Field Theory for the Statistics of Branched Polymers, Gelation, and Vulcanization

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This paper presents a field theory for the statistics of branched polymers and for the gelation transition. The gelation transition with $\Lambda_p\Lambda_L = m$, where Λ_p and Λ_L are the fugacities for polymer number and loop number, is shown to be in the same universality class as the m-state Potts model. A new fixed point governing the statistics of branched polymers in the dilute limit ($\Lambda_p = 0$) in $6-\epsilon$ dimensions with $\nu = \frac{1}{2} + 0.092\epsilon$ and $\eta = -0.073\epsilon$ is located. An old result of Zimm and Stockmayer for the radius of gyration of a Gaussion branched polymer is rederived.

The statistics of polymers in dilute and semidilute solutions is well described by the $n = 0$ limit of the n-vector model in an external field.[1-3] In addition, the statistics of percolating clusters on a lattice[4] with bonds (sites) occupied with probability p and vacant with probability $1-p$ is described by the one-state Potts model[4,5]; and the statistics of treelike percolation is described by the zero-state Potts model.[6] When bifunctional and polyfunctional units are allowed to interact in a polymeric solution, nonlinear polymers are produced.[7] If the reaction is allowed to proceed far enough, an infinite molecule is formed. This is the process of gelation. Alternatively, polyfunctional cross-linking units can be added to semidilute or concentrated solutions of linear polymers. An infinite molecule forms at a critical concentration of cross-linking units. This is the process of vulcanization. Both gelation and vulcanization are percolation processes.[8] The purpose of this note is to introduce a unified model Hamiltonian which can describe the statistics of linear and nonlinear polymers in dilute and semidilute solutions and in the vicinity of the gelation threshold. This model clarifies the relationship between gelation and vulcanization, and percolation.

The Hamiltonian we use is an extension of the n-vector model, partially motivated by previous work[9] on a generalized Hilhorst model.[10] It is defined via

$$\mathcal{H} = \int d^dx \{ \tfrac{1}{2} r\psi^2 + \tfrac{1}{2}(\nabla\psi)^2 + u(\psi^2)^2 - \sum_{f,j} \frac{1}{f!} w_f \psi_{1j}{}^f - H \sum_j \psi_{1j} \}, \tag{1}$$

where $\psi^2 = \sum_{ij}\psi_{ij}{}^2$ where $i = 1, \ldots, n$ and $j = 1, \ldots, m$. In the $n \to 0$ limit, there is a one-to-one correspondence between graphs in a diagrammatic perturbation theory and polymeric configurations. Each f-functional unit is marked by a factor w_f, and each endpoint by a factor H. A typical term in a Taylor expansion for Z containing N_f f-functional units, N_v endpoints, and N_p polymers will be proportional to $(\prod_f w_f{}^{N_f}) H^{N_v} m^{N_p}$. Alternatively, with the use of the fundamental relation $N_v = 2N_p + \sum_f (f-2)N_f - 2N_L$, where N_L is the number of loops, this factor can be re-expressed as $\Lambda_p{}^{N_p}\Lambda_f{}^{N_f}\Lambda_L{}^{N_L}$, where

$$\Lambda_p = mH^2, \quad \Lambda_f = w_f H^{f-2}, \quad \Lambda_L = H^{-2}. \tag{2}$$

Thus, the concentrations of monomers (bifunctional units), polymers, endpoints, f-functional units, and loops, c, c_p, c_v, c_f, and c_L, can be obtained from the free-energy density $F = -\Omega^{-1}\ln Z$, where Ω is the volume, via

$$c = \frac{\partial F}{\partial r}, \quad c_p = -\Lambda_p \frac{\partial F}{\partial \Lambda_p}, \quad c_v = -H\frac{\partial F}{\partial H}, \quad c_f = -\Lambda_f \frac{\partial F}{\partial \Lambda_f}, \quad c_L = -\Lambda_L \frac{\partial F}{\partial \Lambda_L}. \tag{3}$$

