EUROPHYSICS LETTERS 15 November 2000

Europhys. Lett., **52** (4), pp. 413–419 (2000)

Entropic elasticity of phantom percolation networks

O. Farago and Y. Kantor

School of Physics and Astronomy
Raymond and Beverly Sackler Faculty of Exact Sciences
Tel Aviv University - Tel Aviv 69 978, Israel

(received 30 June 2000; accepted 15 September 2000)

PACS. 62.20.Dc – Elasticity, elastic constants.
PACS. 64.60.Fr – Equilibrium properties near critical points, critical exponents.
PACS. 61.43.-j – Disordered solids.

Abstract. – A new method is used to measure the stress and elastic constants of purely entropic phantom networks, in which a fraction p of neighbors are tethered by inextensible bonds. We find that close to the percolation threshold p_c the shear modulus behaves as $(p-p_c)^f$, where the exponent $f \approx 1.35$ in two dimensions, and $f \approx 1.95$ in three dimensions, close to the corresponding values of the conductivity exponent in random resistor networks. The components of the stiffness tensor (elastic constants) of the spanning cluster follow a power law $\sim (p-p_c)^g$, with an exponent $g \approx 2.0$ and 2.6 in two and three dimensions, respectively.

In the gelation process, monomers or short polymers in a fluid solution are randomly cross-linked. At a certain moment during the reaction, a macroscopically large network, *the gel*, spans the system. At this point, the system changes from a fluid-like (sol) to a solid-like (gel) phase that has a finite shear modulus. The *geometry* of gels is frequently described by the percolation model [1]. The percolation geometry is usually defined on a lattice, by randomly occupying a fraction p of the bonds (or sites). The gel point is identified with the percolation threshold p_c, the critical bond (site) concentration above which a spanning cluster is formed. Percolation theory predicts that close to p_c quantities like the average cluster size or the gel fraction have power laws dependence on $(p-p_c)$ with universal exponents, some of which have been measured experimentally for gel systems [2].

Near the sol-gel transition typical polymer clusters are very large, tenuous and floppy. Elastic properties of such systems are primarily determined by the *entropy*, *i.e.*, distortions of a sample barely modify its energy, but they decrease the available phase space (decrease entropy) and, thus, increase the free energy. Like geometrical quantities near p_c, the shear modulus is also expected to follow a power law: $\mu \sim (p-p_c)^f$. de Gennes [3] used an analogy between gel elasticity and conductivity of random resistor networks (RRN), and conjectured that the exponent f should be equal to the exponent t describing the conductivity Σ of RRN close to p_c: $\Sigma \sim (p-p_c)^t$. Alternative theories take different approaches and lead to different exponents [4]. An exact calculation of the critical behavior of μ, which takes into account excluded volume (EV) and entanglements effects, is not yet available. Experimental values of

f, measured for different polymeric systems, are very scattered [5]. One of the reasons for the variety of the experimental results is the mixing of the entropic and energetic contributions to the gel elasticity, which influences the "effective" exponent.

Neglect of EV interactions, *i.e.*, treating a *phantom* system, may strongly modify the physics. Nevertheless, it is frequently done either because in certain situations (such as dense polymer melts) EV interactions effectively cancel out [6], or because from the purely theoretical point of view phantom systems are more tractable and may serve as a starting point for studying real systems. Phantom systems maintain the correct connectivity, which is one of the important characteristics of a polymer network. A feature common to most phantom networks (independently of the detailed shape of the microscopic potential) is the fact that at zero tension the probability density that two distant nodes are separated by $\vec{r}$ takes a Gaussian form $\sim \exp\left[-\frac{1}{2}Br^2\right]$. For linear polymers this is a consequence of the central limit theorem, while for more complicated systems this can be demonstrated numerically [7]. The thermodynamic behavior of a phantom network can, therefore, be described very accurately within a phantom Gaussian network (PGN) model, in which each bond of the network is replaced by a *Gaussian spring* having the energy $E = \frac{1}{2}Kr^2$, where r is its end-to-end distance [8]. Corrections to Gaussian behavior can be studied by considering a phantom nearly Gaussian network (PNGN), in which the springs' energies include an additional small term equal to $\frac{1}{4}ar^4$. In this paper we describe results of a numerical study of the elasticity of tethered phantom percolating networks, and compare our results with the two models [9]. We use a recently developed formalism [10] which enables direct calculation of entropic elastic constants of tethered systems. We show that the shear modulus behaves near p_c like the conductivity of RRN as predicted by the PGN model, while the elastic stiffness tensor of the spanning cluster, which, according to PGN model, is supposed to vanish [9], also exhibits a power law behavior near p_c with a significantly larger critical exponent. The last result is a consequence of the deviation from the Gaussian behavior, and can be understood within the PNGN model [9].

