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Sponge phase of surfactant solutions: An unusual dynamic structure factor

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The dynamics near the symmetry-breaking transition in the sponge phase (L_3) of self-assembling surfactant solutions is considered. The surfactant motion is taken to be diffusive (conserved), while the order parameter for the transition (η) is assumed to follow two channels of relaxation: diffusion (conserved) and leakage (nonconserved). Our dynamical treatment is based on mean-field theory within a time-dependent Landau-Ginzburg approach, whose static limit reproduces an earlier successful theory of the static structure factor. We consider two main regimes: in the first, η relaxes rapidly compared to the surfactant diffusion, while in the second, the opposite limit applies. We find that in the fast-η regime the surfactant dynamical structure factor $S(k,t)$ is exponential in time, but the relaxation rate shows an unusual logarithmic behavior. On the other hand, in the slow-η regime, $S(k,t)$ is very nonexponential in time (although the average relaxation rates show the conventional critical slowing-down effects). We argue that a crossover from the fast-η to the slow-η case occurs as the k vector is increased. Implications for dynamic light scattering from sponge systems are discussed.

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I. INTRODUCTION

There has recently been increasing interest in the so-called sponge phase (or L_3 phase) of self-assembling surfactant systems [1–10]. (For a recent review see Ref. [2].) The sponge phase is typically formed in aqueous surfactant solutions [1,2], although analogues exist in oil-surfactant, and multicomponent, systems [3,10]. The phase is isotropic with no long-range order, though it typically occurs close to a lamellar phase in the phase diagram. In the sponge phase, x-ray and neutron-scattering measurements [8–10] have shown that locally the structure consists of surfactant bilayers. Moreover, light scattering and conductivity studies [10,11] have shown that the membranes form a connected (percolating) structure distributed in space as a random surface [4,5].

A sponge phase contains an infinite bilayer membrane of complex topology, and it is known that such a membrane divides space in two. This means that the phase is solvent *bicontinuous*: it contains two distinguishable regions of solvent, which can be classified arbitrarily as "inside" and "outside" the bilayer that divides them. The case when the total volumes of the "inside" and "outside" solvent regions is equal, called the symmetric (S) sponge phase, is then distinguishable from an asymmetric (A) phase, where these amounts are different. Since the same solvent occupies the "in" and "out" domains, it should be possible to have a continuous (second-order) transition between the S and the A phase [1–4,12]. In fact, such a transition is completely analogous to the second-order phase transition in the Ising spin model, where the "spin-up" clusters correspond to (say) the "in" regions, and the "spin-down" clusters to "out" regions. Note that the asymmetric phase has the same symmetry as a phase of disconnected vesicles and in fact may be connected to it on the phase diagram. In contrast, the unbroken symmetry of the S phase means that one cannot move from it to an ordinary liquid phase without passing through a phase transition.

A typical sponge phase is that of the water-rich H_2O–sodium dodecyl sulfate–pentanol system [1,2]. For this system Roux and co-workers [1] have observed the occurrence of a continuous S-A transition, which is easily detectable in turbidity measurements and is also manifested in a characteristic behavior of the static structure factor $S(k)$, discussed further in Sec. II below. Normally, the S to A transition can be tuned by decreasing the surfactant concentration ϕ and/or varying the amount of cosurfactant. Even for a binary or pseudobinary system, the transition when it occurs generically occupies a line (rather than a point) in the volume-fraction–temperature parameter space. Likewise at fixed temperature and pressure there is a line of transitions in the space defined by surfactant and cosurfactant volume fractions [3,1,2].

The scattering amplitude at long wavelengths (which can be made much larger than the typical "cell size" d of the sponge) was observed to diverge, on approaching this line, like $(\phi-\phi_c)^{-\epsilon}$ where ϕ_c is the critical value of ϕ and the value $\epsilon \simeq 0.5-0.6$ has been extracted. Near the transition the scattering amplitude $S(k)$ becomes effectively independent of ϕ, and develops a contribution proportional to the wavelength $\lambda = 2\pi/k$ [13].

This unusual and characteristic result, $S(k) \sim 1/k$, is in fact the signature of the energy-energy correlation function in the (mean-field approximation of) the Ising model [3], and is quite different from the usual Ornstein-Zernike behavior which for small wavelengths is $S(k) \sim k^{-2}$. This has been explained with the help of a detailed Landau-Ginzburg theory, which has provided good fits to most of the experimental results for static light scattering [3,1,2]. The theory is based on two fluctuating order parameters: one (η) describes the transition from a symmetric to an asymmetric sponge, the other (ρ) describes local fluctuations in the surfactant density. The characteristic static scattering arises because there is no contrast between "inside" and "outside" domains of solvent. The scattering is sensitive to the fluctuations of surfactant density only, and these are coupled quadratically to the order parameter η for the S-A transition. Thus the measured correlation function $S(k)=\langle \rho_k \rho_{-k} \rangle$ has a contribution proportional to $\langle (\eta^2)_k (\eta^2)_{-k} \rangle$, which is the energy-energy correlator in the equivalent Ising model [14–16].

Although the *static* scattering behavior is now reasonably well understood, measurements of the *dynamic* structure factor $S(k,t)$ have so far been limited to regimes far from the S-A transition and to wavelengths of the order of the cell size d of the sponge [8]. Moreover, no theory for $S(k,t)$ at longer wavelengths has yet been presented. Previous theory [17] is limited to qualitative predictions (based on dimensional arguments) for average relaxation times, but these do not address the neighborhood of the S-A transition or the shape of $S(k,t)$ in the time (or frequency) domain. It is interesting to consider whether the unusual character of the phase transition in the sponge phase leaves a special "fingerprint" on the dynamical structure factor, as it does in the static case. We approach this issue theoretically here, and predict that $S(k,t)$ can indeed show very unusual features involving (for example) extreme nonexponential relaxations in time. Below we discuss and delineate several regimes in which different types of relaxation are possible. Although it remains unclear which of our regimes are most relevant to experiment, measurements to determine $S(k,t)$ over a wide k range are currently planned [18], and it is hoped that these will clarify the situation.

In what follows, we use the time-dependent Landau-Ginzburg approach to calculate the dynamical structure factor near the S-A transition. The free energy we use is essentially the same as the one used by Roux *et al.* [3] and by Coulon and co-workers [1,2] for the calculation of the static structure factor. Surfactant molecules are conserved and the relaxation of ρ is therefore taken to be diffusive. However, as discussed in Ref. [17], we expect that the order parameter η for the S-A transition can equilibrate by two different modes: one is leakage of solvent between "inside" and "outside" regions (nonconservative relaxation), and the other is a diffusive process which does not change the total amount of "inside" and "outside" (conservative mode).

Most of our results concern the case when surfactant diffusion is rapid on the time scale of relaxation for fluctuations in η. We believe this is usually the relevant regime for experiments, although (since we assume a nonzero leakage rate) the assumption must fail for sufficiently small wave vectors. In the opposite limit, namely, when the relaxation of η is assumed to be much faster than the surfactant motion, a different approach, formulated some years ago by Halperin and co-workers [14,15,19,16], should be applicable. In this limit the details of the relaxation for η become irrelevant, since this order parameter can be "adiabatically eliminated" to give an effective theory for ρ. (This case is discussed fully in Sec. III B.) Note that in the other limit of main interest to us (slow η), a simple adiabatic elimination of ρ is not enough, since it is precisely the fluctuations of ρ, and not η, that are measured in experiment.

This paper is organized as follows. In Sec. II we review and (in Appendix A) rederive the result of Refs. [1–3] for the static structure factor of the sponge phase. In Sec. III we introduce the different relaxation channels in the sponge (Sec. III A). Thereafter, we first discuss the regime where the bare fluctuations of η of the S-A transition are much faster than those of the surfactant density ρ at the measured wavelength (Sec. III B). For this regime we make use of previous theoretical studies of analogous models, mentioned above [14,16]. We then deal with the opposite limit (fast ρ, slow η), which is of primary interest here, and obtain a general expression for the dynamic structure factor (Sec. III C). In Sec. IV A we analyze the outcome for the case where nonconservative modes dominate the η relaxation, and in Sec. IV B we analyze the outcome for the case where conservative modes dominate. In Sec. V we show consistency of our results, where appropriate, with the dynamical scaling laws introduced by Halperin, Hohenberg, and Ma [15]. Finally, in Sec. VI, we discuss the crossovers between the different relaxation regimes as the wave-vector magnitude is changed, and conclude by summarizing our main predictions for $S(k,t)$ in the various regimes of interest. Some of our main results have been summarized elsewhere [20].

II. THE STATIC STRUCTURE FACTOR

The Landau-Ginzburg free energy of the sponge involves two coupled order parameters [3,1,2]. One parameter is the surfactant density ϕ, or more precisely its deviation from some value ϕ^*, which we write as $\rho=\phi-\phi^*$. The other parameter η is the symmetry-breaking order parameter, which may be defined as the difference in "inside" and "outside" volume fractions:

$$\eta=\psi_{\text{in}}-\psi_{\text{out}} \; . \tag{2.1}$$

An equivalent definition for η can be made in terms of the mean curvature of the membrane $\langle 1/R_1+1/R_2 \rangle$ which vanishes in the symmetric phase. Since both "inside" and "outside" regions contain identical solvent material, there is no scattering contrast between them, and hence ρ is the only order parameter whose correlation function $S(k)=\langle \delta\rho_{\mathbf{k}} \delta\rho_{-\mathbf{k}} \rangle$ (where $\delta\rho=\rho-\langle \rho \rangle$) can be measured by scattering.

Following Coulon and co-workers [1,2], we consider the following Landau-Ginzburg expansion for the thermodynamic potential Φ near the S-A transition:

$$\Phi \equiv F-\frac{\mu}{V}\rho=\int f(\mathbf{r})d\mathbf{r} \; , \tag{2.2}$$

where V is the volume (set to unity below), μ is the surfactant chemical potential, and

$$f(\mathbf{r})=-\mu\rho+\tfrac{1}{2}a\rho^2+\tfrac{1}{4}b\rho^4+\tfrac{1}{2}\gamma_\rho(\nabla\rho)^2+\tfrac{1}{2}A\eta^2+\tfrac{1}{4}B\eta^4 +\tfrac{1}{2}\gamma_\eta(\nabla\eta)^2+\tfrac{1}{2}C\rho\eta^2+\tfrac{1}{2}\gamma_c\eta\nabla\eta\cdot\nabla\rho \; . \tag{2.3}$$

In Eq. (2.3) the first four terms represent a binary-liquid-type expansion for the ρ order parameter, and the next three an Ising-type expansion for η. [A is a constant which can be negative; $B>0$ is required (as usual) for stability.] The remaining two terms are couplings between η and ρ at the lowest order permitted by symmetry. Higher-order couplings are neglected [3,2]. The presence of nonzero coupling constants C and γ_c leads to a critical behavior of ρ near the S-A line, as observed in light-scattering experiments.

The free-energy expansion (2.3) has earlier been used to calculate the sponge S-A phase diagram [2,7] and the static structure factor (at the level of Gaussian-fluctuation theory) [2,3]. The calculation of the latter, in the general case [2], was limited to a perturbation expansion to first order in the coupling terms C and γ_c. However, a simple limit of the theory can be obtained by setting γ_ρ and γ_c identically to zero, and studying the behavior near tricriticality. For this special case, Roux *et al.* [3] were able to calculate exactly the static structure factor, where much of the interesting behavior [such as $S(k)\sim 1/k$] is already present.

