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Paradox in phase transitions with volume change

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In gels, a critical point at which swelling transition becomes continuous, is characterized by vanishing of the bulk modulus K. At this point, however, an instability is triggered by a single mode representing homogeneous expansion while fluctuations with finite wave numbers are still suppressed by the finite shear modulus μ. Critical divergence of the fluctuation spectrum is expected not at this critical point but only in an unstable region. This unusual feature has been overlooked because of small values of μ in previous experiments.

A number of elastic materials undergo phase transitions accompanied by a volume change. The aim here is to raise and try to resolve a paradox in such systems, which seems to have not been discussed seriously in the literature. Our arguments will, however, be limited to polymer gels near their swelling transitions.[1] See a comment on solid materials at the end of this Rapid Communication.

Let us consider an isotropically swollen gel immersed in a solvent. Its volume can be changed discontinuously as a first-order phase transition where an external parameter such as the temperature is varied. Furthermore, Tanaka even reached a critical point of second-order phase transition by changing the degree of ionization of the network and by diminishing the discontinuity at the transition.[2] He also observed enhancement of scattered light intensity on approaching cloud points (or spinodal points).[3]

At the critical point the bulk modulus K and its derivative with respect to ϕ have been claimed to tend to zero.[2] Here,

$$K=\phi(\partial\Pi/\partial\phi)_T=-v(\partial\Pi/\partial v)_T\,, \tag{1}$$

where Π is the omotic pressure, ϕ is the volume fraction of the polymers, and $v=1/\phi$ is the specific volume. The requirement, $K\to 0$ and $(\partial K/\partial\phi)_T\to 0$, will look obvious if we note that Π assumes the following form near the critical point,[2]

$$\Pi=\Pi_c+c_0(T-T_c)+a_0(T-T_c)(\phi-\phi_c)/\phi_c+b_0[(\phi-\phi_c)/\phi_c]^3+\cdots\,, \tag{2}$$

where Π_c, T_c, and ϕ_c are the critical values of Π, T, and ϕ, respectively, and a_0, b_0, and c_0 are constants independent of ϕ and T. We are supposing situations in which Π is fixed at an externally given value $\Pi_{\rm ext}$ (which has been mostly equal to zero in previous experiments).

On the other hand, the correlation function for the Fourier component $\delta\phi_{\mathbf{q}}$ can be calculated in the mean field theory in the form[4]

$$G_{\mathbf{q}}=\langle|\delta\phi_{\mathbf{q}}|^2\rangle=\phi^2/[(K+\tfrac{4}{3}\mu)/k_BT+K_sq^2]\,, \tag{3}$$

where μ is the shear modulus and K_s is a coefficient dependent on the average volume fraction ϕ. The q-dependent term K_sq^2 in the denominator has been introduced to make the intensity to take the Ornstein-Zernike form. The above relation (without the q-dependent term) generally holds in the long wavelength limit $q\to 0$ for any isotropic elastic bodies characterized by the two elastic coefficients, K and μ. For example, it can be obtained by calculating the free-energy increase due to small displacements $\mathbf{u}(\mathbf{r})$ together with the relation $\delta\phi(\mathbf{r})/\phi=-\nabla\cdot\mathbf{u}$.[5] The correlation function has been calculated more generally for affinely deformed gels at long wavelengths.[6]

Now we notice that, even if $K\to 0$, the fluctuation intensity G_q must remain finite unless μ goes to zero at the critical point. Here I believe that μ should be nearly constant near the critical point in gels. Then we are puzzled by the unusual nature of the critical point, determined by $(\partial\Pi/\partial\phi)_T=(\partial^2\Pi/\partial\phi^2)_T=0$, at which critical fluctuations seem to be not enhanced. This, however, apparently contradicts Tanaka's claim that he observed critical divergence of the scattered light intensity.[3] Of course (3) holds only when the wavelength $2\pi/q$ is much shorter than the linear dimension of the system.

A clue to the riddle can be obtained by analyzing kinetics of swelling or shrinking near the critical point.[7] If we consider only a very small displacement $u(r)$ from a position r fixed to a homogeneous reference state of the gel, the stress tensor Π_{ij} due to the displacement can be ex-

pressed in the standard form[5]

$$\Pi_{ij} = -K(\nabla\cdot\mathbf{u})\delta_{ij} - \mu\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{d}\delta_{ij}(\nabla\cdot\mathbf{u})\right). \quad (4)$$