Since H couples to $\sum_j \psi_{ij}$, it is useful to introduce a complete set of orthonormal vectors $e_j{}^l$ with $e_j{}^0 = m^{-1/2}(1, 1, \ldots, 1)$. $\{e_j{}^l\}$ for $l = 1, \ldots, m-1$ is, apart from a scale factor, the set of vectors used by Zia and Wallace[11] to study the m-state Potts model. Thus, we can write

$$\psi_{ij} = \sum_{l=0}^{m} e_j{}^l \psi_i{}^l.$$

Note that $\sum_j e_j{}^l = 0$ for $l = 1, \ldots, m-1$. We now shift ψ_{ij} to produce a Hamiltonian with no linear term

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by writing

$$\psi_{ij} = \sqrt{m}\, Q \delta_{i1} e_j^{\,0} + \varphi_{ij}, \tag{4}$$

where $\langle \varphi_{ij} \rangle = 0$. The Hamiltonian density $\mathfrak{F}$ can be expressed as $\sum_k \mathfrak{F}_k$ where k specifies the power of φ_{ij}. We have

$$\mathfrak{F}_0 = \tfrac{1}{2} m r Q^2 - \sum_f \frac{1}{f!} m w_f Q^f + u m^2 Q^4 - mHQ, \tag{5a}$$

$$\mathfrak{F}_1 = \left(rQ - \sum_f \frac{1}{(f-1)!} w_f Q^{f-1} + 4umQ^3 - H \right) m^{1/2} \varphi_1^{\,0} \tag{5b}$$

$$\mathfrak{F}_2 = \tfrac{1}{2}(r + 4umQ^2)\varphi^2 + \tfrac{1}{2}(\nabla\varphi)^2 - \tfrac{1}{2}\left(\sum_f \frac{w_f}{(f-2)!} Q^{f-2} \right) \sum_j \varphi_{1j}^{\,2} + 4umQ^2(\varphi_1^{\,0})^2, \tag{5c}$$

$$\mathfrak{F}_3 = -\frac{1}{3!} \overline{w}_3^{\,0} \sum_{l_i=0}^{m} \lambda_{l_1 l_2 l_3}^{(3)} \varphi_1^{\,l_1} \varphi_1^{\,l_2} \varphi_1^{\,l_3} + m^{1/2} u_3^{\,0} \varphi_1^{\,0} \sum_l (\varphi_1^{\,l})^2, \tag{5d}$$

$$\mathfrak{F}_4 = u(\varphi^2)^2 - \frac{1}{4!} \overline{w}_4^{\,0} \sum_{l_i=0}^{m} \lambda_{l_1 l_2 l_3 l_4}^{(4)} \varphi_1^{\,l_1} \varphi_1^{\,l_2} \varphi^{l_3} \varphi_1^{\,l_4}, \tag{5e}$$

where

$$\overline{w}_3^{\,0} = \sum_{f \geq 3} w_f Q^{f-3}, \quad \overline{u}_3^{\,0} = 4uQ, \quad \overline{w}_4^{\,0} = \sum_{f \geq 4} w_f Q^{f-4}, \quad \lambda_{l \ldots l_p}^{\,p} = \sum_{j=1}^{m} e_j^{\,l_1} \ldots e_j^{\,l_p},$$

and where we have not written down terms for $k > 4$. The propagator for the field $\varphi_{1j}(\vec{x})$ can be decomposed into a part parallel to $e_j^{\,0}$ and a part perpendicular to $e_j^{\,0}$:

$$G_{1j,1j'}(\vec{x}, \vec{x}') = G_{\parallel}(\vec{x}, \vec{x}') e_j^{\,0} e_{j'}^{\,0} + G_{\perp}(\vec{x}, \vec{x}')(\delta_{jj'} - e_j^{\,0} e_{j'}^{\,0}). \tag{6}$$