In Appendix A we repeat the full calculation of the static structure factor $S(k)$ for the general case, but, in contrast to Ref. [2], we do this nonperturbatively. The result differs only in the presence of "effective" values for certain parameters (i.e., $\overline{\gamma}_\eta$ and $\overline{A}$ below), but this nonperturbative approach is needed if the results are to check with our (nonperturbative) calculation of the dynamic structure factor in Sec. III. We find in the Appendix (assuming [21] $\overline{\gamma}_\eta>0$)

$$[S(k)=\frac{\tilde{a}^{-1}}{1+\xi_\rho^2k^2}+\frac{\tilde{a}^{-2}(C+\frac{1}{2}\gamma_c k^2)^2}{(1+\xi_\rho^2k^2)^2}\times\left[\frac{\eta_0^2\overline{A}^{-1}}{1+\xi_\eta^2k^2}+\frac{1}{16\pi}\overline{\gamma}_\eta^{-2}\xi_\eta\frac{\tan^{-1}(k\xi_\eta/2)}{k\xi_\eta/2}\right]. \tag{2.4}$$

In this equation, ξ_η is the critical correlation length associated with the S-A transition and is given by

$$\xi_\eta^2=\frac{\overline{\gamma}_\eta}{\overline{A}}, \tag{2.5}$$

whereas

$$\xi_\rho^2=\frac{\gamma_\rho}{\tilde{a}} \tag{2.6}$$

defines the (bare) correlation length ξ_ρ associated with the surfactant fluctuations (i.e., that which would arise in the absence of coupling to η). The remaining parameters obey

$$\tilde{a}=a+3b\rho_0^2, \tag{2.7}$$

$$\overline{A}=A+C\rho_0+\eta_0^2\left[3B-\frac{C^2}{\tilde{a}}\right]+\frac{C^2}{2\tilde{a}}\langle\delta\eta^2\rangle, \tag{2.8}$$

$$\overline{\gamma}_\eta=\gamma_\eta+\eta_0^2\frac{C}{\tilde{a}}\left[\frac{C\gamma_\rho}{\tilde{a}}-\gamma_c\right]+\frac{C^2\gamma_\rho\langle\delta\eta^2\rangle}{2\tilde{a}^2}, \tag{2.9}$$

where ρ_0 and η_0 are the spatial averages of ρ and η, respectively.

The mean value η_0 vanishes in the symmetric (S) phase but is nonzero for an asymmetric sponge; if the transition is brought about by variation in the mean surfactant concentration these phases arise for $\rho_0>\rho_c$ and $\rho_0<\rho_c$, respectively, where $\rho_c=-A/C$. Note that the critical density ρ_c vanishes when $A=0$; the combination $\rho_0=\rho_c=0$ and $\tilde{a}=C^2/2B$ defines in fact a double critical end point [2,1]. Since we have defined $\rho_0=\phi-\phi^*$, we may identify ϕ^* as the surfactant density at this high-order critical point [2]. Thus the Landau-Ginzburg expression used above is (for $\tilde{a}=C^2/2B$) an expansion around this point on the (η,ϕ) plane. It can be shown [2] from Eqs. (2.5) and (2.8) that $\xi_\eta\sim|\phi-\phi_c|^{-1}$ where $\phi_c=\rho_c+\phi^*$; the critical exponent 1 is different from the usual mean-field critical exponent $\frac{1}{2}$ due to the presence of the term involving $\langle\delta\eta^2\rangle$ in Eq. (2.8). This term arises [2] when the constraint $\langle\rho\rangle=\rho_0$ is used to eliminate the chemical potential μ (see Appendix A). It leads to Fisher renormalization [22] of the critical exponents, when Eq. (2.8) is solved self-consistently [2] for $\overline{A}$. As a result, for $\phi<\phi_c$, the behavior of the mean Ising order parameter is $\eta_0\sim\phi_c-\phi$, with exponent unity rather than $\frac{1}{2}$.

In the S phase ($\eta_0=0$) the first term in the square brackets of Eq. (2.4) does not contribute. In the A phase ($\eta_0\neq 0$) we can replace $\eta_0^2\overline{A}^{-1}$ in Eq. (2.4) by $(2B-C^2/\tilde{a})^{-1}$ which is a noncritical constant (except on approaching the double critical end point). As the S-A transition is approached from the A phase, when $k\xi_\eta\gg 1$, the second term in the square brackets of Eq. (2.4) dominates so that the $S(k)$ function obtained in the A phase coincides at the critical point with that obtained from the symmetric side, as obviously it should. In this regime $S(k)\sim k^{-1}$, a result quite unusual for liquids, as previously described. On the other hand, when $k\xi_\eta\ll 1$, the first term in the square brackets is just a noncritical constant (or identically zero in the symmetric phase), while the second term diverges critically, being proportional to ξ_η. Hence $S(k)\sim\xi_\eta$ in this regime [23].

The result (2.4) has been shown to fit well the scattering measurements [3,1,2], although because of the number of free parameters involved it seems that only the value of ξ_η obtained from these measurements is accurate. For some systems in which the S-A transition is first order [3,8], the simplified version of the theory as presented in Ref. [3], which has a reduced number of parameters, is found to fit very well. In this limit there is a corresponding simplification of the dynamical theory presented in Sec. III C, as outlined in Ref. [20].

The above calculations are based on a Gaussian-fluctuation treatment and hence give mean-field exponents. As mentioned previously, the results should break down in a critical interval near the S-A transition line, but this interval may be very narrow near a tricritical point. Near such a point, there is a wide region where the mean-field–Gaussian-fluctuation picture is almost exact (with only logarithmic corrections). Moreover, as mentioned earlier, the Landau-Ginzburg expansion Eq. (2.3) is in fact an expansion about a double critical end point which has upper critical dimension $\frac{8}{3}$ and hence gives *exact* mean-field behavior in three dimensions.

Far from any tricritical region of the model, the mean-field exponents will be modified. The appropriate behavior [24,20] can be found by noting that $S(k)$ continues to scale as the energy-energy correlation function. For $k\xi_\eta \ll 1$, the result is that $S(k)$ behaves as $\xi_\eta^{\alpha/\nu}$, and for $k\xi_\eta \gg 1$, $S(k) \sim k^{-\alpha/\nu}$, where α and ν are the usual specific-heat and correlation-length critical exponents: $\alpha=0.12$ and $\nu=0.64$.

We note, however, that so far there is little evidence for anything other than Gaussian-fluctuation behavior in these systems [1,2]. In what follows we focus on calculating the dynamic structure factor within the same Gaussian-fluctuation model that was successfully used for the static case. In the limit of fast-η relaxation (Sec. III B), however, some discussion of true critical regime is given.

III. DYNAMIC STRUCTURE FACTOR

A. Relaxation channels in the sponge

The different hydrodynamic modes expected in the sponge phase were qualitatively discussed by Milner, Cates, and Roux [17]. The relaxation of the S-A order parameter is expected to follow two main channels.

(i) The first channel corresponds to solvent flow within each of the "inside" and "outside" regions, but does not involve crossing of the bilayers. Hence this is a conservative mode, which should be diffusive in nature. By "conservative" it is meant that the total amount of "inside" and "outside" in the (infinite) system cannot change by this mode, but any finite-wavelength perturbation is able to relax. This is true because both of the solvent domains percolate over infinite distances.

(ii) The second channel is related to leakage through the membrane. The leakage might be either due to fluid flow through small defects or holes that could arise at random in the bilayer, or due to diffusion of single solvent molecules across it. Since the statistics of the process are uncertain, we simply introduce a free parameter τ which represents an intrinsic local decay time for the η order parameter arising from this type of relaxation. (In contrast, all the other kinetic parameters that we shall need can be estimated in terms of the solvent viscosity μ_s and the static correlation lengths ξ_ρ and ξ_η.)

The motion of the surfactant order parameter ρ can only be diffusive, since (in the absence of chemical reactions) the overall surfactant density is a conserved quantity. To calculate the relevant diffusion constant, we neglect the very small amount of free surfactant which may be able to diffuse freely through the solvent domains. We may also ignore the diffusion of surfactant molecules within the bilayers, since these are almost incompressible two-dimensional fluids (at wavelengths of interest). Remaining modes are the two-dimensional fluid flow within the films, and the three-dimensional diffusion of the films themselves (which undergo random thermal motion similar to that of polymers in solution). As shown in Ref. [17], both of these modes are coupled hydrodynamically to the solvent, and the resulting relaxation rates are related to the "Zimm time" of pieces of bilayer, as described more formally below.

In studying the dynamics, two main regimes can be distinguished depending on the relative relaxation rates for η and ρ. We consider these now in turn.

B. The fast-η case

First [20], we consider the case where the relaxation of the η order parameter, determined under conditions where ρ is held fixed, are rapid compared to the relaxation of ρ itself. If η is nonconserved ($\tau^{-1}>0$), this condition should always apply in principle for small enough wave vectors k. In this regime ρ represents a slow secular perturbation in the bare Hamiltonian for η. Conversely, the η fluctuations can be adiabatically eliminated [25] from the time-dependent equations for ρ: the rapidly relaxing η field is integrated out, to give an effective Hamiltonian for ρ in which η does not appear at all. This case has been studied in Refs. [14,15]; the dynamic structure factor $S(k,t)=\langle \delta\rho_{\mathbf{k}}(t)\delta\rho_{-\mathbf{k}}(0)\rangle$ should be single exponential in time, with a k-dependent relaxation rate

$$\Gamma_k \equiv D_{\text{eff}}(k)k^2 = \frac{\Lambda_{\text{eff}}(k)k^2}{S(k)} \tag{3.1}$$

which is independent of any details of the η dynamics. Here $S(k)\equiv S(k,0)$ denotes as usual the static structure factor; Λ_{eff} and D_{eff} are effective Onsager and diffusion coefficients. Hence, if Λ_{eff} has no critical behavior, there is a critical slowing down arising solely from the divergence of $S(k)$ (at small k) when $\xi_\eta \to \infty$ Refs. [26,15]. Close to the S-A transition (and in the mean-field approximation) this yields the results [15] $\Gamma_k \sim k^2\xi_\eta^{-1}$ (for $k\xi_\eta \ll 1$), and $\Gamma_k \sim k^3$ (for $k\xi_\eta \gg 1$).

In the sponge phase, however, we must allow for the fact that there is a hydrodynamic coupling between fluctuations in ρ and the solvent velocity field. This can lead to an additional singular behavior in the Onsager coefficient $\Lambda_{\text{eff}}(k)$ in Eq. (3.1) [25,19]. This is simply understood in the language of polymers: patches of bilayer interact hydrodynamically through the Oseen tensor [25,27–29], which in three dimensions decreases with distance as $1/r$. In the small-wave-vector regime ($k\xi_\eta \ll 1$), this coupling leads, within the Kawasaki approximation (in real space), to a limiting value [25,30,27,29]

$$\Lambda_{\text{eff}}(0) = \int d\mathbf{r}\, g(\mathbf{r}) \frac{k_B T}{6\pi\mu_s r}\,, \tag{3.2}$$

where μ_s is the solvent viscosity and $g(\mathbf{r})$ the density-density correlation function [whose Fourier transform is $S(\mathbf{k})$]. One can think of this as defining the hydrodynamic coupling within a "blob" of size ξ_η. In $\mathbf{k}$ space Eq. (3.2) becomes

$$\Lambda_{\text{eff}}(0) = \frac{k_B T}{3\pi^2\mu_s} \int_0^{q_{\max}} S(q)\,dq \tag{3.3}$$

which is now a one-dimensional integral.

Using Eq. (2.4) in Eq. (3.3) one can confirm that if

$\gamma_c \neq 0$ this integral diverges logarithmically with $q_{\max}$. The result arises because $S(q)$ behaves as q^{-1} for $q \to \infty$, and is therefore a direct consequence of the peculiar non-Ornstein-Zernike form of the static correlation function in sponge phases. The novel q dependence comes from the term proportional to $\arctan(q\xi_\eta/2)/q$ in Eq. (2.4), which in real space translates to $g(r)=r^{-2}\exp(-2r/\xi_\eta)$. The same physical divergence of course arises at short real-space separations if this is used in Eq. (3.2). This is reminiscent of the weak divergence that occurs for the hydrodynamic drag on an infinitely thin rod. Indeed one might argue that the density fluctuations in the sponge phase have a fractal dimension of 1 rather than 2 (which would be the usual Ornstein-Zernike case, and would apply for a Gaussian polymer). As a result, the hydrodynamic interaction is only marginal [31,20].

