

# Applicability of the Generalized Stokes–Einstein Equation of Mode-Coupling Theory to Near-Critical Polyelectrolyte Complex Solutions

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Cite This: *ACS Macro Lett.* 2023, 12, 288–294



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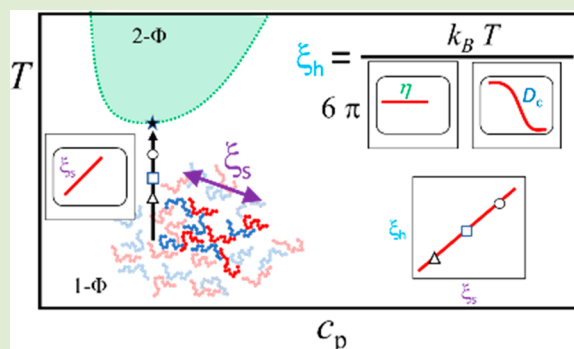


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Supporting Information

**ABSTRACT:** We examine whether the mode-coupling theory of Kawasaki and Ferrell (KF) [Kawasaki, K. *Kinetic Equations and Time Correlation Functions of Critical Fluctuations*. *Ann. Phys.* 1970, 61 (1), 1–56; Ferrell, R. A. *Decoupled-Mode Dynamical Scaling Theory of the Binary-Liquid Phase Transition*. *Phys. Rev. Lett.* 1970, 24 (21), 1169–1172] can describe dynamic light scattering (DLS) measurements of the dynamic structure factor of near-critical polyelectrolyte complex (PC) solutions that have been previously shown to exhibit a theoretically unanticipated lower critical solution temperature type phase behavior, i.e., phase separation upon heating, and a conventional pattern of static critical properties (low angle scattering intensity and static correlation,  $\xi_s$ ) as a function of reduced temperature. Good qualitative accord is observed between our DLS measurements and the KF theory. In particular, we observe that the collective diffusion coefficient  $D_c$  of the PC solutions obeys the generalized Stokes–Einstein equation (GSE),  $D_c = k_B T / 6\pi\eta\xi_s$ , where  $\xi_s$  is specified from our previous measurements and where  $\eta$  is measured by capillary rheometry under the same thermodynamic conditions as in our previous study of these solutions, allowing for a no-free-parameter test of the GSE. We also find that even the wavevector ( $q$ )-dependent collective diffusion coefficient  $D_c(q)$ , measured by varying the scattering angle in the DLS measurements over a large range, is also well-described by the mean-field version of the KF theory. We find it remarkable that the KF theory provides such a robust description of collective diffusion in these complex charged polyelectrolyte blends under near-critical conditions given that charge fluctuations and association of the polymers might be expected to lead to physical complications that would invalidate the standard model of uncharged fluid mixtures.



Dynamic light scattering has proven to be a powerful characterization technique for studying large scale composition fluctuations that are inherent to fluid mixtures near their critical point for phase separation, and the dynamic theory of critical phenomena of Kawasaki and Ferrell (KF)<sup>1,2</sup> provides a useful framework for analyzing this type of data with predictions verified for relatively simple phase separating liquids.<sup>3–5</sup> Douglas has given an accessible review of some of the essential predictions of the theory of dynamic critical phenomena as it applies to phase separating mixtures.<sup>6</sup> The application of this theory to measurements of phase separating polymer solutions has also demonstrated an appreciable agreement, but some new features emerged in these solutions that are apparently associated with the viscoelastic nature of these solutions when the polymer molecular mass becomes very large.<sup>7–9</sup> Aqueous polymer blends of polyelectrolytes having an opposite charge sign can form soluble associates or complexes of greatly reduced net charge in the one-phase region.<sup>10,11</sup> In current parlance, when such solutions have macrophase separated, the polymer-rich component has been termed a complex coacervate and the solvent-rich phase has been termed the supernatant.<sup>12</sup> These charged polymer blend solutions in the one-phase region are often distinguished from

their phase separated counterparts and these solutions are often called polyelectrolyte complex (PC) solutions, based on the presumption that the polymers have formed unspecified charge-neutral complexes (ion pairs) in the one-phase region.<sup>13</sup> This terminology implicitly suggests that polyelectrolyte complexes can be somewhat akin to polyzwitterion polymer solutions, charged polymers containing an equal amount of charges having opposite sign. If we take this heuristic picture literally, we might then expect PC solutions to exhibit both the static and dynamic critical phenomena similar to uncharged fluid mixtures, dramatically simplifying their analysis and characterization. Of course, this simplistic view of PC solutions remains to be tested experimentally.

