

## Dynamic scaling and spontaneous symmetry breaking at the gel point

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The gel point is a continuous transition between fluid and solid states, and therefore exhibits a variety of scaling laws for the linear viscoelastic behavior. These are derived, together with a scaling law for the nonlinear shear relaxation modulus and a sum rule, valid in both fluid and solid states, which has a counterpart in superconductivity. Our results are generic consequences of both dynamic critical phenomena and spontaneous symmetry breaking, and therefore are not equivalent to some previous predictions, based on an analogy with percolation.

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When a sufficient number of permanent cross-links is incorporated into a system of linear polymer chains, either in the melt or in solution, an amorphous solid is formed. This solid is often referred to as a strong gel or rubber, depending upon whether or not a solvent is present. It is amorphous, despite being in equilibrium, because of the frustration due to the combination of the permanent cross-links and the impenetrability of the polymer chains. Cross-linked macromolecular systems are the only systems known to form equilibrium amorphous solids. In using the term *solid* we refer to a system with spontaneously broken translational invariance, and a static shear modulus that is consequently nonzero. In particular, we distinguish between this state and that of a *connected* ensemble of flexible elements (such as polymer chains), which is not obviously or even necessarily a solid. For convenience, we shall refer to the point in the phase diagram, where the transition to the solid state occurs, as the *gel point*, even though the transition is usually called *vulcanization* in the case of rubber.

The phase transition from a fluid to an equilibrium amorphous solid also exhibits unique features. Landau theory predicts that the transition is *not* first order—the usual case for fluid to solid transitions—but instead is continuous [1,2]. We emphasize that this result is non-trivial: In the calculation of the effective Hamiltonian for the tensor order parameter, the coefficient of the relevant cubic invariant could potentially have been positive, which would have led to a first-order transition [3]. This is the only known case of a continuous solidification transition in three dimensions.

The purpose of this paper is to examine the dynamic critical phenomena, which general renormalization-group considerations [4] imply must accompany a continuous transition to the solid state [2]. Our starting point is a dynamic scaling hypothesis for the shear relaxation modulus [5]  $\hat{G}(\omega)$  as a function of frequency  $\omega$ , which is the appropriate response function to consider at a phase transition from the fluid to the solid state.  $\hat{G}(\omega)$  is related to the complex modulus, conventionally denoted as  $G^*(\omega)$ , whose real and imaginary parts are the storage modulus  $G'(\omega)$  and the loss modulus  $G''(\omega)$ , both of which are experimentally observable [6,7] as the number of cross-links  $N$  is varied through the critical value  $N_c$ .

Our results take the form of scaling laws for the moduli and the viscosity  $\eta$ , and relations between the critical exponents characterizing the behavior of these quantities as a function of  $\omega$  and reduced cross-link number  $n \equiv (N_c - N)/N_c$ . We also derive a scaling relation for the nonlinear shear relaxation modulus  $G_{nl}$ . Some, but not all, of these relations have been proposed before on the basis of an analogy with percolation [8], which takes as a *starting point* the existence of a solid, fractal structure at the gel point.

The bases for our work, on the other hand, are twofold. First, the power laws that emerge near the gel point are standard consequences of the dynamic critical phenomena which accompany a continuous phase transition. Our previous work [1,2] not only account for the existence of the transition, but also predicts it to be continuous. Thus, there is no need to make any analogy with percolation, nor to assume that a fractal network forms with a particular fractal dimension [9]. Second, gels are solid, and at the gel point, translational invariance is spontaneously broken [10]. This, and not connectivity, is the principal thermodynamic significance of gelation, and is an aspect that cannot be captured by purely geometrical considerations such as percolation. Spontaneous symmetry breaking implies the *emergence* of rigidity in the system, through the necessary presence [10] of power-law transverse correlations in the strain field, for  $N > N_c$ , and accordingly, as the bulk correlation length  $\xi$  decreases, the shear rigidity increases, with an exponent which we discuss below.

All our predictions are scaling laws and relations between exponents, and should be satisfied regardless of the actual values of the exponents; at this stage, we have nothing to say about these values or the possible universality classes. Thus, our work does not address the issue of a possible concentration dependence of exponents [7]. However, satisfying our scaling laws is a good consistency test, and provides a criterion for checking that the data are in the scaling limit.