A suitable choice for the maximum q cutoff in Eq. (3.3) is $q_{\max}=1/d$ where d ($\sim \xi_\rho$) is the cell size of the sponge. [Since this is the short-length cutoff for the Landau-Ginzburg analysis, we may also assume for consistency that $\xi_\rho > d$.] We then find [20,32] that Λ_{eff} diverges as $\ln(\xi_\eta/\xi_\rho)$ Ref. [33]. Therefore for $\xi_\eta \gg \xi_\rho$ (i.e., close to the transition) and small enough k we obtain [34]

$$D_{\text{eff}}(k \to 0) \sim \frac{k_B T}{\mu_s \xi_\eta} \ln\left[\frac{\xi_\eta}{\xi_\rho}\right] . \tag{3.4}$$

This result resembles the Stokes diffusion coefficient of a rod of width ξ_ρ and length ξ_η Ref. [28]. It differs by the logarithmic factor from the Stokes diffusion coefficient of a sphere of radius ξ_η, which is the Stokes-Kawasaki-type result for a normal Ornstein-Zernike correlation function.

For $k\xi_\eta \gg 1$ one has to use a more general expression than Eq. (3.3) for the effective Onsager coefficient, which becomes explicitly k dependent [25,28]. Physically, this corresponds to separating the system into blobs of size k^{-1} rather than ξ_η. The formal result, which is valid for arbitrary k [and reduces to Eq. (3.3) for $k \to 0$], is [25,28]

$$\Lambda_{\text{eff}}(k) = \frac{k_B T}{4\pi^2 \mu_s k^2} \times \int_0^{q_{\max}} q^2 S(q) \left[\frac{q^2+k^2}{2kq} \ln\left[\frac{k+q}{k-q}\right] - 1 \right] dq . \tag{3.5}$$

For $k\xi_\eta \gg 1$ we then obtain [32] using Eqs. (2.4), (3.5), and (3.1),

$$\Gamma_k \sim \frac{k_B T}{\mu_s} \ln\left[\frac{1}{k\xi_\rho}\right] k^3 \tag{3.6}$$

which demonstrates an unusual k dependence of the relaxation rate. This result differs only in the logarithm from that calculated by *neglecting* hydrodynamics [as discussed following (3.1)].

The above discussion is based on the Gaussian-fluctuation theory using mean-field exponents. It is interesting to see qualitatively the effect of using the exact critical exponents, which become relevant very close to the S-A line far from any tricritical point. In this case, we find that hydrodynamics is irrelevant for the critical behavior [20,32]: the effective Onsager coefficient in Eq. (3.3) is not critical (due to the fact that $\alpha/\nu < 1$) and the conventional Van Hove theory [26] for critical slowing down holds; the critical slowing down is entirely due to the divergence of the structure factor $S(0)$. We then have

$$\Gamma_k \sim \begin{cases} \dfrac{k_B T}{\mu_s \xi_\rho^{1-\alpha/\nu}} \dfrac{k^2}{\xi_\eta^{\alpha/\nu}} & \text{for } k\xi_\eta \ll 1 \\[2ex] \dfrac{k_B T}{\mu_s \xi_\rho^{1-\alpha/\nu}} k^{2+\alpha/\nu} & \text{for } k\xi_\eta \gg 1 \, . \end{cases} \tag{3.7}$$

The calculations given above should apply for sufficiently small values of k, when the (presumed nonconservative) intrinsic relaxation of η is fast compared to the conserved, and therefore slowly relaxing, ρ fluctuations. However, for finite k and close enough to the S-A transition, it is possible instead that the opposite condition would apply. This is because near the transition η is intrinsically critical whereas ρ is not: ρ develops long-wavelength fluctuations only by virtue of its coupling to η. Likewise at a fixed distance from the transition, we expect at some k^* a crossover to a limit where the intrinsic fluctuations of ρ are much faster than those of η. Next we consider in detail this new regime, which we expect to be the relevant one in most experiments. The estimate of the crossover wave number k^* is deferred to Sec. VI.

C. The fast-ρ case

We wish to find the dynamic structure factor $S(k,t) \equiv \langle \delta\rho_{\mathbf{k}}(t)\delta\rho_{-\mathbf{k}}(0)\rangle$ in the regime where the intrinsic relaxation rate for ρ is fast compared to that for η. In this case, ρ can be adiabatically eliminated from the equation governing the dynamics of η, since ρ samples its full equilibrium distribution (conditional on a specified state for η) on a time scale rapid compared to changes in η itself. Therefore slow fluctuations of the order parameter η are controlled by the effective free energy, found by integrating over fluctuations in ρ [cf. Eq. (A13)].

However, since scattering experiments probe only ρ fluctuations, we must after finding the dynamics of η use this to work backwards and compute the fluctuation spectrum for ρ. In this part of the calculation, η represents a slowly varying driving force (of known statistics) on the ρ fluctuations. The coupling between ρ and η is present already in the free energy (2.3) (the terms in C and γ_c). We may exclude the possibility that any further coupling originates from nondiagonal terms in the Onsager matrix for η and ρ; such couplings are forbidden since the motion of ρ must be invariant under the change $\eta \to -\eta$ Ref. [17].

We may therefore assume the following kinetic equations for η and ρ:

$$\frac{\partial}{\partial t}\eta(\mathbf{r},t)=-\frac{1}{\tau}\frac{\delta F_{\text{eff}}}{\delta\eta}+\int d\mathbf{r}'\Lambda_\eta(\mathbf{r}-\mathbf{r}')\nabla^2_{\mathbf{r}'}\frac{\delta F_{\text{eff}}}{\delta\eta(\mathbf{r}')}+\theta(\mathbf{r},t)\ , \tag{3.8}$$

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t)=\int d\mathbf{r}'\Lambda_\rho(\mathbf{r}-\mathbf{r}')\nabla^2_{\mathbf{r}'}\frac{\delta F}{\delta\rho(\mathbf{r}')}+\kappa(\mathbf{r},t)\ . \tag{3.9}$$

The first term on the right in Eq. (3.8) represents the nonconservative motion of solvent across the bilayer from "inside" to "outside" regions. The corresponding kinetic (Onsager) coefficient is simply τ^{-1} as discussed in Sec. III A. The second term in Eq. (3.8) represents conservative (diffusive) motion of η with an Onsager coefficient Λ_η. A similar coefficient for conservative ρ relaxation appears in Eq. (3.9). Thus the dynamics involves three kinetic coefficients in addition to the parameters in the Hamiltonian. In Eqs. (3.8) and (3.9) $\theta(\mathbf{r},t)$ and $\kappa(\mathbf{r},t)$ are white-noise terms whose correlation functions may be determined by the fluctuation-dissipation theorem. These terms do not contribute to the dynamic structure factor $S(k,t)$ and are therefore not discussed further in this paper [35].

In Eqs. (3.8) and (3.9) the Onsager coefficients $\Lambda_\rho(\mathbf{r})$ and $\Lambda_\eta(\mathbf{r})$ for conservative relaxation modes are taken to be nonlocal. This form allows for hydrodynamic interactions to be included [25,27,28,36]. Such interactions arise because the solvent velocity field is generally coupled to fluctuations in the fields η and ρ [see, e.g., Eq. (3.5)]. This could be handled by introducing explicitly a third stochastic equation for the fluctuating velocity field [25,19]; however, this can be avoided if appropriate forms for the nonlocal Onsager coefficients are chosen. Suitable expressions are discussed later in this section.

Within our fast-ρ approximation, fluctuations in η can be described by an autonomous equation which does not involve ρ [namely, Eq. (3.8)]. This allows us to treat η in Eq. (3.9) as time-dependent random source field. Transforming Eqs. (3.8) and (3.9) to the **k** space, and using Eqs. (2.3) and (A13), we obtain (for small $\delta\eta=\eta-\eta_0$ and $\delta\rho=\rho-\rho_0$, and for $\mathbf{k}\neq\mathbf{0}$)

$$\frac{\partial}{\partial t}\delta\eta_{\mathbf{k}}(t)=-L_\eta(k)\delta\eta_{\mathbf{k}}(t)\ , \tag{3.10}$$

where

$$L_\eta=[\tau^{-1}+k^2\Lambda_\eta(k)](\overline{A}+\overline{\gamma}_\eta k^2) \tag{3.11}$$

and

$$\frac{\partial}{\partial t}\delta\rho_{\mathbf{k}}(t)=-L_\rho(k)\delta\rho_{\mathbf{k}}(t)-k^2\Lambda_\rho(k)\zeta_{\mathbf{k}}(t)\ , \tag{3.12}$$

where

$$L_\rho=k^2\Lambda_\rho(k)(\tilde{a}+\gamma_\rho k^2)\ , \tag{3.13}$$

and where $\zeta_{\mathbf{k}}$ is given by

$$\zeta_{\mathbf{k}}=\eta_0(C+\tfrac{1}{2}\gamma_c k^2)\delta\eta_{\mathbf{k}}+\tfrac{1}{2}\sum_{\mathbf{q}}(C+\gamma_c\mathbf{k}\cdot\mathbf{q})\delta\eta_{\mathbf{q}}\delta\eta_{\mathbf{k}-\mathbf{q}}\ . \tag{3.14}$$

The effective source term in the ρ dynamics, $\zeta_{\mathbf{k}}$, includes a part which varies essentially like $(\delta\eta^2)_{\mathbf{k}}$ [i.e., the Fourier transform of $\delta\eta(\mathbf{r})^2$]. As discussed in Sec. II for the static structure factor, one can view the ρ fluctuations as being biased locally with a mean value that varies as η^2 in real space. The structure of the source term ζ in our dynamical calculations precisely reflects this effect.

We can now solve Eq. (3.10) and use the solution to find the source term $\zeta_{\mathbf{k}}(t)$. From Eq. (3.12), we obtain, in terms of ζ_k,

$$S(k,t)=\exp[-L_\rho t]S(k,0)-k^2\Lambda_\rho\int_0^t dt'\exp[-L_\rho(t-t')]\times\langle\zeta_{\mathbf{k}}(t')\delta\rho_{-\mathbf{k}}(0)\rangle\ . \tag{3.15}$$

In Appendix B we calculate explicitly the expectation value $\langle\zeta_{\mathbf{k}}(t)\delta\rho_{-\mathbf{k}}(0)\rangle$. Using the result in Eq. (3.15) and integrating over t', we then obtain

$$\begin{aligned}S(k,t)={}&\exp[-L_\rho(k)t]S(k,0)+k^2\Lambda_\rho(k)\frac{C+\frac{1}{2}\gamma_c k^2}{\tilde{a}+\gamma_\rho k^2}\\&\times\left\{\eta_0^2\overline{A}^{-1}\left[\frac{C+\frac{1}{2}\gamma_c k^2}{1+\xi_\eta^2k^2}\right]\left[\frac{\exp[-L_\eta(k)t]-\exp[-L_\rho(k)t]}{L_\rho(k)-L_\eta(k)}\right]\right.\\&+\frac{1}{2}\sum_{\mathbf{q}}\frac{C+\gamma_c\mathbf{k}\cdot\mathbf{q}}{(\overline{A}+\overline{\gamma}_\eta q^2)[\overline{A}+\overline{\gamma}_\eta(\mathbf{k}-\mathbf{q})^2]}\\&\left.\times\left[\frac{\exp\{-[L_\eta(q)+L_\eta(\mathbf{k}-\mathbf{q})]t\}-\exp[-L_\rho(k)t]}{L_\rho(k)-L_\eta(q)-L_\eta(\mathbf{k}-\mathbf{q})}\right]\right\}\ .\end{aligned} \tag{3.16}$$

The static structure factor $S(k,0)$ appearing on the right in Eq. (3.16) is precisely as given by Eq. (2.4).

Equation (3.16) is the most important result of this paper. Obviously it is a complicated expression, but one that can be reduced to simpler forms in many limiting cases, several of which are discussed below. Note that, for the symmetric (S) phase $\eta_0=0$ and the first term in the large curly brackets does not appear. On the other hand, in the asymmetric (A) phase we can replace $\eta_0^2\overline{A}^{-1}$ in Eq. (3.16) by $(2B-C^2/\tilde{a})^{-1}$ which is a noncritical constant.