While most previous experimental studies of PC solutions have emphasized the influence of salt on the phase boundaries,

**Received:** November 4, 2022

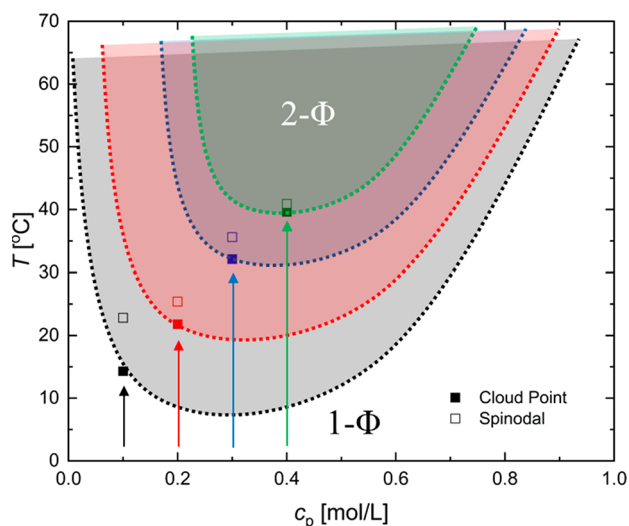
**Accepted:** February 6, 2023

**Published:** February 10, 2023



our group recently found the unanticipated result that these charged polymer blends can also exhibit phase separation upon heating or a lower critical solution temperature type phase behavior,<sup>14,15</sup> as found in many other types of water-soluble polymers.<sup>16,17</sup> Many aspects of the phase behavior of this important class of charged blend solutions remain to be studied, and the present work is an initial study of the critical dynamics of these complex solutions. Given the growing interest in phase separation in solutions forming PCs in connection with the formation of complex biological structures and in association with diverse disease states when these structures do not form or function as required, and in emulating these materials in synthetic biocompatible materials of medical and materials science interest,<sup>18</sup> we note that a better understanding of the dynamics of these solutions is clearly a topic of broad fundamental and practical interest.

Our previous work established the temperature ( $T$ )-dependent phase diagram and static critical behavior of the PC solutions. In Figure 1, we schematically illustrate the



**Figure 1.** Schematic of the pseudobinary lower critical solution phase boundary for different initial polymer concentrations at fixed total salt concentration. The cloud point from laser transmittance measurements and spinodal points from static laser light scattering are shown from ref 15. The dashed lines marking the phase boundary between the one-phase ( $1 - \Phi$ ) and shaded two-phase ( $2 - \Phi$ ) regions are projections of the  $T - c_s - c_p$  phase envelope and added as a visual aid.

binodal at a fixed total salt concentration ( $c_s$ ) of our PC solution where  $c_p$  is the polymer concentration. The details of the static critical behavior of this PC near-critical mixture are described elsewhere<sup>15</sup> with the  $T - c_p - c_s$  phase surface consistent with the liquid state theory by Ylitalo and Wang.<sup>19</sup> We note that both the static correlation length  $\xi_s$  and the scattering intensity at zero angle  $I(0)$  measured by static light scattering diverge upon approaching the phase boundary in the one-phase region and the critical properties were quantified within the standard critical phenomena framework. The present note focused on the dynamic critical behavior of these solutions.

The present Letter applies a relatively standard theory of dynamic critical phenomena as a tentative framework for analyzing DLS observations on the same PC solutions in the one-phase region and near the phase boundary determined in our previous study. We admit at the outset that these are

multicomponent mixtures and that the polymer chains are polydisperse, and, moreover, we assume that these complex mixtures can be described approximately as pseudobinary mixtures. This type of approximation has many precedents. Previous studies of mixtures of charged surfactant molecules<sup>20</sup> and polymer blends<sup>21–23</sup> and uncharged polymer blends dissolved in organic solvents<sup>24,25</sup> have indicated that the standard theory of dynamic critical phenomena and the pseudobinary approximation together provide a reasonable description of multicomponent mixtures near their critical point, and we find that the same situation appears to hold for our near-critical PC solutions. Based on these assumptions, we utilize the dynamic theory of KF as the framework over a range of  $c_p$  and  $T$  in which composition fluctuations associated with incipient phase separation are appreciable.