Using the fact that $\lambda_{0,0,\ldots,l_p}^{(p)} = 0$ for $l_p \neq 0$, one can easily verify that $G_{\perp}(\vec{x}, \vec{x}')$ measures correlations between endpoints on a single polymer, whereas $G_{\parallel}(\vec{x}, \vec{x}')$ measures correlations between endpoints on any polymers. Q is nonzero as long as H is nonzero. It can be expressed as

$$Q = H\chi \equiv \Lambda_L^{-1/2} \chi, \tag{7}$$

where χ has well-defined large- and small-H limits. It therefore follows that

$$mQ^2 = mH^2\chi^2 = \Lambda_p \chi^2, \quad u_3^{\,0} = 4uQ = 4u\Lambda_L^{-1/2}\chi,$$

and

$$\overline{w}_3^{\,0} = \sum_f w_f H^{f-3} = \Lambda_L^{1/2} \left(\sum_f \Lambda_f \chi^{f-3} \right).$$

With this information, we consider some special cases of interest.

(1) $u = 0$, $\Lambda_L = 0$, $\Lambda_f = 0$ *for* $f > 3$.—This is the case of a Gaussian branched polymer with no closed loops considered by Zimm and Stockmayer[12] and by de Gennes.[13] In this case, $\mathfrak{F}_k \equiv 0$ for $k \geqslant 3$, and the problem can be solved exactly. From Eqs. (6b) and (6c), we have

$$r\chi - \tfrac{1}{2}\Lambda_3 \chi^2 - 1 = 0 \tag{8a}$$

$$G_{\parallel}^{-1} = G_{\perp}^{-1} = G^{-1} = r - \Lambda_3 \chi + q^2. \tag{8b}$$

Defining $G_N(q)$ to be the Laplace transform of G, $\int_{-i\infty}^{i\infty} e^{Nr} G(r, q)\, dr$, we can calculate the average separation ξ between endpoints of a branched polymer containing N monomer units. We find

$$\xi^2 = -G_N^{-1}(dG_N/dq^2)|_{q=0} \sim N^{1/2} \Lambda_3^{-1/4}. \tag{9}$$

The average number of trifunctional units $\langle N \rangle = (\Lambda_3 / Z_N)(dZ_N / d\Lambda_3)$, where $Z_N = \int_{-i\infty}^{i\infty} e^{Nr} Z(r)\, dr$, is proportional to $\Lambda_3^{1/2} N$, yielding $\xi^2 \sim N \langle N_3 \rangle^{-1/2}$. This has the same dependence on N and $\langle N_3 \rangle$ as the radius of gyration (rather than the average endpoint separation) calculated by Zimm and Stockmayer[12] and by de Gennes[13] using χ rather than Z to determine $\langle N_3 \rangle$ via $\langle N_3 \rangle = (\Lambda_3 / \chi_N)(d\chi_N / d\Lambda_3)$, where $\chi_N = \int_{-i\infty}^{i\infty} e^{Nr} \chi(r)\, dr$.

(2) $u \neq 0$ *and* $\Lambda_p \neq 0$.—In this case, there is a splitting between $\varphi_1^{\,0}$ and $\varphi_1^{\,l}$, $l = 1, \ldots, m-1$, with $\varphi_1^{\,l}$ becoming critical first. (φ_{ij} for $i > 1$ is also noncritical as long as any $\Lambda_f > 0$.) Thus to study the critical properties of this case, a new effective Hamiltonian for $\varphi_1^{\,l}$ can be obtained by tracing over $\varphi_1^{\,0}$ and φ_{ij}, $i > 1$. The resulting Hamiltonian has exactly the same symmetry as the m-state Potts model.[4,5,11] *Thus gelation with* $\Lambda_p \Lambda_l = m$ *is in the same universality class as the* m*-state Potts model, and critical exponents for gelation will vary continuously with* $\Lambda_p \Lambda_L$. If $\Lambda_L = 0$, there are no closed loops and the gelation process is described by the zero-state Potts

model. We will argue later that in most cases of experimental interest, $\Lambda_p\Lambda_L = 1$ implying that gelation is in the same universality class as percolation in agreement with previous predictions.[8]