In Appendix C we argue that, for the regime of rapid ρ relaxation to which Eq. (3.16) refers (rather than the fast-η limit considered in Sec. III B), the inequality $L_\rho(k) \gg L_\eta(k)$ always applies. While the same inequality cannot hold for all q in the sum in Eq. (3.16), it may be checked that so long as either $L_\rho t \gg 1$ or $(\xi_\eta/\xi_\rho)^{1/3}(k\xi_\eta)^{2/3} \gg 1$ [37], the part of the sum for which the inequality $L_\rho(k) \gg L_\eta(q)$ does not hold is negligible [38]. Under these conditions, we obtain a simplified form for $S(k,t)$ by formally taking the limit $L_\rho/L_\eta \to \infty$ while keeping $L_\rho t$ of arbitrary magnitude. Making use of Eq. (2.4) for $S(k,0)$ [39], we then obtain

$$S(k,t)=\frac{\exp[-L_\rho(k)t]}{\tilde{a}+\gamma_\rho k^2}+\frac{(C+\frac{1}{2}\gamma_c k^2)^2}{(\tilde{a}+\gamma_\rho k^2)^2}\left\{\eta_0^2\overline{A}^{-1}\frac{\exp[-L_\eta(k)t]}{1+\xi_\eta^2 k^2}+Y(k,t)\right\}, \tag{3.17}$$

where we have defined

$$Y(k,t)=\frac{1}{(2C+\gamma_c k^2)}\times\sum_{\mathbf{q}}\frac{C+\gamma_c\mathbf{k}\cdot\mathbf{q}}{(\overline{A}+\overline{\gamma}_\eta q^2)[\overline{A}+\overline{\gamma}_\eta(\mathbf{k}-\mathbf{q})^2]}\times\exp\{-[L_\eta(\mathbf{q})+L_\eta(\mathbf{k}-\mathbf{q})]t\} . \tag{3.18}$$

Note that the result reduces, as it should, to the static structure factor for $t=0$ Ref. [40]; the first term in $\exp[-L_\rho t]$ ensures this even if it gives a negligible contribution at larger times. Moreover, Eq. (3.17) can also be obtained from the defining equation $S(k,t)\equiv\langle\rho_{\mathbf{k}}(t)\rho_{-\mathbf{k}}(0)\rangle$ by writing $\rho_{\mathbf{k}}(t)=\bar{\rho}_{\mathbf{k}}(t)+\Delta_{\mathbf{k}}(t)$, where the biased mean is $\bar{\rho}_{\mathbf{k}}(t)=-\zeta_{\mathbf{k}}(t)/(\tilde{a}+\gamma_\rho k^2)$ and we assume that the fluctuation $\Delta_{\mathbf{k}}(t)$ decays rapidly from its initial value: $\langle\Delta_{\mathbf{k}}(t)\Delta_{-\mathbf{k}}(0)\rangle=(\tilde{a}+\gamma_\rho k^2)^{-1}\exp[-L_\rho(k)t]$.

To make Eq. (3.17) useful, knowledge of the three kinetic parameters involved is required. While an estimation of the leakage time τ is rather difficult, we can comment on the form of the Onsager coefficients $\Lambda_\eta(k)$ and $\Lambda_\rho(k)$ or, equivalently, the diffusion coefficients

$$D_\eta\equiv\Lambda_\eta(k)(\overline{A}+\overline{\gamma}_\eta k^2) , \tag{3.19}$$

$$D_\rho\equiv\Lambda_\rho(k)(\tilde{a}+\gamma_\rho k^2) . \tag{3.20}$$

Within the Kawasaki-Stokes approximation [25,28], the incorporation of hydrodynamic interactions leads to the generalized Stokes laws

$$D_\eta(k)=\frac{k_B T}{6\pi\mu_s\xi_\eta}\Omega(k\xi_\eta) , \tag{3.21}$$

$$D_\rho(k)=\frac{k_B T}{6\pi\mu_s\xi_\rho}\Omega(k\xi_\rho) , \tag{3.22}$$

each of which can be obtained by combining Eq. (3.5) with a suitable Ornstein-Zernike expression for the correlation function. (Note that, in the case of ρ, this diffusion constant is that which would arise without coupling to η, and is therefore of a conventional form rather than the anomalous type obtained in Sec. III B [19].) In Eqs. (3.21) and (3.22), μ_s is the solvent viscosity, and $\Omega(x)$ is a scaling function which has the following limits: $\Omega(x)\to 1$ for $x\to 0$ and $\Omega(x)\sim x$ for $x \gg 1$. (The latter leads as required to a k^3 behavior of the relaxation rate at large k.) More precisely [25,28]

$$\Omega(x)=\tfrac{3}{4}x^{-2}[1+x^2+(x^3-x^{-1})\tan^{-1}x] . \tag{3.23}$$

Restoring finally the nonconservative decay term ($\sim\tau^{-1}$) for η, the relaxation rates may be written as

$$L_\eta(k)=\frac{\overline{\gamma}_\eta}{\tau}\frac{1}{\xi_\eta^2}(1+\xi_\eta^2 k^2)+D_\eta k^2 \tag{3.24}$$

and

$$L_\rho(k)=D_\rho k^2 , \tag{3.25}$$

where the D's obey Eqs. (3.21) and (3.22).

The multiexponential decay of $Y(k,t)$ in Eq. (3.18) should lead to a clear fingerprint of the slow dynamics of the underlying S-A order parameter (η) as observed by scattering from the surfactant density (ρ). This term is also responsible for the characteristic arctangent scattering form for $t=0$ (see Appendix A): the same physics that leads to the breakdown of Ornstein-Zernike scattering for $S(k,0)$ leads here to a nonexponential time dependence. This is explored more fully in Sec. IV where we calculate $Y(k,t)$ for some special cases.

IV. CONSERVATIVE AND NONCONSERVATIVE RELAXATION

A. Nonconservative case

Here we discuss the case where the relaxation of η is dominated by the leakage process, so the relaxation is nonconservative. If $\tau^{-1} \gg k^2\Lambda_\eta(k)$ Eq. (3.24) reduces to

$$L_\eta\simeq\frac{\overline{\gamma}_\eta}{\tau}\frac{1}{\xi_\eta^2}(1+\xi_\eta^2 k^2) . \tag{4.1}$$

For this case we have derived the following scaling form for $Y(k,t)$ (see Appendix D):

$$Y(k,t)=\frac{1}{16\pi}\overline{\gamma}_\eta^{-2}\xi_\eta U(k\xi_\eta,t/\tau_a) , \tag{4.2}$$

where

$$\tau_a^{-1}=\frac{\overline{\gamma}_\eta}{\tau\xi_\eta^2} \tag{4.3}$$

and where the scaling function $U(x,z)$ is given in Eq. (D2).

The function $U(k\xi_\eta,t/\tau_a)$ is a strongly nonexponential function of time t. Its precise form may be found by numerical integration. However, for small k ($k\xi_\eta \ll 1$)

we can replace $U(x,z)$ by $U(0,z)$, which obeys

$$U(0,z)=(1+4z)[1-\Phi((2z)^{1/2})] -2(2z/\pi)^{1/2}\exp(-2z)\ , \qquad (4.4)$$

where $\Phi(u)$ is the usual error function [41] $[\Phi(u)=2/\sqrt{\pi}\int_0^u e^{-t^2}dt]$. Hence the relaxation rate of $Y(k,t)$ in this limit scales as ξ_η^{-2}, the well-known mean-field result for critical slowing down in systems where hydrodynamic interactions do not dominate [42]. Combining Eqs. (4.2), (4.4), and (3.17) yields a relatively simple expression for $S(q,t)$ which could be a useful form for fitting to experimental results; for example, in a symmetric sponge we have

$$S(k,t)=\frac{\exp[-L_\rho t]}{\tilde{a}+\gamma_\rho k^2}+\frac{1}{16\pi}\frac{(C+\frac{1}{2}\gamma_c k^2)^2}{(\tilde{a}+\gamma_\rho k^2)^2}\bar{\gamma}_\eta^{-2}\xi_\eta \times\left[(1+4t/\tau_a)[1-\Phi((2t/\tau_a)^{1/2})]-2\left[\frac{2t}{\tau_a\pi}\right]^{1/2}\exp(-2t/\tau_a)\right]\ , \qquad (4.5)$$

where the first term is not critical, and may be small in practice.

The asymptotic behavior of the scaling function $U(0,z)$ is as follows:

$$U(0,z)\simeq\begin{cases}1-3.19z^{1/2} & \text{for } z\ll 1\\ 0.20z^{-3/2}e^{-2z} & \text{for } z\gg 1\ .\end{cases} \qquad (4.6)$$

Hence for small k (i.e., for $k\xi_\eta \ll 1$) the anomalous relaxation is manifested at short times as $Y(k,t)\propto 1-\text{const}\times t^{1/2}$ and at long times as $Y(k,t)\propto t^{-3/2}\exp[-\text{const}\times t]$. We see that $S(k,t)$ has an algebraic prefactor even at long times, and the relaxation is never purely exponential [43].

We now consider (4.3) in the high-k regime $(k\xi_\eta \gg 1)$, which of course encompasses all k when one is at the critical point $(\xi_\eta \rightarrow \infty)$. In this case we find that

$$Y(k,t)=\tfrac{1}{16}\bar{\gamma}_\eta^{-2}\frac{\tilde{U}(t/\tau_b)}{k}\ , \qquad (4.7)$$

where

$$\tau_b^{-1}=k^2\frac{\bar{\gamma}_\eta}{\tau} \qquad (4.8)$$

and where $\tilde{U}(z)$ is given by Eq. (D10). This shows that the relaxation rate is proportional to k^2 in this regime. The scaling function $\tilde{U}(z)$ has the following asymptotic forms (Appendix D):

$$\tilde{U}(z)\simeq\begin{cases}1-1.02z^{1/2} & \text{for } z\ll 1\\ 0.25z^{-1/2}e^{-z} & \text{for } z\gg 1\ .\end{cases} \qquad (4.9)$$

At short times this implies that $Y(k,t)\propto 1-\text{const}\times t^{1/2}$, as for the low-$k$ limit discussed above (though the constant is different). At long times we obtain $Y(k,t)\propto t^{-1/2}\exp[-\text{const}\times t]$, which again has a power-law prefactor.

In Fig. 1 we present a logarithmic-linear plot of the scaling function $U(0,z)$ (which is relevant to the limit of small $k\xi_\eta$) as a function of the reduced time z. It is clear that $U(0,z)$ is a strongly nonexponential function, especially for short times. The same applies for the high-wave-vector limit $k\xi_\eta \rightarrow \infty$ for which the corresponding scaling function $\tilde{U}(z)$ is plotted in Fig. 2.

B. Conservative case

We now turn to the case where τ^{-1} in Eq. (3.18) is so small that it can be neglected. In this case we can use without modification the Kawasaki approximation for the hydrodynamic relaxation rate as given in Eq. (3.21).

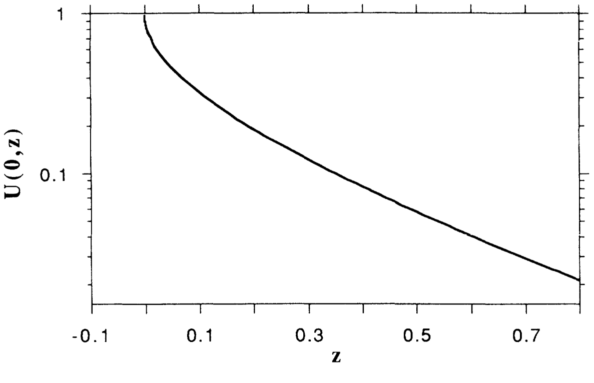

FIG. 1. Nonconserved η, and $k\xi_\eta=0$. Scaling function $U(0,z)$ against the reduced time $z=t/\tau_a$ on a logarithmic-linear plot. τ_a is given by Eq. (4.3).

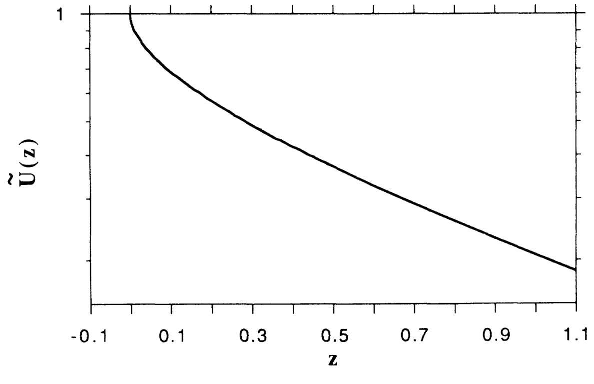

FIG. 2. Nonconserved η, and $k\xi_\eta \rightarrow \infty$. Scaling function $\tilde{U}(z)$ against the reduced time $z=t/\tau_b$ on a logarithmic-linear plot. τ_b is given by Eq. (4.8).