As mentioned above, there is nothing particularly unusual about the way in which dynamic scaling phenomena manifest themselves near the gel point, given that the transition to the solid state is continuous. Thus, much of the phenomenology developed in this paper has its direct counterpart in other systems where the spontaneous

breaking of a continuous symmetry is probed by transport measurements. In particular, we shall mention the similarity with fluctuation phenomena in the vicinity of the superconducting transition, with the complex modulus  $G^*$  playing the role of the superfluid density  $\rho_s$ , and the shear relaxation modulus  $\hat{G}(\omega)$  being the analog of the frequency-dependent conductivity  $\hat{\sigma}(\omega)$ .

*Dynamic scaling.* For a shear flow with velocity field  $\mathbf{v}=(v_x, v_y, v_z)$ , where  $v_x=k(t)y$  and  $v_y=v_z=0$ , the  $xy$  component of the shear stress tensor is related to the rate of strain  $k(t)$  by the shear relaxation modulus  $G(t)$  through

$$\sigma_{xy}(t) = \int_{-\infty}^{\infty} dt' G(t-t')k(t'). \quad (1)$$

Causality requires that  $G(t-t')=0$  for  $t'>t$ . In a polymer system, it is conventional to assume that there are two additive contributions to  $G$ , one coming from the solvent, the other,  $G^p(t)$ , from the polymers themselves. Thus  $G(t)=\eta_s\delta(t)+G^p(t)$ , where  $\eta_s$  is the solvent viscosity. In a steady shear flow,  $\sigma_{xy}=\eta k$ , where the static viscosity is  $\eta=\eta_s+\int_0^{\infty} dt' G(t')$ .

In a time-dependent flow, it is convenient to consider the Fourier-transform variables denoted by a caret: thus  $\hat{\sigma}_{xy}(\omega)=\hat{G}(\omega)\hat{k}(\omega)$ , where, for example,

$$\hat{G}(\omega) \equiv \int_{-\infty}^{\infty} dt e^{-i\omega t} G(t).$$

We define the complex modulus  $G^*(\omega)=i\omega\hat{G}(\omega)$ , with real and imaginary parts  $G'(\omega)$  and  $G''(\omega)$ , respectively.

The dynamic scaling hypothesis for the shear relaxation modulus  $\hat{G}(\omega, n)$  asserts that

$$\hat{G}(\omega, n) = n^{-\gamma} F_{\pm}(\omega\tau_0), \quad (2)$$

where  $n \equiv (N_c - N)/N_c$ ,  $F_{\pm}$  is a scaling function and  $\tau_0$  is the relaxation time of the zero wave-number mode, given in terms of the correlation length  $\xi(n)$  by  $\tau_0 = \tau_m \xi(n)^z$ . Here  $\tau_m$  is some microscopic relaxation time, and  $z$  is the dynamic critical exponent. Near the transition, the correlation length diverges with an exponent  $\nu$ :  $\xi(n) = \xi_0^{\pm} |n|^{-\nu}$ , where  $\xi_0^{\pm}$  is the bulk correlation length in the solid (-) or fluid phase (+), well away from the transition. The frequency-dependent viscosity is defined to be  $\hat{\eta}(\omega, n) = G^*(\omega, n)/i\omega$ , and so is equal to  $\hat{G}$ . Thus the exponent  $\gamma$  describes the divergence of the zero frequency or static viscosity  $\eta(n) \equiv \lim_{\omega \rightarrow 0} \hat{\eta}(\omega, n)$ , in the limit that  $n \rightarrow 0+$ , as long as the scaling function  $F_+(x)$  tends towards a constant value independent of  $x$  as  $x \rightarrow 0$ . Hence, well away from the transition, and for  $n > 0$ , the complex modulus in the fluid phase must have the form

$$G^*(\omega, n) = g_1^+(n)(i\omega) + g_2^+(n)(i\omega)^2 + O((i\omega)^3), \quad (3)$$

where the  $g_i^+(n)$  are real coefficients. In the limit  $n \rightarrow 0+$ , the coefficient  $g_1^+(n) \sim n^{-\gamma}$ .

In the solid phase, the complex modulus does not vanish as  $\omega \rightarrow 0$ , by definition, and so has the form

$$G^*(\omega, n) = g_0^-(n) + g_1^-(n)(i\omega) + g_2^-(n)(i\omega)^2 + O((i\omega)^3), \quad (4)$$

where  $g_0^-(n) \propto |n|^{\beta}$  for  $n \rightarrow 0-$ : This describes the onset of rigidity in the solid phase as the cross-link number is

increased above the critical value. The terminology  $\beta$  for the exponent is nonstandard; for now, we shall regard  $\beta$  as arbitrary, but we will show later that it has the value  $\nu$  in three dimensions. This result follows from spontaneous symmetry breaking, and we do not see how it could be obtained from percolation analogs. This form  $G^*$  requires that the complex viscosity *in the solid phase* has the form at low frequencies

$$\hat{\eta}(\omega, n) = \lim_{\epsilon \rightarrow 0} \frac{g_0^-(n)}{i\omega + \epsilon}. \quad (5)$$

In writing Eq. (5), we have used causality to resolve the singularity at  $\omega=0$ : Thus, the real part of the complex viscosity has a delta function at  $\omega=0$ , which is another signature of the solid state. This is the analog of the London equation in the theory of superconductivity [11]. In addition, we will show below that this effect can be quantified in principle, using an application of the  $f$ -sum rule.