The basic observable in DLS measurements on solution mixtures near their critical point is the decay rate  $\Gamma(q)$  of spontaneous composition fluctuations, a quantity that depends on the observational scale (scattering wavevector,  $q$  ( $q = (4\pi n/\lambda) \sin(\theta/2)$ ) determined by the scattering angle ( $\theta$ ), the refractive index of the solvent ( $n$ ), and the wavelength ( $\lambda$ ) of the incident light in vacuum) probed by the light scattered from the solution. Guenoun et al. have directly visualized critical fluctuations in a model critical mixture near its critical point,<sup>26</sup> which has provided qualitative insight into the origin and physical nature of composition fluctuations in critical fluid mixtures. At large length scales or low scattering wavevector  $q$ , the KF framework predicts that the relaxation of dynamic composition fluctuations in solution should occur as a diffusive process with a corresponding collective diffusion coefficient,  $D_c$  defined by  $\Gamma(q)/q^2$  in the limit of low  $q$  where  $\Gamma(q)$  defines the rate of the relaxation process. The KF theoretical framework<sup>1,2</sup> also predicts that the effective  $D_c$  depends on  $q$  at high  $q$  because of the constrained motion of the molecules in the dynamic domains rich in one or the other solvent, a phenomenon that is also observed in DLS measurements in polymer solutions in good solvents at high  $q$  because of the evident constrained motion of the polymer segments in the polymer chains.<sup>27–30</sup> In both of these systems, hydrodynamic interactions play a key role in the high  $q$  scaling of  $\Gamma(q)$ , which in the mean-field KF mode-coupling theory scales as  $\Gamma(q) \sim q^3$  in both near-critical<sup>1,2</sup> and polymer solutions in good and marginal solvents employing the same type of mean-field approximation.<sup>27–31</sup> The form of KF theory normally discussed, and considered below as a framework for analyzing our DLS data, is a dynamical mean-field variant of KF theory in the sense that fluctuation effects derived from the coupling between concentration and momentum fluctuations are neglected in this theory. These fluctuation effects, which lead to a divergence of the viscosity extremely near the critical point, are distinct from the critical fluctuation effects found in the static critical behavior that give rise to changes in the overall shape of the phase boundary, and in the static critical exponents describing the scattering properties of near-critical fluids from their mean-field values. Importantly, these fluctuation effects have *no detectable effect* on the generalized Stokes–Einstein equation (GSE) between the collective diffusion coefficient  $D_c$  and the static correlation length  $\xi_s$  measured previously<sup>15</sup> and independent measurements of the *observed* solution viscosity  $\eta$ , whose determination is described in the [Supporting Information \(SI\)](#).

The KF theory for the dynamic structure factor of near-critical mixtures makes precise predictions for the contribution

of critical fluctuations to  $D_c$  in terms of the static correlation length of solution  $\xi_s$  and the viscosity  $\eta$  of the solution. In particular, the contribution to  $D_c$  arising from composition fluctuations is predicted to follow a GSE in a mean-field approximation<sup>1,2</sup>

$$D_c = \lim_{q \rightarrow 0} \Gamma(q)/q^2 = k_B T / 6\pi\eta\xi_s \quad (1)$$

where  $\Gamma(q)$  is the decay rate from the dynamic structure factor and  $\xi_s$  formally replaces the particle size parameter in the corresponding well-known Stokes–Einstein equation describing the diffusion of a particle at infinite dilution. Note that the viscosity  $\eta$  in eq 1 is the shear viscosity of the polymer solution, a quantity that depends appreciably on the solute composition, salt concentration, and temperature. Viscoelastic effects in near-critical high molecular mass polymer solutions can apparently give rise to the significant deviations from the predictions of the KF mode-coupling theory such as the emergence of additional relaxation modes in the dynamic structure factor observed by Kostko et al.<sup>9</sup> that are not encompassed by the KF theory and by an interesting progressive suppression of the viscosity anomaly with increasing polymer mass noted by Tanaka et al.<sup>32</sup> when the solutions are in the entangled dynamics regime. Given that we have thoroughly studied  $\xi_s$  in our former work,<sup>15</sup> all we require to test the GSE for our PC solutions is the experimental determination of  $\eta$ . Measurements of  $\eta$  were made using a specially developed temperature-controlled small-volume pressure-control mode capillary rheometer. Salient details relating to the apparatus, experimental protocol, and the measurements themselves are described in the SI.

