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Colored noise in the dynamics of aqueous protein solutions

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We show that the experimental results on the concentration fluctuations in aqueous solutions of bovine eye lens protein γ_{II}-crystallin along the critical isochore, obtained by Fine *et al.* [Phys. Rev. Lett. **74**, 198 (1994)] using quasielastic light scattering, can be explained using our recently proposed theory on the dynamics of polymer solutions with spatiotemporal correlated noise. This theory is characterized by two parameters λ and τ, which are the correlation length and correlation time, respectively, of the colored noise. Our theory gives the nonexponential decay in the time autocorrelation function observed in experiment. Fitting the averaged experimental decay rate of Fine to our theory, we predict the solution viscosity and τ to be about 0.05N s/m^2 and 0.02–0.05 s, respectively, and it is independent of the correlation length parameter λ.

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An aqueous protein solution is a binary mixture of large protein molecules and small water molecules. The static critical behaviors of such solutions have been established experimentally [1–3] to be that of a three-dimensional system with short-range interactions and scalar order parameters. The dynamic critical behaviors of such solutions have not been so thoroughly investigated experimentally. The only previous work was that of Ishimoto and Tanaka [4], who made quasielastic light scattering (QLS) measurements at a single fixed wave number of the fluctuations of lysozyme along the critical isochore. Recently, Fine *et al.* [5] carried out QLS measurements to characterize concentration fluctuations in aqueous solutions of bovine eye lens protein γ_{II}-crystallin along the critical isochore. This was a significant experimental advance over the work of Ishimoto and Tanaka in that many different wave numbers were used and the temperatures were much closer to the critical temperature. This more thorough investigation of the critical dynamics revealed new and unexpected behavior. Specifically, they found that the dynamic structure function exhibited a significant deviation from exponential decay. Moreover, they found that the wave number and temperature dependence of the average rate of decay of the concentration fluctuations were consistent with the theory for critical dynamics in binary liquid mixtures [6] only if they allowed both the background viscosity and the background contribution to the decay rate to be unusually large. In fact, the background viscosity had to be assumed to be 300 to 500 times that of water.

The purpose of this paper is to show that the experimental results of Fine *et al.* can be readily explained within the framework of our recently proposed theory [7] for the critical dynamic of polymer solutions with spatiotemporal correlated, or colored, noise. The solution viscosity predicted by our theory is an order of magnitude smaller than that predicted by the Kawasaki theory for critical dynamics in binary liquid mixtures [6].

In this theory, the dynamic structure function $g(\mathbf{k},t)$ of a polymer solution has the form

$$g(\mathbf{k},t)=g(k)\frac{(1+\lambda^2k^2)e^{-\Gamma_k t}-\tau\Gamma_k e^{-(1+\lambda^2k^2)t/\tau}}{1+\lambda^2k^2-\tau\Gamma_k}\ , \tag{1}$$

where $g(k)$ is the static structure function, and λ and τ are the correlation length and correlation time, respectively, of the colored noise. The decay rate Γ_k has the form

$$\Gamma_k=\frac{k_BT}{6\pi\eta_s\xi}k^2F(k\xi)\ . \tag{2}$$

Here k_B is the Boltzman constant, k is the wave number, and η_s is the viscosity of the solution. ξ is the correlation length of the protein and is taken to be of the form $\xi=\xi_0[(T-T_c)/T_c]^{-0.61}$, with $\xi_0=7$ Å and the critical temperature $T_c=2.057\pm0.005\,^\circ\text{C}$ [3,5]. The function $F(x)$ has the form [7,8]

$$F(x)=\tfrac{3}{4}\frac{1+x^2}{x^3}[x+(x^2-1)\ \arctan\,(x)]\ . \tag{3}$$

For the case of white noise, λ and τ equal zero, and we have a single exponential decay [8]

