 5(1), 181–202 (2014).
- [6] Sutherland, D. N., "A theoretical model of floc structure," J. Colloid Interface Sci. 25(3), 373–380 (1967).

- [7] Lazzari, S., L. Nicoud, B. Jaquet, M. Lattuada, and M. Morbidelli, "Fractal-like structures in colloid science," Adv. Colloid Interface Sci. 235, 1–13 (2016).
- [8] Lu, P. J., J. C. Conrad, H. M. Wyss, A. B. Schofield, and D. A. Weitz, "Fluids of clusters in attractive colloids," Phys. Rev. Lett. 96(2), 028306 (2006).
- [9] Xiong, W., and X. Wang, "Nonlinear responses of carbon black-filled polymer solutions to forced oscillatory shear," J. Non-Newtonian Fluid Mech. 282, 104319 (2020).
- [10] Wu, K., J. Zou, and X. Wang, "Impacts of filler loading and particle size on the transition to linear-nonlinear dichotomy in the rheological responses of particle-filled polymer solutions," J. Rheol. 66(3), 605–618 (2022).
- [11] Xiong, W., and X. Wang, "Linear-nonlinear dichotomy of rheological responses in particle-filled polymer melts," J. Rheol. 62(1), 171–181 (2018).
- [12] Liu, A. J., and S. R. Nagel, "Jamming is not just cool any more," Nature 396(6706), 21–22 (1998).
- [13] Trappe, V., V. Prasad, L. Cipelletti, P. Segre, and D. A. Weitz, "Jamming phase diagram for attractive particles," Nature 411(6839), 772–775 (2001).
- [14] Ciamarra, M. P., M. Nicodemi, and A. Coniglio, "Recent results on the jamming phase diagram," Soft Matter 6(13), 2871–2874 (2010).
- [15] O'Hern, C. S., L. E. Silbert, A. J. Liu, and S. R. Nagel, "Jamming at zero temperature and zero applied stress: The epitome of disorder," *Phys. Rev. E* 68(1), 011306 (2003).
- [16] Robertson, C. G., and X. Wang, "Isoenergetic jamming transition in particle-filled systems," Phys. Rev. Lett. 95(7), 075703 (2005).
- [17] Wang, X., and C. G. Robertson, "Strain-induced nonlinearity of filled rubbers," Phys. Rev. E 72(3), 031406 (2005).
- [18] Roland, C. M., Chap. 5, in Viscoelastic Behavior of Rubbery Materials (Oxford University, New York, 2011).
- [19] Wang, X., J. E. Hall, S. Warren, J. Krom, J. M. Magistrelli, M. Rackaitis, and G. G. A. Bohm, "Synthesis, characterization, and application of novel polymeric nanoparticles," Macromolecules 40(3), 499–508 (2007).
- [20] Wang, X., V. J. Foltz, M. Rackaitis, and G. G. A. Böhm, "Dispersing hairy nanoparticles in polymer melts," Polymer 49(26), 5683–5691 (2008).
- [21] Hergenrother, W. L., W. C. Kiridena, J. H. Pawlow, J. D. Ulmer, C. G. Robertson, M. C. David, and J. D. Quinn, "Nanoparticle fillers and methods of mixing into elastomers," US Patent 10,407,522 (2019).
- [22] Rodewald, S., S. K. Henning, and B. E. Burkhart, "Process for synthesizing functionalized styrene monomer," US patent 6,670,471 (2003).
- [23] Won, Y.-Y., S. P. Meeker, V. Trappe, D. A. Weitz, N. Z. Diggs, and J. I. Emert, "Effect of temperature on carbon-black agglomeration in hydrocarbon liquid with adsorbed dispersant," Langmuir 21(3), 924–932 (2005).
- [24] Aoki, Y., and H. Watanabe, "Rheology of carbon black suspensions.: III. Sol-gel transition system," Rheol. Acta 43(4), 390–395 (2004).
- [25] Aoki, Y., "Rheological characterization of carbon black/varnish suspensions," Colloids Surf. A Physicochem. Eng. Asp. 308(1–3), 79–86 (2007).
- [26] Yang, Y., E. A. Grulke, Z. G. Zhang, and G. Wu, "Temperature effects on the rheological properties of carbon nanotube-in-oil dispersions," Colloids Surf. A Physicochem. Eng. Asp. 298(3), 216–224 (2007).
- [27] Fuchs, M., and M. E. Cates, "Theory of nonlinear rheology and yielding of dense colloidal suspensions," Phys. Rev. Lett. 89(24), 248304 (2002).