We will discuss the problem for general spatial dimensionality d because our results can then be applied to constrained gels allowed to swell only in one or two directions.[6] The equation of motion is of the form[4]

$$\rho\frac{\partial^2}{\partial t^2}u_i + \gamma\frac{\partial}{\partial t}u_i = -\sum_j \frac{\partial}{\partial x_j}\Pi_{ij}, \quad (5)$$

where ρ is the mass density and γ is the friction coefficient. In gels the friction term is dominant due to relative motion between the network and the solvent. Hence we obtain

$$\frac{\partial}{\partial t}u_i = D\left(\nabla^2 u_i + \epsilon\frac{\partial}{\partial x_i}(\nabla\cdot\mathbf{u})\right), \quad (6)$$

where

$$D = \mu/\gamma, \quad (7)$$

$$\epsilon = K/\mu + (1-2/d). \quad (8)$$

The quantity $g \equiv \nabla\cdot\mathbf{u}$ simply obeys the diffusion equation

$$\frac{\partial}{\partial t}g = D(1+\epsilon)\nabla^2 g. \quad (9)$$

Notice that the following combination of K and μ appears in (9):

$$\mu(1+\epsilon) = K + [2(d-1)/d]\mu, \quad (10)$$

which is inversely proportional to the intensity G_q in the limit $q \to 0$ as shown in (3). Obviously the stability requires $1+\epsilon > 0$. At the boundary between the gel and the surrounding solvent, the following relation must be satisfied:

$$\sum_j \Pi_{ij} n_j = 0, \quad (11)$$

where $\mathbf{n}$ is the outward normal unit vector to the surface. Using (4) and (8) we rewrite (11) as

$$(\epsilon-1)(\nabla\cdot\mathbf{u})n_i + (\mathbf{n}\cdot\nabla)u_i + \sum_j n_j\left(\frac{\partial}{\partial x_i}u_j\right) = 0. \quad (12)$$

Thus we are led to the following eigenvalue problem:

$$\nabla^2 u_i + \epsilon\frac{\partial}{\partial x_i}(\nabla\cdot\mathbf{u}) = -\lambda(1+\epsilon)u_i, \quad (13)$$

with the boundary condition (12).

For simplicity we consider a spherical gel with the boundary at $r = R$ and seek only spherical solutions of the form

$$u_i = u x_i/r, \quad (14)$$

where u depends only on the radius r. Then there is no shear stress and (12) and (13) are simplified as

$$\frac{\partial}{\partial r}\left(\frac{\partial}{\partial r} + \frac{d-1}{r}\right)u = -\lambda u, \quad (15)$$

$$(1-\epsilon)(d-1)u(R) = (1+\epsilon)Ru'(R), \quad (16)$$

where $u'(r) = \partial u/\partial r$. The solution to (15) is expressed as

$$u = r^{-(d-2)/2}J_{d/2}(\lambda^{1/2}r), \quad (17)$$

where $J_\nu(z)$ is the Bessel function of order ν. The equation for λ is of the form

$$zJ_{d/2-1}(z)/J_{d/2}(z) = 2(d-1)/(1+\epsilon), \quad (18)$$

where $z = \lambda^{1/2}R$ and use has been made of $dJ_\nu(z)/dz = J_{\nu-1}(z) - \nu z^{-1}J_\nu(z)$. If the gel is stable, we should have a series of positive numbers, $0 < z_0 < z_1 < \cdots$, and the nth eigenvalue λ_n is given by $\lambda_n = (z_n/R)^2$. Here we are interested in the case $z_0 \cong 0$. Because the left-hand side of (18) may be expanded as $d - z^2/(d+2) + \cdots$ for $|z| \ll 1$, we then find

$$z_0^2 \cong \frac{d(d+2)}{1+\epsilon}\left(\epsilon - \frac{d-2}{d}\right) = d(d+2)K/\mu(1+\epsilon). \quad (19)$$

Namely, if $\epsilon \cong \epsilon_c \equiv (d-2)/d$ or $0 < K \ll \mu$, there appears a slow relaxation mode with the following relaxation rate:

$$\Omega_0 = D(1+\epsilon)z_0^2/R^2 \cong d(d+2)K/(\gamma R^2). \quad (20)$$

From (14) and (17) the eigenvector $\mathbf{u}_0(\mathbf{r})$ for this mode may be expanded as

$$\mathbf{u}_0(\mathbf{r}) = [1 - \text{const}\times(z_0 r/R)^2 + \cdots]\mathbf{r}. \quad (21)$$

