PHYSICAL REVIEW E VOLUME 50, NUMBER 1 JULY 1994

Dynamics of concentration fluctuations in polymer solutions with spatiotemporal correlated noise

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(Received 4 February 1994)

We study the problem of concentration fluctuations in polymer solutions under the influence of spatiotemporal correlated noise. We find that in contrast to the case of white noise, where the dynamic structure function is characterized by a single decay rate Γ_k which is given in terms of the static structure function $g(k)$ in the colored noise case, the decay rate takes a different form depending on a characteristic wave vector κ, given by the solution of the equation $1+\xi^2\kappa^2-\tau\Gamma_\kappa=0$, with ξ being the correlation length of the polymers and τ being the correlation time of the colored noise. For the wave vector $k \ll \kappa$, the decay rate is Γ_k, just as in the white noise case. For $k=\kappa$, the decay rate is Γ_κ, but the decay is modified by an extra factor $(1+\Gamma_\kappa t)$ where t is the time. For $k \gg \kappa$, the decay rate is $(1+\xi^2k^2)/\tau$. Since our result should hold as long as the correlation time τ is not exactly zero, it should lead to experimentally verifiable consequences in dynamic light scattering in polymer solutions in short time scales.

PACS number(s): 36.20.−r, 05.70.Ln, 05.40.+j, 02.50.−r

I. INTRODUCTION

Many problems in nonequilibrium statistical mechanics are modeled by Langevin equations [1–6]. For instance, the application of Langevin equations to describe surface growth [7–13] and self-organized criticality [14,15] are recent active areas of research. In these equations, a stochastic term $\eta(\mathbf{r},t)$ is added to the macroscopic and deterministic equation of the form

$$\frac{\partial\psi}{\partial t}=f([\psi(\mathbf{r},t)],\nabla\psi,\nabla^2\psi)+\eta(\mathbf{r},t)\ . \tag{1}$$

Here $\psi(\mathbf{r},t)$ is the relevant variable of the system and the first term on the right-hand side is a deterministic force. $\eta(\mathbf{r},t)$ is a stochastic term called noise, which is usually assumed to be Gaussian and accounts for either internal degrees of freedom or fluctuations in the constraint imposed externally on the system. In the first case, the noise is called internal noise and is assumed to be white noise. That means the value of the random field at a given point and at a given time does not depend on its value at other points or at other times:

$$\langle\eta(\mathbf{r},t)\eta(\mathbf{r}',t')\rangle=2A\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\ , \tag{2}$$

where A is the strength of the noise and $\langle\ \rangle$ denotes an average over the probability distribution of the random field. In the case of external noise, or noise coming from fluctuations in the constraints imposed externally on the system, the correlations of the random field between different points and times could be nonzero. In this case, the spectrum of the noise in both momentum k and frequency ω is no longer constant, so one speaks of colored noise. Colored noise is of practical interest in many branches of physics and in engineering and has been extensively studied [16–22]. Recently, colored noise has also been used in nonequilibrium surface growth models [9,13].

The most famous example of colored noise is the Ornstein-Uhlenbeck process, which is Gaussian and has zero mean and a correlation given by [6,23]

$$\langle\zeta(\mathbf{r},t)\zeta(\mathbf{r}',t')\rangle=\frac{A}{\tau}e^{-|t-t'|/\tau}\delta(\mathbf{r}-\mathbf{r}')\ , \tag{3}$$

where τ is the correlation time of the colored noise, i.e., a measure of its memory in time. The stochastic differential equation which governs its evolution is

$$\frac{\partial\zeta}{\partial t}=-\frac{1}{\tau}\zeta(t)+\frac{1}{\tau}\eta(t)\ , \tag{4}$$

where $\eta(t)$ is white noise following (2) without spatial dependence.

Recently Garcia-Ojalvo, Sancho, and Ramirez-Piscina [24] proposed a generalization of this very simple idea to take into account the finite correlations in space as well. The simplest stochastic differential equation modeling such a noise is the following reaction-diffusion equation:

$$\frac{\partial\zeta}{\partial t}=-\frac{1}{\tau}(1-\lambda^2\nabla^2)\zeta+\frac{1}{\tau}\eta(\mathbf{r},t)\ , \tag{5}$$

where $\eta(\mathbf{r},t)$ is again a white noise term obeying (2) and λ is the correlation length of the colored noise. We [25] have calculated the correlation which is a generalization of (3) to colored noise obeying (5). Its spatial Fourier transform has the form

$$\langle\zeta(k,t)\zeta(k',t')\rangle=\frac{A}{\tau}\frac{\exp[-|t-t'|/\tau-\lambda k^2|t-t'|/\tau]}{1+\lambda^2k^2}\times\delta(\mathbf{k}-\mathbf{k}')\ . \tag{6}$$

This reduces to the white noise case (3) for λ and (τ) equal to zero.

