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Neutral polymer slow mode may signify an incipient growth-frustrated domain-forming glass

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Kivelson, *et al.* [J. Chem. Phys. **101**, 2391 (1994)] propose a model for glass-forming liquids based on the potential existence of frustration-limited structures. Frustration-limited structures are *equilibrium* supramolecular assemblages. The maximum size of an assemblage is limited by geometric constraints. Here I propose that the "slow mode" found in the quasielastic light scattering spectra of some but not all neutral polymer solutions corresponds to the presence of an *incipient* growth-frustrated domain-forming glass in these solutions. A physical picture is proposed for the origin of frustration in polymer solutions.

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I. INTRODUCTION

Recently, Kivelson *et al.* [1] proposed a model for glasses based on the appearance in glass-forming liquids of geometrically frustrated equilibrium domains. The model does not specify whether glass formation corresponds to the actual presence of domains, or if it corresponds to a favored length scale that would be exhibited by these domains if they were present. The model does not specify the detailed nature of the domains; it does present an exemplary structure that might in a particular system have the hypothesized properties of the hypothesized domains. This model's treatment [1–4] of the size and density of domains explains static light scattering by glass-forming liquids, especially features encountered during heating-cooling cycles and above the melting temperature T_m of the bulk crystalline phase. The temperature dependences of the viscosity of 11 glass-forming (both strong and fragile) one-component liquids and three polymer melts were reduced by the model to a single universal curve.

Our interest here is in polymer solutions, not in the single-component liquids treated in Ref. [1]. Because the systems here have more than one component, concentration joins temperature as a significant variable. As discussed below, the effects discussed in Ref. [1] as occurring if temperature is reduced are mirrored by the effects discussed here as concentration is increased.

The central effect considered here is the polymer slow mode, as phenomenologically observed in quasielastic light scattering spectra $S(q,t)$ of neutral polymers in good and θ solvents. At lower concentrations, $S(q,t)$ is characterized by a single nearly exponential relaxation. At elevated polymer concentrations, in some solutions *but not others* $S(q,t)$ gains a second conspicuously nonexponential mode. The nonexponential mode typically has a much longer mean relaxation time than does the exponential mode, leading to its being denoted the "polymer slow mode." There is an extensive literature on properties of the nonexponential mode, including its dependences on scattering vector, polymer concentration and molecular weight, solvent quality, and temperature.

Kivelson *et al.* [1] demonstrate that certain physical properties of representative polymer melts, notably the temperature dependence of the viscosity, behave as though glass formation in polymer melts is due to the formation in the melt of frustration-limited equilibrium domains. In this paper, I propose that certain physical properties of some nondilute polymer solutions, notably the polymer slow mode, are consistent with incipient glass formation in solution due to the formation of similar frustration-limited equilibrium domains. The polymer solutions treated here differ from polymer melts of Ref. [1]. In the melts, the apparent viscosity diverges as temperature is reduced. In the solutions, glass formation is only incipient. With increasing concentration, solution viscosities increase, but remain well below the range of viscosities that characterize glasses.

A prior consideration [5] of polyelectrolyte solutions led to the proposal that the polyelectrolyte "extraordinary phase" observed in quasielastic light scattering spectroscopy spectra of low-salt polyelectrolyte solutions [6] corresponds to the appearance of a cluster-forming glass [7,8] in these solutions. The cluster-forming glasses described by Mel'cuk *et al.* and Johnson *et al.* [7,8] and proposed to be found in polyelectrolyte solutions have dynamic properties which differ from the dynamic properties noted here for neutral polymers. We therefore believe that the glass transition proposed below for neutral polymer solutions differs from the cluster-forming phenomena proposed [5] to explain the polyelectrolyte extraordinary phase.

Section II of this paper describes the model of Kivelson *et al.* [1] for glass-forming liquids containing frustration-limited domains. Section III summarizes the modern literature on polymer nonexponential modes. Section IV matches the model against the phenomenology, showing that they are highly consistent. Implications of these results are treated in Sec. V.

II. THE KIVELSON GLASS

We first consider the glass model of Ref. [1] and suggest how it might be extended to solutions. Kivelson *et al.* [1] propose that the glassy properties of many single-component liquids arise because the liquids form equilibrium molecular domains that are not crystallites of the equilibrium solid phase. The hypothesized domains are thermodynamically

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stable. However, they do not grow to arbitrarily large sizes because geometric frustration prevents unlimited growth. Domains form, and grow to a largest size permitted by geometric frustration. Further heating or cooling leads to changes in the concentration of domains, but the size of the individual domains is determined by packing constraints and is bounded above, regardless of the temperature. The domains, or perhaps favored length scales associated with the potential presence of domains, enhance the viscosity at low temperatures.

This glass model characterizes structures by invoking an unspecified order parameter **O**, envisioning a qualitative coarse-grained Hamiltonian for **O** to be

$$H=-\sum_{ij}\ \alpha_{ij}\mathbf{O}_i\cdot\mathbf{O}_j+\sum_{ij}\ \gamma_{ij}\mathbf{O}_i\cdot\mathbf{O}_j\,. \qquad (1)$$

Kivelson *et al.* [3] propose that **O** might be a local bond orientation variable representing how particles are packed around each other. Equivalently, **O** could be a spherical harmonic of the density of nearby particles around each atomic center. The actual physical nature of **O** is not critical to the model's development in Ref. [1], because the clustering behavior is entirely determined by the mathematical form of Eq. (1) and is substantially independent of the physical nature of **O**. In Eq. (1), the sums go over all pairs i,j of particles, α_{ij} represents an energetically favorable short-range interaction that vanishes unless i and j are near neighbors, while β_{ij} represents a longer-range, energetically unfavorable interaction.