In a homogeneous deformation we distort the boundaries of a system is such a way that a separation $\vec{R}$ between a pair of surface points is modified into $\vec{r}$, which is linearly related to $\vec{R}$ via a position-independent matrix. In this case the new squared distance $r^2 = R_iR_j(\delta_{ij} + 2\eta_{ij})$, where the subscripts denote Cartesian coordinates, δ_{ij} is the Krönecker delta, η_{ij} is the Lagrangian strain tensor, and summation over repeated indices is implied. The stress and elastic stiffness tensors, σ_{ij} and C_{ijkl}, respectively, are then defined as the coefficients of the expansion of the free energy density in the strain variables: $f(\{\eta\}) = f(\{0\}) + \sigma_{ij}\eta_{ij} + \frac{1}{2}C_{ijkl}\eta_{ij}\eta_{kl} + \ldots$ Close to p_c, percolation networks "forget" the details of the lattice and behave like isotropic systems, and therefore the stress tensor $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} \equiv \sigma \equiv -P$, where P is the pressure. Isotropic systems have only three *different* non-vanishing elastic constants: $C_{11} \equiv C_{xxxx} = C_{yyyy} = C_{zzzz}$; $C_{12} \equiv C_{xxyy} = C_{yyzz} = C_{zzxx} = \ldots$; and $C_{44} \equiv \frac{1}{2}(C_{xyxy} + C_{xyyx}) = \frac{1}{2}(C_{yzyz} + C_{yzzy}) = \ldots$, which are related by $C_{11} = C_{12} + 2C_{44}$. Frequently, one finds it more useful to describe the elastic behavior in terms of the *shear* modulus $\mu \equiv C_{44} - P$, and the *bulk* modulus $\kappa \equiv \frac{1}{2}(C_{11} + C_{12})$ (for two-dimensional (2D) systems), or $\kappa \equiv \frac{1}{3}(C_{11} + 2C_{12} + P)$ (for three-dimensional (3D) systems). In a percolation phantom system the contributions of the different clusters are additive. Each finite cluster, not connected to the boundaries of the system, contributes as a single atom of an ideal gas. Thus N_0 free finite clusters confined within volume V at temperature T produce stress equal to $\sigma = -\frac{N_0kT}{V}$, and elastic constant $C_{44} = \frac{N_0kT}{V}$, where k is the Boltzmann constant. Although both C_{44} and P are affected by the presence of finite clusters, we observe that the (ideal gas) contribution of the finite clusters cancels out in the definition definition of μ. Since finite clusters play such unremarkable role in the problem of elasticity, we will disregard them