Therefore the above mode represents slow homogeneous swelling or shrinking with only small density inhomogeneities. However, this mode has been overlooked by Tanaka.[7] For example, if $u_i(\mathbf{r},0) = a_0 x_i/r$ at $t = 0$, the subsequent time development is expressed as

$$u_i(\mathbf{r},t) = a_0(x_i/r)\sum_{n=0}^{\infty} a_n u_n(r)\exp(-\Omega_n t), \quad (22)$$

where $u_n(r)$ is the nth eigenfunction of (15) and $\Omega_n = D(1+\epsilon)z_n^2/R^2$, z_n being the nth solution to (18). As $z_0 \to 0$ we can prove $a_0 u_0(R) = 1 - z_0^2/[(d+2)\times(d+4)] + \cdots$ and $a_n u_n(R) \propto K/\mu$ for $n \geq 1$. Namely, the first mode $n = 0$ dominates in (22), leading to

$$u_i(\mathbf{r},t) \cong a_0(x_i/r)\exp(-\Omega_0 t) \text{ for } |K/\mu| \lesssim 1. \quad (23)$$

Even for general shapes of the gel, the corresponding slow mode can be readily calculated by expanding $\mathbf{u}$ as $\mathbf{r} + O(r^3)$. After some calculations we find up to first order in $\epsilon - \epsilon_c = K/\mu$,

$$\Omega_0 \cong d^2 K/(\gamma R_g^2) \quad (24)$$

where R_g is the gyration radius defined by $VR_g^2 = \int d\mathbf{r}\, r^2$, V being the total volume of the gel and the integral being limited within the gel. More generally, if the first term in (5) is not negligible, Ω_0 is determined by

$$-\rho\Omega_0^2 + \gamma\Omega_0 \cong d^2 K/R_g^2. \quad (25)$$

Next we examine how the free energy F due to small deformations behaves at small K. It is expressed as[5]

$$F=\int d\mathbf{r}\left[\tfrac{1}{2}Kg^2+\tfrac{1}{4}\mu\sum_{i,j}\left(\partial_i u_j+\partial_j u_i-\frac{2}{d}g\delta_{ij}\right)^2\right], \quad (26)$$

where $g=\nabla\cdot\mathbf{u}$. Let the eigenfunctions and the eigenvalues of (12) and (13) be $\hat{\mathbf{u}}_{ip}$ and λ_p with $p=0,1,2,\ldots$. Expanding $u_i(\mathbf{r})$ as $u_i(\mathbf{r})=\sum_{p=0}^{\infty}A_p\hat{\mathbf{u}}_{ip}$, we find

$$F=\tfrac{1}{2}\mu(1+\epsilon)\sum_{p=0}^{\infty}\lambda_p C_p A_p^2, \quad (27)$$

where $C_p=\int d\mathbf{r}\sum_i|\hat{\mathbf{u}}_{ip}|^2$. Thus the variables A_p are independently Gaussian with variance $k_BT/[\mu(1+\epsilon)\lambda_p C_p]$ near equilibrium.

We have thus shown that only a single mode representing a homogeneous volume change becomes marginal as $K\to 0$ and an instability takes place for $K<0$. Furthermore, in the transient process to a new swollen (or shrunken) state, we should find no appreciable inhomogeneities like domain structures as long as $|K|\ll\mu$. This is because such inhomogeneities are suppressed by the finite shear modulus on the time scale of R_g^2/D which is supposed to be faster than $1/\Omega_0$. Phase separation into two phases can be expected only for $|K|\gtrsim\mu$. The instability point $K=0$ is thus completely different from the usual critical point in other equilibrium systems in which an infinite number of long wavelength fluctuations are enhanced. We should consider the point $K=0$ to represent a mechanical instability point rather than a thermodynamic instability point.

The form of Π near the critical point (2) also suggests that there should be a finite transition probability even for $K>0$ between two different stable states determined by $\Pi=$const. In the case $K\ll\mu$, this is the problem of metastability for a single mode without any spatial dependence. The transition rate should be proportional to the factor $\exp(-\Delta F/k_BT)$, ΔF being the free-energy barrier. Some calculations show that ΔF is proportional to the total volume V as

$$\Delta F/k_BT\sim VK^2/\mu k_BT. \quad (28)$$

The above rate is, however, extremely small in most conditions and there should be hysteresis in experiments.

There is a considerable difficulty to explicitly calculate correlation functions in finite systems.[8] Here we express the correlation function for the deviation $\delta\phi(\mathbf{r})$ in the following expansion form:

$$\langle\delta\phi(\mathbf{r}_1)\delta\phi(\mathbf{r}_2)\rangle=\frac{k_BT}{\mu(1+\epsilon)}\sum_{p=0}^{\infty}\frac{1}{\lambda_p}C_p^{-1}\hat{\psi}_p(\mathbf{r}_1)\hat{\psi}_p(\mathbf{r}_2), \quad (29)$$

where $\hat{\psi}_p(r)=\nabla\cdot\hat{\mathbf{u}}_p$. The first term $p=0$ gives rise to a contribution nearly equal to k_BT/KV for $0<K\lesssim\mu$, whereas the contribution from large p should be insensitive to the boundary condition with its dominant part being the Fourier transform of (3). The first term diverges as $K\to 0$ signaling the onset of the instability, but it is virtually negligible in magnitude unless V is very small. Equation (29) also shows that the fluctuation of the total volume, $\delta V\cong-\int d\mathbf{r}\,\delta\phi(\mathbf{r})$, is Gaussian with variance k_BTV/K as $K\to 0$ as ought to be the case. On the other hand, if $K<0$, an instability occurs and then the first mode A_0 should exhibit large fluctuations in the transient stage.[9]

