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Is the Polyelectrolyte Extraordinary Phase a Cluster-Forming Glass?

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ABSTRACT: The polyelectrolyte extraordinary diffusion regime encountered in low-salt polyelectrolyte solutions is proposed to be a material example of the cluster-forming glasses simulated by Johnson et al. Features common to both types of system include (i) cluster formation, (ii) slow/glassy dynamics in which clusters participate while individual molecules move relatively freely, and (iii) a peak in the static structure factor at nonzero scattering vector that scales with the interaction strength. The neutral polymer slow mode also seen with light scattering spectroscopy has quite different properties and corresponds to a different class of glassy dynamics.

Introduction

Mel'cuk et al.,[1] Johnson et al.,[2] and Klein et al.[3] have reported extensive computer simulations of fluids as they are taken to low-temperature, high-density glass transitions. These authors find that as the glass is approached, their systems have certain characteristic features, notably the formation of long-lived clusters that dominate aspects of the system's dynamics. Various interparticle potentials were used in these simulations, including a repulsive two-body potential with a mean-field limit and a two-dimensional Lennard-Jones potential. In the original papers, the terms "clumps" and "clusters" were used to differentiate particular sorts of particle aggregates. Here the systems discussed in refs 1−3 are collectively termed "cluster-forming glasses".

This paper compares characteristic features of cluster-forming glasses[1−3] with certain characteristic features of polyelectrolyte solutions. In particular, as observed by Lin et al.,[4] solutions of many polyelectrolytes exhibit a phenomenology that was then described as the "ordinary" (high salt)−"extraordinary" (low salt) transition in their dynamics. Characteristic features of the polyelectrolyte extraordinary phenomenology appear below. These characteristic features are shown to resemble closely the characteristic features of the cluster-forming glasses studied by Klein, Gould, and collaborators.[1−3] It is proposed below that the polyelectrolyte extraordinary regime in fact provides a material exemplar of a cluster-forming glass.[1−3] What is meant here by "glass"? This question is considered further immediately in the Discussion. It is momentarily sufficient to say that a "cluster-forming glass" is a system having the properties described by Klein, Gould, and collaborators.

The polyelectrolyte extraordinary regime is sometimes referred to as a "phase". However, there is no good thermodynamic evidence that the appearance of the extraordinary-regime behavior in polyelectrolyte solutions is accompanied by a thermodynamic phase transition. The lack of a thermodynamic phase transition between the polyelectrolyte ordinary and extraordinary regimes has a direct similarity to the glass transition in many fluids, namely, that there is no good thermodynamic evidence that the formation of a glass uniformly involves a true thermodynamic phase transition from the fluid state. Indeed, as shown below there is substantial evidence in at least some polyelectrolyte systems that the extraordinary "regime" is better viewed as a class of thermal excitation of the system and that references to ordinary and extraordinary phases or regimes are actually references to the relaxations of two classes of excitation of the same system.

The next section of the paper discusses characteristic features of cluster-forming glasses. The following section presents the corresponding characteristic features of polyelectrolyte solutions. Similarities between cluster-forming glasses and the polyelectrolyte extraordinary regime are identified. A final section discusses more general implications of this analysis.

Simulations of Cluster-Forming Glasses

Mel'cuk et al.[1] and Johnson et al.[2] report extensive simulations of a two-component, two-dimensional supercooled Lennard-Jones system. As this system is cooled, one can observe the formation of clusters. These clusters have little density contrast with the surrounding fluid, so it is challenging to identify which Lennard-Jones particles belong to them. Mel'cuk et al.[1] and Johnson et al.[2] used a geometric definition appropriate to their two-dimensional system: particles that are in particularly regular hexagonal groups with their neighbors and that have sufficiently small kinetic energies are part of a cluster, and particles that are nearest neighbors and parts of clusters are taken to be part of the same extended cluster.

In the Lennard-Jones system, the temperature dependence of the cluster diffusion coefficient D_c reveals the existence of a glass transition; D_c goes to zero as the glass temperature is approached. In contrast to D_c, the single-particle diffusion coefficient D_s is insensitive to the glass transition. As the system's temperature is reduced, D_s decreases smoothly, while the time τ_e required to relax energy fluctuations increases. However, at all temperatures studied in the simulations, single particles diffuse and energy fluctuations are able to relax.

Mel'cuk et al. and Johnson et al. compare their findings with results on a near-mean-field system, a fluid having a pairwise-repulsive interparticle potential taken to a near-mean-field (long range, weak) limit. In a near-mean-field system, particles are observed to form very long-lived clusters [termed "clumps" by the original authors to distinguish them from the clusters in a Lennard-Jones system] as T is reduced. The clumps in

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a near-mean-field system are actual regions of higher particle density; they are readily identified.

Mel'cuk et al. remark on the "... qualitatively different dynamical behavior of the single particle and cluster properties." Unlike many experimental systems, in which single-particle diffusion substantially stops when a glass forms, in a near-mean-field system below the spinodal temperature T_s individual particles can still diffuse. At the same density, the diffusion coefficient D_c of the clumps becomes very small as the temperature is reduced. Single-particle properties are not affected by the glass transition; conversely, clump formation and the glass transition are not evident in single-particle properties. In a near-mean-field cluster-forming glass, the glass transition thus corresponds to clump dynamics, not to single-particle dynamics.