Now we derive the form of the complex viscosity at the gel point. At nonzero frequency, assuming that it remains finite, we require that as  $n \rightarrow 0+$ ,  $\hat{G}(\omega, n)$  is independent of  $n$ . In the scaling regime, this means that  $F_+(x) \sim x^{-\gamma/\nu}$  as  $x \rightarrow \infty$ , so that the  $n$  dependence cancels from Eq. (2). Thus, we conclude that

$$\hat{G}(\omega, 0) \sim (-i\omega)^{-\gamma/\nu}, \quad (6)$$

where we have included the correct factor of  $i$ , in accordance with the Kramers-Kronig relations. Thus, there should also be a universal phase lag  $\delta$  at the gel point [12], with  $\delta \equiv \tan^{-1}(G''/G') = \pi\gamma/2z\nu$ . Power-law behavior of the storage and loss moduli at the gel point has indeed been reported [6,7].

Next, we derive a scaling law relating the exponent describing divergence of the viscosity in the fluid state to that describing the onset of rigidity in the solid state. For nonzero frequency, Eq. (5) implies that the scaling function  $F_-(x)$  behaves as  $1/x$  when  $x \rightarrow 0$ . Thus, the scaling hypothesis becomes

$$\hat{G}(\omega, n) \sim \frac{|n|^{-\gamma+\nu z}}{i\omega}, \quad (7)$$

which in conjunction with Eq. (4) implies that

$$\beta = -\gamma + \nu z. \quad (8)$$

Thus, the viscosity diverges with an exponent  $\gamma = -\beta + \nu z$ . For this to be a true divergence, and not a cusp, we require  $\nu z > \beta$ .

Away from the gel point, there should still be vestiges of the power laws described above, which will be observable as crossover phenomena. Thus, for  $n \neq 0$ , but at high frequency where  $\omega n^{-\nu z} \gg 1$ , the large  $x$  behavior of the scaling functions  $F_{\pm}(x)$  is probed. Whereas the behavior of  $\hat{G}(\omega)$  at low frequency will deviate from pure power-law behavior, such behavior will be recovered at high frequencies  $\omega \gg \omega_0(n)$ , where  $\omega_0(n) \sim n^{\nu z}$ .

*Nonlinear response.* We can also use scaling ideas to describe the *nonlinear response* of the system at the gel point. The arguments below were used to analyze the scaling of the nonlinear conductivity near the superconducting transition [13]. We define the *nonlinear* shear re-

laxation modulus  $G_{nl}(k)$  at zero frequency by the relation between stress and rate of strain

$$\sigma_{xy} = G_{nl}(k)k, \quad (9)$$

where  $k$  is the rate of strain, and we are implicitly discussing the fluid phase. We can write down a scaling hypothesis for  $G_{nl}$  by noting two facts: first,  $G_{nl}$  has the same dimensions as the linear shear relaxation modulus, and second, the dimensions of  $k$  are inverse time. Near the gel point, then,  $k$  must scale with the relaxation time  $\tau_0$ . Hence  $G_{nl}(k, n) = n^{-\gamma} \Gamma(k\xi(n)^{-\gamma})$ , with  $\Gamma$  being a scaling function. At the gel point,  $\xi \rightarrow \infty$ , and in order that  $G_{nl}(k, n)$  remain finite, the  $n$  dependence of  $G_{nl}$  must cancel out: this requires that  $\Gamma_{\pm}(x) \sim x^{-\gamma/\nu}$  as  $x \rightarrow \infty$ . Hence, we obtain a scaling law for the dependence of the nonlinear shear relaxation modulus on strain rate, at the gel point

$$G_{nl}(k, 0) \sim k^{-\gamma/\nu}. \quad (10)$$

As in the linear case, there is also a crossover phenomenon slightly away from the gel point: when  $kn^{-\nu} \gg 1$ , we have  $G_{nl}(k, n) \sim k^{-\gamma/\nu}$ .