In this paper we apply spatiotemporal colored noise to the problem of concentration fluctuation in polymer solutions. The Fourier transform $c_\mathbf{k}$ of the polymer segment density $c(\mathbf{r})$ is assumed to be described by the phenomenological Langevin equation [26]

$$\frac{\partial c_\mathbf{k}}{\partial t}=-\Gamma_\mathbf{k}c_\mathbf{k}+r_\mathbf{k}(t)\ , \tag{7}$$

where $\Gamma_{\mathbf{k}}$ is given in terms of the static structure function $g(k)$, and $r_{\mathbf{k}}(t)$ is a stochastic noise term. We calculated the dynamic structure function which is related to the time correlation function $\langle c_{\mathbf{k}}(t)c_{\mathbf{k}'}(t')\rangle$ for the case of spatiotemporal colored noise of the form (5) and (6). We find that contrary to the white noise case, where the dynamic structure function is characterized by a single decay rate given by $\Gamma_{\mathbf{k}}$, in the colored noise case the decay rate of the dynamic structure function has a different form depending on a characteristic wave vector κ given by the solution of the equation $1+\lambda^2\kappa^2-\tau\Gamma_\kappa=0$. For $\mathbf{k} \ll \kappa$, the decay rate is $\Gamma_{\mathbf{k}}$, just as in the white noise case. For $k=\kappa$, the decay rate is Γ_κ, but the decay is modified by an extra factor $(1+\Gamma_\kappa t)$ where t is the time. For $k \gg \kappa$, the decay rate is $(1+\lambda^2k^2)/\tau$. Also, from the scaling form of the static structure function, it follows that $\lambda=\xi$, where ξ is the correlation length of the polymers. Therefore there is only one free parameter, which is the correlation time τ of the colored noise. At the θ point of the polymer, where the correlation length ξ diverges, there is again only one decay rate $\Gamma_{\mathbf{k}}$. Our result for the behavior of the dynamic structure function should hold as long as τ is not exactly zero. Therefore it should lead to verifiable experimental predictions in dynamic light scattering in polymer solutions in short time scales.

In Sec. II we will review the background theory on the dynamics of concentration fluctuations in polymer solutions. In Sec. III we will discuss dynamic light scattering in the case of white noise. In Sec. IV we will describe our result for dynamic light scattering in the case of spatiotemporal colored noise. Section V covers discussions and conclusions.

II. DYNAMICS OF CONCENTRATION FLUCTUATIONS

Let us first consider the static properties of concentrated polymer solutions in equilibrium. Let $\mathbf{R}_{\alpha n}$ be the position of the nth segment of the αth chain. The equilibrium distribution function for $\mathbf{R}_{\alpha n}$ is given by [27]

$$\Psi[\mathbf{R}_{\alpha n}] \propto \exp\{-(U_0[\mathbf{R}_{\alpha n}]+U_1[\mathbf{R}_{\alpha n}])/k_BT\} , \tag{8}$$

where

$$U_0[\mathbf{R}_{\alpha n}]/k_BT=\sum_{\alpha,n}\frac{3}{2b^2}(\mathbf{R}_{\alpha n}-\mathbf{R}_{\alpha,n-1})^2 \tag{9}$$

is the energy of the chain connectivity and

$$U_1[\mathbf{R}_{\alpha n}]/k_BT=\tfrac{1}{2}\sum_{\alpha,\beta}\sum_{n,m} v\delta(\mathbf{R}_{\alpha n}-\mathbf{R}_{\beta m}) \tag{10}$$

is the Edward Hamiltonian for the excluded volume interaction, which includes both the intramolecular interaction $\alpha=\beta$ and the intermolecular interaction $\alpha\neq\beta$. Here b is the effective bond length or Kuhn length of the polymers, v is the excluded volume parameter which can be regarded as the virial coefficient between the segments, and k_B is the Boltzmann constant.

Instead of describing the problem in terms of $\mathbf{R}_{\alpha n}$, it is more convenient to focus attention on the local segment density $c(\mathbf{r})$, which can be considered as collective coordinates, defined by [27,28]

$$c(\mathbf{r})=\sum_{\alpha,n}\delta(\mathbf{r}-\mathbf{R}_{\alpha n}) , \tag{11}$$

and consider the distribution function $\Psi(c(\mathbf{r}))$ for $c(\mathbf{r})$. This method is effective if the physical quantity under consideration can be expressed by $c(\mathbf{r})$. For the mathematical development, it is convenient to use the Fourier transform of $c(\mathbf{r})$:

$$c_{\mathbf{k}}=\frac{1}{V}\int d^3r\, \exp(i\mathbf{k}\cdot\mathbf{r})c(\mathbf{r})=\frac{1}{V}\sum_{\alpha,n}\exp(i\mathbf{k}\cdot\mathbf{R}_{\alpha n}) , \tag{12}$$

$$\begin{aligned} c(\mathbf{r})&=\sum_{\mathbf{k}} c_{\mathbf{k}}\exp(-i\mathbf{k}\cdot\mathbf{r}) \\ &=\frac{V}{(2\pi)^3}\int d^3k\, c_{\mathbf{k}}\exp(-i\mathbf{k}\cdot\mathbf{r}) , \end{aligned} \tag{13}$$

where V is the volume. In the representation of $\{c_{\mathbf{k}}\}$, not all $c_{\mathbf{k}}$ are independent of each other since $c_{\mathbf{k}}$ and $c_{-\mathbf{k}}$ are related by