If a near-mean-field system is equilibrated at elevated temperature, and quenched to below the spinodal temperature T_s, clumps form. The details of the clump structure depend on the quench history. In quenched systems, clumps are not mobile on observed time scales and do not form crystals. The free energy surface is complex with many minima, suggesting that after the quench the system has formed a metastable glass.

In the near-mean-field system, glass formation is also evident in the static structure factor $S(q)$, which has a peak at some scattering vector $q_0 \neq 0$. The characteristic distance $2\pi/q_0$ is the typical distance between particles within a cluster. As temperature is reduced, at first the peak height χ increases, while the peak width w declines. However, $S(q_0)$ does not increase indefinitely with falling temperature. There is a lower temperature below which $S(q_0)$ is substantially independent of T. Johnson et al.[2] show that over a range of temperatures χ and w both follow scaling laws $\sim (T - T_s)^x$, x being a scaling exponent. In Johnson et al.'s system, there is no strong peak at $q = 0$ because the system has a liquidlike density. (The particles have a diameter $\sim 2/\gamma$ and a spacing $\sim 2/\gamma$.)

In discussing their observations, Mel'cuk et al.[1] propose that the behavior of their Lennard-Jones system arises from an "incipient thermodynamic instability". They note that other interactions, such as the Gaussian potential in its near-mean-field limit, yield systems in which there is neither a spinodal nor a thermodynamic glass transition.[5] If one accepts the implication that there are several classes of glassy system, differentiated by their dynamics, it becomes of interest to inquire for each glass which class of dynamics is being observed. Evidence discussed below suggests that polymer solutions provide examples of two different types of glassy dynamics.

The Polyelectrolyte Extraordinary Regime

The appearance of a nominal polyelectrolyte extraordinary transition was first noted by Lin et al.,[4] who used light scattering spectroscopy to measure the mutual diffusion coefficient D_m of aqueous solutions of poly-L-lysine. D_m at first increased with declining solution ionic strength. Over a modest range of ionic strength both D_m and the absolute scattering intensity then decreased dramatically. Finally, D_m was nearly independent of salt concentration c_s over several further decades of c_s. D_m at low c_s was also several orders of magnitude smaller than D_m measured in high-salt solutions. The low-salt regime in which D_m is independent of c_s corresponds approximately to the regime in which c_s is substantially less than the concentration of counterions present because the polyelectrolyte has been fully or partially neutralized.

Until relatively recently, observations on the nature of the polyelectrolyte slow mode remained complex and controversial. Major technical improvements that aided understanding the extraordinary regime include (i) the advent of full-time-domain 100% efficient exponential-sampling correlators for quasi-elastic light scattering spectroscopy and (ii) the use of absolute intensity standards to determine the true intensity of each spectral mode. This discussion proceeds in reverse chronological order, beginning with current understanding of the nominal ordinary and extraordinary regimes and referring back to earlier observations that illuminate particular phenomenologies. A definitive set of current papers on the extraordinary regime is provided by work of Sedlak,[6] Sehgal and Seery,[7] and Ermi and Amis.[8] This is not a review[9] article; most of the earlier literature is not referenced.

Sedlak[6] measured light scattering spectra of solutions of sodium polystyrene sulfonate, molecular weights 5000−1.2 × 10^6 Da, for polymer concentrations $c_p \in 0.5-50$ g/L and NaCl concentrations $c_s \in 5 \times 10^{-6}-5.0$ M, using pure benzene as an absolute intensity standard. Sedlak found that most though not quite all of his spectra were bimodal. Depending on polymer molecular weight, the diffusion coefficient D_f corresponding to the fast mode increased several- to 50-fold with decreasing c_s. The increase, which is most prominent for the largest polymers, is substantially confined to the regime $0.1 \le c_s \le 0.001$ M. The diffusion coefficient D_s corresponding to the slow mode is generally nearly independent of c_s; D_s is 2 or more orders of magnitude smaller than the fast-mode diffusion coefficient in the low salt limit. D_f and D_s do not approach a common limit at large c_s, showing that it is inappropriate to describe the ordinary and extraordinary modes as a "splitting of the diffusion coefficient".

Sedlak[6] introduced the use of an absolute intensity standard, a small-molecule liquid, as a tool for examining the polyelectrolyte extraordinary regime. Sedlak demonstrated that the absolute scattering amplitude of the fast mode falls 10-fold with decreasing ionic strength, while simultaneously the absolute magnitude of the slow mode increases from zero or nearly zero until the slow mode dominates the spectrum. Sedlak used dialysis to reduce the ionic strength of a single solution, showing not only that is it true that the slow mode is more intense in solutions of low ionic strength but also that the slow mode increases in its absolute intensity when salt is physically removed from a given solution. Sedlak inferred from his data that the slow mode arises from transient structures that grow in number or scattering power as salt concentration is lowered.