A simple example of a Hamilton with this structure appears in a multidimensional Ising model in which the **O** are spin variables on a lattice, α_{ij} is a nearest-neighbor ferromagnetic interaction, and β_{ij} represents long-range frustration effects. Qualitatively, this Hamiltonian makes it energetically favorable to form domains in which $\mathbf{O}_i\cdot\mathbf{O}_j$ is locally large. However, over large distances there is frustration: It becomes energetically unacceptable to have $\langle\mathbf{O}_i\cdot\mathbf{O}_j\rangle\gg 0$ for $\|i-j\|\gg 1$. For this Hamiltonian, at low temperatures the system forms a defect-laden pattern of locally ordered domains.

There is no requirement that **O** be a functional of the density. As noted by Kivelson *et al.* [3], if **O** were not a functional of the density, it would couple to the density (and hence to the static structure factor) only indirectly. Let $\mathbf{O}(\mathbf{k},t)$ and $\mathbf{A}(\mathbf{k},t)$ denote the spatial fourier transforms of the densities $\mathbf{O}(\mathbf{r},t)$ and $\mathbf{A}(\mathbf{r},t)$ of the order parameter and the particles, respectively. When $\mathbf{k}\to 0$ the simple correlation function $\langle\mathbf{O}(\mathbf{k},t)\mathbf{A}(-\mathbf{k},t)\rangle$ must vanish because **O** and **A** have different symmetry properties. However, while a bilinear coupling $\mathbf{B}=\langle\mathbf{O}(\mathbf{k},t)\mathbf{O}(-\mathbf{k}+\mathbf{q},t)\mathbf{A}(-\mathbf{q},t)\rangle$ is not required to vanish in the small $\mathbf{k},\mathbf{q}$ limit, **B** has a diffuse **q** dependence, leading to an absence of sharp structure-implying peaks in $\langle\mathbf{A}(\mathbf{k},t)\mathbf{A}(-\mathbf{k},t)\rangle$. For dynamic couplings, while $\langle\mathbf{O}(\mathbf{k},t)\dot{\mathbf{A}}(-\mathbf{k},t+\tau)\rangle$ is obliged to vanish by time reversal symmetry at $\tau=0$, the coupling $\langle\mathbf{O}(\mathbf{k},t)\dot{\mathbf{A}}(-\mathbf{k},t+\tau)\rangle$ can be nonzero when $\tau\neq 0$. (For a suitable choice of an $\dot{\mathbf{A}}$, and an **O** like that envisioned by in Ref. [1], such nonzero time-displaced dynamic couplings have recently been observed in simulations [9].)

How might a coarse-grained frustration-inducing Hamiltonian arise in a fluid? Reference [1] notes observations by Boerdijk [10], Frank and Kasper [11], Bernal [12], Hoare [13], and Stillinger [14] that spherical molecules often prefer to pack locally in body-centered icosahedra. However, overlapping simple body-centered icosahedra are not space filling, so they cannot be the basis for a true crystalline phase. If one attempts to pack icosahedra, one rapidly creates voids or finds regions in which neighboring molecules need to interpenetrate. Attempting to pack icosahedra in a space-filling way creates crystal defects and strain energies that diverge with the volume of the icosahedral domain. The formation of large icosahedral domains is energetically prohibitive, the prohibition being an example of "geometric frustration." Frustration-limited domains resemble the transient van der Waals–stabilized cryptocrystallites of Rouse's [16] treatment of viscoelasticity in concentrated polymer solutions, in that the domains and cryptocrystallites both create local regions having long correlation times.

Kivelson *et al.* [1] analyze the free energy of their proposed domains as functions of domain stability and system temperature T. The melting temperature T_{mi} of the icosahedral crystallites could be higher than the freezing temperature T_{ms} of the simple liquid. When T is reduced below T_{mi} the liquid therefore attempts to freeze into icosahedral crystals; imperfect icosahedral domains grow until they encounter geometric frustration. These domains are thermodynamically stable with respect to the liquid, but are not an orthodox thermodynamic phase because their volume is not unlimited. In the temperature range $T_{ms}<T<T_{mi}$, crystallites of the crystalline phase are superheated and hence unstable. When the system is heated from below until it is warmer than T_{ms}, crystals of the stable phase rapidly disappear. Heating the system above T_{ms} does not cause the frustrated domains to decompose; the domains are stable up to T_{mi}, and may be metastable, once formed, even if they are not stable. In experimental support of these predictions, Kivelson *et al.* note experiments by Fischer *et al.* [15] showing that unspecified glassy-related aggregates do not disappear rapidly when heated above T_{ms}, until some much higher temperature T_{mi} is attained.

Reference [1] finally proposes that the fundamental temperature in their model is closely related to the melting temperature T_{mi} of the icosahedral domains, because the equilibrium number of domains goes to zero as $T\to T_{mi}$ from below, but scales with $T-T_{mi}$ at lower temperatures. They therefore propose that T_{mi} (and not the Vogel-Fulcher temperature T_o or the glass temperature T_g) is the fundamental temperature for describing glass formation. Indeed, they show that the activation energy for the viscosity of a range of fragile, strong, and polymeric glass-forming liquids scales naturally with $T_{mi}-T$.