*Consequences of symmetry breaking.* Up to this point, we have presented the consequences which follow from the fact that the transition to the solid state is a continuous transition, rather than a first-order transition. Now, we briefly discuss the consequences of the fact that a continuous symmetry—translational invariance—is spontaneously broken at this transition. The most important consequence from our point of view is that the long-wavelength free-energy density governing the elasticity of the solid state is

$$F(u_{ij}(\mathbf{r})) = \frac{1}{2} [2\mu u_{ij}^2(\mathbf{r}) + \lambda u_{kk}(\mathbf{r})^2], \quad (11)$$

where  $u_{ij}(\mathbf{r})$  is the stress tensor, and  $\lambda$  and  $\mu$  are the Lamé coefficients for an isotropic solid. In particular,  $\mu$  is the static shear modulus given by  $g_0^-(n) = \lim_{\omega \rightarrow 0} G^*(\omega, n)$  when  $n < 0$ . The form of Eq. (4) implies that this is a real quantity. The long-wavelength free-energy density  $F$  should scale as  $\xi(n)^{-d}$  near the transition, whereas the individual gradient terms in  $F$  must scale as  $\xi(n)^{-2}$ . Thus, we can determine the scaling of  $g_0^-(n)$  near the transition:  $g_0^-(n)\xi^{-2} \sim \xi^{-d}$ , which implies that  $g_0(n) \sim \xi^{2-d}$ , and so the exponent governing the growth of the static shear modulus in the solid state just below the transition point is

$$\beta = \nu(d - 2). \quad (12)$$

Thus, in three dimensions,  $\beta = \nu$ , as announced earlier. This result imposes an additional constraint on the scaling laws which we have derived, and is a consequence of the fact that rigidity is a thermodynamic phenomenon and not an architectural one.

*Sum rule.* An interesting signature of the symmetry breaking at the gel point is an apparent violation of a rigorous sum rule, valid for viscoelastic materials. The

sum rule may be derived by recalling that the real and imaginary parts of  $\hat{G}(\omega)$  are related by the Kramers-Kronig relations. At frequencies above some cutoff  $\omega_c$ , the real part of  $\hat{G}(\omega)$ , namely,  $G''(\omega)/\omega$ , tends to zero, because the response to an external driving force is purely inertial, and therefore there cannot be any dissipation. Thus, in the integral relating the real and imaginary parts of  $\hat{G}(\omega)$ , the upper limit is actually  $\omega_c$ . Hence, for high frequencies  $\omega \gg \omega_c$ , the response is independent of whether or not the system is solid or liquid, and we obtain the sum rule

$$\int_0^{\infty} \frac{G''(\omega')}{\omega'} d\omega' = \lim_{\omega \rightarrow \infty} G'(\omega). \quad (13)$$

We emphasize that the constant on the right-hand side of Eq. (13) is the *same* for both solid and liquid, and should also be essentially model independent. For example, the right-hand side has the value  $\pi n k_B T / 2$  for both Rouse and Zimm dynamics, where  $n$  is the monomer density and  $k_B T$  is Boltzmann's constant times temperature. In the solid phase, the sum rule will appear to be violated if the integral is performed for  $\omega > 0$ , because of the appearance of a delta function at the origin, as shown by Eq. (5). Although the cutoff frequency  $\omega_c$  is very high, the "missing" spectral weight may occur at accessible frequencies, and may be observable by comparing  $G''(\omega)/\omega$  slightly above and below the transition. Corresponding effects occur at the superconducting transition [14].

*Conclusion.* In the theory of superconductivity, the complex modulus  $G^*$  is the counterpart of the superfluid density, whereas the shear relaxation modulus  $\hat{G}(\omega)$  is the counterpart of the complex conductivity. This is a direct consequence of Eqs. (3) and (4). The scaling behavior of  $G^*$ , described above, parallels a similar argument in the theory of superconductivity [15] for the scaling of the superfluid density with temperature. In the theory of superconductivity, it is the superfluid density which quantifies the rigidity of the wave function of the condensate.

Combining our dynamic scaling results with symmetry breaking as expressed by Eq. (12), we find that above the transition, the viscosity diverges with the exponent  $\gamma = \nu(z - 1)$ . The loss and storage moduli are power-law functions of frequency at the gel point, scaling as  $\omega^{1/z}$ . The phase angle at the gel point is  $\delta = \pi(z - 1)/2z$ , and the nonlinear shear modulus also has a power-law dependence on strain rate, with an exponent of  $-(z - 1)/z$ . Finally, the analysis reported here would be applicable to other three-dimensional systems exhibiting a continuous solidification transition, if they should exist.

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