In practice, the time development of the slow mode discussed above can be followed only when the time $1/\Omega_0$ is less than the observation time. For example, a 2.5% polyacrylamide gel in Refs. 3 and 4 had a very small shear modulus μ of order 2×10^2 dyn/cm^2 and the diffusion constant D defined by (7) was of order 10^{-7} cm^2/sec far from the spinodal point.[10] Therefore, for macroscopic sizes of gels, the temperature can be lowered into a region in which $K+\frac{4}{3}\mu\cong 0$ without any appreciable volume change. In the above gel the scattered light intensity indicated the relation

$$(K+\tfrac{4}{3}\mu)/k_BT=3.6\times10^{20}(1/T_s-1/T)\text{cm}^{-3}\text{deg}^{-1},$$

where T_s was the temperature at a cloud point. Then the temperature region in which $|K|<\mu$ should have had a width of order 1 deg. It is now very desirable to detect the difference of the temperature of $K=0$ and that of $K+\frac{4}{3}\mu=0$ by observing both swelling and light scattering.[11]

We remark that the slow mode at $K\cong 0$ strongly depends on the macroscopic boundary conditions, whereas the fluctuation enhancement at $K+\frac{4}{3}\mu=0$ does not as long as gels are kept isotropic. The former even becomes nonexistent if the gel surface is clamped to solid walls. Interestingly the point at which the swelling transition becomes continuous and the point of fluctuation enhancement can coincide if gels are allowed to change their shapes only in one direction.[12] This is simply because shear deformations are not induced by uniaxial volume changes. In accord with this, (10) indicates that the diffusion constant for $\nabla\cdot\mathbf{u}$ in (9) is just equal to K/γ for $d=1$. There should be a rich variety of experiments on instabilities and critical phenomena in constrained gels with various boundary conditions.[6,12]

Also in crystals an analogous mechanical instability can occur without critical enhancement of acoustic modes. For example, this condition is $C_{11}+2C_{12}\to 0$ with $C_{12}<0$ in cubic crystals, where C_{ij} are the stiffness constants in the usual notation. This condition can in fact be realized in some crystals,[13] in which, however, μ is not a small quantity and the two points of $K=0$ and $K+\frac{4}{3}\mu=0$ are much separated.

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[1]T. Tanaka, Physica A **140**, 261 (1986), and references quoted therein.

[2]T. Tanaka, Phys. Rev. Lett. **20**, 820 (1978). He found a critical point at zero osmotic pressure and called it a critical end point. Note that it is an intersection point of a critical line and the surface $\Pi=0$. Hence in the usual sense of the terminology [R. B. Griffiths, J. Chem. Phys. **60**, 195 (1974)] it is only one particularly chosen critical point on the critical line

and is not a critical end point. The latter would be located in the region $\Pi < 0$ as an end point of the critical line if it would exist.

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[4]T. Tanaka, L. O. Hocker, and G. B. Benedek, J. Chem. Phys. **59**, 5151 (1973).

[5]L. D. Landau and E. M. Lifschitz, *Theory of Elasticity* (Pergamon, New York, 1986). Here the positivity of K and μ is concluded to follow from thermodynamic stability against small deformations. If the argument there is applicable to the case of gels, G_q can diverge only when the gel is brought into a metastable or unstable region.

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[7]T. Tanaka, E. Sato, Y. Hirokawa, S. Hirotsu, and J. Peetermans, Phys. Rev. Lett. **25**, 2455 (1985).

[8]See for example, G. Satten and D. Ronis, Physica A **125**, 281 (1984).

[9]M. Suzuki, Adv. Chem. Phys. **46**, 195 (1981).

[10]In Ref. 3 the inverse $1/\gamma$ was shown to diverge as $T \rightarrow T_s$ as in critical fluids. However, I believe that it should level off at $T = T_s$ due to a resistive effect of the finite shear modulus μ.

[11]Tanaka calculated the curve of $K = 0$ as the spinodal curve in Fig. 3 of Ref. 2. This definition is misleading as we have shown. Note also that there is a branch at small ϕ for the curve of $K = 0$ ($N \sim S$ in Fig. 3). However, such a low-density branch does not exist for the curve of $K + \frac{4}{3}\mu = 0$.

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