In summary, the model of Ref. [1] predicts the following. In a glass-forming single-component liquid one can find equilibrium domains that have reproducible sizes, are substantially larger than single molecules, but are not crystallites of the equilibrium solid phase. Correspondingly, the static structure factor $S(q)$ shows excess amplitude, perhaps with structure at low angle, persisting into the nonsupercooled melt. The fundamental temperature is for analyzing glassy behavior is T_{mi}, the temperature at which domains decompose into the simple fluid. The domain concentration is larger at low temperature. Relaxation to equilibrium of the number density of domains may be very slow. The viscosity tracks the number density of domains, so that the domain number density and the viscosity scale in the same way with temperature, namely, both scale in $(T_{mi}-T)^x$.

Reference [1] did not treat quasielastic scattering spectra. The model implies that when there are domains whose order parameter is coupled to the density, translational diffusion of intact domains yields in the limit of very low q a q^2-dependent diffusive relaxation in $S(q,t)$. At larger q, structural relaxations dominated by an internal length scale lead to q-independent relaxation rates. The line shape of the relaxation in $S(q,t)$ is partially determined by the distribution of domain sizes. If the domains are nondilute, interactions between domains may also perturb their dynamics.

Reference [1] treated viscosity but not viscoelasticity. The model implies: If glassy viscosity arises from domains or superdomains rather than a length scale that the domains create, the longest relaxation time is a domain lifetime τ_c. Not necessarily with observable amplitudes, τ_c supplies the longest relaxation time in $S(q,t)$, in the mechanical spectrum $G(t)$, and in the depolarized scattering spectrum if one is detectable.

Kivelson *et al.* [1] treated one-component melts at constant pressure. Their thermodynamic control variable was the temperature. Here we consider two-component solutions, largely at fixed temperature, the accessible thermodynamic variable being the concentration. It is here proposed that there is a rational analogy between temperature and concentration dependences, and that the analogy allows one to apply the model of Ref. [1] to solutions. The analogy maps high temperature melts onto dilute solutions. At high temperature or low polymer concentration, the polymer molecules have a simple liquid behavior, with no domains being present. A reduction in temperature is mapped onto an increase in concentration. With decreasing temperature or increasing concentration, one eventually reaches a solid line: the melt crystallizes, while the solution reaches a solubility limit beyond which lies a solid phase in equilibrium with a saturated solution. However, in the liquid phase before the solid line is reached, decreasing temperature or increasing concentration makes it thermodynamically favorable to form stable or metastable local growth-frustrated domains. Beyond a limiting temperature T_{mi} or the corresponding concentration, the domain concentration increases with decreasing temperature or increasing concentration. In the melt, the domains persist with cooling into the supercooled fluid, obstructing crystallization, leading to a glass: a highly viscous noncrystalline system. In solutions, the direct analogy to supercooling is supersaturation. However, many polymer:solvent combinations are miscible in all proportions, so supersaturation does not arise. Nonetheless, with decreasing temperature or increasing polymer concentration, more and more domains form in solution, leading to a great increase in viscosity at elevated c.

The two following sections consider available information on the polymer slow mode and related phenomena, and compare with expectations based on domain formation models. First information is presented coherently sorted by source, so that readers can see when multiple phenomena were unambiguously seen by one laboratory at one time in one system. The paper then advances by comparing each predicted behavior against all data that tests that prediction.

What are the central predicted phenomena? Factors that enhance domain formation by creating favorable entropic or enthalpic terms, such as increasing the polymer concentration, reducing the temperature, or reducing the solvent quality, will enhance the amplitude of the slow mode. If the order parameter for the domains couples to the density, the onset of the slow mode will be correlated with changes in the static light scattering intensity. In light scattering spectra, at very small q domains are seen to diffuse, with a slow diffusive mode having $S(q,t)\sim q^2$. At larger q, domain relaxations have a characteristic length scale and time, leading to a nearly q-independent slow relaxation. Domain relaxations create the slowest mode, so the slowest relaxations of $S(q,t)$, the VH mode, and the viscoelastic $G(t)$ will have the same characteristic time. Fluctuations in the domain number may have ultraslow relaxations. To form domains, polymer coils might be obliged to interpenetrate substantially, requiring that the polymer concentration must exceed the polymer overlap concentration c^* before domain formation occurs.

III. THE POLYMER NONEXPONENTIAL MODE

There is an extensive literature on light scattering spectra of nondilute polymer solutions. The pre-1988 literature was largely obtained with linear correlators, which are not well-suited to studying spectra that have an extremely wide range of relaxation times. Also, much early work fit spectra to one or two pure exponentials; the outcome of fitting a nonexponential form to a simple exponential is ambiguous. The discussion here is largely restricted to more recent literature on spectra obtained with exponential-sampling correlators; however, earlier measurements found useful qualitative results. True gels such as the gelatin system studied by Ren *et al.* [17] are not considered here.

There were early disagreements as to whether the polymer slow mode represents a real phenomenon or a laboratory artifact, e.g., underfiltered dust or polymer polydispersity. There is now broad but not universal agreement that the dynamic structure factor $S(q,t)$ of some polymer solutions shows bimodal behavior at elevated concentrations. How may these modes be represented? In some papers, spectra are described as sums of groups of similar exponentials. In other papers, spectra are approximated as

$$S(q,t)=[A_1\exp(-\theta_1 t^{\beta})+A_2\exp(-\theta_2 t^{\beta'})]^2+B. \quad (2)$$

Here A_1 and A_2 are mode amplitudes, θ_1 and θ_2 are mode decay rates, β and β' are stretching parameters, and B is the spectral base line. The literature assigns several cognomens to these modes. The descriptors "sharp" and "broad" refer to single nonexponential modes. The sharp mode is typically nearly a pure exponential ($\beta \in 0.85$–1.0); the broad mode contains an extensive range of relaxation times (β typically 0.5 or less). The sharp mode, which often decays at shorter times than the broad mode, appears to be continuous with the single relaxation seen in dilute solution. The broad mode becomes apparent at elevated concentrations.