$$c_{-\mathbf{k}}=c_{\mathbf{k}}^* . \tag{14}$$

In order to generalize this approach to dynamical problems, a central assumption is made that the set of coordinates $\{c_{\mathbf{k}}\}$ are good variables for characterizing the state of the system, and that a closed equation can be constructed for their evolution. This approach is quite analogous to the critical dynamics for binary solutions of low molecular weight [29], where the dynamics of the system is described by the phenomenological Langevin equation [26]

$$\frac{\partial}{\partial t}c_{\mathbf{k}}=-\sum_{\mathbf{k}'}L_{\mathbf{k}\mathbf{k}'}\frac{\partial U(\{c_{\mathbf{k}}\})}{\partial c_{\mathbf{k}'}}+r_{\mathbf{k}} , \tag{15}$$

where $U(\{c_{\mathbf{k}}\})$ is the free energy, $L_{\mathbf{k}\mathbf{k}'}$ are phenomenological kinetic coefficients, and $r_{\mathbf{k}}$ are Gaussian random variables satisfying

$$\langle r_{\mathbf{k}}\rangle=0 , \quad \langle r_{\mathbf{k}}(t)r_{\mathbf{k}'}(t')\rangle=2k_BTL_{\mathbf{k}\mathbf{k}'}\delta(t-t') , \tag{16}$$

where T is the temperature. For polymers, the validity of this equation is not obvious since the description of the polymeric system by the collective coordinates $\{c_{\mathbf{k}}\}$ disregards the chain connectivity, and therefore neglects the entanglement effect. However, for time scales shorter than the repetition time τ_d, this is not a serious problem, and many experiments related to concentration fluctuations are concerned with the short time-scale motion.

In the Gaussian approximation [26] the free energy $U(\{c_{\mathbf{k}}\})$ is given by

$$U(\{c_{\mathbf{k}}\})=\frac{V}{c}k_BT\sum_{\mathbf{k}}\frac{1}{g(k)}c_{\mathbf{k}}c_{-\mathbf{k}} , \tag{17}$$

where $g(k)$ is the static structure function and c is the average concentration.

To determine $L_{\mathbf{k}\mathbf{k}'}$, we use the Langevin equation for $\mathbf{R}_{\alpha n}$, the position vector of the nth segment in the αth chain [26]

$$\frac{\partial}{\partial t}\mathbf{R}_{\alpha n}=\sum_{\beta,m}\mathbf{H}_{\alpha n\beta m}\cdot\left[-\frac{\partial U[\mathbf{R}_{\alpha n}]}{\partial R_{\beta m}}+\mathbf{f}_{\beta m}\right], \tag{18}$$

where $\mathbf{H}_{\alpha n\beta m}=\mathbf{H}(\mathbf{R}_{\alpha n}-\mathbf{R}_{\beta m})$ is the mobility matrix, with m and n denoting segment and α and β denoting the chain numbers, respectively. It has the form [26]

$$\mathbf{H}_{\alpha n\beta m}=\int\frac{d^3q}{(2\pi)^3}\frac{I-\hat{\mathbf{q}}\hat{\mathbf{q}}}{\eta_s q^2}\exp[i\mathbf{q}\cdot(\mathbf{R}_{\alpha n}-\mathbf{R}_{\beta m})]\ , \tag{19}$$

where I is the identity matrix, η_s is the viscosity, and $\mathbf{f}_{\beta m}$ is the random force on the mth segment of the βth chain with moments given by

$$\begin{gathered}\langle\mathbf{f}_{\alpha n}(t)\rangle=0\ ,\\ \langle f_{\alpha nI}(t)f_{\beta mJ}(t')\rangle=2k_BT\delta_{\alpha\beta}\delta_{mn}\delta_{IJ}\delta(t-t')\ .\end{gathered} \tag{20}$$

where I, $J=x$, y, or z denote the components of the random force $\mathbf{f}$. Equation (18) can be rewritten as

$$\frac{\partial}{\partial t}\mathbf{R}_{\alpha n}=-\sum_{\beta,m}\mathbf{H}_{\alpha n\beta m}\cdot\frac{\partial U[\mathbf{R}_{\alpha n}]}{\partial\mathbf{R}_{\beta m}}+\mathbf{r}_{\alpha n}\ , \tag{21}$$

with

$$\mathbf{r}_{\alpha n}=\sum_{\beta m}\mathbf{H}_{\alpha n\beta m}\cdot\mathbf{f}_{\beta m}\ , \tag{22}$$

and

$$\begin{gathered}\langle\mathbf{r}_{\alpha n}(t)\rangle=0\ ,\\ \langle\mathbf{r}_{\alpha n}(t)\mathbf{r}_{\beta m}(t')\rangle=2k_BT\mathbf{H}_{\alpha n\beta m}\delta(t-t')\ .\end{gathered} \tag{23}$$