We thereby find the following scaling form:

$$Y(k,t)=\frac{1}{16\pi}\overline{\gamma}_\eta^{-2}\xi_\eta F(k\xi_\eta,t/\tau_c)\ , \tag{4.10}$$

where τ_c obeys

$$\tau_c^{-1}=\frac{k_BT}{6\pi\mu_s\xi_\eta^3} \tag{4.11}$$

and is the "Zimm time" of a blob of linear size ξ_η. The full form of the scaling function $F(k\xi_\eta,t/\tau_c)$ is given in Eq. (D17).

In the low-k regime $(k\xi_\eta \ll 1)$ we can use $F(x,z)\simeq F(0,z)$ for which we obtain a simple expression

$$F(0,z)=\frac{4}{\pi}\int_0^\infty dy\frac{y^2}{(1+y^2)^2}\exp[-2zy^2\Omega(y)] \tag{4.12}$$

which has the following asymptotic forms [44]:

$$F(0,z)\simeq\begin{cases}1-2.29z^{1/3} & \text{for } z \ll 1\\ 0.20z^{-3/2} & \text{for } z \gg 1\ .\end{cases} \tag{4.13}$$

Hence in the short-time limit $Y(k,t)\propto 1-\text{const}\times t^{1/3}$. For long times the relaxation becomes a *purely algebraic decay in time*: $Y(k,t)\propto t^{-3/2}$. This contrasts with the conservative case discussed in Sec. IV A and is obviously a very unusual behavior for $S(k,t)$.

For the high-k limit $(k\xi_\eta \gg 1)$ we obtain in the conservative case the following scaling form:

$$Y(k,t)=\tfrac{1}{16}\overline{\gamma}_\eta^{-2}\frac{\tilde{F}(t/\tau_d)}{k}\ , \tag{4.14}$$

where

$$\tau_d^{-1}=\frac{k_BT}{6\pi\mu_s}k^3 \tag{4.15}$$

and where the scaling function $\tilde{F}(z)$ is given in Eq. (D21). Here the relaxation rate scales as k^3. The following asymptotic forms are obtained (Appendix D):

$$\tilde{F}(z)\simeq\begin{cases}1-0.87z^{1/3} & \text{for } z \ll 1\\ 0.27z^{-1/3}e^{-1.18z} & \text{for } z \gg 1\end{cases} \tag{4.16}$$

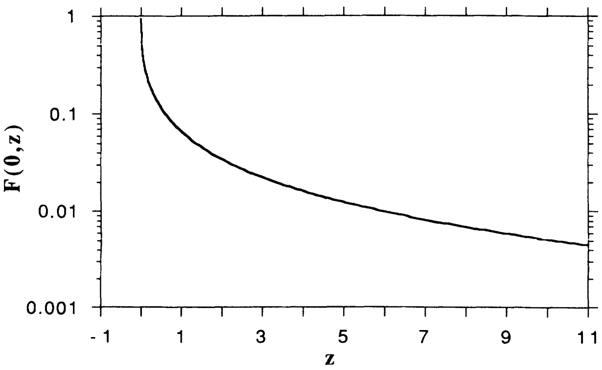

FIG. 3. Conserved η, and $k\xi_\eta=0$. Scaling function $F(0,z)$ against the reduced time $z=t/\tau_c$ on a logarithmic-linear plot. τ_c is given by Eq. (4.11).

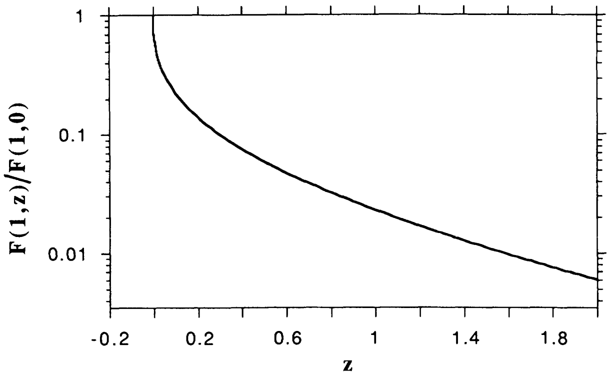

FIG. 4. Conserved η, and $k\xi_\eta=1$. Normalized scaling function $F(1,z)$ against the reduced time $z=t/\tau_c$ on a logarithmic-linear plot. τ_c is given by Eq. (4.11).

so that $Y(k,t)\propto 1-\text{const}\times t^{1/3}$ at short times, and $Y(k,t)\propto t^{-1/3}\exp(-\text{const}\times t)$ at long times. The algebraic prefactor here, $t^{-1/3}$, is different from the one obtained in long-time limit for nonconservative relaxation, Eq. (4.9). The scaling function $F(x,z)$ is plotted in Figs. 3 and 4 for reduced wave vectors $x=0$ and 1 $(x=k\xi_\eta)$, and the scaling function $\tilde{F}(z)$ (relevant for large $k\xi_\eta$) is plotted in Fig. 5.

C. Combined case

When the two relaxation channels for η are comparable we have to use a scaling function of three variables. We can write

$$Y(k,t)=\overline{\gamma}_\eta^{-2}\xi_\eta W(k\xi_\eta,t/\tau_a,t/\tau_c)\ , \tag{4.17}$$

where τ_a and τ_c are given by Eqs. (4.3) and (4.11). For $k\xi_\eta \gg 1$ this reduces to

$$Y(k,t)=\overline{\gamma}_\eta^{-2}k^{-1}\tilde{W}(t/\tau_b,t/\tau_d)\ , \tag{4.18}$$

with Eqs. (4.8) and (4.15) for τ_b and τ_d. The scaling functions $W(x,y,z)$ and $\tilde{W}(y,z)$ can be found numerically in a similar way to those introduced above.

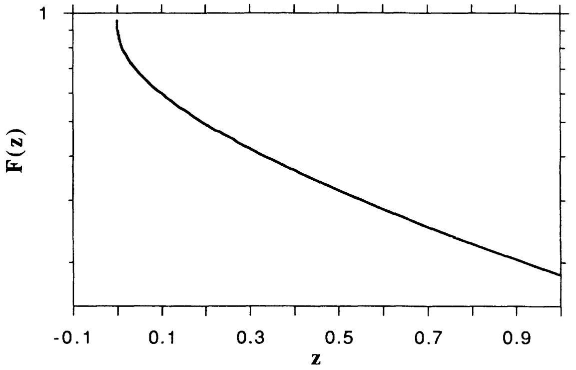

FIG. 5. Conserved η, and $k\xi_\eta\rightarrow\infty$. Scaling function $\tilde{F}(z)$ against the reduced time $z=t/\tau_d$ on a logarithmic-linear plot. τ_d is given by Eq. (4.15).

V. EFFECTIVE RELAXATION TIMES: DYNAMICAL SCALING

In the previous sections we have discussed in some detail the *shape* of the time-relaxation function for the dynamic structure factor. Most previous theories of dynamics near a phase transition deal mainly with the calculation of an *effective relaxation rate* Γ_k which does not contain detailed information about the line shape [14,15,19,16]. In the present context, the effective relaxation rate can be computed from Eq. (3.16) according to

$$\frac{1}{\Gamma_k}=\frac{\int_0^\infty dt\, S(k,t)}{S(k,0)} \; . \tag{5.1}$$

The (extended) dynamical scaling hypothesis (of Halperin, Hohenberg, and Ma [15]) then states

$$S(k,t)=S(k,0)f(\Gamma_k t) \; , \tag{5.2}$$

where $f(x)$ is some scaling function. We now check that our results for the fast-ρ limit (and for the symmetric phase) obey this dynamical scaling law. We consider as before the two regimes (i) $k\xi_\eta \ll 1$ and (ii) $k\xi_\eta \gg 1$. For nonconservative relaxation of η, we can easily find using Eq. (3.16) in Eq. (5.1) the results (i) $\Gamma_k \sim \xi_\eta^{-2}$, and (ii) $\Gamma_k \sim k^2$. In the case of conservative relaxation of η (where the Onsager coefficients are renormalized due to the hydrodynamic coupling) we obtain for the corresponding cases (i) $\Gamma_k \sim \xi_\eta^{-3}$ and (ii) $\Gamma_k \sim k^3$. It is clear from these results that the dynamic scaling hypothesis (5.2) is consistent with the scaling forms found in Sec. IV.

VI. DISCUSSION AND CONCLUSIONS

We now want to determine the different regimes of applicability of the results discussed in Secs. III and IV. As discussed in Sec. III B, the results reported there for the fast-η regime should apply to the ultimate $k \to 0$ limit, where the relaxation should be pure exponential. But as k increases we should have a crossover to the behavior reported in Secs. III C and IV (slow η). First, we assume the crossover to occur when $k\xi_\eta \ll 1$. Equating the effective relaxation rate of the fast-η case

$$\Gamma_k \sim \frac{k_B T}{\mu_s \xi_\eta} \ln\left[\frac{\xi_\eta}{\xi_\rho}\right] k^2 \tag{6.1}$$

with

$$\Gamma_k \sim \frac{\bar{\gamma}_\eta}{\tau}\frac{1}{\xi_\eta^2}+\frac{k_B T}{\mu_s \xi_\eta^3} \tag{6.2}$$

which corresponds to the slow-η calculation [45], we can estimate the crossover wave vector to be at

$$k^* \sim \frac{1}{(\xi_\eta)^{1/2}}\left[\frac{\bar{\gamma}_\eta \mu_s}{k_B T \tau \ln(\xi_\eta/\xi_\rho)}\right]^{1/2} \; . \tag{6.3}$$

If the system is not too close to the transition (or for large leakage time τ), such that

$$\xi_\eta \ll \frac{k_B T}{\mu_s} \ln\left[\frac{\xi_\eta}{\xi_\rho}\right] \bar{\gamma}_\eta^{-1} \tau \tag{6.4}$$

the regime $k^* \ll k \ll \xi_\eta^{-1}$ is wide enough to have a crossover to Eq. (6.2) and to the other results for the slow-η regime, before our assumption of $k\xi_\eta \ll 1$ fails.

If the condition (6.4) is reversed, namely, if

$$\xi_\eta \gg \frac{k_B T}{\mu_s} \ln\left[\frac{\xi_\eta}{\xi_\rho}\right] \bar{\gamma}_\eta^{-1} \tau \tag{6.5}$$

we have, contrary to our original assumption, a crossover in the high-k region ($k^*\xi_\eta \gg 1$), so that k^* is no longer given by (6.3). Instead, we have to equate the result of the slow-η calculation for $k\xi_\eta \gg 1$:

$$\Gamma_k \sim \frac{k_B T}{\mu_s} \ln\left[\frac{1}{k\xi_\rho}\right] k^3 \tag{6.6}$$

with

$$\Gamma_k \sim \frac{\bar{\gamma}_\eta}{\tau} k^2 + \frac{k_B T}{\mu_s} k^3 \tag{6.7}$$

corresponding to the fast-η calculation for $k\xi_\eta \gg 1$. We then obtain

$$k^* \ln\left[\frac{1}{k^*\xi_\rho}\right] \sim \frac{\bar{\gamma}_\eta \mu_s}{k_B T \tau} \; . \tag{6.8}$$

To summarize, if $k^*\xi_\eta \ll 1$ then it is given by Eq. (6.3); in this case (i) for $k \ll k^*$, Γ_k is given by Eq. (6.1), (ii) for $k^* \ll k \ll \xi_\eta^{-1}$, Γ_k is given by (6.2), and (iii) for $\xi_\eta^{-1} \ll k$, Γ_k is given by (6.7). If, on the other hand, $k^*\xi_\eta \gg 1$ then it obeys Eq. (6.8), and in this case (i) for $k \ll \xi_\eta^{-1}$, Γ_k is given by Eq. (6.1), (ii) for $\xi_\eta^{-1} \ll k \ll k^*$, Γ_k is given by (6.6), and (iii) for $k^* \ll k$, Γ_k is given by (6.7). Considering the relaxation function, for $k \ll k^*$ we expect single exponential decay, while for $k \gg k^*$ we predict nonexponential decay as discussed in Sec. IV.