Modes may also be characterized as "fast" or "slow" by reference to an average decay time. A broad stretched exponential, expanded as a sum of exponentials, includes terms decaying at very short times. A description that focused on early time rather than average behavior of a nonexponential mode might identify a broader mode as faster—having some faster components—even though it had the longer average decay time.

There are a range of specific results. This is not a review paper; only details relevant to this paper are given.

Balloge and Tirrell [18] report static and dynamic light scattering from polymethylmethacrylate: methyl methacrylate using materials from several suppliers. M_w covered the range 60–703 kDa. Samples exhibiting a spectral broad mode also exhibit an anomalous enhancement of their static light scattering intensities. The apparent radii of gyration increase with increasing polymer concentration. For a 179 kDa poly-methylmethacrylate (PMMA), R_g increases from the few hundred angstroms of a single molecule to >2000 Å. Other samples exhibit at large c neither a broad mode nor elevated light scattering. Balloge and Tirrell did not determine why only some samples showed a broad mode. While highly monodisperse materials showed the broad mode, and extensively polydisperse samples showed only the sharp mode, mixtures of several highly monodisperse samples continued to show broad mode activity.

Brown and Stepanek [19] studied 2.95-MDa polystyrene:-ethylacetate over temperatures from $+70$ to $-45\,°\mathrm{C}$ at concentrations 2–72 g/l (from the overlap concentration c^* up to $42c^*$). At lower concentrations ($<4c^*$) spectra were nearly single exponential. For $c>4c^*$, careful decomposition of spectra (in which relaxations are seen over four or more orders of magnitude in time) into sums of exponentials identified fast, intermediate, and slow modes, the modes seemingly having about the same fractional widths in ln(t). The fast and slow modes scale as q^2. The intermediate mode has a nonzero $q \rightarrow 0$ intercept. The amplitudes of the two faster modes are relatively independent of q. The amplitude of the slowest mode increases sharply at small angle, consistent with this mode arising from domains that have a substantial spatial extent. At high temperature, the fast mode is dominant; as the temperature is reduced, first the slow and then the intermediate mode dominates. Brown and Stepanek inferred that the slow mode corresponds to transient domains of chains. Brown and Stepanek's observation that the slow modes are only seen at larger c is consistent with other work: Eisele and Burchard [20] (for 570-kDa polyvinylpyrrilidone in water and alcohol) and Balloge and Tirrell [18] both found that the broad mode only appears for $c>c^*$.

Nicolai *et al.* [21] report spectra of 1.28-, 3.8-, and 5.48-MDa polystyrenes in the good solvent cyclohexane. Spectra were analyzed with inverse Laplace transform methods leading to spectral descriptions in terms of groups of pure exponentials. In relatively dilute solutions, $S(q,t)$ is nearly a pure exponential with a q^2-dependent relaxation rate. Well into the semidilute concentration regime, a far more complex spectral structure is found: The fastest modes scale as q^2; the corresponding D is considerably faster than the D for the same chains obtained using classical gradient methods. Over a wide range of q, the slowest modes are nearly independent of q. However, at very small q the slowest mode goes to zero linearly in q^2. With increasing q, an increasing distribution of additional decays becomes apparent between the fastest and slowest relaxations. With increasing c, q and M being fixed, the fastest relaxations become faster, but the slowest relaxations slow dramatically. With increasing M, q and c being fixed, the fastest relaxations are unchanged, while the slowest relaxations slow substantially.

In a separate paper, Nicolai *et al.* [22] apply quasielastic light scattering and dynamic mechanical methods to study polystyrene (M_w in the range 0.83–8.42 MDa) in dioctyl phthalate (DOP) as a function of polymer concentration and temperature. DOP is a θ solvent at $22\,°\mathrm{C}$. Polymer concentrations were limited to $c>c^*$, c^* in Ref. [22] being the overlap concentration obtained from the radius of gyration R_g. Relaxation time distributions were calculated from $S(q,t)$ and from the dynamic modulus $G(t)$ [as determined from the storage and loss moduli $G'(\omega)$ and $G''(\omega)$]. For $S(q,t)$, the fastest mode had a q^2-dependent relaxation time, while slower modes were q independent. The longest significant relaxation time τ inferred from $S(q,t)$, and the longest relaxation time inferred entirely separately from $G(t)$ are very nearly the same over a ten fold range of polymer concentration and four orders of magnitude variation in τ. Lowering the temperature through the θ point greatly increases the amplitude in $S(q,t)$ of the polymer slow mode.

Brown and Stepanek [23] observed light scattering spectra of 4.9-MDa polystyrene in a series of θ solvents. $S(q,t)$ at fixed c in a series of θ solvents is independent of the relative density of the polymer and the solvent, the relative density being changed by varying the solvent. Spectra consistently show a fast relatively exponential decay and a broad decay largely relaxing at longer times. At higher temperatures the sharp mode is more important. The broad mode is dominant at lower temperatures. Brown and Stepanek observed the VH (depolarized) as well as the conventional VV spectrum, finding that the VH spectrum substantially relaxes on shorter time scales than the VV spectrum relaxes, but that the longest relaxation times of the VV and VH spectra are very nearly the same. Over a range of larger angles, the decay rate of the fast mode was q^2 dependent while the slow relaxations were very nearly independent of q.