Fourier transforming the last equation:

$$\begin{aligned}\frac{\partial}{\partial t}c_{\mathbf{k}}(t)&=\frac{1}{V}\sum_{\alpha,n}i\mathbf{k}\cdot\frac{\partial\mathbf{R}_{\alpha n}}{\partial t}\exp(i\mathbf{k}\cdot\mathbf{R}_{\alpha n})\\ &=\frac{1}{V}\sum_{\alpha n,\beta m}i\mathbf{k}\cdot\left[-\mathbf{H}_{\alpha n\beta m}\cdot\frac{\partial U[\mathbf{R}_{\alpha n}]}{\partial R_{\beta m}}+\mathbf{r}_{\alpha n}\right]\\ &\qquad\times\exp(i\mathbf{k}\cdot\mathbf{R}_{\alpha n})\ .\end{aligned} \tag{24}$$

Comparing with (15), we have

$$r_{\mathbf{k}}(t)=\frac{1}{V}\sum_{\alpha n}i\mathbf{k}\cdot\mathbf{r}_{\alpha n}(t)\exp(i\mathbf{k}\cdot\mathbf{R}_{\alpha n})\ . \tag{25}$$

Using (25) and (23), it follows that

$$\begin{aligned}\langle r_{\mathbf{k}}(t)r_{\mathbf{k}}(t')\rangle&=-\frac{1}{V^2}\sum_{\alpha n,\beta m}\mathbf{k}\cdot\langle\mathbf{r}_{\alpha n}(t)\mathbf{r}_{\beta m}(t')\rangle\cdot\mathbf{k}'e^{i(\mathbf{k}\cdot\mathbf{R}_{\alpha n}+\mathbf{k}'\cdot\mathbf{R}_{\beta m})}\\ &=-\frac{1}{V^2}\sum_{\alpha n,\beta m}2k_BT\delta(t-t')\mathbf{k}\mathbf{k}':\mathbf{H}_{\alpha n\beta m}\exp(i\mathbf{k}\cdot\mathbf{R}_{\alpha n}+i\mathbf{k}'\cdot\mathbf{R}_{\beta m})\ .\end{aligned} \tag{26}$$

Using (19) for $\mathbf{H}$, we have

$$\begin{aligned}\langle r_{\mathbf{k}}(t)r_{\mathbf{k}'}(t')\rangle&=-\frac{2}{V^2}\delta(t-t')k_BT\int\frac{d^3q}{(2\pi)^3}\frac{\mathbf{k}\cdot\mathbf{k}'-(\mathbf{k}\cdot\hat{\mathbf{q}})(\mathbf{k}'\cdot\hat{\mathbf{q}})}{\eta_s q^2}\sum_{\alpha n,\beta m}\exp[i(\mathbf{k}+\mathbf{q})\cdot\mathbf{R}_{\alpha n}+i(\mathbf{k}'-\mathbf{q})\cdot\mathbf{R}_{\beta m}]\\ &=-2\delta(t-t')k_BT\int\frac{d^3q}{(2\pi)^3}\frac{\mathbf{k}\cdot\mathbf{k}'-(\mathbf{k}\cdot\hat{\mathbf{q}})(\mathbf{k}'\cdot\hat{\mathbf{q}})}{\eta_s q^2}c_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}'-\mathbf{q}}\ .\end{aligned} \tag{27}$$

Comparing (27) and (16), we have

$$L_{\mathbf{k}\mathbf{k}'}=-\int\frac{d^3q}{(2\pi)^3}\frac{\mathbf{k}\cdot\mathbf{k}'-(\mathbf{k}\cdot\hat{\mathbf{q}})(\mathbf{k}'\cdot\hat{\mathbf{q}})}{\eta_s q^2}c_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}'-\mathbf{q}}\ . \tag{28}$$

Equations (15), (17), and (28) give a nonlinear equation for $c_{\mathbf{k}}$. To proceed further, we use the preaveraging approximation, i.e., replace $L_{\mathbf{k}\mathbf{k}'}$ by its average in equilibrium [26],

$$\begin{aligned}L_{\mathbf{k}\mathbf{k}'}\to\langle L_{\mathbf{k}\mathbf{k}'}\rangle_{\mathrm{eq}}&=-\int\frac{d^3q}{(2\pi)^3}\frac{\mathbf{k}\cdot\mathbf{k}'-(\mathbf{k}\cdot\hat{\mathbf{q}})(\mathbf{k}'\cdot\hat{\mathbf{q}})}{\eta_s q^2}\\ &\qquad\times\langle c_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}'-\mathbf{q}}\rangle_{\mathrm{eq}}\ .\end{aligned} \tag{29}$$

Now the equilibrium average $\langle c_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}'+\mathbf{q}}\rangle_{\mathrm{eq}}$ is just the static structure function:

$$\langle c_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}'-\mathbf{q}}\rangle_{\mathrm{eq}}=\frac{c}{V}g(\mathbf{k}+\mathbf{q})\delta_{\mathbf{k}-\mathbf{k}'}\ . \tag{30}$$

This gives

$$\langle L_{\mathbf{k}\mathbf{k}'}\rangle_{\mathrm{eq}}=\delta_{\mathbf{k}-\mathbf{k}'}L_{\mathbf{k}}\ , \tag{31}$$

with

$$L_{\mathbf{k}}=\frac{c}{V}\int\frac{d^3q}{(2\pi)^3}\frac{k^2-(\mathbf{k}\cdot\hat{\mathbf{q}})^2}{\eta_s q^2}g(\mathbf{k}+\mathbf{q})\ . \tag{32}$$