Sedlak[6] also determined how the slow and fast mode amplitudes depend on polymer concentration c_p and molecular weight M at fixed c_s, showing that the fast mode intensity (normalized by polymer concentration) decreases with increasing c_p, while simultaneously the slow mode intensity greatly increases. At elevated c_p (30 g/L), the slow mode remains visible even at high (1 M) salt concentration. The dependence of the fast mode amplitude on c_s is larger at large M, making the apparent ordinary-extraordinary transition more dramatic at large M. Sedlak and Amis[10] studied the dependence of slow mode properties on polymer molecular weight and concentration, finding D_s fell with increasing c_p, especially at large M. At large c_p, a 200-fold increase in M could reduce D_s nearly 100-fold; at the same elevated c_p, a 200-fold increase in M increases the radius of gyration of the apparent transient structures, as inferred from static light scattering, by only 2-fold, with most of the increase occurring at the largest molecular weights.

Sehgal and Seery[7] studied light scattering by polystyrene sulfonate in N-dimethylformamide, a nonaqueous solvent having an extremely large dielectric constant. Sehgal and Seery's results are in part similar to Sedlak's, but Sehgal and Seery made many additional important observations. In particular, in N-dimethylformamide light scattering spectra show bimodal relaxations at all salt concentrations, removing any possibility that the extraordinary relaxation appears only on one side of a dynamic phase transition. Both relaxation rates are linear in q^2; correspondingly, both modes correspond to diffusive relaxation by the excitations that scatter light. From measurement of the mode amplitudes as a function of q, the fast mode corresponds to Rayleighian scatterers (objects far smaller than a light wavelength), but the slow mode corresponds to structures with a mean-square dimension R_g of 70 nm at smaller (<0.004 M) salt concentrations and 50 nm at larger (>0.04 M) salt concentrations. D_s of the slow mode does increase with increasing c_s. However, the 30% decline in cluster size R_g with increasing c_s does not explain a more than 3-fold increase in D_s over the same range of c_s. Furthermore, most of the change in R_g occurs within a single central decade in c_s, but the change in D_s with increasing c_s occurs smoothly over almost 3 decades in c_s.

The results of Sedlak[6] differ from those of Sehgal and Seery[7] in one respect, namely that in the former set of results the amplitude of the slow mode grows monotonically as c_s is reduced, but in the latter set of results this amplitude has a maximum near $c_s = 0.1$ M and falls roughly 2-fold at either lower or higher salt concentrations.

Ermi and Amis[8] present static light scattering and elastic neutron scattering measurements of poly(N-methyl-2-vinylpyridinium chloride) in D_2O, covering $4 \times 10^{-4} \le q \le 0.2$ Å^{-1} for polymer concentrations of 3, 15, and 30 g/L. Combination of neutron and light scattering measurements cover a far wider range of q than would otherwise be possible; $S(q)$ shows a broad peak centered at $q = 0$ and a single side peak.

The central peak in the light and neutron scattering data corresponds to structures with radii of gyration of 88−90 nm, nearly independent of polymer concentration. The side peaks from Ermi and Amis's data[8] were here fit to a form

$$S(q) = B + Sq + \frac{H}{(q - q_0)^2 + \Gamma^2} \qquad (1)$$

where B and S describe the baseline and influence of the central peak, q_0 is the side-peak center, Γ/q_0 is the normalized side-peak half-width at half-maximum, and H/Γ^2 is the side-peak amplitude. As seen in Figure 1, the center, width, and height of the side peak in $S(q)$ all depend on polymer concentration. From the figure, with increasing c_p the side peak moves to larger q with $q_0 \sim c_p^{0.41}$, becomes narrower with ($\Gamma/q_0 \sim c_p^{-0.10}$), and becomes taller, though for the height a power law ($H/\Gamma^2 \sim c_p^{0.39}$) only gives a moderately accurate description of the data.

The data of Sedlak[6] and Sehgal and Seery[7] put prior observations of the ordinary−extraordinary transition in a new light. As small c_s, only the slow mode contributes significantly to the spectrum. With increasing c_s, the fast mode eventually dominates the spectrum. With the more limited digital correlators available in earlier decades, it would have been very difficult to identify the weaker of the two decay modes in the presence of more intense of the two decay modes, so a change in the identity of the dominant mode would readily have been interpreted as a dramatic change in the relaxation time of a single mode.

Clearly, one can generate slow modes by contaminating a polyelectrolyte solution with dust, the dust being removable by filtration. The interesting question, however, is whether there are also slow modes that are not due to dust contamination. The available experimental data suffice to reject proposals that polyelectrolyte slow modes always arise from particulate contaminants, whose scattering becomes visible when scattering by the polymer itself is electrostatically suppressed at small c_s. From measurements of Sedlak,[6] reducing c_s does reduce the scattering intensity of the fast mode. However, contrary to Sedlack's observation that the absolute intensity of the slow mode increases at low c_s, no obvious mechanism permits scattering by dust to become more intense at small c_s. Furthermore, Smits et al.[11] have shown that dilution with solvent at fixed ionic strength selectively eliminates the polyelectrolyte slow mode, while the fast mode remains visible. Like the results of Sedlak,[6] the phenomenology of Smits et al. cannot be explained as dilution of dust particles by dust-free solvent, because dilution would affect the intensities of fast polymer and slow dust modes in equal proportions and would remove both modes simultaneously.

Smits et al.[11] do note that filtration of low-salt solutions through very small (0.05−0.1 μm) filters sometimes removes the slow mode in a reversible way. Their observations are consistent with the (sometimes) reversible disruption of multipolymer structures by passage through the filter.

