Reversible Thermal Gelation in Soft Spheres

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Upon heating, concentrated solutions of star polymers and block copolymer micelles in a good solvent, representing soft spheres, undergo a reversible gelation. This phenomenon is attributed to the formation of clusters causing a partial dynamic arrest of the swollen interpenetrating spheres at high temperatures. A phase diagram analogous to that of sterically stabilized colloids is proposed.

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A wide range of soft materials such as colloids, emulsions, and foams undergo a jamming transition at low temperatures and/or high volume fractions, which is characterized by a solidlike rheological response [1,2]. The jammed systems are thought to belong to the fragile state of matter and often exhibit a signature of a glass. These features have been assembled recently in a proposed phase diagram for jamming involving temperature, density, and stress [1]. On the other hand, for synthetic polymers, a main representative of soft matter, cooling leads to vitrification or reversible gelation; the latter is due to changes in microstructure, in the absence of other interactions such as electrostatic, enthalpic, or hydrogen bonding [3]. A combination of these effects may drive complex systems such as block copolymer micelles to different gel phases or crystals [4]. The above classification of liquid-solid transitions may not be complete, however, in view of the emergence of a novel class of materials encompassing both polymeric and colloidal characteristics, tunable at the chemistry level, and known as ultrasoft polymeric spheres [5]. Hence, unexpected effects of temperature on the behavior of dense suspensions of these systems in a fluid could be anticipated.

In this Letter we demonstrate a counterintuitive reversible gelation transition observed in star polymers and giant micelles upon heating. These materials are suspended in good solvents and characterized by excluded volume interactions only. We describe the phenomenon based on the findings from different and complementary experimental techniques, identify its origin, and propose an alternative jamming phase diagram.

Using chlorosilane chemistry and anionic polymerization, star polybutadienes of nominal functionality \( f = 128 \) and arm molecular weights 28 000, 56 000, and 80 000 g/mol, coded as 12 828, 12 856, and 12 880, respectively, have been synthesized recently [5]. This new class of chemically homogeneous materials exhibits liquidlike ordering above the overlap concentration [6] and an ultrasoft interaction potential [7]; these are also reflected in their rich dynamic response [8]. Further, there is indirect evidence of a crystallization transition in a narrow concentration range [9]. When dissolved in decane, a good solvent for polybutadiene, the three stars have a hydrodynamic radii \( R_h = 26, 38, \) and 48 nm, respectively, at 20 °C. Giant block copolymer micelles were prepared from a high molecular weight poly(styrene-b-isoprene) of about \( 2 \times 10^6 \) g/mol dispersed in decane, a selective good solvent for polyisoprene. They were found to exhibit the features of multiarm stars with \( f = 1500 \) and \( R_h = 480 \) nm at 20 °C [10]. The structure and dynamics of concentrated solutions of these spherical objects (in the range 10–15 times the overlap concentration \( c^* \)) have been explored at different temperatures using shear rheology, small angle neutron scattering (SANS), dynamic light scattering (DLS), and pulsed field gradient NMR (PFG-NMR).

Figure 1(a) depicts typical dynamic frequency sweeps for a 4.6 wt % solution of 12 880 in the temperature range...
from 20 to 35°C. It is clear that as the temperature increases the material behavior changes drastically from viscous liquid \((G' \sim \omega^2, G'' \sim \omega, G'' > G')\) to a weak elastic solid \((G' > G''\) and nearly virtually independent of frequency in the experimental window), accompanied by a sudden increase in the values of the moduli. The reproducibility of these results at different times after cooling to room temperature confirms the reversibility of the process and is consistent with visual observation of the transition [11]. The same phenomenon is manifested in the dynamic jumps of the viscoelastic moduli during a temperature ramp experiment [a typical example is depicted in Fig. 1(b) for a 5 wt% solution of 12 856 from 30 to 65°C]. The combination of frequency and temperature sweeps allows the determination of the liquid-solid transition temperature, which we denote as \(T_{gel}\), since the materials behave as nearly critical gels at the transition, exhibiting \(\tan\delta \sim \omega^0\) [12(a)]. For all stars it is found that as the concentration increases \(T_{gel}\) decreases (lower inset of Fig. 2). Apart from the low values of the shear moduli, the weakness of the solid is manifested in steady shear experiments showing a continuous thinning behavior [12(b)].

This counterintuitive reversible transition is characterized by a slow kinetics; typically, about 10 h are needed to recover the steady state liquid behavior upon cooling from the “solid” regime, or 2 h to create an “equilibrium” solid on heating. This situation is reminiscent of phase separation kinetics [13]; however, this possibility is excluded for these solutions as SANS and DLS experiments did not show any increase of the scattered intensity across \(T_{gel}\) [12(b)] (see upper inset of Fig. 2 and inset of Fig. 3 below). These findings exclude the possibility of chemical cross-linking or solidification due to solvent evaporation.