- [28] Tanaka, T., "Gels," Sci. Am. 244(1), 124–138 (1981).
- [29] Rasool, N., T. Yasin, J. Y. Heng, and Z. Akhter, "Synthesis and characterization of novel pH-, ionic strength and temperature-sensitive hydrogel for insulin delivery," Polymer 51(8), 1687–1693 (2010).

- [30] Park, T. G., "Temperature modulated protein release from pH/ temperature-sensitive hydrogels," Biomaterials 20(6), 517–521 (1999).
- [31] Kabanov, A. V. and S. V. Vinogradov, "Nanogel networks including polyion polymer fragments and biological agent compositions thereof," U.S. Patent 6,696,089 (2004).
- [32] Chauveteau, G., R. Tabary, M. Renard, and A. Omari, "Method for preparing microgels of controlled size," US Patent 6,579,909 (2003).
- [33] Park, D., W. Wu, and Y. Wang, "A functionalizable reverse thermal gel based on a polyurethane/PEG block copolymer," Biomaterials 32(3), 777–786 (2011).
- [34] Kraus, G., "Mechanical losses in carbon-black-filled rubbers," J. Appl. Polym. Sci.: Appl. Polym. Symp. 39, 75–92 (1984).
- [35] Hamaker, H. C., "The London-van der waals attraction between spherical particles," Physica 4(10), 1058–1072 (1937).
- [36] Witten, T., M. Rubinstein, and R. Colby, "Reinforcement of rubber by fractal aggregates," J. Phys. II 3(3), 367–383 (1993).
- [37] Huber, G., and T. A. Vilgis, "On the mechanism of hydrodynamic reinforcement in elastic composites," Macromolecules 35(24), 9204–9210 (2002).
- [38] Huber, G., T. A. Vilgis, and G. Heinrich, "Universal properties in the dynamical deformation of filled rubbers," J. Phys.: Condens. Matter 8(29), L409–L412 (1996).
- [39] Heinrich, G., and M. Klüppel, "Recent advances in the theory of filler networking in elastomers," Adv. Polym. Sci. 160, 1–44 (2002).
- [40] Lin, M. Y., H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, and P. Meakin, "Universality in colloid aggregation," Nature 339, 360–362 (1989).
- [41] Chiew, Y. C., and E. D. Glandt, "Percolation behaviour of permeable and of adhesive spheres," J. Phys. A: Math. Gen. 16, 2599–2608 (1983).
- [42] Bergenholtz, J., and M. Fuchs, "Gel transitions in colloidal suspensions," J. Phys.: Condens. Matter 11, 10171–10182 (1999).
- [43] Bergenholtz, J., and M. Fuchs, "Nonergodicity transitions in colloidal suspensions with attractive interactions," Phys. Rev. E 59(5), 45706–5715 (1999).
- [44] Ramakrishnan, S., V. Gopalakrishnan, and C. F. Zukoski, "Clustering and mechanics in dense depletion and thermal gels," Langmuir 21, 9917–9925 (2005).
- [45] Somogyi, B., F. E. Karasz, L. Trón, and P. R. Couchma, "The effect of viscosity on the apparent decomposition rate on enzyme-ligand complexes," J. Theor. Biol. 74(2), 209–216 (1978).
- [46] Welch, G. R., B. Somogyi, J. Matkó, and S. Papp, "Effect of viscosity on enzyme-ligand dissociation II.: Role of the microenvironment," J. Theor. Biol. 100(2), 211–238 (1983).
- [47] Deegan, R. D., R. L. Leheny, N. Menon, S. R. Nagel, and D. C. Venerus, "Dynamic shear modulus of tricresyl phosphate and squalane," J. Phys. Chem. B 103(20), 4066–4070 (1999).
- [48] Vlassopoulos, D., "Colloidal star polymers: Models for studying dynamically arrested states in soft matter," J. Polym. Sci. Part B: Polym. Phys. 42(16), 2931–2941 (2004).
- [49] Kaiser, A., and A. M. Schmidt, "Phase behavior of polystyrene-brush-coated nanoparticles in cyclohexane," J. Phys. Chem. B 112(7), 1894–1898 (2008).
- [50] Truzzolillo, D., D. Vlassopoulos, and M. Gauthier, "Thermal melting in depletion gels of hairy nanoparticles," Soft Matter 9(38), 9088–9093 (2013).
- [51] Mongcopa, K. I. S., R. Poling-Skutvik, R. Ashkar, P. Butler, and R. Krishnamoorti, "Conformational change and suppression of the Θ-temperature for solutions of polymer-grafted nanoparticles," Soft Matter 14(29), 6102–6108 (2018).