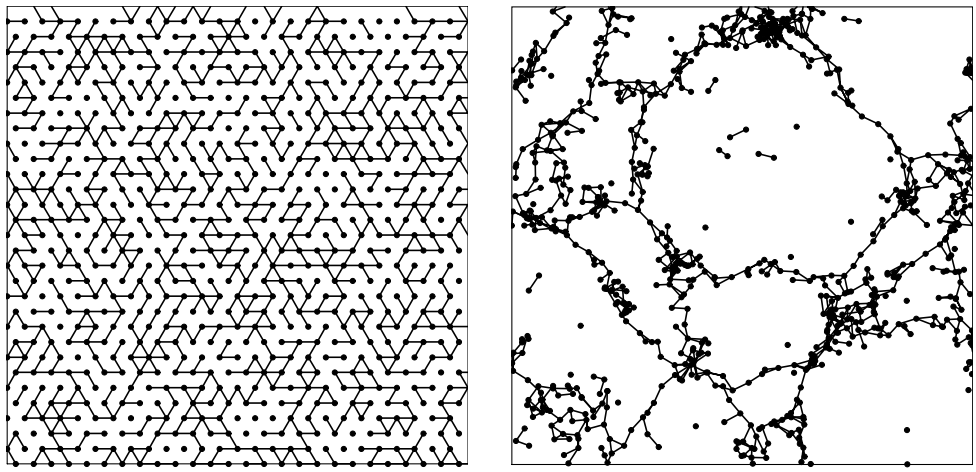

Fig. 1 – Part of initial (a) and equilibrated (b) configurations of the 2D system ($p = 0.405$, $b = 1.05$).

completely, and in the remainder of this work the stress, elastic constants and elastic moduli will refer to the contribution of the spanning cluster alone. The latter depends on the details of the potential and connectivity. However, in the case of PGN few simple properties exist [9]: 1) Since the energy of a Gaussian spring is proportional to r^2, while the squared distances between the points on the boundaries are linear in η_{ij}, it can be shown that the free energy of the spanning cluster does not include quadratic terms in η_{ij}, and therefore its $C_{ijkl} = 0$. 2) The stress tensor is *equal* to the conductivity tensor of an equivalent resistor network in which each spring of the spanning cluster with a force constant K is replaced by a resistor of conductance K. For isotropic PGNs $\mu = \sigma = \Sigma$, where Σ is the conductivity of the equivalent resistor network, and we, thus, find that $f = t$. In the PNGN model near p_c, σ and μ are still dominated by the Gaussian term rather than by the non-Gaussian perturbation, and we recover the equality $f = t$. Non-Gaussian corrections are manifested by non-vanishing elastic constants, which for percolation PNGNs are expected to behave as $C \sim (p - p_c)^g$ with $g > f$ [9].

In this work we investigate the elastic behavior of networks for which the problem of mixing of the entropic and energetic components does not exist. Our system consists of point-like atoms connected by "tethers" that have no energy, but simply limit the distance of a connected pair to be smaller than some value b. Since the internal (potential) energy of the system vanishes, its thermodynamic behavior is *purely* entropic. We generated the (quenched) topologies by considering the bond percolation problem on 2D triangular ($p_c = \frac{\pi}{9} \sim 0.349$) and 3D faced-centered-cubic ($p_c \simeq 0.12$) lattices, with a fraction p of bond present. Each present bond was replaced by a tether, while each site became an "atom" without EV, and the system was allowed to move in *continuum*. Figure 1(a) depicts an initial 2D configuration of the system, which equilibrates into configuration of the kind depicted in fig. 1(b). As expected, finite clusters and dangling ends of the spanning cluster contract relative to their linear size in the initial quenched construction [11]. The size of the backbone, on the other hand, is fixed by the boundary conditions and, therefore, it looks like a collection of loops of the size of the percolation correlation length.