SANS measurements over a wide temperature range across the transition (Fig. 2) indicate that the liquidlike order remains unchanged. More interestingly, the peak position \(q_{\text{max}}\) of maximum scattering intensity \((q\) being the scattering wave vector\), and thereby the core distance, remains insensitive to temperature variations, but a slightly stronger arm interpenetration \([6(a),8]\) is suggested by the small intensity decrease upon heating (upper inset of Fig. 2), which is attributed to the form factor decay of the swollen stars. The latter is not accompanied by appreciable arm stretching as evidenced by the unchanged \(q\) dependence of the scattered intensity at high \(q\)’s (with a slope of about \(-4/3\) at all temperatures) [14]. Note that the intensity \(I(q)\) data with virtually constant width exclude the possibility of crystallization.

In these systems excluded volume effects represent the only kind of interaction among the polymeric spheres and the solvent is good with improving quality as temperature increases. This is derived from the increasingly positive second virial coefficient and increasing star size \(R_h\) (swelling of about 18% for a temperature increment of

![FIG. 2. Scattering intensity \(I\) from SANS measurements of 12 856/d-decane 6 wt% in a wide temperature range \((\bigcirc: 15°C; \bigtriangledown: 20°C; \bigtriangledown: 30°C \sim T_{gel}; \bigtriangleup: 40°C; \bigdiamond: 50°C; \blacklozenge: 60°C; \blacktriangle: 70°C)\). Upper inset: Temperature dependence of scattered peak intensity \(I_{\text{peak}}\) (open symbols) and inverse peak location \(q_{\text{peak}}\) (closed symbols) for three solutions in d-decane: 12 856 wt% \((\bigcirc), 12 828 8.3\) wt% \((\bigtriangleup)\), and 12 828 9.4 wt% \((\bigtriangledown)\). Lower inset: \(T_{gel}\) for various star polymer solutions (12 828: \(\bigcirc\); 12 856: \(\bigtriangleup\); 12 880: \(\bigtriangledown\)) as a function of total polymer concentration.](image1)

![FIG. 3. Intermediate scattering function \(C(q, t)\) of 12 828/d-decane 9.5 wt% solution \((T_{gel} \approx 25°C)\) at \(q = 0.033\) nm\(^{-1}\) and temperatures 15°C \((\bigcirc\), liquid\) and 50°C \((\bigtriangleup\), solid\). Upper inset: Corresponding distribution of relaxation times from inverse Laplace transformation of \(C(q, t)\), \(L(t)\), times the normalized (to the solvent) total light scattering intensity \(I^*\) (allowing one to compare intensities of modes directly), against the relaxation time reduced with the solvent viscosity, \(\tau/\eta\). Lower inset: Normalized incoherent structure factor \(S_{inc}(q, t)\) as a function of \(q^* t\) for 12 828/d-decane 8.3 wt% \((T_{gel} \approx 45°C)\) at different measurement times \((\bigtriangleup: 23 ms; \bigcirc: 53 ms; \bigdiamond: 103 ms; \blacklozenge: 203 ms; \blacktriangle: 503 ms)\). Solid symbols denote low temperature (25°C) and open symbols high temperature (50°C). Solid lines indicate Fickian diffusion, whereas the dotted line shows the frozen motion of the high-temperature clusters, within the experimental time (see text).](image2)
40 °C), measured by DLS in dilute solution [12(b)]. In the nondilute regime, the measured intermediate scattering function \( C(q,t) \) (depicted in Fig. 3 for a 5 wt % 12856 solution at \( q = 0.033 \text{ nm}^{-1} \) clearly reveals the expected \([8]\) two-step relaxation behavior at low temperatures in the liquid regime, with the fast mode due to total concentration fluctuations (cooperative diffusion) and the slow mode due to self-diffusion; the latter can be detected by DLS because of the small functionality polydispersity of the stars. The characteristics of the contributing dynamic processes (relaxation rate \( \Gamma \) and amplitude) are best extracted by the Laplace inversion of \( C(q,t) \). The diffusive nature \((\Gamma = Dq^2 < 1)\) of the two processes of \( C(q,t) \) at 15 °C (Fig. 3) is confirmed by measurements at various \( q \)’s. However, at high temperatures in the solid regime an additional slow “cluster” mode appears, which is reminiscent of the long-range density fluctuations in supercooled liquids \([15]\); in contrast to that case, here the clusters melt upon cooling, with a kinetics analogous to that explored in the rheological studies \([12(b)]\). The amplitude of \( C(q,t) \), scaled by the total scattering intensity, in the upper inset of Fig. 3 (displaying for simplicity only the first two modes), suggests that the cooperative mode (which scales with the solvent viscosity, \( \eta \)) loses intensity (a drop of 30%) upon heating from 15 to 50 °C. Thus, the combination of SANS and DLS demonstrates the absence of crystallization and an enhanced arm interpenetration upon heating.