For the regime $k \gg k^*$, it should be useful to distinguish between regimes where either the conservative rate or the nonconservative rate dominate. Indeed, although both terms in (6.7) contribute, for large enough k values the conservative relaxation becomes dominant; we denote this crossover by k^{**}. In Tables I and II we summarize

TABLE I. Effective relaxation rates Γ_k and corresponding relaxation functions in different k regimes, for the case $k^* \ll \xi_\eta^{-1}$, where $k^* \sim [1/(\xi_\eta)^{1/2}][\bar{\gamma}_\eta \mu_s / k_B T \tau \ln(\xi_\eta/\xi_\rho)]^{1/2}$ and $k^{**} \sim \bar{\gamma}_\eta \mu_s / k_B T \tau$.

	$k < k^*$	$k^* < k < \xi_\eta^{-1}$	$\xi_\eta^{-1} < k < k^{**}$	$k^{**} < k$
Γ_k	$\frac{k_B T}{\mu_s \xi_\eta} \ln\left[\frac{\xi_\eta}{\xi_\rho}\right] k^2$	$\frac{\bar{\gamma}_\eta}{\tau}\frac{1}{\xi_\eta^2}+\frac{k_B T}{\mu_s \xi_\eta^3}$	$\frac{\bar{\gamma}_\eta}{\tau} k^2 + \frac{k_B T}{\mu_s} k^3$	$\frac{k_B T}{\mu_s} k^3$
$Y(k,t)$	exponential	Eq. (4.17)	Eq. (4.18)	Eqs. (4.14), (4.16)

TABLE II. Same as Table I but for the case $k^* \gg \xi_\eta^{-1}$, where k^* obeys $k^* \ln(1/k^*\xi_\rho) \sim \bar{\gamma}_\eta \mu_s / k_B T \tau$, and $k^{**} \sim \bar{\gamma}_\eta \mu_s / k_B T \tau$.

	$k < \xi_\eta^{-1}$	$\xi_\eta^{-1} < k < k^*$	$k^* < k < k^{**}$	$k^{**} < k$
Γ_k	$\frac{k_B T}{\mu_s \xi_\eta} \ln\left[\frac{\xi_\eta}{\xi_\rho}\right] k^2$	$\frac{k_B T}{\mu_s} \ln\left[\frac{1}{k \xi_\rho}\right] k^3$	$\frac{\bar{\gamma}_\eta}{\tau} k^2$	$\frac{k_B T}{\mu_s} k^3$
$Y(k,t)$	exponential	exponential	Eqs. (4.7), (4.9)	Eqs. (4.14), (4.16)

the effective rates obtained for the four different regimes of k values. The corresponding relaxation functions associated with these regimes are also noted.

The above discussion is based on the mean-field treatment and should therefore hold close enough to a tricritical point (or to the double critical end point). Far from these high-order points, the mean-field exponents should be replaced by "exact" exponents. A complete dynamical analysis for this case is, however, beyond the scope of this paper.

Nonetheless our mean-field results exemplify the unusual decay profiles that can be expected from dynamic light scattering in sponge phases. According to Eq. (3.17), $S(k,t)$ decays essentially in two steps: A fast single-exponential decay, in which only $\tilde{a}^{-1}(1+\xi_\rho^2 k^2)^{-1}$ decays, followed by a slow highly nonexponential decay in which the critical part of $S(k)$ decays. This is a clear effect, which should be easily amenable to experimental check. The crossover time from the single-exponential decay to the multiexponential one should roughly scale as $\sim [D_\rho k^2]^{-1}$ [Eq. (3.22)]. Obviously, for a clearcut observation of both regimes the two terms in Eq. (3.18) [for $S(k)$] have to be comparable.

Our results suggest that dynamic light scattering should be a powerful probe of relaxation behavior in sponge phases. To extract the best information from the data it will be important to study *decay profiles* as well as simply the average relaxation rates as a function of k and ξ_η. The predicted regimes of nonexponential decay, and (for example) the marked differences between conserved and nonconserved η, indicate that careful study of dynamic light-scattering data may enable key dynamical parameters of sponge phases (such as the leakage time τ) to be estimated for the first time. We hope that experimental work to test our new predictions will be forthcoming in the near future.

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APPENDIX A: THE STATIC STRUCTURE FACTOR

1. Formalism

Here we calculate $S(k)$ in a nonperturbative way. This calculation closely follows the perturbation calculation of Ref. [2]. First we consider the free energy for small fluctuations $\delta\rho = \rho - \rho_0$, where ρ_0 is the average value of ρ. Expanding the free-energy density (2.3) up to quadratic terms in $\delta\rho$, we obtain (omitting a constant)

$$f(\mathbf{r}) = -\tilde{\mu}\delta\rho + \tfrac{1}{2}\tilde{a}\delta\rho^2 + \tfrac{1}{2}\gamma_\rho(\nabla\delta\rho)^2 + \tfrac{1}{2}\tilde{A}\eta^2 + \tfrac{1}{4}B\eta^4 + \tfrac{1}{2}\gamma_\eta(\nabla\eta)^2 + \tfrac{1}{2}\gamma_c\eta\nabla\eta\cdot\nabla\delta\rho + \tfrac{1}{2}C\delta\rho\eta^2 , \tag{A1}$$

where we have defined

$$\tilde{a} = a + 3b\rho_0^2 , \tag{A2}$$

$$\tilde{A} = A + C\rho_0 , \tag{A3}$$

$$-\tilde{\mu} = a\rho_0 + b\rho_0^3 - \mu . \tag{A4}$$

It will be shown below that the constraint $\langle\rho\rangle = \rho_0$ leads to $\tilde{\mu} = C\langle\eta^2\rangle/2$ or equivalently

$$\mu = a\rho_0 + b\rho_0^3 + \tfrac{1}{2}C\langle\eta^2\rangle . \tag{A5}$$

Defining the Fourier transform of any field $h(\mathbf{r})$ by $h(\mathbf{r}) = \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} h_{\mathbf{k}}$ and taking the volume V to be unity, we obtain $\Phi = \sum_{\mathbf{k}} f(\mathbf{k})$ with

$$f(\mathbf{k}) = -\tilde{\mu}\delta\rho_{\mathbf{k}}\delta(\mathbf{k}) + \tfrac{1}{2}(\tilde{a} + \gamma_\rho k^2)\delta\rho_{\mathbf{k}}\delta\rho_{-\mathbf{k}} + \tfrac{1}{2}(\tilde{A} + \gamma_\eta k^2)\eta_{\mathbf{k}}\eta_{-\mathbf{k}} + \tfrac{1}{4}B\sum_{\mathbf{q},\mathbf{q}'}\eta_{\mathbf{q}}\eta_{\mathbf{k}-\mathbf{q}}\eta_{\mathbf{q}'}\eta_{-\mathbf{k}-\mathbf{q}'} + \tfrac{1}{2}\delta\rho_{-\mathbf{k}}\sum_{\mathbf{q}}(C + \gamma_c\mathbf{k}\cdot\mathbf{q})\eta_{\mathbf{q}}\eta_{\mathbf{k}-\mathbf{q}} \tag{A6}$$

[$\delta(k)$ is the Dirac δ function]. We must keep track of any terms in $\delta\rho_{\mathbf{k}=0}$ so as to obtain Eq. (A5) for μ, although these do not affect our result for $S(k)$. To obtain the correlation function (static structure factor) $S(k) \equiv \langle\delta\rho_{\mathbf{k}}\delta\rho_{-\mathbf{k}}\rangle$ we add to $f(\mathbf{k})$ a source term $\epsilon_k\delta\rho_{\mathbf{k}}\delta\rho_{-\mathbf{k}}$ and calculate $S(k)$ according to

$$S(k) = \frac{-(\partial/\partial\epsilon_k)\left[\int\prod_{\mathbf{k}} d\rho_{\mathbf{k}}d\eta_{\mathbf{k}}e^{-\Phi}\right]_{\epsilon_k=0}}{\int\prod_{\mathbf{k}} d\rho_{\mathbf{k}}d\eta_{\mathbf{k}}e^{-\Phi}} . \tag{A7}$$

Since the coupling to η is linear in $\rho_{\mathbf{k}}$ it is possible to carry the integration over the $\rho_{\mathbf{k}}$ variables exactly. First we rewrite $f(\mathbf{k})$ as

$$f(\mathbf{k})=\tfrac{1}{2}(\tilde a+\gamma_\rho k^2+2\epsilon_k)\left[\delta\rho_{\mathbf{k}}+\frac{\zeta_{\mathbf{k}}-\tilde\mu\delta(\mathbf{k})}{\tilde a+\gamma_\rho k^2+2\epsilon_k}\right]\times\left[\delta\rho_{-\mathbf{k}}+\frac{\zeta_{-\mathbf{k}}-\tilde\mu\delta(\mathbf{k})}{\tilde a+\gamma_\rho k^2+2\epsilon_k}\right]+\tfrac{1}{2}(\tilde A+\gamma_\eta k^2)\eta_{\mathbf{k}}\eta_{-\mathbf{k}}+\tfrac{1}{4}B\sum_{\mathbf{q},\mathbf{q}'}\eta_{\mathbf{q}}\eta_{\mathbf{k}-\mathbf{q}}\eta_{\mathbf{q}'}\eta_{-\mathbf{k}-\mathbf{q}'}+\frac{C\tilde\mu\eta_{\mathbf{k}}\eta_{-\mathbf{k}}-\zeta_{\mathbf{k}}\zeta_{-\mathbf{k}}}{2(\tilde a+\gamma_\rho k^2+2\epsilon_k)} \tag{A8}$$

(omitting a constant), where

$$\zeta_{\mathbf{k}}=\tfrac{1}{2}\sum_{\mathbf{q}}(C+\gamma_c\mathbf{k}\cdot\mathbf{q})\eta_{\mathbf{q}}\eta_{\mathbf{k}-\mathbf{q}}\ . \tag{A9}$$

We then obtain from Eq. (A7) (for $\mathbf{k}\neq 0$)

$$S(k)=\frac{1}{\tilde a+\gamma_\rho k^2}+\frac{1}{(\tilde a+\gamma_\rho k^2)^2}\langle\zeta_{\mathbf{k}}\zeta_{-\mathbf{k}}\rangle_{f_{\text{eff}}}\ , \tag{A10}$$

where $\langle\ \rangle_{f_{\text{eff}}}$ means average with the following effective Hamiltonian for $\{\eta_{\mathbf{k}}\}$:

$$f_{\text{eff}}=\tfrac{1}{2}(\tilde A+\gamma_\eta k^2)\eta_{\mathbf{k}}\eta_{-\mathbf{k}}+\tfrac{1}{4}B\sum_{\mathbf{q},\mathbf{q}'}\eta_{\mathbf{q}}\eta_{\mathbf{k}-\mathbf{q}}\eta_{\mathbf{q}'}\eta_{-\mathbf{k}-\mathbf{q}'}-\frac{\zeta_{\mathbf{k}}\zeta_{-\mathbf{k}}}{2(\tilde a+\gamma_\rho k^2)}+\frac{C\tilde\mu\eta_{\mathbf{k}}\eta_{-\mathbf{k}}}{2(\tilde a+\gamma_\rho k^2)}\ . \tag{A11}$$

The origin of Eq. (A10) is very clear from the form of Eq. (A8): $-\zeta_{\mathbf{k}}/(\tilde a+\gamma_\rho k^2)$ is essentially the average of $\delta\rho_{\mathbf{k}}$ (for $\mathbf{k}\neq 0$) and $(\tilde a+\gamma_\rho k^2)^{-1}$ is its variance. Note that for $\gamma_c=0$ we simply have $\zeta_{\mathbf{k}}\propto(\eta^2)_{\mathbf{k}}$. Thus the fluctuating field ρ describing the surfactant density is everywhere biased by an amount that varies as η^2. To obtain a Gaussian approximation for f_{eff}, we should expand f_{eff} to order $\delta\eta^2$ where $\delta\eta=\eta_0$ and η_0 is the average of η. η_0 therefore minimizes the $k=0$ component of f_{eff}, namely,

$$\left[A+C\rho_0+C\frac{\tilde\mu}{\tilde a}\right]\eta_0+\left[B-\frac{C^2}{2\tilde a}\right]\eta_0^3=0\ . \tag{A12}$$