Therefore the Langevin equation (15) becomes

$$\frac{\partial}{\partial t}c_{\mathbf{k}}(t)=-L_{\mathbf{k}}\frac{\partial U(\{c_{\mathbf{k}}\})}{\partial c_{-\mathbf{k}}}+r_{\mathbf{k}}(t)\ . \tag{33}$$

In the Gaussian approximation, $U(\{c_{\mathbf{k}}\})$ is given by (17). Thus the Langevin equation (33) becomes

$$\frac{\partial c_{\mathbf{k}}}{\partial t}=-\Gamma_{\mathbf{k}}c_{\mathbf{k}}+r_{\mathbf{k}}(t)\ , \tag{34}$$

where

$$\Gamma_{\mathbf{k}}=\frac{V}{c}k_BT\frac{L_{\mathbf{k}}}{g(k)}\ , \tag{35}$$

or using (32),

$$\Gamma_{\mathbf{k}}=k_B T\int \frac{d^3 g}{(2\pi)^3}\frac{g(\mathbf{k}+\mathbf{q})}{g(k)}\frac{k^2-(\mathbf{k}\cdot\hat{\mathbf{q}})^2}{\eta_s q^2} . \tag{36}$$

Equation (34) is the basic equation for the dynamics of concentration fluctuation. We will study this equation for the case of spatiotemporal colored noise. But first we will review the case when $r_{\mathbf{k}}$ is white noise.

III. DYNAMIC LIGHT SCATTERING WITH WHITE NOISE

Equation (34) has the solution

$$c_{\mathbf{k}}(t)=\int_{-\infty}^{t} ds \exp[-\Gamma_{\mathbf{k}}(t-s)]r_k(s) . \tag{37}$$

For white noise, (16) becomes

$$\langle r_{\mathbf{k}}\rangle=0 , \quad \langle r_{\mathbf{k}}(t)r_{\mathbf{k}'}(t')\rangle=2k_B T L_{\mathbf{k}}\delta_{\mathbf{k}-\mathbf{k}'}\delta(t-t') . \tag{38}$$

Using (37) and (38) we obtain the time correlation function

$$\langle c_{\mathbf{k}}(t)c_{-\mathbf{k}}(t')\rangle=\langle c_{\mathbf{k}}c_{-\mathbf{k}}\rangle\exp(-\Gamma_{\mathbf{k}}|t-t'|) . \tag{39}$$

Here the dynamic structure function

$$g(\mathbf{k},t)\equiv\frac{V}{c}\langle c_{\mathbf{k}}(t)c_{-\mathbf{k}}(0)\rangle=g(k)\exp(-\Gamma_{\mathbf{k}}t) \tag{40}$$

is a single exponential decay with time. The exponential decay is correct for $t\rightarrow 0$. In fact, $\Gamma_{\mathbf{k}}$ as given in (36) is the exact initial decay rate [26]. However, theory is still lacking for the behavior in the whole time scale. Experimentally, it has been observed [30–32] that in some systems, the structure factor does not decrease in a single exponential manner and has a long tail. The long timescale behavior is considered to be related to the topological interaction due to the impossibility of chain crossing. However, quantitative theory is not yet given. In the next section we will discuss the effect of spatiotemporal colored noise on the dynamic structure function. But first we want to give the form of $\Gamma_{\mathbf{k}}$ in the Gaussian approximation in which the distribution of $c_{\mathbf{k}}$ is Gaussian [26]. In that case, the static structure function $g(k)$ has the form [26]

$$g(k)=\frac{12}{b^2(k^2+\xi^{-2})} , \tag{41}$$

where b is the Kuhn length and ξ is the correlation length

$$\xi=b^2/(12cv)^{1/2} , \tag{42}$$

with v the excluded volume parameter in the Edward Hamiltonian. Using this form of the static structure function in (36), one finds [26]

$$\begin{aligned}\Gamma_{\mathbf{k}}&=\frac{k_B T}{4\pi^2\eta_s}\int_0^{\infty} dq\frac{1+k^2\xi^2}{1+q^2\xi^2}q^2\left(\frac{k^2+q^2}{2kq}\ln\left|\frac{k+q}{k-q}\right|-1\right)\\&=\frac{k_B T}{6\pi\eta_s\xi}k^2F(k\xi) ,\end{aligned} \tag{43}$$

where

$$F(x)=\frac{3}{4}\frac{1+x^2}{x^3}[x+(x^2-1)\tan^{-1}x] . \tag{44}$$

IV. DYNAMIC LIGHT SCATTERING WITH SPATIOTEMPORAL CORRELATED NOISE

Instead of the white noise (38), we can use spatiotemporal colored noise with correlations [24,25]

$$\begin{aligned}&\langle r_{\mathbf{k}}\rangle=0,\\&\langle r_{\mathbf{k}}(t)r_{\mathbf{k}'}(t')\rangle=\frac{k_B T\delta_{\mathbf{k}-\mathbf{k}'}L_{\mathbf{k}}}{(1+\lambda^2k^2)\tau}\\&\qquad\times\exp[-(1+\lambda^2k^2)|t-t'|/\tau] ,\end{aligned} \tag{45}$$

where the two parameters λ and τ are the correlation length and correlation time of the colored noise. For λ and τ equal to zero, (45) reduces back to the white noise case (38). For $\lambda=0$, (45) reduces to the well known Ornstein-Uhlenbeck process of temporal colored noise. Equation (45) represents a natural generalization of the Ornstein-Uhlenbeck process to take into account finite correlations in space as well as in time.