On the other hand, the main result with respect to the self-diffusion (Fig. 3) is that, whereas it slows down on going through the transition, it does not follow the dramatic increase of the macroscopic viscosity (\( G'' \) in Fig. 1). This implies the presence of dynamic heterogeneities in the system as it is heated above \( T_{gel} \). To address this point more rigorously we carried out the PFG-NMR measurements on a 12828 star solution in perdeuterated decane. As indicated in the lower inset of Fig. 3, which depicts the normalized incoherent structure factor \( S_{inc}(q,t) \) as a function of \( q^2 t \) for different measurement times, at low temperatures the classical Fickian diffusion is recovered, with mean squared displacement \( \langle \Delta r^2 \rangle \sim t \); on the other hand, at high temperatures, the short time Fickian diffusion (slowed down upon heating) is accompanied by an ultraslow mode (frozen within the experimental window). The fact that the latter process is independent of \( q \) points to the presence of a distinct population (rather than in-cage diffusion \([16]\)), which accounts for up to 50% of the star population, based on the normalized \( S_{inc}(q,t) \) value; this population represents clusters which diffuse very slowly (beyond the experimental time) in the system.

The above unambiguous evidence suggests the following mechanism of the detected reversible thermal gelation: as the temperature increases, the solvent quality improves and the peripheral blobs of the interacting liquid-ordered soft spheres swell; consequently, due to overall incompressibility of the system, in order to accommodate themselves in the same volume, the spheres increase their arms’ overlap, but not to a large extent because of the strong excluded volume repulsions. This eventually leads to a dynamic frustration of the systems due to the formation of clusters of a few “trapped” spheres, in equilibrium with “free” spheres. This is manifested by the formation of a macroscopic solid, retaining its soft order, but with the signature of a nearly critical gel as judged from rheology and PFG-NMR, in which some restricted internal mobility is retained, as evidenced from DLS and PFG-NMR \([12]\). The cartoon in the inset of Fig. 4 attempts to catch a snapshot of this situation with the hypothetical bold periphery circumscribing an area of dynamic arrest (cluster). In view of Fig. 3, a low degree of clustering apparently suffices for the macroscopic immobilization of the system \([17]\).

This thermal gelation phenomenon, which has not been reported before \([18]\) and does not apply to stars of low functionality, leads to an alternative jamming phase diagram, where solids are formed upon heating. Figure 4 shows such a diagram for the star polymers investigated here; the excluded volume parameter is related to the temperature and taken as \( v = 1 - \alpha/T \) \([19]\) where the parameter \( \alpha \) is temperature independent, relates to the theta conditions for the specific system, and is given here an arbitrary value of 100 K. The effective volume fraction \( \phi_{eff} \) is essentially the volume fraction of the spherical stars (or micelle) by considering their overall dimensions as if they were hard spheres; it is taken from the weight concentration using the density of the systems, which involves their size \( R_h \). The fact that \( \phi_{eff} \) exceeds unity is due to arm interpenetration. The virtual collapse of the data (shown in the lower inset of Fig. 2) for the three different stars and the micelle is a striking result suggesting a universal behavior for this class of soft materials, which are characterized by significant softness (the size ratio of “grafted” layer to
central core is up to about 100 times larger than in “conventional” micelles or steric colloids used so far [20]). In addition, the apparent resemblance to the generalized phase diagram of small micelles interacting through screened Coulomb repulsions, which, however, exhibit crystalline order in the solid phase [20], demonstrates how the volume fraction of these jammed systems can increase with temperature apart from density, offering a new route to reversible gelation. This further shows that large changes in such systems can be induced by rather small changes in external forces [21]. The implications in the jamming of soft matter when the effects of heating are considered may be profound.

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[11] For example, a sample of 12 856 at \( c = 6.9 \) wt % is immobile at room temperature, whereas it flows when stored in the deep freezer (about \(-10 ^\circ C\)) for several hours.
[12] (a) T. Sato et al., Macromolecules 33, 1686 (2000); (b) D. Vlassopoulos et al. (unpublished).
[15] E. W. Fischer, Physica (Amsterdam) 201A, 183 (1993). Note that the present systems were ergodic, as judged from the high value of \( C(q, t) \) at short times in Fig. 3 (almost full contrast).
[17] Even the presence of a small percentage of such clusters could yield a solidike response. For example, during crystallization, 1% of crystals was found to be sufficient for a similar macroscopic behavior [H. H. Winter and M. Mours, Adv. Polym. Sci. 134, 165 (1997)].
[18] Even when a swelling of grafted colloids upon heating was detected, a solidike behavior was not observed [M. D. Croucher and T. H. Milkie, Faraday Discuss. Chem. Soc. 76, 261 (1983)].