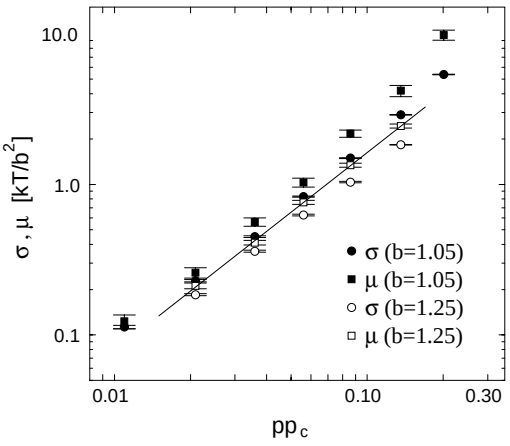

Fig. 2

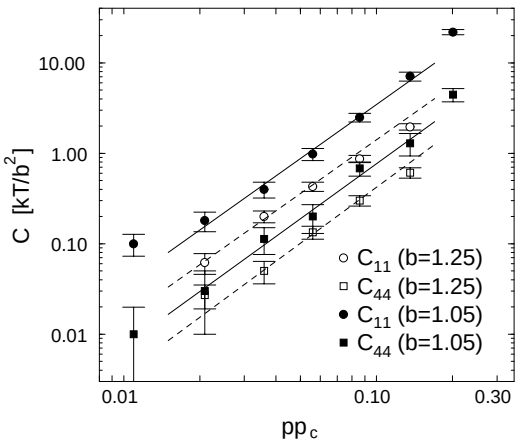

Fig. 3

Fig. 2 – Logarithmic plot of the stress σ and the shear modulus μ as a function of $(p - p_c)$, for 2D systems. The slope of the solid line is 1.35. Results are in kT/b^2 units.

Fig. 3 – Logarithmic plot of the elastic constants C_{11} and C_{44} as a function of $(p-p_c)$, for 2D systems. The slope of the lines is ≈ 2. Results are in kT/b^2 units.

The non-interacting character of phantom networks significantly simplifies the numerical procedure: 1) Since we are not interested in the (trivial) contribution of the finite clusters, they were removed from the simulations. 2) Dangling ends of the spanning cluster do not contribute neither to the stress nor to the elastic constants and, therefore, they can also be removed. Thus, for every quench we identified the backbone (using the "burning" algorithm [12], which was slightly modified to deal with the periodic boundary conditions applied in the simulations) and explored the configuration space using a Monte Carlo (MC) updating scheme [13] in which the conventional Metropolis single atom steps are replaced by collective steps of chains of atoms. At each MC time unit we made a number of move attempts (with acceptance probability ~ 0.5) equal to the number of atoms. In the 2D simulations, we used a 120×138 triangular lattice (that has an aspect ratio very close to 1) with nearest-neighbor spacing $b_0 \equiv 1$, and a number of quenched topologies that ranged from $N_t = 200$ for p closest to p_c, down to $N_t = 20$ far from p_c. In the 3D simulations we used systems of 24^3 cubic unit cells (each containing 4 atoms), *i.e.* of linear size $L = 24\sqrt{2}b_0$, with nearest-neighbor spacing $b_0 \equiv 1$, and $30 \leq N_t \leq 150$. The duration of the MC run of each individual sample was *at least* 50 times larger than the relaxation time which we estimated from the expression $\tau = dkTL^2\rho/(\pi^2\mu s^2)$, where s is the (average) distance an atom moves in one MC time unit, ρ is the number density of atoms, and d is the dimensionality of the system [14]. The value of μ in this expression was taken, *a posteriori*, from the simulations. We used a new method enabling the direct measurement of the stress and elastic constants from the probability densities of finding maximally extended tethers [10]. The error estimates are affected by the fluctuations in the values of the measured quantities between the different quenches, and to a lesser extent by the thermal uncertainties within each sample. The error bars appearing in the graphs correspond to one standard deviation of the average.

In our system we can vary only two non-trivial parameters: bond concentration p, and the maximal tether length b (measured in the units of the nearest-neighbor spacing b_0). Figure 2