Since the static correlation length  $\xi_s$  plays an important role in our test of whether the GSE describes our near-critical PC solutions, we briefly describe the physical significance of this property, and how we estimated it experimentally in our previous work.  $\xi_s$  describes the average size of the composition fluctuations that generally arise in fluid mixtures upon approaching their phase boundaries, and  $\xi_s$  for near-critical mixtures can rather generally be estimated from the Ornstein–Zernike relation for the static structure factor  $S(q)$ ,<sup>34</sup>

$$S(q) = S(q=0) / [1 + (q\xi_s)^2] \quad (2)$$

$S(q)$  is proportional to the excess scattering intensity at zero angle,  $I(0)$ . Notably,  $S(q=0)$  in the long wavelength limit ( $q \rightarrow 0^+$ ) is directly related to the solution osmotic compressibility.<sup>34</sup> Again, it should be admitted that this mean-field expression for  $S(q)$  under near-critical conditions is not exact, but this simplified expression for  $S(q)$  is sufficient for most static critical phenomena studies, as the corrections to this expression are rather small.<sup>35</sup> We next check whether the GSE is consistent with our DLS measurements on near-critical PC solutions.

Our model polyelectrolyte blend solution involves two synthetic strong polyelectrolytes—potassium poly(styrenesulfonate) (KPSS) and poly(diallyldimethylammonium) bromide (PDADMAB)—which are dissolved with charge stoichiometry in aqueous solutions with KBr as the added salt. The polyelectrolytes were prepared and purified as described previously<sup>15</sup> where KPSS had  $M_w = 196$  kg/mol with  $\bar{D} = 2.8$  and PDADMAB had  $M_w = 60$  kg/mol with  $\bar{D} = 2.8$  relative to poly(2-vinylpyridine) standards, where  $M_w$  is the relative mass-average molecular mass and  $\bar{D}$  is the polydispersity. Since the polyelectrolyte counterions and

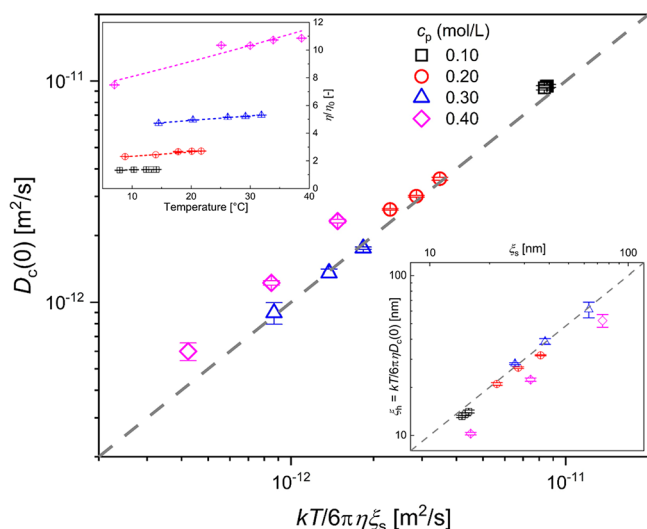
added salt ions are indistinguishable, we define the total salt concentration ( $c_s$ ) by the added KBr ( $c_{s,\text{add}}$ ) and the counterions introduced by the two polyelectrolytes, such that  $c_s = c_{s,\text{add}} + c_p/2$ . We study  $c_p$  values from 0.10 to 0.40 mol/L at fixed  $c_s = 1.80$  mol/L throughout using the spinodal and cloud point phase boundary data and static scattering properties determined previously.<sup>15</sup> Figure 1 shows a schematic of the phase boundary for the cloud point and spinodal points that are approached by DLS upon heating, as performed on a modified Brookhaven BI-200SM spectrometer equipped with a 532 nm wavelength laser (Coherent VERDI) and a digital autocorrelator (Brookhaven TurboCorr), functioning under the vv-polarization mode. The autocorrelated scattered intensity as a function of delay time ( $\tau$ ) was converted to the baseline-normalized second-order autocorrelation function  $g_2(q, \tau)$  and then the first-order correlation function,  $g_1(q, \tau)$ , through the Siegert relation,  $g_2(q, \tau) = 1 + \alpha|g_1(q, \tau)|^2$ , where  $\alpha$  is the coherence factor and  $q = (4\pi n/\lambda) \sin(\theta/2)$  is the scattering vector at the scattering angle  $\theta$ .<sup>36</sup> In this study, all  $g_1(q, \tau)$  up to  $c_p = 0.40$  mol/L displayed a single decay mode; therefore, they were fit to the stretched exponential function