The solution of (34) for $c_{\mathbf{k}}$ is still given by (37). Calculating the time correlation $\langle c_{\mathbf{k}}(t)c_{\mathbf{k}'}(t')\rangle$ for the case of spatiotemporal colored noise (45), we obtain (see Appendix A)

$$\begin{aligned}\langle c_{\mathbf{k}}(t)c_{\mathbf{k}'}(t')\rangle=&\frac{k_B T\delta_{\mathbf{k}-\mathbf{k}'}L_{\mathbf{k}}}{(1+\lambda^2k^2)[(1+\lambda^2k^2)^2-\tau^2\Gamma_{\mathbf{k}}^2]}\\&\times\left[\frac{(1+\lambda^2k^2)}{\Gamma_{\mathbf{k}}}e^{-\Gamma_{\mathbf{k}}|t-t'|}\right.\\&\left.\qquad-\tau e^{(1+\lambda^2k^2)|t-t'|}\right] .\end{aligned} \tag{46}$$

For $t=t'$, we have

$$\langle c_{\mathbf{k}}(t)c_{-\mathbf{k}}(t)\rangle=\frac{k_B T L_{\mathbf{k}}}{(1+\lambda^2k^2)\Gamma_{\mathbf{k}}(1+\lambda^2k^2+\tau\Gamma_{\mathbf{k}})} . \tag{47}$$

The static structure function $g(k)$ is given by

$$\begin{aligned}g(\mathbf{k})&=\frac{V}{c}\langle c_{\mathbf{k}}(t)c_{-\mathbf{k}}(t)\rangle\\&=\frac{V}{c}k_B T\frac{L_{\mathbf{k}}}{(1+\lambda^2k^2)\Gamma_{\mathbf{k}}(1+\lambda^2k^2+\tau\Gamma_{\mathbf{k}})} ,\end{aligned} \tag{48}$$

with $L_{\mathbf{k}}$ and $\Gamma_{\mathbf{k}}$ given by (32) and (36). The dynamic structure function is given by

$$\begin{aligned}g(\mathbf{k},t)&=\frac{V}{c}\langle c_{\mathbf{k}}(t)c_{-\mathbf{k}}(0)\rangle\\&=g(k)\frac{(1+\lambda^2k^2)e^{-\Gamma_k t}-\tau\Gamma_{\mathbf{k}}e^{-(1+\lambda^2k^2)t/\tau}}{1+\lambda^2k^2-\tau\Gamma_{\mathbf{k}}} .\end{aligned} \tag{49}$$

For λ and τ equal to zero, (49) reduces to the white noise case (40). In order to discuss the consequence of (49) we need to know some properties of the function $\Gamma_{\mathbf{k}}$. In the Gaussian approximation, $\Gamma_{\mathbf{k}}$ is given by Eqs. (43) and (44). From Eqs. (43) and (44) one finds that

$$\Gamma_{\mathbf{k}}=\frac{k_B T}{16\eta_s}k^3 , \quad k\xi \gg 1 \tag{50}$$

and

$$\Gamma_{\mathbf{k}}=\frac{k_B T}{16\pi\eta_s\xi}k^2 , \quad k\xi \ll 1 . \tag{51}$$

From (49) and (50) we can see that unless τ is exactly zero, for large enough k, the denominator in (49) will change sign. Let us denote by κ the value of k at which the denominator in (49) vanishes,

$$1+\lambda^2\kappa^2-\tau\Gamma_\kappa=0 . \tag{52}$$

At this value of k, the exponentials in (49) become equal and the numerator in (49) also vanishes. For k close to κ, let $\tau\Gamma_k=1+\lambda^2\kappa^2\pm\epsilon$. In the limit $\epsilon\to 0$, we have

$$g(\kappa,t)=g(\kappa)(1+\Gamma_\kappa t)\exp(-\Gamma_\kappa t) , \quad k=\kappa . \tag{53}$$

For any finite τ, at $k \ll \kappa$, we have $1+\kappa^2k^2 \gg \tau\Gamma_k$ and we have the white noise behavior (40) of one decay rate Γ_k. For $k=\kappa$, the decay rate is given by Γ_κ, but the decay is modified by the extra factor $(1+\Gamma_\kappa t)$, as is given in (53). For $k \gg \kappa$, such that $1+\lambda^2k^2 \ll \tau\Gamma_k$, the decay is given by the second exponent, with decay rate $(1+\lambda^2k^2)/\tau$. We can therefore write the behavior of the dynamic structure function in these different k regions as

$$g(\kappa,t)=\begin{cases} g(k)e^{-\Gamma_k t} , & k \ll \kappa \\ g(\kappa)(1+\Gamma_\kappa t)e^{-\Gamma_\kappa t} , & k=\kappa \\ g(k)e^{-(1+\lambda^2k^2)t/\tau}, & k \gg K \end{cases} \tag{54}$$

with κ given by (52). For a general wave vector k, the decay consists of a sum of two exponentials as given in (49).