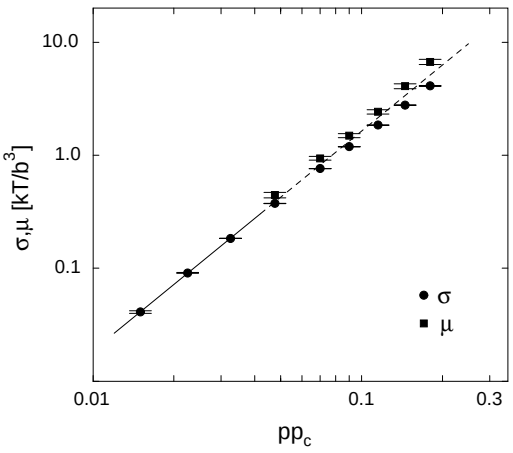

Fig. 4

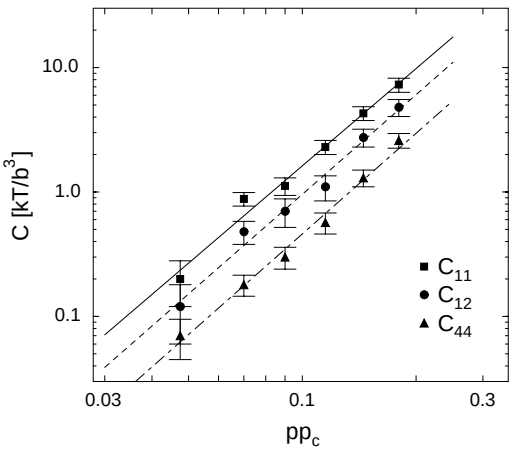

Fig. 5

Fig. 4 – Logarithmic plot of the stress σ and the shear modulus μ as a function of $(p - p_c)$, for 3D systems with $b = 1.05$. The slope of the solid line is 1.95. Results are in kT/b^3 units.

Fig. 5 – Logarithmic plot of the elastic constants C_{11}, C_{12}, and C_{44} as a function of $(p - p_c)$, for 3D systems with $b = 1.05$. The slope of different lines is ≈ 2.65. Results are in kT/b^3 units.

depicts our results for σ and μ as a function of $(p - p_c)$ for 2D systems with $b = 1.05$ and $b = 1.25$. It clearly demonstrates that close to p_c, the network becomes Gaussian: First, the difference between μ and σ decreases as we approach p_c, which implies that the elastic constant $C_{44} = \mu - \sigma$ vanishes faster than both quantities. Second, when plotted in kT/b^2 units, the values of σ and μ in systems with different b converge towards each other. This is explained by the facts that a) the stress of a 2D PGN depends only on the topology of the network and the value of the springs force constant K; and b) for the tethered networks, the *effective* K is proportional to kT/b^2 [8]. Third, the value of f extracted from the the graphs is $f = 1.35 \pm 0.10$, very close to the value of the conductivity exponent $t = 1.297 \pm 0.007$ in 2D [15]. A similar result for the exponent f has been obtained by Plischke *et al.* [16]. They used central force networks in which both entropy and energy contribute to the elastic properties and, by examining systems at several temperatures, removed the energetic component. Close to p_c the elasticity of central force systems is completely dominated by entropy, and their result for f reflects this fact.

In fig. 3 we present our results for the elastic constants C_{11} and C_{44}, which are supposed to vanish in the purely Gaussian case. Shorter tethers correspond to larger values of the elastic constants, since they represent more stretched networks, which exhibit stronger deviations from Gaussian behavior. Despite almost an order-of-magnitude difference between C_{11} and C_{44} for the same b, and half an order-of-magnitude difference between the same constants for the different values of b, all the results can be described by a power law $(p - p_c)^g$, with the same exponent $g = 2.0 \pm 0.2$, which is significantly larger than f. (We do not show the elastic constant C_{12}, which has large statistical uncertainties that prevent the exact determination of the power law. The results are, however, consistent with the power laws for the other constants.) To further ascertain the universality of g, one would need to increase b to even larger values. This, however, would further decrease the values of the elastic constants which

in our method of simulations [10] would increase the statistical uncertainties, and require increase of the simulation length beyond our computational ability.

Our results for the 3D networks with $b = 1.05$ are shown in figs. 4 and 5. Again, the validity of the PGN model is supported by the observation that σ and μ converge towards each other as we approach p_c, following power laws with $f = 1.95 \pm 0.05$, which agrees with the conductivity exponent $t = 2.003 \pm 0.047$ in 3D [17]. The elastic constants also follow power laws with an exponent $g = 2.65 \pm 0.15$. Note that our results confirm the relation $C_{11} = C_{12} + 2C_{44}$, which indicates that close to p_c, percolating networks behave as isotropic systems. At $p = 1$ the system has a lower (cubic) symmetry, and there is a gradual deviation from this relation with increasing p beyond the regime shown in fig. 5.