Sedlak[6] and Ermi and Amis[8] both measured apparent radii of large domains in polyelectrolyte solutions via the angular dependence of static light and neutron scattering intensities. Sedlak found concentration-dependent radii of gyration R_g of 64−89 nm, R_g decreasing with increasing c_p, in solutions of 5 kDa polystyrene sulfonate. The R_g of the aggregates of 5 kDa polymer is far larger than R_g of the individual polymer chains. Ermi and Amis, studying a 281 kDa polymer, found R_g of their clusters to be independent of concentration.

In polyelectrolyte solutions, single-particle dynamics show less dramatic behaviors than the behaviors encountered for the light scattering spectra. Wilcoxon and Schurr,[12] Zero and Ware,[13] and Schmitz and Ramsay[14] all studied the extraordinary phase with electrophoretic light scattering (ELS). In these experiments, the polymers were not dilute, while the apparent polymer aggregates correspond formally to a second macrocomponent in the system, so interpretation of ELS spectra is nontrivial. Fortunately, light-scattering electrophoretic spectra of two- and three-component dilute and nondilute solutions were examined theoretically by this author,[15] including effect of chemical reactions on the spectra. In these papers, one component was the solvent,

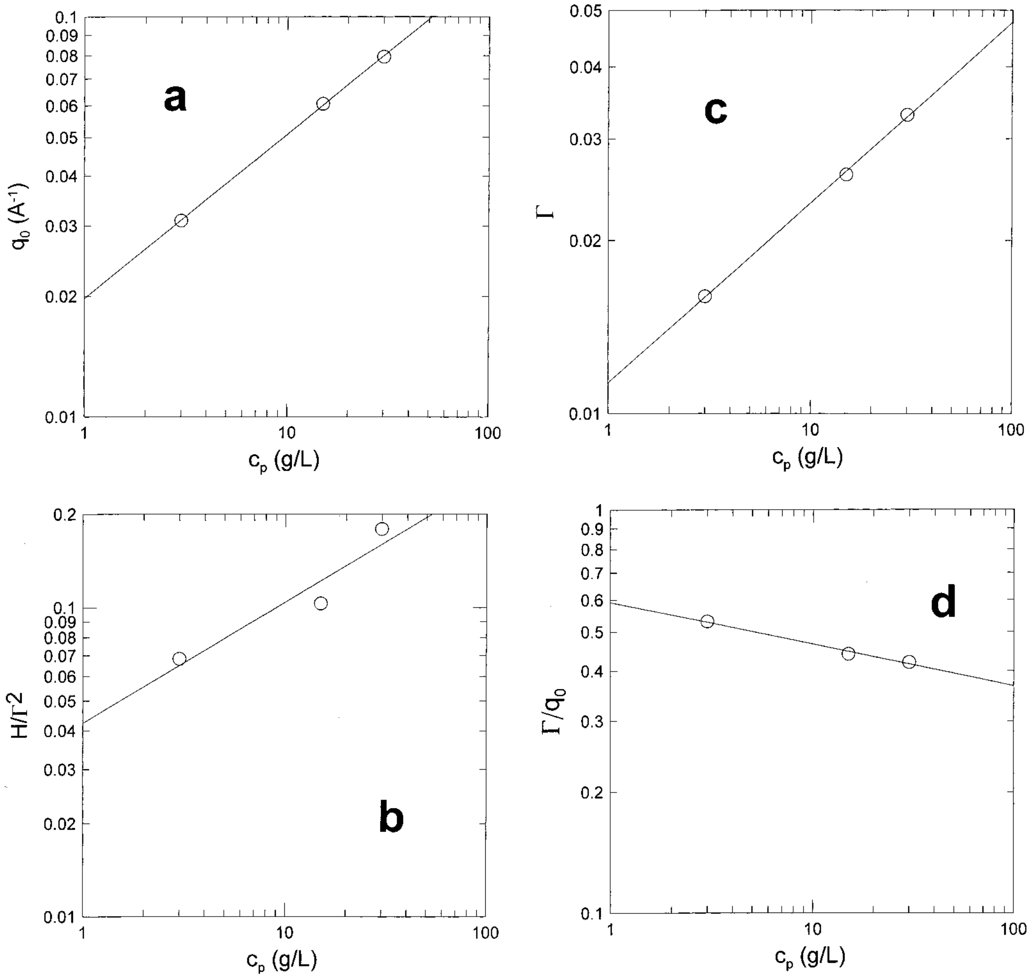

Figure 1. (a) Peak center, (b) peak height, (c) peak width, and (d) normalized peak width for the first $q \neq 0$ peak, as functions of concentration, from the small-angle neutron scattering data of Ermi and Amis[8] on poly(*N*-methyl-2-vinylpyridinium chloride) in D_2O with no added salt.

and the other components were the one or two macrocomponents that scattered light. In the case of a simple fast chemical reaction linking two macrocomponents, light scattering electrophoresis spectra should simply show the average behavior of the scatterers, with no indication in the spectrum that two macrocomponents are present. If any chemical reactions are slow and the solution is dilute, ELS will readily obtain D_m of a dominant scatterer. At elevated concentrations the diffusion coefficient inferred from the ELS line width is not necessarily the zero-field mutual diffusion coefficient coefficient of the scattering species.