$$g(\mathbf{k},t)=g(k)\exp(-\Gamma_k t)\ . \tag{4}$$

The experimental data of Fine *et al.* [5] exhibited nonexponential decay of the dynamic structure function, characterized by a distribution of decay rates $G(\Gamma_i)$, so that $g(\mathbf{k},t)=g(k)\sum_i G(\Gamma_i)e^{-\Gamma_i t}$. Fine *et al.* estimated the distribution $G(\Gamma_i)$ by using a constrained regularization algorithm [9]. From this distribution they obtained the average decay rate Γ_{av} at different temperatures T and wave number k. From Fig. 3 of their paper, we can read off the average experimental decay rates Γ_{av} at the wave number $k=1.04\times10^5$ cm^{-1}, at different temperatures, which we show in Table I. The values of Γ_{av} cannot be read off with great accuracy from Fig. 3 of Ref. [5], but they are sufficiently accurate for our purpose here.

In order to explain their experimental results, Fine

TABLE I. Average experimental decay rates Γ_{av}, obtained from Fig. 3 of Ref. [5], at wave number $k=1.04\times10^5\ \mathrm{cm}^{-1}$, at different temperatures.

$(T-T_c)/T_C$	$\Gamma_{\mathrm{av}}(s^{-1})$
0.02	250
0.009	50
0.006	33
0.003	22
0.002	12

et al. [5] invoked the mode-coupling theory of Kawasaki [6] for the critical dynamics of binary liquid mixtures. In this theory, the decay rate Γ may be written as $\Gamma=\Gamma_B+\Gamma_C$, where Γ_B and Γ_C are the background and the critical contributions, respectively, to Γ. The accepted expressions for Γ_B and Γ_C are [10]

$$\Gamma_B=\frac{k_BTk^2}{6\pi\eta_B\xi}\left[\frac{1+k^2\xi^2}{k_c\xi}\right], \tag{5}$$

$$\Gamma_C=\frac{k_BTk^2}{6\pi\eta\xi}\mathcal{K}(k\xi)\left[1+\frac{k^2\xi^2}{4}\right]^{z_\eta/2}, \tag{6}$$

with $\mathcal{K}(x)=(3/4x^2)[1+x^2+(x^3-x^{-1})\arctan(x)]$ and k_c a system-dependent constant. The viscosity $\eta=\eta_B(Q_0\phi)^{z_\eta}$, where η_B is the background viscosity, Q_0 is a system-dependent constant, and z_η is an exponent that characterizes the divergence of the viscosity. The two system-dependent quantities Q_0 and k_c are related by $k_c\sim[4e^{4/3}/3\pi]Q_0$ [1,11]. Fine *et al.* compared the average experimental values Γ_{av} with the theoretical predictions by treating k_c and η_B as adjustable parameters and found that the best fit was obtained with $\eta_B=(3\pm2)\times10^2\eta_{\mathrm{H_2O}}$ (where $\eta_{\mathrm{H_2O}}$ is the viscosity of water) and $k_c^{-1}=(1.2\pm0.5)\times10^3$ Å.

Fine *et al.* considered this value of the viscosity to be "unusually large" and that the Kawasaki theory did not provide an adequate description of the behavior in aqueous protein solutions.

The purpose of our work here is to apply an alternative theory [7] to the analysis of the experimental data of Fine *et al.* Unfortunately, the actual experimental data of their quasielastic light scattering data, or the time autocorrelation function of the photocounts, are not readily available. Therefore, we can fit our theory only to their published result, which is given in the form of an averaged decay rate Γ_{av}, shown in Table I. At fixed time t we will fit their averaged experimental decay function at different temperatures, $\exp[-\Gamma_{\mathrm{av}}(T)t]$ to the expression multiplying the static structure function $g(k)$ in (1):

$$\frac{(1+\lambda^2k^2)e^{-\Gamma_k(T,\eta_s)t}-\tau\Gamma_k(T,\eta_s)e^{-(1+\lambda^2k^2)t/\tau}}{1+\lambda^2k^2-\tau\Gamma_k(T,\eta_s)}.$$