Wang *et al.* [24] report spectra of 185- and 233-kDa polystyrene in diethylmalonate and diethylphthalate. Contrary to Brown and Stepanek [23], polystyrene:diethylmalonate spectra of Wang *et al.* show only a single sharp q^2-dependent mode. This work reached polymer concentrations up to 522 g/l, more than $18c^*$, without seeing a broad mode. Wang *et al.* [24] conclude, from the spectra of these nominally well-entangled solutions, that chain entanglements do not by themselves give rise to a polymer broad mode. However, when the same polystyrene sample was dissolved in diethylphthalate, Wang *et al.* observed two modes. Clearly, polydispersity or sample contamination can lead to a broad mode. Disparate results of Wang *et al.* in two solvents show that the broad mode is not due to polydispersity, because with a single polymer sample the mode can be made to appear or disappear by changing the solvent. Wang *et al.* propose that they disagree with Brown and Stepanek [23] because Brown and Stepanek's samples are polydisperse. However, the one literature study of polydispersity, due to Balloge and Tirrell [18], found the broad mode to be associated with the initially monodisperse samples, while the initially polydisperse samples did not show a broad mode, the inverse of the interpretation proposed by Wang *et al.* Polydispersity therefore does not appear likely to be responsible for the differences between Refs. [23] and [24]. The observed differences might instead reflect the nearly 20-fold difference in polymer molecular weight between the two studies.

Wang and Zhang [25] studied light scattering spectra of 2.88-MDa monodisperse polystyrene in diethylphthalate, finding distinct sharp ($\beta=0.99$) and broad ($\beta'=0.21$) modes. In this system, the mean relaxation rate $\Gamma_{sh}=\langle\tau\rangle^{-1}$ of the sharp mode scales as q^2. The corresponding mean relaxation rate Γ_{br} for the broad mode goes to zero at very small q, but is independent of q over a wide range of larger q. Γ_{sh} increases with concentration for c up to $10c^*$, and then levels off. No measurements were reported for $c<c^*$. The fraction of the spectral amplitude in the broad mode increases slowly with increasing concentration. In CCl_4 solutions, the same polymer sample [26] largely had the same spectral behavior. However, in Ref. [26] $S(q,t)$ was measured for $c \ll c^*$, finding that the fractional amplitude of the sharp mode rises toward unity, and conversely the slow mode fades away, as the polymer concentration is reduced toward zero.

Sun and Wang [27] examined 183-kDa polystyrene in the good solvent benzene, finding a mode structure very similar to that reported by Wang and Zhang [25] for polystyrene:diethylphthalate. Sun and Wang also examined spectra of 16.7-kDa polystyrene at a polymer weight fraction of 0.276. A broad mode appears in the spectrum, even though the 16.7 kDa is less than half the minimum molecular weight M_e for entanglement in this polymer, not to mention that the effective M_e was here extensively increased by the fourfold dilution from the melt. In benzene/diethylphthalate, Sun and Wang also found ultraslow spectral relaxations. The broad mode amplitude declined for up to five weeks after dissolving samples.

Stepanek and Brown [28] studied 2 kDa–20 MDa polystyrene:benzene, decomposing spectra into a sharp mode and no fewer than three broad mode components. Over a substantial range of M, relaxation times of the four modes were separated by one or more orders of magnitude. In addition to a q^2-dependent sharp mode, Stepanek identified (a) a broad ($\beta\in 0.4-0.8$) mode scaling as $q^0 M^{2.3}$, (b) a pure-exponential q^2-dependent mode, and (c) a very slow q^2-dependent mode. The modes were interpreted as arising, respectively, from (a) relaxation via reptation ($M^{2.3}$ being the molecular weight dependence expected for consistency with shear viscosity data [29]), (b) a diffusion mode characteristic of the distance between entanglement points, this distance containing a substantial number of polymer blobs, and (c) a mode characteristic of the diffusion of particulates with $R \approx 3R_g$.

Faraone *et al.* [30] studied 75–800 kDa PMMA:acetone and 35-kDa polyethylene oxide (PEO): water, at concentrations up to 20% and 30%, respectively. The PEO solutions show no broad mode, even at concentrations far above the overlap concentration. The broad mode amplitude of 75-kDa PMMA solutions increased dramatically between 15% and 20% concentration. Faraone *et al.* [30] found that their sharp mode was diffusive: $\langle\Gamma\rangle \sim q^2$ for $q^2 \in 2-11\times 10^{10}$ cm^{-2}. Their broad mode was nearly independent of q^2.

Ioan *et al.* [31] studied static and dynamic light scattering and rheology of 334-, 506-, and 2660-kDa dextrans in water for concentrations up to 65% w/v. Above 15% w/v, a pronounced slow mode appeared in $S(k,t)$, while Berry plots show that the static scattering intensity gains a low-angle peak. At approximately the same concentration, $d \ln \eta / d \ln c$ increased markedly, while above this concentration the storage modulus $G'(\omega)$ has a low-frequency plateau indicating the presence of a weak gel.

Phillies *et al.* [32] compared static and dynamic light scattering from 1-MDa hydroxypropylcellulose in water, $0 \leq c \leq 15$ g/l with scattering spectra of optical probes having diameters $14 \leq d \leq 282$ nm in the same solutions. They found that hydroxypropylcellulose: water gains a slow mode above a narrow concentration range centered at 6 g/l; there is no corresponding feature in the static light scattering intensity. A variety of spectral features suggest that the slow mode has a characteristic length scale in the range 50–70 nm, which is approximately the polymer's hydrodynamic radius.

IV. SLOW MODES AS REFLECTIONS OF INCIPIENT GLASSES

This section compares the predictions from Sec. II for glassy solutions with the observations of polymer properties given in Sec. III.