In problems of interest[15] in 1971–1973, the two macrocomponents linked by a chemical reaction were two charge states of the same protein, linked by the very fast proton binding and release to the solvent. In the polyelectrolyte problem, the two species of interest are apparently single polymer chains and an aggregate. So long as the exchange reaction in which single chains join and leave aggregates is rapid, electrophoretic light scattering measures the averaged electrophoretic mobility and diffusion coefficient of all scattering molecules. If such reactions are slower, more complex situations arise.

Wilcoxon and Schurr[12] used electrophoretic light scattering to measure the electrophoretic mobility μ_e and diffusion coefficient *D* (from the width of the ELS peak) for 84.7, 197, and 475 kDa poly-L-lysine as functions of the concentration of added salt. For most salt concentrations, the dependence of μ_e on c_s qualitatively tracks the c_s dependence of D_f seen by Sedlak.[6] Wilcoxon and Schurr found that μ_e increases as c_s is reduced, until a maximum in μ_e is reached at low but nonzero salt concentration.

Wilcoxon and Schurr note seeing at least one clearly bimodal light scattering spectrum, which appears to be the first recognition that light scattering spectra could show the ordinary and extraordinary relaxations simultaneously. They also noted difficulties near the apparent ordinary–extraordinary transition with observing the ELS spectrum. As they noted, their difficulties were consistent with a bimodal broadening of the ELS spectrum by two diffusive modes—one mode that gave the observed width and a second mode that was too broad to see easily. The simultaneous observation of two diffusive modes in the ELS spectrum is consistent with the theoretical analysis of ref 15 if the exchange reaction of polymers between monomer and the hypothesized aggregate is not too rapid and if the solution is nondilute.

Zero and Ware[13] used fluorescence recovery after photobleaching and electrophoretic light scattering to measure the self-diffusion coefficient D_s and electrophoretic mobility μ_e of low-salt solutions of 90 kDa poly-L-lysine. For added salt concentrations in the range 0–10 mM KCl, in which the mutual diffusion coefficient (interpreted assuming unimodal behavior of the light scattering spectra) rose sharply by an order of magnitude, D_s increased smoothly from 4.0×10^{-7} to 6.0×10^{-7} cm^2/s (approximately 50%), while μ_e increased smoothly from 1.9 to 2.5 μm cm/(V s) (approximately 30%). Zero and Ware[13] concluded that D_s and μ_e behave "... precisely as theory would predict for a random-coil polyion" and that neither parameter shows "any anomalous behavior through the ordinary−extraordinary phase transition." Recently, Seery has performed FRAP on sodium polystyrenesulfonate/dimethylformamide, finding results qualitatively the same as those found in aqueous solutions.[16]

Schmitz and Ramsay[14] report light scattering electrophoresis data on poly-L-lysine obtained by using a sinusoidally oscillating electric field. They found with increasing field strength and small c_s that the diffusion coefficient of the scattering objects increased with increasing field, and simultaneously the apparent scattering intensity of the electrophoretically mobile scatterers declined. The apparent diffusion coefficient obtained from ELS in the high-field limit approached the high-salt-concentration limit of D_m as observed with conventional light scattering spectroscopy. At low salt concentrations, the apparent diffusion coefficient from ELS measurements at low field approached the extraordinary-regime mutual diffusion coefficient, as determined by light scattering spectroscopy. Schmitz and Ramsay concluded that their data are consistent with a polymer slow mode that is due to polymer aggregates in solution, the aggregates being fragile enough to be dispersed with an applied current: At high field, D from ELS primarily reflects the diffusion of isolated polymer chains, because at high field the aggregates are broken up by their rapid electrophoretic motion; single-chain diffusion is rapid. At low field and low salt, D for ELS reflects scattering by the dominant species, namely the slowly diffusing aggregates.

Comparison: Glasses and Polyelectrolyte Solutions

In this section, the characteristic features of cluster-forming glasses are compared with the characteristic features of polyelectrolyte solutions showing extraordinary regime behavior.

Cluster-forming glasses have several significant characteristic features: (a) The component particles form identifiable clusters or clumps, which may be mobile away out of the low-temperature and mean-field limits. (b) The slow dynamics of the glass are characteristics of the clusters. Single-particle dynamics are relatively unaffected by the glass transition. (c) In at least some systems one observes a peak in $S(q)$ for some $q \neq 0$. The height and width of the peak satisfy scaling relations in $(T - T_s)$.

Polyelectrolyte solutions showing "extraordinary regime" behavior exhibit the same characteristic features that serve to identify cluster-forming glasses. In making this comparison, a modest complication arises in that data on polyelectrolyte systems is largely athermal. Experimentally, the average interaction potential $\langle \beta U \rangle$ is varied not by changing the temperature but by changing the concentration of polymers (and hence the typical interparticle distances) or by changing the concentration of added salt (and hence the range of the electrostatic interactions). It is formally possible to alter $\langle \beta U \rangle$ by varying T. However, in polyelectrolyte solutions, changing the temperature changes the dielectric constant of the solvent (a feature vigorously exploited by Sehgal and Seery[7]), the degree of dissociation of the polyelectrolyte, and (in aqueous solution) the pH of the water, so that βU may depend on temperature more substantially through the potential U than through the temperature $T = (k_B \beta)^{-1}$.