$$g_1(q, \tau) = A \exp[-(\Gamma(q)\tau)^\beta] \quad (3)$$

where the amplitude parameter ( $A$ ) was found to be in the range from 0.7 to 0.8 and the stretched exponent,  $\beta$ , of the relaxation function was found to range between 0.78 and 0.93 (Figure S1). The KF theory<sup>1,2</sup> predicts that  $\beta = 1$ , but a variable value of  $\beta$  is often observed in experimental studies of complex fluids. The fitted values of both  $A$  and  $\beta$  were found to be insensitive to  $q$  in our measurements.

We next estimate  $D_c = D_c(q=0)$  by plotting of  $\Gamma(q)$  versus  $q^2$  where  $D_c$  is identified with the slope at low  $q$  (Figure S1, inset). Deviations of  $\Gamma(q)$  from a linear scaling with  $q^2$  at large  $q$  were also observed as functions of concentration and temperature. These observations are a consequence of the large fluctuations in these mixtures. Having estimated  $D_c$ , we are now able to test the GSE.

Figure 2 shows a comparison of our  $D_c$  estimates with the GSE,  $D_c = k_B T / 6\pi\eta\xi_s$  for four polymer concentrations  $c_p$  and for a range of experimental  $T$ . The abscissa in the main figure includes independent data sets of  $\xi_s$  and  $\eta$ . The relative ( $\eta/\eta_0$ ) solution viscosity (upper inset) at the requisite  $T$  where  $\eta_0$  is the solvent viscosity includes the effect of added salt. The prediction of the GSE is shown in the figure as the dashed line. From a survey of a broad range of experimental conditions involving variable  $T$  and  $c_p$ , we conclude that the GSE is consistent with our experimental observations to within the uncertainty in these measurements. We note that we do not observe a rapid increase in viscosity consistent with a divergence in the vicinity of the critical temperature, as often reported for critical fluid mixtures, but the observation of this type of viscosity anomaly is known to require a highly precise temperature control and a careful treatment of shear thinning effects and other complications that accompany this phenomenon.<sup>33</sup> Under these experimental conditions where the temperature differs from the critical temperature by several degrees, the solutions are always Newtonian. The relative viscosity does increase as the temperature approaches the critical temperature. More careful measurement close to the critical point<sup>15</sup> would be useful in the future. The lower inset shows the relationship between the magnitude of the static correlation length  $\xi_s$  and the dynamic correlation length  $\xi_h$



**Figure 2.** Test of GSE for a model polyelectrolyte complex solution where observations are made over a wide range of temperatures and polymer concentrations. The top inset of relative ( $\eta/\eta_0$ ) solution viscosity was obtained by capillary viscometry with the dashed lines as a guide to the eye. The bottom inset shows the proportionality of the dynamic correlation length versus static correlation length as derived from the inverse relation of eq 1 as an alternative presentation. Uncertainties (error bars) are estimated by one standard deviation from the fits and may be smaller than the symbols.

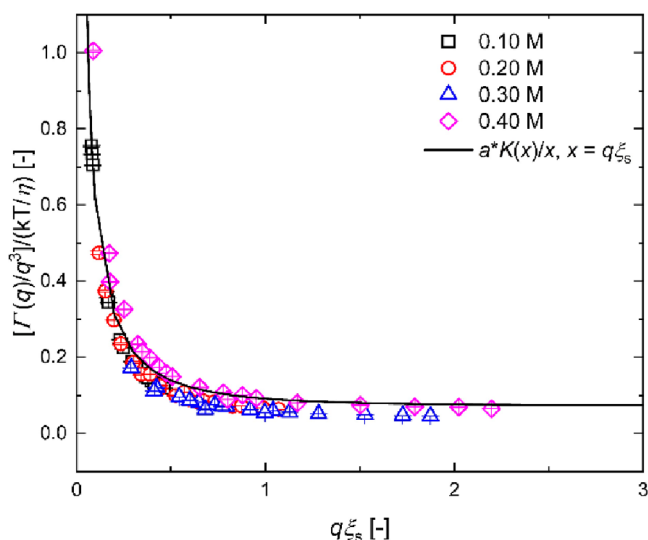
inferred from the GSE. A proportionality between these quantities (dashed line) is required by the KF theory.