If the order parameter identifying the domains couples to the concentration, domain formation will create regions of particularly low or high particle concentration. Larger concentration fluctuations will scatter more light, the enhanced scattering amplitude being q dependent if the domains are sufficiently extended. Balloge and Tirrell [18] report that enhanced, q-dependent static scattering and polymer slow modes were either both present or both absent. Enhanced scattering and the broad mode thus have a common source. Scatterers had radii up to 2000 Å, far larger than single molecules, consistent with scatterers being chain domains. Similarly, Ioan *et al.* [31] found that enhanced static scattering and the slow mode appear at approximately the same concentration. On the other hand, Phillies *et al.* [32] found for hydroxypropylcellulose:water that the appearance of the slow mode is not correlated with a marked change in static scattering.

For sufficiently small q, the model implies that $S(q,t)$ has a mode reflecting domain center-of-mass motion. This mode is diffusive, so at small q its relaxation rate Γ_{br} scales as q^2, going to zero at low q. As predicted, Nicolai [21] and Wang and Zhang [24,25] find for the broad mode that $\Gamma_{br}\to 0$ at very small q. At large q, $S(q,t)$ will track domain internal modes. A frustration-limited domain has a fixed internal length scale ξ, leading to internal mode relaxation times determined by ξ, and thus to q-independent mode relaxation times. Indeed, over a wide range of larger q, Refs. [21–25] agree that the relaxation rate of the broad mode is nearly independent of q.

A more detailed mode decomposition by Brown and Stepanek [19,28] found within in their broad mode a slowest q^2-dependent group of relaxations and an intermediate mode that scaled as q^0. At low q, the very slow q^2-dependent mode had the larger amplitude, while at larger q the q^0 mode had the larger amplitude. The *dominant* broad mode relaxation thus scales as q^2 at small q and as q^0 at large q.

To form a region of high concentration in nondilute solution, the polymer coils would appear to need to interpenetrate. Substantial chain interpenetration and thus domain formation largely occurs above the overlap concentration c^*, suggesting that the broad mode should primarily be apparent for $c>c^*$. Consonantly, Eisele and Burchard [20] and Balloge and Tirrell [18] report that the polymer broad mode becomes visible at $c>c^*$, while Ioan, *et al.* [31] and Phillies *et al.* [32] agree that there is a cutoff concentration below which the slow mode is not visible. Wang *et al.* [24] measured mode amplitudes in polystyrene CCl_4, finding that the broad mode amplitude goes sharply to zero as $c\to 0$.

The model implies that, except at extremely small q, $S(q,t)$, the VH spectrum, and $G(t)$ have a common largest relaxation time τ_c, because the longest relaxation times arise from the same domain relaxations. There is no reason to expect that a mode contributes equally to $S(q,t)$, the VH spectrum, and $G(t)$: While their longest relaxation times are the same, the three relaxation spectra have different shapes. Brown and Stepanek [23] report, as predicted, that their VV and VH spectra have the same longest relaxation times. Nicolai *et al.* [22] show that $S(q,t)$ and $G(t)$ have the same longest relaxation time.

Kivelson *et al.* [1] note that the relaxation of the domain number density to equilibrium may be extremely slow. Relaxations in the number density of domains would be seen as a relaxation in the amplitude of the slow mode. Ultraslow relaxations of the polymer slow mode amplitude are indeed found: Sun and Wang [27] report that the broad mode amplitude relaxes to equilibrium over a five week period.

Within the model, the broad mode amplitude should be affected by variables that affect the number and size of the equilibrium domains in solution, notably solvent quality, temperature, and polymer concentration:

(a) Attractive interactions between chain segments are weaker in good solvents than in θ solvents, so domain formation should be less pronounced in good solvents than in θ solvents. In agreement with this predicted dependence on solvent quality, multiple observations [18–30] agree that the broad mode is weak or absent in good solvents and stronger in θ solvents.

(b) Domain formation and thus the broad mode amplitude should be more pronounced at lower temperatures. Nicolai *et al.* [21] and Brown and Stepanek [23] report an increase in the broad mode intensity at lower temperatures. Brown and Stepanek [19] found that the sharp mode dominates at high temperature. At lower temperatures first a broad q^2-dependent mode and then a q^0 mode dominates. This change in dominant mode is consistent with the increased importance of domains in solution at lower T. Domains or superdomains grow to their limiting size as T is reduced, so at fixed q, as domains become larger, internal, q-independent relaxations replace q^2-dependent center-of-mass motion as the dominant apparent relaxation.

(c) Domain formation should be enhanced at elevated concentrations. Indeed, Nicolai *et al.* [21] and Ioan *et al.* [31] found that the broad mode slows with increasing c or M. Wang, *et al.* [25] and Faraone *et al.* [30] found that the amplitude of the slow mode increases with increasing concentration.

In summary, a wide range of properties of the polymer broad mode (including the dependence of its amplitude and linewidth on scattering vector, polymer concentration, molecular weight, solvent quality, and temperature) indicate that the polymer broad mode arises from the presence in solution of equilibrium domains of polymer chains. Domain lifetimes inferred from VV and VH light scattering spectra match the viscoelastic terminal relaxation time, implying a direct correlation between the presence of the domains and the solution viscoelastic properties in these systems. The characteristics observed for polymer solutions that exhibit a slow mode are thus precisely the characteristics expected from the glass model of Kivelson *et al.* [1] as generalized to polymer solutions. However, the solutions considered here in general have viscosities well below those of true glasses, so we are discussing liquids, not glasses. Polymer solutions showing the polymer slow mode thus have properties consistent with their being exemplars of an *incipient* Kivelson glass whose viscosity has not yet diverged.