Characteristic features of low-salt polymer systems that resemble features of cluster-forming glasses include the following:

(1) There is direct experimental evidence for the presence of clusters. Sehgal and Seery[7] and Ermi and Amis[8] measured elastic light and neutron scattering of polyelectrolyte solutions. They observed a peak in $S(q)$ at $q = 0$, the peak corresponding to objects that scatter both light and neutrons and that have $R_g \in 50-90$ nm depending on environment.

The bimodal dynamic structure factor $S(q,t)$ obtained from light scattering spectroscopy[6,7] is consistent with $S(q)$ if one interprets the slow mode as corresponding to cluster diffusion and the fast mode as corresponding to motions of single chains. As demanded by this interpretation, the line widths of the fast and slow modes of $S(q,t)$ are both $\sim q^2$, consistent with the two modes reflecting the diffusion of slowly and rapidly moving objects.[7] Furthermore, the angular dependence of the intensities of the two modes shows that the fast mode corresponds to the movements of small ($R_g \ll \lambda$) objects, while the slow mode corresponds to the movements of objects with an $R_g \approx 50-70$ nm.[7] The size inferred from the slow mode matches the cluster R_g obtained from static light scattering.

When solution properties are changed, the intensities and decay rates of the two modes respond to the changes as expected from the interpretation that the slow mode corresponds to clusters of polymer chains, the interpretation that aggregation is driven by electrostatic interactions between polymer chains, and Le Chatelier's principle. In specific, if one reduces c_s, interchain electrostatic interactions should become stronger; experimentally, with decreasing c_s the clusters remain the same[7] or increase[6] in scattering power and, by inference, in number or optical contrast. If one increases c_p, aggregation should be favored; experimentally with increasing c_p the single chain mode becomes fainter while the cluster mode becomes more intense.[6] Moreover, at larger c_p the clusters remain stable to higher salt concentration.[6] Finally, if solutions are diluted at fixed ionic strength, aggregation should become less favorable. Experimentally, as solutions are diluted, the slow cluster diffusion mode, and by implication the slowly diffusing clusters, disappear from light scattering spectra, leaving behind the faster mode marking single chain motions.[11]

Increasing the applied field in an ELS experiment leads to an apparent D from the ELS spectrum that is close to D_s, consistent with disruption of the aggregates at high field, leaving behind single chains.[14] The slow mode is also sometimes reversibly eliminated by passing low-salt polyelectrolyte solutions through small-pore filters.[11] Reversibility is consistent with the interpretation that filtration disrupts polymer aggregates, which can re-form after being disrupted, but is not consistent with an interpretation that filtration removes particulate contaminants.

(2) In polyelectrolyte solutions, single-particle dynamics are relatively insensitive to the ordinary−extraordinary transition. In particular, the polymer self-diffusion coefficient (obtained from fluorescence recovery

after photobleaching) and the polymer electrophoretic mobility increase smoothly by 30−50% as one moves from circumstances in which the slow mode dominates the light scattering spectrum to circumstances in which the fast mode dominates the light scattering spectrum.[13]

(3) The static structure factor $S(q)$ has a peak[8] at nonzero q. The line shift, width, and (more approximately) height of this side peak all follow scaling laws in the interaction strength, as measured by the polymer concentration c_p.

Characteristic features (1), (2), and (3) of the extraordinary mode of low-salt polyelectrolyte solutions match one-to-one the major characteristic features (a), (b), and (c) of cluster-forming glasses. I therefore here propose that low-salt polyelectrolyte solutions are material exemplars, accessible to convenient experimental study, of cluster-forming glasses.

The one obvious difference between the simulated cluster-forming glasses and the polyelectrolyte solutions is readily explained. In the simulations, calculations of $S(q)$ show at most a weak peak at $q = 0$. In contrast, the polymer solutions show a strong $q = 0$ peak, corresponding to objects of size 50−90 nm. The difference follows immediately from the densities at which the two systems were studied. The polyelectrolyte solutions are at low polymer concentration, so that it is relatively easy to produce concentration fluctuations. In contrast, the simulations are performed at liquidlike densities of clusters, so it is relatively difficult to produce fluctuations in the density of clusters. Thus, the polyelectrolyte solutions have large peaks in $S(q)$ near $q = 0$, while the cluster-forming glasses show only weak peaks at very low q.

The proposed interpretation does not explain mechanistically why polyelectrolytes form clumps in low-salt solution. The interpretation does, however, tie experimental observations on low-salt polyelectrolyte dynamics to a specific family of simulational models of glassy dynamics. When other characteristic properties of cluster-forming glasses emerge from simulations, it will be of interest to determine whether those features are encountered in polyelectrolyte solutions. Conversely, experimental data on the polyelectrolyte extraordinary regime may suggest novel questions for simulational study.

As a specific example of simulations suggesting further experiments, there is evidence[17] for the Lennard-Jones cluster-forming glasses that clusters of clusters can arise at low temperature and high density. If such a phenomenon were to occur in the polymer solutions, it would reveal itself as additional structure in $S(q)$ at very low q, corresponding to distances $\geq$ 100 nm. The corresponding q range would be attainable from light scattering or (taking advantage of nonaqueous solvents) low-angle elastic infrared scattering.

Discussion

It remains unclear how charged polyelectrolytes, their counterions, added salt, and the solvent conspire to create polymer aggregates.