The effective Hamiltonian also includes some terms of higher than quadratic order in k, which are of no physical significance as they are omitted in the original expansion Eq. (A6). Therefore it is enough to expand f_{eff} to order k^2. We thus find (omitting a constant)

$$f_{\text{eff}}=\tfrac{1}{2}(\overline{A}+\bar\gamma_\eta k^2)\delta\eta_{\mathbf{k}}\delta\eta_{-\mathbf{k}}\ , \tag{A13}$$

where

$$\overline{A}=\tilde A+3\eta_0^2\left[B-\frac{C^2}{2\tilde a}\right]+C\frac{\tilde\mu}{\tilde a} \tag{A14}$$

and

$$\bar\gamma_\eta=\gamma_\eta+\eta_0^2\frac{C}{\tilde a}\left[\frac{C\gamma_\rho}{2\tilde a}-\gamma_c\right]+\frac{C\tilde\mu\gamma_\rho}{\tilde a^2}\ . \tag{A15}$$

The constraint $\langle\delta\rho\rangle=0$ then leads to $\tilde\mu=C\langle\eta^2\rangle/2$ [see Eq. (A5)]. [If the effective free energy Eq. (A13) is used to calculate $\langle\delta\eta^2\rangle$, then Eqs. (A14) and (A15) become self-consistent equations for $\overline{A}$ and $\bar\gamma_\eta$ which lead to Fisher renormalization of the critical exponents. This is discussed in Ref. [2] and we do not dwell on this point here.] Thus within the Gaussian approximation for η we have in the S phase $\overline{A}=\tilde A+C^2\langle\delta\eta^2\rangle/(2\tilde a)$ and $\bar\gamma_\eta=\gamma_\eta+C^2\gamma_\rho\langle\delta\eta^2\rangle/(2\tilde a^2)$.

In what follows we assume that γ_c is not too large so that $\bar\gamma_\eta$ is positive [21]. [More precisely we require $\gamma_c<\gamma_\eta\tilde a/(\eta_0^2C)+C\gamma_\rho/\tilde a$.] According to Eqs. (A9) and (A10) and (A13)–(A15), the structure factor is then obtained as

$$S(k)=\frac{1}{\tilde a+\gamma_\rho k^2}+\frac{1}{(\tilde a+\gamma_\rho k^2)^2}\left[\eta_0^2(C+\tfrac{1}{2}\gamma_c k^2)^2\langle\delta\eta_{\mathbf{k}}\delta\eta_{-\mathbf{k}}\rangle_{f_{\text{eff}}}+Q(k)\right]\ , \tag{A16}$$

where we have defined

$$Q(k)\equiv\tfrac{1}{4}\sum_{\mathbf{q},\mathbf{q}'}(C+\gamma_c\mathbf{k}\cdot\mathbf{q})(C-\gamma_c\mathbf{k}\cdot\mathbf{q}')\times\langle\delta\eta_{\mathbf{q}}\delta\eta_{\mathbf{k}-\mathbf{q}}\delta\eta_{\mathbf{q}'}\delta\eta_{-\mathbf{k}-\mathbf{q}'}\rangle_{f_{\text{eff}}}\ . \tag{A17}$$

The calculation of $Q(k)$ is similar to the perturbation calculation of Ref. [2], but we nonetheless repeat it in the second part of this appendix, where we show that

$$S(k)=\frac{1}{\tilde a+\gamma_\rho k^2}+\frac{(C+\frac{1}{2}\gamma_c k^2)^2}{(\tilde a+\gamma_\rho k^2)^2}\times\left[\frac{\eta_0^2\overline{A}^{-1}}{1+\xi_\eta^2k^2}+\frac{1}{16\pi}\bar\gamma_\eta^{-2}\xi_\eta\frac{\tan^{-1}[k\xi_\eta/2]}{k\xi_\eta/2}\right]. \tag{A18}$$

This differs from the perturbative result of Refs. [1,2], in that effective values of coefficients replace bare ones: $\overline{A}$ replaces $\tilde A$ and $\bar\gamma_\eta$ replaces γ_η. In the symmetric phase $\eta_0=0$ so that the first term in the square brackets does not appear. In the asymmetric phase ($\eta_0\neq 0$) we may use Eqs. (A12) and (A14) to equate $\eta_0^2\overline{A}^{-1}$ in (A18) by $(2B-C^2/\tilde a)^{-1}$, which is a noncritical constant.

2. Calculation of Eq. (A18)

Here we calculate $Q(\mathbf{k})$ of Eq. (A17) as in Ref. [2]. The quartic correlation function can be written in terms of sums of products of quadratic correlation functions since the distribution is Gaussian [16]. We then obtain (for any $\mathbf{k}\neq\mathbf{0}$)

$$\langle\delta\eta_{\mathbf{q}}\delta\eta_{\mathbf{k}-\mathbf{q}}\delta\eta_{\mathbf{q}'}\delta\eta_{-\mathbf{k}-\mathbf{q}'}\rangle=\frac{\delta(\mathbf{k}+\mathbf{q}'-\mathbf{q})+\delta(\mathbf{q}+\mathbf{q}')}{(\overline{A}+\bar\gamma_\eta q^2)[\overline{A}+\bar\gamma_\eta(\mathbf{k}-\mathbf{q})^2]} \tag{A19}$$

and we thus obtain

$$Q(k)=\tfrac{1}{2}(C+\tfrac{1}{2}\gamma_c k^2)\sum_{\mathbf{q}}\frac{C+\gamma_c\mathbf{k}\cdot\mathbf{q}}{(\overline{A}+\overline{\gamma}_\eta q^2)[\overline{A}+\overline{\gamma}_\eta(\mathbf{k}-\mathbf{q})^2]}\ . \tag{A20}$$

Converting the sum to an integral [i.e., dividing by $(2\pi)^3$], performing the angular integration, and changing the variables to $x=k\xi_\eta$ and $y=q\xi_\eta$ where $\xi_\eta^2=\overline{\gamma}_\eta/\overline{A}$ leads to

$$Q(k)=(C+\tfrac{1}{2}\gamma_c k^2)^2 Y(k)\ , \tag{A21}$$

where

$$Y(k)=\frac{1}{8\pi^2}\overline{A}^{-2}[Y_1(k)+Y_2(k)]\ , \tag{A22}$$

$$Y_1(k)=\frac{\gamma_c}{(C+\gamma_c k^2/2)\xi_\eta^5}\left\{\frac{1}{4x}\int_0^\infty y\ln\left[\frac{1+(x+y)^2}{1+(x-y)^2}\right]dy-\int_0^\infty\frac{y^2}{1+y^2}dy\right\}\ , \tag{A23}$$

$$Y_2(k)=\frac{1}{2\xi_\eta^3 x}\int_0^\infty\frac{y}{1+y^2}\ln\left[\frac{1+(x+y)^2}{1+(x-y)^2}\right]dy\ . \tag{A24}$$

Although both integrals in (A23) diverge, $Y_1(k)$ is identically zero, as may be proved by integrating the first term by parts; evaluating the resulting integrals, we obtain

$$\begin{aligned}Y_1(k)=&\frac{\gamma_c}{(C+\gamma_c k^2/2)\xi_\eta^5}\\&\times\left\{\frac{1}{8x}(1-x^2-y^2)\ln\left[\frac{1+(x+y)^2}{1+(x-y)^2}\right]\right.\\&+\tfrac{1}{2}(y-\tan^{-1}[y-x]-\tan^{-1}[y+x])\\&\left.-y+\tan^{-1}[y]\right\}\Bigg|_{y=0}^{y=\infty}=0\ .\end{aligned} \tag{A25}$$

The integral in $Y_2(k)$ is easily effected to give [41]

$$Y_2(k)=\frac{\pi}{\xi_\eta^3 x}\tan^{-1}[k\xi_\eta/2] \tag{A26}$$

so that we finally obtain

$$Q(k)=\frac{1}{16\pi}(C+\tfrac{1}{2}\gamma_c k^2)^2\overline{\gamma}_\eta^{-2}\xi_\eta\frac{\tan^{-1}[k\xi_\eta/2]}{k\xi_\eta/2} \tag{A27}$$

which leads directly to Eq. (A18).

APPENDIX B: CALCULATION OF $\langle\zeta\rho\rangle$

To calculate $\langle\zeta_{\mathbf{k}}(t)\delta\rho_{-\mathbf{k}}(0)\rangle$ in Eq. (3.15) we again observe that $\delta\rho_{-\mathbf{k}}(0)$ can be replaced by [46] $-\zeta_{\mathbf{k}}(0)/(\tilde{a}+\gamma_\rho k^2)+\Delta_{\mathbf{k}}(0)$ where $\Delta_{\mathbf{k}}$ is the fluctuation of $\rho_{\mathbf{k}}$ around its mean value $-\zeta_{\mathbf{k}}/(\tilde{a}+\gamma_\rho k^2)$; clearly $\langle\Delta_{\mathbf{k}}\rangle=0$ and it does not contribute to Eq. (3.15). We therefore obtain

$$\begin{aligned}\langle\zeta_{\mathbf{k}}(t)\delta\rho_{-\mathbf{k}}(0)\rangle=-\frac{1}{\tilde{a}+\gamma_\rho k^2}\Bigg\{&\eta_0^2(C+\tfrac{1}{2}\gamma_c k^2)^2\langle\delta\eta_{\mathbf{k}}\delta\eta_{-\mathbf{k}}\rangle\exp[-L_\eta(\mathbf{k})t]\\&+\tfrac{1}{4}\sum_{\mathbf{q},\mathbf{q}'}(C+\gamma_c\mathbf{k}\cdot\mathbf{q})(C-\gamma_c\mathbf{k}\cdot\mathbf{q}')\langle\delta\eta_{\mathbf{q}}\delta\eta_{\mathbf{k}-\mathbf{q}}\delta\eta_{\mathbf{q}'}\delta\eta_{-\mathbf{k}-\mathbf{q}'}\rangle\\&\times\exp\{-[L_\eta(\mathbf{q})+L_\eta(\mathbf{k}-\mathbf{q})]t\}\Bigg\}\end{aligned} \tag{B1}$$

and using Eq. (A19) we get explicitly

$$\begin{aligned}\langle\zeta_{\mathbf{k}}(t)\delta\rho_{-\mathbf{k}}(0)\rangle=-\frac{1}{\tilde{a}+\gamma_\rho k^2}\Bigg\{&\eta_0^2\frac{(C+\tfrac{1}{2}\gamma_c k^2)^2}{\overline{A}+\overline{\gamma}_\eta k^2}\exp[-L_\eta(\mathbf{k})t]\\&+\tfrac{1}{2}(C+\tfrac{1}{2}\gamma_c k^2)\sum_{\mathbf{q}}\frac{C+\gamma_c\mathbf{k}\cdot\mathbf{q}}{(\overline{A}+\overline{\gamma}_\eta q^2)[\overline{A}+\overline{\gamma}_\eta(\mathbf{k}-\mathbf{q})^2]}\exp\{-[L_\eta(\mathbf{q})+L_\eta(\mathbf{k}-\mathbf{q})]t\}\Bigg\}\ .\end{aligned} \tag{B2}$$

Substituting Eq. (B2) in Eq. (3.15) and integrating over t' we obtain Eq. (3.16).

APPENDIX C: ADIABATIC LIMIT

To justify the claim made in Sec. III B, we note that close enough to the transition, $\xi_\eta \gg \xi_\rho$. We assume that scattering wave vectors of interest always obey $k\xi_\rho \ll 1$. (In many systems we expect that ξ_ρ is of the order of the cell size d so this restriction is necessary any way for the Landau-Ginzburg approach to be applicable.) Therefore for $k\xi_\eta \ll 1$, we have $D_\eta \ll D_\rho$ (namely, critical slowing down). On the other hand, for $k\xi_\eta \gg 1$, we have $D_\eta \sim k$ and (since $k\xi_\rho \ll 1$)$D_\rho \sim \xi_\rho^{-1}$; hence $D_\eta \ll D_\rho$.