V. SUBSIDIARY ISSUES

In the original papers of Kivelson *et al.*, the frustrated domains were proposed to have dimensions in the range 1–5 nm. Domains of larger size (ca. 100 nm) are reported by Fischer, *et al.* [15], but these domains were treated by Ref. [1] as not being rheologically significant. Here we are discussing domains with sizes in the range 50–200 nm, but identifying them with 5-nm domains of Kivelson *et al.* and not their 200-nm domains. In understanding this identification, recall that the basic unit of length is size of the individual domain-forming molecules. In the discussion of Ref. [1], the individual molecules are a few tenths of a nanometer across, and the interesting domains are an order of magnitude larger. Here the basic unit is a polymer coil of size R_g, and the domains in some cases are only fivefold larger. The fundamental question is then not why the domains here are so large, but why they are so small *in natural units* relative to domains of Ref. [1]. A possible explanation is that polymer coils can interpenetrate, so an object having ten polymer coils from side to side has far less linear extent than the sum of ten polymer coils measured each in isolation.

Light scattering measurements do not prove that the domains are regions of elevated concentration. Domains would also scatter light if they were regions of unusually low concentration. While conditions that enhance the slow mode amplitude (e.g., θ solvent condition) are conditions that enhance chain attractions, data here do not resolve between (1) discontinuous local regions of high concentration embedded in regions of low concentration, (2) a continuous spongelike high concentration region, in which scatterers are embedded in low concentration globules, and (3) a bicontinuous mesh of small and large concentration regions.

I have not proposed a physical model for frustration in polymers. Indeed, Kivelson *et al.* [1] speculate that the properties of glass-forming fluids may arise from a length scale implicit to frustration and not from the actual formation of domains. However, for the model to be applicable there needs to be some physical effect that leads to frustration. How might domains of polymer chains be subject to frustration? Suppose domains contained relatively well-packed chains. Each domain is then surrounded by a corona of reentrant polymer loops present because chains leave the domain, and then reenter the domain or a neighboring domain. Entrant and reentrant loops are disordered, so they are less dense than the domain. If the mean length of well-packed chain between reentrance points is independent of the size of the domain, the number of reentrant loops increases linearly with the mass of chain in the domain (and hence with the domain's volume). The volume available at the domain's surface to accommodate the reentrant loops increases only in proportion to the surface area of the domain. There is then a square-cube law conflict. With increasing domain size reentrance becomes impossible because there is no more space in the corona for additional loops. Increases in domain size become energetically prohibitive. Frustration based on reentrant loop density provides a much softer constraint on maximum domain size than does frustration based on hard-core packing constraints. Correspondingly, the resistance of a polymer domain to growth is less than the resistance of geometrically frustrated near-hard-sphere domains to further growth. Indeed, some experimental data [21] support the interpretation that domains grow at elevated c.

The hypothesized importance of domain formation to polymer solution dynamics does not speak to the validity of reptatory, hydrodynamic, or other descriptions of polymer dynamics. Whether domains form or not, in concentrated solution chains might be constrained to diffuse largely parallel to their own contour, largely perpendicular to their own contour, or isotropically. If polymer solutions showing a slow mode become viscoelastic because they contain incipient Kivelson glasses, the viscoelastic behavior arises in the first instance from static properties, namely, domain formation. However, chain motions still control viscoelasticity: The domain lifetime giving the slow decay in $G(t)$ is determined by polymer dynamics. If the domains were to be relaxed by, e.g., reptation, then the reptation time and other reptation scaling properties would manifest themselves in the viscoelastic properties of the solution via the intermediation of the domains.

A picture of long chains passing alternately through ordered domains, in which chain motion is slow, and disordered regions, in which chain motion is rapid, is not novel. This picture is precisely the picture presented by any of the heavy-bead models of polymer melt dynamics. These models are examined in detail by Skolnick and Yaris [36], who show to the level of precision of the model that heavy-bead models correctly predict the standard phenomenology for polymer melt dynamics, including not only the molecular weight dependences of the self-diffusion coefficient D and the viscosity η, but also the crossover molecular weights for D and η, couplings between center-of-mass motion and internal coordinates, and single-bead correlation functions. The growth-frustrated domain model provides a critical physical enhancement of the heavy-bead models, namely, it provides a mechanism that makes some beads ''heavy'' and restricts their dynamics.

It appears that domain formation is in part controlled by variables that have not yet been identified. Balloge and Tirrell [18] compared polystyrenes from multiple suppliers. Under identical experimental conditions, only some samples show a broad spectral mode. Similarly, Brown and Stepanek [23] and Wang *et al.* [24] both studied polystyrene:diethylmalonate, disagreeing as to whether or not this system has a slow mode. Balloge and Tirrell's data are all from a single lab, using a common set of protocols and instruments. Repeatable sample-to-sample variations must therefore inhere in the material components, not the experimental methods. These data, however, tell us what is not responsible for the appearance of the slow mode, rather than finding which variables are responsible for the slow mode.

A previous paper [5] treated the polyelectrolyte ''extraordinary phase'' [6], which is a slow mode apparent in the light scattering spectra of nondilute polyelectrolyte solutions, especially at low-salt concentrations. Its properties match the properties expected for scattering from the ''clusters'' and ''clumps'' found by Mel'cuk *et al.* and Johnson *et al.* [7,8], in their simulations on supercooled two-dimensional Lennard-Jones systems. In particular, the slow mode of the polyelectrolyte extraordinary phase arises from translational diffusion of long-lived clumps.