The simulations of refs 1−3 provide one interesting insight. The reported clusters and clumps arise not only in Lennard-Jones systems but also in systems with purely repulsive pair interactions, in which clustering is driven by many-body effective interactions. Because clustering can be observed with particles that always repel each other, one may not advance from an observation that observable clusters form to a conclusion that the pair force is attractive at some ranges.

The phenomenological properties of the polymer slow mode (its scattering intensity, decay rate, and dependence on polymer and solution properties) suggest how forces responsible for polymer aggregates might arise. In particular, Sedlak[6] found that R_g of an aggregate can be much larger than R_g of its individual chains, while Sedlak and Amis[10] found that R_g of an aggregate only depends weakly on M of its component polymers. These findings are consistent with an interpolymer force with a more-or-less constant magnitude per pair of interacting chain segments. Changing the polymer molecular weight would change the number of segments per polymer chain, but inserting occasional breaks in a chain would only affect the forces between a very few segment pairs. Changing the polymer molecular weight would leave most segment−segment forces unchanged, leading to an aggregate whose stabilizing forces are relatively independent of M. The stabilizing forces would be determined by the polymer charge per unit length, the solution ionic strength, and the solvent dielectric constant. By measuring the dramatic change in $S(q,t)$ as temperature is changed in a solvent (dimethylformamide) whose dielectric constant e depends very strongly on T, Sehgal and Seery[7] provide relatively direct evidence that cluster formation is sensitive to ϵ. Ha and Liu[18] have shown how counterion-mediated forces can lead to a net attractive force between like-charged rods.

If the polymer molecular weight were large enough, R_g of an individual chain would be larger than the radii (50−90 nm) of reported aggregates, in which case aggregate size should become markedly dependent on polymer molecular weight. This regime may have been approached by Sedlak and Amis.[10] Further experiments at larger M might yield novel phenomenology.

Sedlak and Amis[10] noted that D_s of an aggregate depends on polymer molecular weight far more strongly than R_g does. This observation is not surprising. The aggregates are diffusing in a nondilute polymer solutions, not in a simple solvent. The diffusion coefficients of rigid spheres moving though nondilute polymer solutions depend strongly on polymer molecular weight.[19] Also, from the limited experimental data[20] on sphere diffusion in solutions of substantially neutralized polyelectrolytes, zero- and low-salt polymer solutions are far more effective at retarding sphere diffusion than are elsewise identical high-salt polymer solutions. The phenomenology of Sedlak and Amis[10] would be obtained, namely D_s would depend on M, c_p, and c_s far more strongly than R_g does, if aggregates diffuse like rigid objects.

An interesting issue that I have not yet treated directly is the nature of the “glass” in a cluster-forming glass. As noted by one of the referees,[21] the term “glass” is used to refer both to (1) systems that appear not to be at true equilibrium and that do not reach equilibrium on observable time scales and (2) equilibrium systems having a relaxation that is far slower than the system’s other relaxations. In polyelectrolyte solutions, the extraordinary regime appears to be a slow mode in an equilibrium system. Evidence supporting the interpretation that the clusters are equilibrium objects includes observations that cluster formation apparently can be disrupted by filtration, increasing the ionic strength, or elevated electric fields in electrophoresis, but on removing the disruptive stimulus the apparent clusters generally return. It does not appear possible to rule out an alternative interpretation that the glassy clusters are small nonequilibrium structures that reversibly adsorb polyelectrolyte chains. Under this alternative interpretation, scattering, diffusion, and electrophoresis data would refer to the reversible adsorptive of polyelectrolyte chains, the adsorption making the nonequilibrium cores visible, but the nanoscopic filtrable cores would not themselves be equilibrium structures.

In this note I have not compared the polyelectrolyte extraordinary regime with the “polymer slow mode” seen in nondilute solutions of some neutral polymers in good solvents. Understanding of the polymer slow mode mode is complicated by the difficulty that it is not visible in the spectra of all solutions. While some neutral polymer solutions show bimodal light scattering spectra, others do not.

The study of the polymer slow mode via light scattering spectroscopy has been substantially advanced by modern correlator technology, as shown, e.g., by recent results of Faraone et al.[22] Faraone et al. studied poly(methyl methacrylate) (PMMA) in acetone and poly(ethylene oxide) (PEO) in water. PMMA molecular weights ranged from 10^4 to 8×10^5 Da; the PEO had $M_w = 35$ kDa.

PEO solutions only showed a single spectral mode. For PMMA solutions, under some conditions Faraone et al. found a mode that substantially decayed at short times (a “fast” mode) and a mode that substantially decayed at longer times (a “slow” mode). The modes were both evident at concentrations below the chain overlap concentration ϕ^*. Above ϕ^* the modes became substantially more pronounced. Faraone et al.[22] fit their field correlation functions to a sum of two stretched exponentials $\exp(-(t/\tau)^\beta)$, the fitting parameters τ and β being used used to compute a mean decay rate Γ of each mode.

The modes differ substantially in their q dependences. The fast mode is nearly exponential, with $1 \geq \beta \geq 0.9$; Γ of the fast mode scales linearly in q^2. In contrast, τ, β, and hence Γ of the slow mode are independent of q. The neutral polymer slow mode and the polyelectrolyte extraordinary mode then differ markedly in their q dependences. In polyelectrolyte solutions the fast and slow modes are both[7] diffusive, with $\Gamma \sim q^2$ and $\Gamma \approx 0$ as $q \to 0$. In solutions of neutral polymers in good solvents, the line shape of the slow mode is largely independent of q.