In ref. [9] we used PNGN model to derive bounds on the exponent g, which is a consequence of non-Gaussian behavior: $3t - 2\nu(d-1) \leq g \leq 4(t-1) - \nu(3d-4)$, where ν is the correlation length exponent. The perturbative derivation of the bounds was self-consistent only for $d \geq 3$. We note that our result for g in $d = 3$ is, within the statistical uncertainty, consistent with the bounds $2.48 \leq g \leq 2.60$. One should keep in mind, however, that the PNGN model assumes that the coefficient of the quartic perturbation term to the Gaussian spring energy is a constant number, while for the tethered network model its effective value may depend on the mean stress and, thus, on the position of the bond in the network.

In conclusion, we studied the critical elastic behavior of purely entropic phantom model with topology of a percolating network. The microscopic tethering potential is very different from a Gaussian spring. Nevertheless, diluted networks become very "floppy" so that the potentials become effectively Gaussian and, consequently, the shear modulus behaves as the conductivity of RRN. The non-trivial power law dependence of the elastic constants of the spanning cluster on $(p - p_c)$ is a signature of a deviation from the Gaussian behavior, and is controlled by a critical exponent significantly larger than the exponent of conductivity. Since g characterizes a "sub-leading" behavior, a detailed study of a broad class of potentials is needed to verify its universality.

* * *

We greatly appreciate the support of E. Bielopolski and Ch. Sofer from the Tel Aviv University Computation Center, and of G. Koren from the High Performance Computing Unit at the Inter University Computation Center. This work was supported by the Israel Science Foundation through Grant No. 177/99.

REFERENCES

[1] Stauffer D. and Aharony A., *Introduction to Percolation Theory* (Taylor and Francis, London) 1992.

[2] Adam M. and Lairez D., *Physical Properties of Polymeric Gels*, edited by J. P. Cohen Addad (J. Wiley and Sons, Chichester) 1996, p. 87 and references therein.

[3] de Gennes P. G., *J. Phys. (Paris) Lett.*, **37** (1976) L1.

[4] See, *e.g.*, Daoud M. and Coniglio A., *J. Phys. A*, **14** (1981) L301; Castillo H. M. and Goldbart P. M., *Phys. Rev, E*, **58** (1998) R24.

[5] A partial list of experimental works from the last decade: Carciun F., Galassy C. and Roncari E., *Europhys. Lett.*, **41** (1998) 55; Adam M., Lairez D., Karpasas K. and Gottlieb M., *Macromol.*, **30** (1997) 5920; Colby R. H., Gillmor J. R. and Rubinstein M., *Phys. Rev. E*, **48** (1993) 3712; Devreux F., Boilot J. P., Chaput F., Mailier M. and Axelox M. A. V., *Phys. Rev. E*, **47** (1993) 2689; Axelox M. A. V. and Kolb M., *Phys. Rev. Lett.*, **64** (1990) 1457. See also ref. [2].

[6] de Gennes P. G., *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca) 1979.
[7] Kantor Y., Kardar M. and Nelson D. R., *Phys. Rev. A*, **35** (1987) 3056.
[8] See, *e.g.*, Farago O. and Kantor Y., *Eur. Phys. J. E*, **3** (2000) 253
[9] Farago O. and Kantor Y., cond-mat/0006004, to be published in *Phys. Rev. E.*
[10] Farago O. and Kantor Y., *Phys. Rev. E*, **61** (2000) 2478.
[11] Cates M. E., *Phys. Rev. Lett.*, **53** (1984) 926.
[12] Herrmann H. J., Hong D. C. and Stanley H. E., *J. Phys. A*, **17** (1984) L261.
[13] Jaster A., *Physica A*, **264** (1999) 134.
[14] This expression is a generalization of eq. (4.7) in ref. [7].
[15] Grassberger P., *Physica A*, **262** (1999) 251.
[16] Plischke M. and Joós B., *Phys. Rev. Lett.*, **80** (1998) 4907; Plischke M., Vernon D. C., Joós B. and Zhou Z., *Phys. Rev. E*, **60** (1999) 3129.
[17] Gingold D. B. and Lobb C. J., *Phys. Rev. B*, **42** (1990) 8220.