If the static structure function $g(k)$ is assumed to have the scaling form [26,33] $g(k)=f_1(\xi k)$ with ξ the correlation length of the polymer, as is shown explicitly in the Gaussian approximation in (41), then from (32) and (36), both L_k and Γ_k would have scaling forms $L_k=f_2(k\xi)$ and $\Gamma_k=f_3(k\xi)$. Then Eq. (48) implies that $\lambda=\xi$, where the correlation length ξ of the polymer is given by (42) in the Gaussian approximation. Therefore the only free parameter in the spatiotemporal colored noise is the correlation time τ of the noise. At the θ point of the polymers, the excluded volume parameter v vanishes. In that case, the polymer correlation length ξ diverges according to (42). Then (49) shows that the decay of the dynamic structure function is again a single exponent with decay rate Γ_k.

V. DISCUSSIONS AND CONCLUSIONS

We have presented the result for the dynamics of concentration fluctuations in polymer solutions with spatiotemporal colored noise. We find that the decay rate of the dynamic structure function takes a different form depending on a characteristic value of the wave vector κ given by the solution of the equation $1+\xi^2\kappa^2-\tau\Gamma_\kappa=0$, where ξ is the correlation length of the polymers and τ is the correlation time of the colored noise. For $k \ll \kappa$, the decay rate is Γ_k, just as in the white noise case. For $k=\kappa$, the decay rate is Γ_κ, but the decay is modified by an extra factor $(1+\Gamma_\kappa t)$, where t is the time. For $k \gg \kappa$ the decay rate is $(1+\xi^2k^2)/\tau$. At the θ point of the polymer when the polymer correlation length diverges, the decay of the dynamic structure function is again a single exponent with decay rate Γ_k. Since the description of the polymer system by the collective coordinates $\{c_k\}$ disregards the chain connectivity and therefore neglects the entanglement effect, it applies only for time scales shorter than the repetition time τ_d. This is not a serious problem, since many experiments related to concentration fluctuations are concerned with the short time-scale motion. In this case our result should hold as long as the correlation time τ of the colored noise is not exactly zero. Therefore we expect that our result has verifiable consequences in dynamic light scattering experiments on polymer solutions in short time scales.

Our spatiotemporal colored noise given in (45) is of short range in space and time. The effect of long range colored noise on a dynamical system has also recently been studied [9,13]. Its effect on the dynamics of nonequilibrium systems is even more drastic. In many cases, long range correlated noise even changes the dynamic universality class of the system [9,13]. The effect of long range colored noise on the concentration fluctuations of polymer solutions will be a subject of future study.

ACKNOWLEDGMENTS

This work was supported in part, through the Timbuktu Academy, by the Department of the Navy, Office of Naval Research (ONR Grant No. N00014-93-1-1368), and by the National Science Foundation (NSF Grant No. HRD-9108590).

APPENDIX A

Using (37) and (45) we write

$$\begin{aligned}\langle c_{\mathbf{k}}(t)c_{-\mathbf{k}}(t')\rangle &= \int_{-\infty}^{t} ds \int_{-\infty}^{t'} ds' \exp[-\Gamma_{\mathbf{k}}(t-s)]\exp[-\Gamma_{-\mathbf{k}}(t'-s')]\langle r_{\mathbf{k}}(s)r_{-\mathbf{k}'}(s')\rangle \\ &= \frac{k_B T L_{\mathbf{k}}}{\tau(1+\lambda^2k^2)}\int_{-\infty}^{t} ds \int_{-\infty}^{t'} ds' e^{-\Gamma_{\mathbf{k}}(t-s)} e^{-\Gamma_{-\mathbf{k}}(t'-s')} e^{-(1+\lambda^2k^2)|s-s'|/\tau} .\end{aligned} \tag{A1}$$

We first calculate for the case $t<t'$. In this case (A1) can be written as

$$\langle c_{\mathbf{k}}(t)c_{-\mathbf{k}}(t')\rangle=\frac{k_B T L_{\mathbf{k}}}{\tau(1+\lambda^2k^2)}e^{-\Gamma_{\mathbf{k}}(t+t')}\int_{-\infty}^{t}dse^{\Gamma_{\mathbf{k}}}\left[\int_{-\infty}^{s}ds'e^{\Gamma_{\mathbf{k}}s'}e^{(1+\lambda^2k^2)(s'-s)/\tau}+\int_{s}^{t'}ds'e^{\Gamma_k s'}e^{(1+\lambda^2k^2)(s-s')/\tau}\right]. \tag{A2}$$