The relaxational mode structure of neutral polymers in solution is usefully compared to the mode structure of a Kivelson glass.[23] In a Kivelson glass, cluster growth following supercooling is subject to geometric frustration. Translation diffusion over long distances is predicted to be relatively rapid, leading to a q^2-dependent fast mode. The slow mode of a Kivelson glass is due to structural relaxation between frustrated clusters; the relaxation rate is determined by the cluster size, not the scattering vector. In a Kivelson glass, the relaxation time of the slow mode is therefore independent of q.

In its relaxational behavior, the neutral polymer modes show the behavior expected for a Kivelson[23] glass, namely the relaxation rate of the fast mode is diffusive and scales as q^2, while the relaxation rate of the slow mode is independent of q. The neutral polymer modes do not match the modes of a cluster-forming glass, in that the relaxation rate of the neutral polymer slow mode scales as q^0 rather than q^2.

It thus appears that polymer solutions provide material realizations of several different theoretical models of glass formation, namely the cluster-forming glass and the Kivelson glass. It is difficult to reconcile this existence of realizations of multiple theoretical models with any hypothesis that there is a universal model of glass dynamics, unless the model is so ecumenical as to treat the cluster-forming and Kivelson glasses as special cases of the same general behavior.

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References and Notes

(1) Mel’cuk, A. I.; Ramos, R. A.; Gould, H.; Klein, W.; Mountain, R. D. *Phys. Rev. Lett.* **1995**, *75*, 2522−2525.
(2) Johnson, G.; Mel’cuk, A. I.; Gould, H.; Klein, Mountain, R. D. *Phys. Rev. E* **1998**, *57*, 5707−5718.
(3) Klein, W.; Gould, H.; Tobochnik, J.; Alexander, F. J.; Anghel, M.; Johnson, G. *Phys. Rev. Lett.* **2000**, *85*, 1270−1273.
(4) Lin, S. C.; Lee, W. I.; Schurr, J. M. *Biopolymers* **1978**, *17*, 1041.
(5) Klein, W.; Gould, H.; Ramos, R. A.; Clejan, I.; Mel’cuk, A. I. *Physica A* **1994**, *205*, 738−746. Greave, N.; Klein, W. *J. Math. Phys.* **1977**, *18*, 1735.
(6) Sedlak, M. *J. Chem. Phys.* **1996**, *105*, 10123−10133.
(7) Sehgal, A.; Seery, T. A. P. *Macromolecules* **1998**, *31*, 7340−7346.
(8) Ermi, B. D.; Amis, E. J. *Macromolecules* **1998**, *31*, 7378−7384.
(9) Recent excellent reviews include: Foerster, S.; Schmidt, M. Polyelectrolytes in Solution. *Adv. Polym. Sci.* **1995**, *120*, 51−133. Schmitz, K. S. *Macroions in Solution and Colloidal Suspension*; VCH Publishers: New York, 1993.
(10) Sedlak, M.; Amis, E. J. *J. Chem. Phys.* **1991**, *96*, 817−825.
(11) Smits, R. G.; Kuil, M. E.; Mandel, M. *Macromolecules* **1994**, *27*, 5599−5608.
(12) Wilcoxon, J. P.; Schurr, J. M. *J. Chem. Phys.* **1982**, *78*, 3354−3364.
(13) Zero, K.; Ware, B. R. *J. Chem. Phys.* **1984**, *80*, 1610−1616.
(14) Schmitz, K. S.; Ramsay, D. J. *Macromolecules* **1985**, *18*, 933−938.
(15) (a) Phillies, G. D. J. *J. Chem. Phys.* **1973**, *59*, 2613−2617. (b) Phillies, G. D. J. M.S. Thesis, MIT, 1971.
(16) Seery, T. A. P. Private communication, 2001.
(17) Gould, H. Private communication, 2001.
(18) Ha, B.-Y.; Liu, A. J. *Phys. Rev. E* **1999**, *60*, 803−813.
(19) Phillies, G. D. J.; Ullmann, G. S.; Ullmann, K.; Lin, T.-H. *J. Chem. Phys.* **1985**, *82*, 5242−5246.
(20) Phillies, G. D. J.; Malone, C.; Ullmann, K.; Ullmann, G. S.; Rollings, J.; Yu, L.-P. *Macromolecules* **1987**, *20*, 2280−2289.
(21) Anonymous, private communication.
(22) Faraone, A.; Magazu, S.; Maisano, G.; Ponterio, R.; Villari, V. *Macromolecules* **1999**, *32*, 1128−1133.
(23) (a) Kivelson, S. A.; Kivelson, D.; Fischer, T. M.; Knobler, C. M. *J. Chem. Phys.* **1994**, *101*, 2391−2397. (b) Tarjus, G.; Kivelson, D.; Kivelson, S. *Supercooled Liquids: Advances and Novel Applications*; Fourkas, J. T., Kivelson, D., Mohanty, U., Nelson, K. A., Eds.; ACS Symposium Series 676; American Chemical Society: Washington, DC, 1997.

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