However, the polyelectrolyte slow mode of Ref. [5] and the neutral polymer slow mode discussed here differ in major physical properties. The neutral polymer slow mode is independent of q except at very small q, as expected for scattering from domains in a Kivelson glass [1] in which relaxations are dominated by internal dynamics. In contrast, the polyelectrolyte slow mode linewidth Γ_s is linear in q^2, corresponding to diffusive cluster motion, over a full range of q^2.

Furthermore, the glasses of Refs. [7,8] and [1] differ substantially in the statisticomechanical control of their domain sizes and domain size distributions. In the glasses envisioned by Mel'cuk *et al.* and Johnson *et al.* [7,8], '' . . . the free energy . . . has many minima . . . the system remains trapped in a local free energy minimum . . . . The minimum the system chooses appears to depend on the quench history.'' [8]. In contrast, the domains in the frustration-limited glasses envisioned by Kivelson *et al.* [1] are equilibrium structures having characteristic sizes determined by competition between short-range intermolecular attractions and many-particle geometric frustration effects.

Experimentally, Sedlak [38–40] has shown that nanofiltration of polyelectrolyte solutions changes the domain size distribution, reducing *or increasing* the size of a typical domain, and that the altered distribution has no tendency even over very long times (years) to return to its previous form. From the prior paragraph, these are the properties expected for a cluster-forming glass [7,8], and not a frustration-limited glass. For solutions of neutral polymers, there does not appear to be a definitive study comparable to Sedlak's recent work. The systematic work of Streletzky *et al.*, culminating in Ref. [32] and references therein, identified through multiple paths a characteristic length scale in hydroxypropylcellulose:water; a well-defined length scale is a characteristic of a frustration-limited glass. While Ref. [32] did use multiple filter sizes, which were not identified as changing experimental outcomes, the work does not completely exclude the possibility that the effects seen by Sedlak [38–40] are encountered in hydroxypropylcellulose solutions.

An alternative set of models for the slow mode, recently reviewed by Candau [37], proposes that the mode arises from coupling of concentration fluctuations to fluctuations and relaxation of viscoelastic stress. This alternative model is supported by some of the primarily pre-1990 measurements largely not considered here. The viscoelastic coupling model seems to face several challenges, including the following.

(a) At very low q, when the diffusive relaxation time is longer than the hypothesized reptation tube-release time, the slow mode is predicted to disappear, contrary to data above indicating that the slow mode is more prominent at low scattering angle. Of course, one may always propose that at still lower q one finds the desired behavior.

(b) Specifying the polymer species, polymer molecular weight, and choice of solvent (and, hence, the solvent quality) appears within the viscoelastic model to determine the visibility of the mode, contrary to results of Balloge and Tirrell [18].

(c) Under the viscoelastic coupling model, polymers that are too short to entangle have no tubes—according to the tube models—from which they might escape, lack a prolonged viscoelastic plateau, and thus should exhibit no slow mode. However, Sun and Wang [27] find a slow mode in solutions of 16.7-kDa polystyrene. Contrariwise, Faraone *et al.* [30] found no slow mode in some extremely concentrated, large-molecular-weight polymer solutions that should have been substantially entangled.

(d) The polymer slow mode is not a universal behavior. Explanations of a nonuniversal slow mode in terms of a universal cause, such as solution viscoelasticity, are therefore intrinsically suspect.

Finally, the primary experimental rationale for interpreting the slow mode as arising from viscoelastic coupling is that $S(q,t)$ and $G(t)$, when both are observed in the same system, have the same longest relaxation time, suggesting that one phenomenon controls the other. The interpretation here in terms of the Kivelson glass model reverses this rationale by making the relationship between the longest relaxation times of $S(q,t)$ and $G(t)$ concomitant rather than causal. The longest relaxation times of $S(q,t)$ and $G(t)$ both arise from the structural relaxation time of the domains, and are therefore equal to each other because they have a common external cause. An interpretation of the slow mode as arising from the terminal viscoelastic relaxation is thus not necessary as well as is inconsistent with some data.

The glass temperature refers to a property of the solvent-free solid. The systems here are mostly solvent with modest amounts of added polymer. There are experimental data on the significance of a glass temperature for solvent:polymer systems, notably the temperature and concentration dependence of the diffusion of mesoscopic probes through low-molecular-weight neutralized polyacrylic acid [33], intermediate molecular weight polyacrylic acid [34], and high-molecular-weight dextrans [35]. The temperature dependence of the probe diffusion coefficient D_p is determined by the temperature dependence of the solvent viscosity η_o. Once the temperature dependence of η_o is removed from D_p, there was no residual temperature dependence of D_p available for reduction to a glass temperature. These results are perhaps unsurprising, because most of the mass of each system is solvent, not polymer. References [33–35] suggest that reduction of data here relative to some glass temperature would not have a dramatic outcome.

Finally, the glass model makes a different prediction as to the correlation between light scattering and viscosity. There is a lowest concentration c_t at which domains form. Within the model, the polymer slow mode is only apparent for $c > c_t$. At larger concentrations, the number density of domains increases. The domains make a contribution to the solution viscosity, but only for $c > c_t$. At lower concentrations, there are no domains. Therefore, a treatment of the viscosity, made for $c < c_t$, would not include domains. Extrapolation of such a treatment to larger concentrations would break down at $c = c_t$. A difference between the actual and extrapolated viscosities should therefore begin at the concentration at which the slow optical mode first becomes apparent, and should increase as concentration is further increased. In exact analogy to the natural temperature variable $T - T_{mi}$ found by Kivelson *et al.* [1] to be significant for glass formation in pure liquids, for solutions the natural concentration variable should be $c - c_t$.

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