Calculating the integrals we obtain

$$\langle c_{\mathbf{k}}(t)c_{-\mathbf{k}}(t')\rangle=\frac{k_B T L_{\mathbf{k}}}{(1+\lambda^2k^2)[(1+\lambda^2k^2)^2-\tau^2\Gamma_{\mathbf{k}}^2]}\times\left[\frac{1+\lambda^2k^2}{\Gamma_{\mathbf{k}}}e^{\Gamma_{\mathbf{k}}(t-t')}-\tau e^{-(1+\lambda^2k^2)(t-t')}\right].$$

A similar equation can be obtained for the case $t>t'$. Therefore we have in general

$$\langle c_{\mathbf{k}}(t)c_{-\mathbf{k}}(t')\rangle=\frac{k_B T L_{\mathbf{k}}}{(1+\lambda^2k^2)[(1+\lambda^2k^2)^2-\tau\Gamma_{\mathbf{k}}^2]}\times\left[\frac{1+\lambda^2k^2}{\Gamma_{\mathbf{k}}}e^{-\Gamma_{\mathbf{k}}|t-t'|}-\tau e^{-(1+\lambda^2k^2)|t-t'|/\tau}\right].$$

[1] C. W. Gardiner, *Handbook of Stochastic Methods* (Springer-Verlag, Berlin, 1990).

[2] P. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).

[3] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8, p. 267.

[4] S. Kai, S. Wakabayashi, and M. Imasaki, Phys. Rev. A **33**, 2612 (1986).

[5] H. Haken, *Laser Light Dynamics* (North-Holland, Amsterdam, 1985).

[6] W. Horsthemke and R. Lefever, *Noise Induced Transitions* (Springer-Verlag, Berlin, 1984).

[7] F. Family and T. Vicsek, *Dynamics of Fractal Surfaces* (World Scientific, Singapore, 1990).

[8] M. Kardar, G. Parisi, and Y.-C. Zhang, Phys. Rev. Lett. **56**, 889 (1986).

[9] E. Medina, T. Hwa, M. Kardar, and Y.-C. Zhang, Phys. Rev. A **39**, 3053 (1989).

[10] S. Das Sarma and P. I. Tamborenea, Phys. Rev. Lett. **66**, 325 (1991); Z.-W. Lai and S. Das Sarma, *ibid.* **66**, 2324 (1991).

[11] D. E. Wolf and J. Villain, Europhys. Lett. **13**, 389 (1990).

[12] T. Sun, H. Guo, and M. Grant, Phys. Rev. A **40**, 6763 (1989).

[13] P. M. Lam and F. Family, Phys. Rev. A **44**, 7939 (1991).

[14] T. Hwa and M. Kardar, Phys. Rev. Lett. **62**, 1833 (1989).

[15] P. M. Lam and F. Family, Phys. Rev. E **47**, 1570 (1993).

[16] J. Masoliver, K. Lindenberg, and B. J. West, Phys. Rev. A **34**, 2351 (1986).

[17] M. A. Rodriquez and L. Pesquera, Phys. Rev. A **34**, 4532 (1986).

[18] S. M. Rytov, Yu. A. Kravtsov, and V. I. Tatarski, *Principles of Statistical Radio Physics* (Springer-Verlag, Berlin, 1987), Vol. 1; Yu. L. Klimontovich, *The Kinetic Theory of Electromagnetic Processes* (Springer-Verlag, Berlin, 1983).

[19] R. F. Pawula and S. O. Rice, IEEE Trans. Inf. Theory **IT-32**, 63 (1986).

[20] R. F. Pawula, Phys. Rev. A **35**, 3102 (1987); **36**, 4996 (1987).

[21] J. Masoliver, Phys. Rev. A **45**, 706 (1992).

[22] K. Lindenberg, B. J. West, and J. Masoliver, in *Noise in Nonlinear Dynamical Systems,* edited by F. Moss and P. V. E. McCintock (Cambridge University Press, Cambridge, England, 1989), Vol. 1.

[23] J. M. Sancho, M. San Miguel, S. Katz, and J. D. Gunton, Phys. Rev. A **26**, 1589 (1982).

[24] J. Garcia-Ojalvo, J. M. Sancho, and L. Ramirez-Piscina, Phys. Rev. A **46**, 4670 (1992).

[25] P. M. Lam and D. Bagayoko, Phys. Rev. E **48**, 3267 (1993).

[26] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).

[27] S. F. Edwards, Proc. Phys. Soc. London **88**, 265 (1966).

[28] S. F. Edwards and M. Muthukumar, Macromolecules **17**, 586 (1984).

[29] K. Kawasaki, Ann. Phys. (N.Y.) **61**, 1 (1970); K. Kawasaki and J. D. Gunton, in *Progress in Liquid Physics,* edited by C. Croxton (Wiley, New York, 1978).

[30] E. J. Amis and C. C. Han, Polymers **23**, 1403 (1982); E. J. Amis, P. A. Janmey, J. D. Ferry, and H. Yu, Macromolecules **16**, 441 (1983).

[31] E. Eisele and W. Burchard, Macromolecules **17**, 1636 (1984).

[32] W. Brown, Macromolecules **17**, 66 (1984).

[33] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979), Chap. 3.