We next consider the more stringent test of the KF theory for the wavevector dependence of  $\Gamma(q)$ . The KF theory<sup>1,2</sup> in its mean-field theory form predicts an approximate form of the crossover expression for  $\Gamma(q)$  in the absence of the correction for the near-critical viscosity anomaly:

$$\begin{aligned}\Gamma(q) &= q^2 D_c(0) K(x) \\ &= q^2 D_c(0) \cdot \frac{3}{4x^2} [1 + x^2 + (x^3 - x^{-1}) \arctan x]\end{aligned}\quad (4)$$

where  $x = q\xi_s$ . We then see that  $\Gamma(q)$  reduces to  $q^2 D_c(0)$  in the long wavelength limit  $x \ll 1$  and to  $(3\pi/8)q^3 \xi_s^3 (k_B T / 6\pi\eta\xi_s) = q^3 (k_B T / 16\eta) \sim q^3$  at large  $q$ , i.e.,  $x \gg 1$ , corresponding to spatial scales smaller than  $\xi_s$ . Incorporating the same type of fluctuation effect that causes the shear viscosity to diverge at the critical point leads to a slight change<sup>1,5</sup> of the high- $q$  scaling exponent for  $\Gamma(q)$  to a value of about 3.069 (ref 37), but this correction term is normally neglected in studies of dynamic critical phenomena because of its relatively small size and the lack of any exact closed functional form to describe this type of correction for general  $q$ . Burstyn et al.<sup>5</sup> have described a simple interpolation function replacing  $K(q)$  in eq 4 that addresses these small corrections to the mean-field version of KF theory, but we feel that the uncertainties of our measurements do not justify such refinement. Moreover, the use of the Ornstein–Zernike approximation to approximately describe the static scattering intensity in eq 2 involves a similar approximation<sup>35</sup> so that the use of the mean-field KF theory is theoretically consistent with our modeling of the static scattering.

Figure 3 shows the reduced decay rate,  $[\Gamma(q)/q^3]/(k_B T/\eta)$ , as a function of the reduced wavevector,  $x = q\xi_s$ . Based on eq 4, the reduced decay rate should be proportional to  $K(x)/x$  in the entire  $q$  range following  $[\Gamma(q)/q^3]/(k_B T/\eta) = (k_B T / 6\pi\eta\xi_s) \times$



**Figure 3.** Reduced decay rate  $[\Gamma(q)/q^3]/(k_B T/\eta)$  as a function of  $q\xi_s$ . The solid line represents the best fit to  $aK(x)/x$ , where the prefactor parameter  $a$  is the only fitting parameter and  $K(x)$  is the Kawasaki function.<sup>1,2</sup> Note that the mean deviation from mean-field KF theory is approximately 10%, whereas the relative viscosity is a factor as large as 1100%. Uncertainties (error bars) are estimated by one standard deviation from the fits and propagated and may be smaller than the symbols.

$[K(x)/q]/(k_B T/\eta) = K(x)/6\pi x$ . All the data points for the reduced relaxation rate form a master curve that is consistent to within experimental uncertainty with the transition from a low- $q$  and high- $q$  scaling,  $\Gamma \sim q^2$  and  $\Gamma \sim q^3$ , respectively. Considerable superposition is achieved for all data points across four different  $c_p$  and several  $T$ , and regardless of the proximity to the critical polymer concentration (0.43 M<sup>15</sup>), giving a near universal plateau value of  $0.061 \pm 0.001$ . This asymptote estimate is reasonably close to the mean-field KF theory prediction,  $1/6\pi \approx 0.053$ , where  $\pm$  denotes one standard deviation of the estimated prefactor from our fits. We note the change in the shear viscosity of the polymer solution  $\eta$  relative to the pure solvent  $\eta_0$  under the same thermodynamic conditions ranging from 10% up to 1100%, indicating the importance of the solution viscosity  $\eta$  in achieving the observed near universal curve.