We conclude that in the regime where $\xi_\eta \gg \xi_\rho$ we have $D_\rho \gg D_\eta$. This implies that in the regime $k \gg \tilde{k}^*$, where

$$\tilde{k}^*=\frac{1}{\xi_\eta}\left[\frac{\overline{\gamma}_\eta}{\tau D_\rho}\right]^{1/2}\ , \tag{C1}$$

we have $L_p(k) \gg L_\eta(k)$. Comparing Eqs. (C1) and (6.3), we see that $\tilde{k}^*$ is smaller than k^*, the crossover wave vector between fast- and slow-η relaxation regimes. Hence in the slow-η regime where the approach of Sec. III B applies ($k \gg k^*$), we always have $L_p(k) \gg L_\eta(k)$.

APPENDIX D: SCALING FUNCTIONS

1. The nonconservative case

In this case the angular integration in Eq. (3.18) can be carried out in terms of known functions. We first obtain [with scaling variables $x = k\xi_\eta$, $z = t/\tau_a$ as defined in (4.3)]

$$Y(k,t) = \frac{1}{16\pi}\bar{\gamma}_\eta^{-2}\xi_\eta\{U(x,z)+U_2(x,z)+U_3(x,z)\}\ , \tag{D1}$$

where

$$U(x,z) = \frac{1}{\pi x}\int_0^\infty dy\frac{y}{1+y^2}\exp[-z(1+y^2)] \times\{\mathrm{Ei}(-[1+(x+y)^2]z) - \mathrm{Ei}(-[1+(x-y)^2]z)\}\ , \tag{D2}$$

$$U_2(x,z) = \frac{\gamma_c}{2\pi x z\xi_\eta^2}\int_0^\infty dy\frac{y}{1+y^2}\exp[-z(1+y^2)] \times(\exp\{-[1+(x+y)^2]z\} - \exp\{-[1+(x-y)^2]z\})\ , \tag{D3}$$

and

$$U_3(x,z) = \frac{\gamma_c}{2\pi x\xi_\eta^2}\int_0^\infty dy\, y\exp[-z(1+y^2)] \times\{\mathrm{Ei}(-[1+(x+y)^2]z) - \mathrm{Ei}(-[1+(x-y)^2]z)\}\ , \tag{D4}$$

where $\mathrm{Ei}(x)$ is the exponential integral function [41] $[\mathrm{Ei}(x) = -\int_{-x}^\infty(e^{-t}/t)dt]$. We have found *numerically* that

$$U_2(x,z)+U_3(x,z)=0 \tag{D5}$$

for an exhaustive range of values of x and z (although we are not able to prove this analytically). This result is the generalization to $z \neq 0$ of Eq. (A25) (which corresponds to the $z=0$ limit). The validity of Eq. (D5) is essential in obtaining the scaling form Eq. (4.2) which is given in terms of $U(x,z)$ defined in Eq. (D2) above.

For $x \to 0$ we find from Eq. (D2) the following useful expression:

$$U(0,z) = (1+4z)[1-\Phi((2z)^{1/2})] - 2(2z/\pi)^{1/2}\exp(-2z)\ , \tag{D6}$$

where $\Phi(u)$ is the usual error function [41] $[\Phi(u) = 2/\sqrt{\pi}\int_0^u e^{-t^2}dt]$. For $z \ll 1$ (short times) we therefore have

$$U(0,z) \simeq 1 - 4\left[\frac{2}{\pi}\right]^{1/2} z^{1/2} + 4z - \frac{8}{3}\left[\frac{2}{\pi}\right]^{1/2} z^{3/2} + o(z^{5/2}) \tag{D7}$$

and for $z \gg 1$ (long times) it is

$$U(0,z) \simeq \frac{1}{2\sqrt{2\pi}}\frac{\exp[-2z]}{z^{3/2}}\ . \tag{D8}$$

For larger x ($=k\xi_\eta$) values, $x \leq 1$, we find, for $z \to \infty$,

$$U(x,z) \simeq \frac{1}{2\sqrt{2\pi}}\frac{1}{1+x^2}\frac{\exp[-\frac{1}{2}(4+x^2)z]}{z^{3/2}}\ . \tag{D9}$$

Considering now the result (D2) at large k we find that for $k\xi_\eta \to \infty$, $Y(k,t)$ is given by Eq. (4.7) where the scaling function $\tilde{U}(z)$ is given by

$$\tilde{U}(z) = \frac{1}{\pi}\int_0^\infty \frac{dy}{y}\exp(-zy^2)\{\mathrm{Ei}(-(1+y)^2 z) - \mathrm{Ei}(-(1-y)^2 z)\} \tag{D10}$$

with

$$z = k^2\frac{\gamma_\eta}{\tau}t\ . \tag{D11}$$

For $z \ll 1$ we obtain

$$\tilde{U}(z) \simeq 1 - \frac{4\sqrt{2}}{\pi^{3/2}}z^{1/2} \tag{D12}$$

and for $z \gg 1$ we have

$$\tilde{U}(z) \simeq \frac{\sqrt{2}}{\pi^{3/2}}\frac{e^{-z}}{z^{1/2}}\ . \tag{D13}$$

2. The conservative case

In this case as well the scaling result (4.10) is not evident at first sight. Converting the sum in Eq. (3.18) to an integral, we first obtain

$$Y(k,t) = \frac{1}{8\pi^2}\bar{\gamma}_\eta^{-2}\xi_\eta^2\tilde{Y}(k,t)\ , \tag{D14}$$

where

$$\tilde{Y}(k,t) = \frac{1}{C+\frac{1}{2}\gamma_c k^2}\int_0^\infty dq\int_{-1}^1 dx\frac{q^2(C+\gamma_c kqx)}{(1+\xi_\eta^2 q^2)[1+\xi_\eta^2(k^2+q^2-2kqx)]} \times\exp\{-D_0 t\xi_\eta^{-1}[q^2\Omega(q\xi_\eta)+(k^2+q^2-2kqx)\Omega((k^2+q^2-2kqx)^{1/2}\xi_\eta)]\}\ , \tag{D15}$$

where $D_0=k_BT/(6\pi\mu_s)$ and $\Omega(x)$ is given by Eq. (3.23). We have checked *numerically* that

$$\tilde{Y}(k,t;\gamma_c)=\tilde{Y}(k,t;\gamma_c=0) \tag{D16}$$

although we were not able to find an analytical proof for this relation. It is the equivalent of Eq. (D5), and is a generalization to Eq. (A25) which corresponds to the $t=0$ case. Equation (D16) leads to the scaling form (4.10), with the scaling function $F(x,z)$ given by

$$F(x,z)=\frac{2}{\pi}\int_0^\infty dy\int_{-1}^{1} du\,\frac{y^2}{(1+y^2)(1+x^2+y^2-2xyu)}\exp\{-z[y^2\Omega(y)+(x^2+y^2-2xyu)\Omega((x^2+y^2-2xyu)^{1/2})]\}\;. \tag{D17}$$

For $x=0$ (i.e., when $x\ll 1$) we simply obtain

$$F(0,z)=\frac{4}{\pi}\int_0^\infty dy\,\frac{y^2}{(1+y^2)^2}\exp[-2zy^2\Omega(y)] \tag{D18}$$

which for $z\gg 1$ behaves as

$$F(0,z)\simeq\frac{1}{2(2\pi)^{1/2}}z^{-3/2}\;. \tag{D19}$$

In the regime $k\xi_\eta\gg 1$, we can use $\Omega(x)\to\alpha x$ for $x\to\infty$ where $\alpha=3\pi/8$, to obtain

$$Y(k,t)=\tfrac{1}{16}\gamma_\eta^{-2}\frac{\tilde{F}(D_0k^3t)}{k}\;, \tag{D20}$$

where

$$\tilde{F}(z)=\frac{2}{\pi^2}\int_0^\infty dy\int_{-1}^{1} du\,\frac{\exp\{-\alpha z[y^3+(1+y^2-2yu)^{3/2}]\}}{1+y^2-2yu}\;. \tag{D21}$$

For $z\ll 1$ it then follows from (D21)

$$\tilde{F}(z)\simeq 1-0.87z^{1/3} \tag{D22}$$

(where the numerical constant 0.87 has been obtained by numerical integration), and for $z\gg 1$

$$\tilde{F}(z)\simeq\frac{4\Gamma(1/3)}{3\pi^2(2\alpha)^{1/3}}\frac{\exp(-\alpha z)}{z^{1/3}} \tag{D23}$$

[$\Gamma(x)$ is the usual gamma function [41]].

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[21] The expression for $\overline{\gamma}_\eta$ implies that in the asymmetric phase ($\eta_0 \neq 0$) and for very large γ_c [i.e., $\gamma_c > \gamma_\eta \tilde{a}/(\eta_0^2 C) + C\gamma_\rho/\tilde{a}$] $\overline{\gamma}_\eta$ is negative; hence small-wavelength fluctuations are preferable. In this case one has to retain the k^4 terms in the expansion for stability. This leads to a preferable wave vector k_s that minimizes the free energy, and we find $k_s = [2\tilde{a}(C\tilde{a}\gamma_c - \tilde{a}^2\gamma_\eta/\eta_0^2 - C^2\gamma_\rho)/(\tilde{a}\gamma_c - 2C\gamma_\rho)^2]^{1/2}$. While normally we do not expect such a strong coupling between the gradients of η and ρ [cf. Eq. (2.3)], we note that this may suggest formation of domains in the asymmetric phase, with a characteristic domain radius $r_s \sim 1/k_s$. In this work, however, we limit the discussion to positive $\overline{\gamma}_\eta$.

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[32] This result has been independently obtained by S. Ramaswamy (private communication).

[33] This assumes $\gamma_c/C < d^2$, which is consistent with our earlier assumption that $\overline{\gamma}_\eta > 0$.

[34] Far from the transition, D_{eff} is approximately given by $D_{\text{eff}} \simeq (k_B T/\mu\xi_\rho)(\{1 + K(C^2/\overline{\gamma}_\eta^2\tilde{a})\xi_\rho[K'' + \ln(\xi_\eta/\xi_\rho)]\}/[1 + K'(C^2/\overline{\gamma}_\eta^2\tilde{a})\xi_\eta])$, where K, K', and K'' are numerical constants.

[35] Note, however, that these white-noise terms are essential for a calculation of the dynamics of the perturbed static structure factor following a jump experiment $\langle \rho_{\mathbf{k}}(t)\rho_{-\mathbf{k}}(t)\rangle$.

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[37] This criterion arises by noting that for $\tilde{q}\xi_\eta \gg 1$, where $\tilde{q}$ is defined by $L_\eta(\tilde{q}) = L_\rho(k)$, the weight factor in front of the exponential terms is negligibly small.

[38] In writing Eq. (3.8) we have already assumed the adiabatic limit $L_\rho(k) \gg L'_\eta(k)$ where $L'_\eta(k)$ is different from $L_\eta(k)$ only by the fact that the latter is calculated using the effective parameters $\overline{A}$ and $\overline{\gamma}_\eta$ rather than $\tilde{A}$ and γ_η.

[39] Actually we make use of the equivalent equations (A16), (A17), and (A20).

[40] In fact this is true even if the criterion $(\xi_\eta/\xi_\rho)^{1/3}(k\xi_\eta)^{2/3} \gg 1$, used to derive it, is not obeyed.

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[42] Of course, such interactions may play some part in the determination of τ but since the relaxation is local this is independent of the distance from the transition.

[43] Although the form of Eq. (3.18) suggests that for long enough times modes near $q = 0$ contribute, the phase-space weight in modes with $q > 0$ increases as q^2. Essentially one has an integral of the form $\int_0^\infty dq\, q^2 e^{-q^2 t - 2t/\tau_a}$ which scales as $t^{-3/2} e^{-2t/\tau_a}$.

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[45] We have implicitly assumed that the crossover from Eq. (6.1) to (6.2) scales with k^*.

[46] In fact we can rigorously justify this in a similar way to the derivation of Eq. (A10).