(3) $u \neq 0$; $\Lambda_p = 0$.—This corresponds to the dilute limit of branched polymers (with or without loops). From Eq. (5c), it is easy to see that $\varphi_1{}^0$ and $\varphi_1{}^l$ are simultaneously critical in this case, whereas φ_{ij} for $i \geqslant 2$ is not. The critical properties of this limit are described by a new fixed point in $6-\epsilon$ dimensions. Recursion relations immediately generate a new term in $\mathfrak{F}_3$, $(m^{3/2}/3!)v_3(\varphi_1{}^0)^3$, that scales as $\Lambda_L{}^{-3/2}$. Since we will want the freedom to allow $\Lambda_L \to 0$, we develop differential[14] renormalization-group[15] recursion relations in $6-\epsilon$ dimensions[16] for $x = K_6(\overline{w}_3)^2$, $y = K_6\overline{w}_3 u_3$, and $z = K_6(\overline{w}_3{}^3 v_3)^{1/2}$, where $(2\pi)^6 K_6 = \Omega_6$, the solid angle subtended by a sphere in six dimensions. We obtain

$$dx/dl = \epsilon x + \tfrac{3}{2}x^2 - 20xy, \tag{10a}$$

$$dy/dl = \epsilon y + \tfrac{3}{2}xy - 22y^2 + \tfrac{1}{2}z^2, \tag{10b}$$

$$dz/dl = \epsilon z + xz - 26yz + 56y^3/z - 6xy^2/z, \tag{10c}$$

$$\eta = \tfrac{1}{6}x - \tfrac{4}{3}y;\; \nu^{-1} = 2 + \tfrac{5}{6}x - \tfrac{20}{3}y, \tag{10d}$$

with initial values $x_0 = K_6\Lambda_3{}^2\Lambda_6$, $y_0 = 4K_6 u\Lambda_3\chi$, $z_0 = 0$. This set of equations has one stable fixed point with $x=0$, $y = 0.055\epsilon$, and $z = 0.148\epsilon$ with exponents $\eta = -0.073\epsilon$ and $\nu = \frac{1}{2} + 0.092\epsilon$. The stability exponents[17] for this fixed point are $\lambda_x = -0.090\epsilon$, $\lambda_1 = -\epsilon$, and $\lambda_2 = -1.2336\epsilon$. There are two other unstable fixed points with positive u. Note that the critical properties of branched polymers with and without loops in the dilute limit are in the same universality class in $6-\epsilon$ dimensions.

The natural variables for the model presented here are the fugacities for a number of polymers, Λ_p, number of f-functional units, Λ_f, etc. The most natural experimental variables are the densities $c, c_p, \ldots$. In polydisperse systems with not too much dispersion, the relations in Eq. (4) can be used to convert from fugacities to densities. This is easily done in the mean-field limit by performing a Legendre transform to $\Gamma(Q) = F + mHQ$ and using $\mathfrak{F}_0$ for F. Then

$$c_f = -w_f\frac{\partial\Gamma}{\partial w_f},\quad c = \frac{\partial\Gamma}{\partial r},\quad c_v = Q\frac{\partial\Gamma}{\partial Q},$$

$$c_p = -m\frac{\partial\Gamma}{\partial m} + mHQ. \tag{11}$$

In the mean-field limit, $c_v = 2c_p + \sum_f(f-2)c_f$ so that $c_L = 0$. Using Eqs. (11) and (5c), we obtain

$$G_\perp{}^{-1} = c^{-1}[c_p - \tfrac{1}{2}\textstyle\sum_f(f-1)(f-2)c_f] + q^2. \tag{12}$$