In summary, these measurements of the off-critical and near-critical dynamics of a series of phase-separating KPSS–PDADMAB complex solutions using DLS indicates only one relaxation mode up to 0.40 mol/L of polyelectrolyte complex, which is associated with the large-scale composition fluctuations near phase separation, as previously confirmed by separate static light scattering measurements where only an  $\approx 8\%$  difference in light scattering contrast<sup>15</sup> ( $dn/dc_p$ ) was present between polyelectrolytes. A proportionality of the static and dynamic correlation lengths is predicted by the GSE with the solution viscosity  $\eta$  rather than the solvent viscosity. A crossover from a  $\Gamma \sim q^2$  to a  $\Gamma \sim q^3$  scaling was also observed where  $\Gamma(q)/q^3$  normalized by  $(k_B T/\eta)$  can be described by a universal curve of reduced wavevector  $q\xi_s$  that is well described by mean-field KF theory.<sup>1,2</sup>

Although our experimental findings on the dynamics of the total concentration fluctuations in a model near-critical PC solution are seemingly in good accord with the mean-field Kawasaki–Ferrell mode-coupling theory of critical dynamics, additional fluctuation effects associated with charge fluctua-

tions are clearly a possibility that should be considered in the future. For example, Muthukumar has recently discussed this type of charge-based mode-coupling effect in polyelectrolyte solutions where additional relaxation modes were predicted and observed experimentally.<sup>38,39</sup> It is currently not clear whether these charge fluctuation effects are generally suppressed by neutralization accompanying polymer complexation in our case, which gives added interest for the present observations. The formation of soluble ion pairs via interpolyelectrolyte neutralization in dilute solution was observed by isothermal titration calorimetry<sup>40–43</sup> and in the dilute phase after phase separation with vanishingly small free polyelectrolytes by simulation.<sup>44</sup> Moreover, additional relaxation processes are conceivable from the presence of ion–dipole, dipole–dipole, and multipole interactions that can arise when oppositely charged chain segments form complexes.<sup>45,46</sup> The DLS study by Kostko et al.<sup>9</sup> found that the viscoelasticity of high molecular mass polymer solutions led to observed deviations from the KF theory in near-critical solutions of this kind. We anticipate that solution viscoelasticity might likewise be a complication in PC solutions in which supramolecular assembly becomes prevalent or in cases in which the polymer molecular mass is similarly very high so that entanglement effects become important, as in the work of Kostko et al.<sup>9</sup> and Tanaka et al.<sup>32</sup>

In our previous paper quantifying the static critical behavior of our PC solution, we observed nonclassical static critical indices ( $c_p = 0.40$  mol/L,  $\nu_{\text{eff}} = 0.79 \pm 0.06$ )<sup>15</sup> for the static correlation length, consistent with the Ising model estimate with an enhancement in magnitude due to Fisher renormalization.<sup>47</sup> Such behavior is common in multicomponent and molecularly polydisperse fluids including ternary solvent mixtures,<sup>48,49</sup> polydisperse polymer solutions,<sup>50</sup> and diluted neutral critical polymer blends,<sup>24</sup> rather than ionic fluid mixtures or strongly associating fluids, where the long-range interactions or the presence of large-scale supramolecular assemblies<sup>51</sup> might also be expected to greatly diminish the reduced temperature range over which non-mean-field fluctuation effects are observed. In ionic fluids, this suppression of non-mean-field fluctuation is naturally expected to be larger than that in fluids having a lower dielectric constant because the range of the charge interaction is longer in such fluids.<sup>52–57</sup> This same type of effect is often invoked to rationalize the relatively narrow reduced temperature width of the critical region of neutral polymer blends in comparison to small molecule mixtures.<sup>58–60</sup> In our near-critical fluid mixture, non-mean-field fluctuation effects are clearly *enhanced* rather than suppressed in magnitude, as commonly found in neutral nonassociating near-critical fluid mixtures. The physical reason why our polyelectrolyte solutions conform to such a simple dynamic critical behavior seems to be far from obvious, and there is evidently a need to study other PC solutions to ascertain the generality of our observations.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00647>.

Dynamic light scattering and capillary viscometer measurement methods and data are summarized, and estimates of the overlap concentration are provided (PDF)

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### Notes

The authors declare no competing financial interest.

Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply the materials are necessarily the best available for the purpose.

The symbol M used to represent mol/L is not in SI units but was used to adhere to the conventions of the Journal.

## ■ ACKNOWLEDGMENTS

We acknowledge partial support from the National Institute of Standards and Technology Materials Genome Initiative.

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