In a least-squares-fit procedure, we minimize the difference squared S, defined as

$$S(\lambda,\eta,\tau,t)\equiv\sum_{i=1}^{5}\left[\exp[-\Gamma_{\mathrm{av}}(T_i)t]-\frac{(1+\lambda^2k^2)e^{-\Gamma_k(T_i,\eta_s)t}-\tau\Gamma_k(T_i,\eta_s)e^{-(1+\lambda^2k^2)t/\tau}}{1+\lambda^2k^2-\tau\Gamma_k(T_i,\eta_s)}\right]^2, \tag{7}$$

where $\Gamma_{\mathrm{av}}(T_i,\eta_s)$ is the decay rate given in (2) at the temperature T_i. The summation in (7) is over the five temperatures given in Table I. As can be seen from (2), the temperature dependence of Γ_k enters both in the explicit factor k_BT and in the temperature dependence of the correlation length ξ of the protein. We minimize the difference squared $S(\lambda,\eta_s,\tau,t)$ at fixed values of the noise correlation length parameter λ and the time t, to obtain the solution viscosity η_s and the noise correlation time τ. For the parameter λ we fix it at two values: $\lambda=0$ and $\lambda=\xi$, the latter being the correlation length of the protein. The values of the parameters η_s and τ that minimize the difference squared S are shown for different values of the time t in Table II for $\lambda=0$ and in Table III for $\lambda=\xi$. From Tables I and II we estimate the correlation time τ of the noise to be from 0.02 to 0.05 s and the viscosity of the solution to be about 0.05 N s/m², which is about 30 times that of water. The value of the solution viscosity predicted by our theory is about one order of magnitude less than that predicted by the Kawasaki

TABLE II. Correlation times τ of the colored noise and solution viscosity η_s, obtained by minimizing Eq. (7), at different times t for $\lambda=0$.

$t(s)$	$\tau(s)$	$\eta_s(\mathrm{N\,s/m^2})$
0.2	0.019	0.05
0.4	0.060	0.06
0.6	0.017	0.07
0.8	0.024	0.06
1.0	0.029	0.06
2.0	0.048	0.06

TABLE III. Correlation times τ of the colored noise and solution viscosity η_s, obtained by minimizing Eq. (7), at different times t for $\lambda=\xi$.

$t(s)$	$\tau(s)$	$\eta_s(\mathrm{N\,s/m^2})$
0.2	0.020	0.05
0.4	0.013	0.10
0.6	0.019	0.06
0.8	0.026	0.06
1.0	0.033	0.06
2.0	0.053	0.06

theory. These estimates seem to be insensitive to the correlation length parameter λ of the colored noise and to the time t for $t=0.2$ to $t=2.0$. Since the viscosity of the solution has not been measured directly, we would encourage direct measurement of the solution as a test of our theory. At first sight, our theory of colored noise, having three parameters, λ, τ, and η_s, seems to contain more adjustable parameters than the Kawasaki theory. But as it turns out, our theory is insensitive to the parameter λ. The Kawasaki theory also contains two adjustable parameters, the background viscosity η_B and k_c. In our theory, the parameter τ has the physical meaning of the correlation time of the colored noise, which is the driving force for the dynamics of the protein.

In summary, we have shown that the nonexponential decay of the time autocorrelation function observed experimentally in the dynamics of aqueous solutions of protein in water can be explained by our recently proposed theory for the dynamics of concentration fluctuations in polymer solutions with colored noise. We fitted the averaged experimental decay to our theory and determined the viscosity η_s of the solution and the correlation time τ of the colored noise. We found that the correlation time τ of the colored noise and the viscosity of the solution η_s are insensitive to the correlation length λ of the noise; we estimate τ to be of the order 0.02–0.05 s and η_s to be about 0.05 $\mathrm{N\,s/m^2}$. The solution viscosity predicted by our theory is an order of magnitude smaller than that predicted by the Kawasaki theory. The discrepancy between our theory and that of Kawasaki can only be settled by a direct experimental measurement of the solution viscosity. Since in our opinion the viscosity of this protein solution and the correct theory for its dynamics is not just an academic question but an important issue, we strongly encourage such measurements.

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