When $c_f = 0$, this agrees with previous results[2,18] for polydisperse linear polymers. Gelation occurs when $c_p = \frac{1}{2}\sum_f(f-1)(f-2)c_f$. This is to be compared with the Flory result[19] relating the fraction of reacted endgroups $p = 1 - [2c_p + (f-2)c_f][2c + fc_f]^{-1}$ to the fraction of endgroups on f-functional units $\rho = fc_f[2c + fc_f]$ at gelation via $p\rho[1 - p(1-\rho)]^{-1} = (f-1)^{-1}$. It is easy to verify that Eq. (12) with only one value for f is equivalent to Flory's result as long as $c \gg c_p - c_f$. One would expect both theories to give the same critical surface for gelation since they are both loopless theories. Since $c = \partial\Gamma/\partial r$ is expected to be valid for $c \gg c_p - c_f$, it is not surprising that the two theories agree only in this limit. Equation (12) provides an explicit verification that the correlation length near the vulcanization threshold is given by $\xi^2 = N(\Delta\rho/\rho_c)^{-1}$, where $N = 2c/c_v$, the average number of monomers per primary polymer, and $\rho_c = \frac{1}{2}c_v/c = N^{-1}$. This relation was used by de Gennes[20] to show that the critical region for the vulcanization transition is small when N is large.

We now return to the question of what value m has in an actual gelation transition. In such a transition, one begins with a concentration c of bifunctional units which we denote by A-A and a concentration c_f of f-functional units denoted by R-A_f, leading to a concentration $N_v{}^0/\Omega = c_v{}^0 = 2c + fc_f$ of functional endgroups A. Chemical reactions between the functional groups are allowed to proceed. Each reaction reduces the number of endpoints (unreacted functional groups) by 2. Thus after R reactions, $N_v = \Omega c_v = \Omega c_v{}^0 - 2R$. If one assumes equal reactivity of all functional groups, then there is no restriction on the number of loops or polymers produced. Using the above and Eq. (2), one can replace $\Lambda_p{}^{N_p}\Lambda_f{}^{N_f}\Lambda_L{}^{N_L}$ by $\Lambda_p{}^{-R}(\Lambda_f\Lambda_p)^{N_f}(\Lambda_p\Lambda_L)^{N_L}$ in the partition sum. Since the number of loops in the reaction is not restricted, the sum should give all values of N_L equal weight in the sum. This is accomplished by setting $\Lambda_p\Lambda_L = m = 1$. Thus the gelation process is in the same universality class as percolation. In the vulcanization process, N_v is fixed and four-functional units are added. Here there is no restriction other than $2N_p \leqslant N_v - 2N_4$ on N_p. Thus m must be unity in the product $w_4{}^{N_4}H^{N_v}m^{N_p}$ in order to weight all values of N_p equally. By choosing trifunctional units of the form A-R-B_2 and bifunctional units A-B and allowing interactions to occur only between A and B but not between A and A or B and B, it is possible to restrict the number of loops to a maximum of one per polymer ($N_L \leq N_p$). Thus, it is possible to approach gelation described essentially by a zero-state Potts model. If a number N_3' of trifunctional groups A_2-R-B are added to a solution of A-R-B_2 and A-B's, it is possible to increase the maximum number of allowed loops to $N_p + N_3'$. It may, therefore, be possible to create a distribution of molecules with well defined $\Lambda_p \Lambda_m$ between zero and one by allowing reactions to proceed to a certain point, diluting the system to inhibit intermolecular interactions, allowing the reaction to continue to another point, and then removing some solvent to recreate a more concentrated solution.

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Sea-Level Muon Charge Ratio of Cosmic Rays at High Energies

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The charge ratio of cosmic-ray muons with energies up to 1 TeV in the zenith-angle range 68°–82° has been measured. The data clearly show an enhancement of the charge ratio with increasing energy thus indicating a "normal" mass composition of galactic cosmic rays.

The charge ratio of cosmic-ray muons at sea level provides the only information on the mass composition of the primary cosmic-ray flux, in particular on the ratio of neutrons (bound in nuclei) to all nucleons,[1] in the energy range beyond 10^{11} eV. The mass composition is an essential tool to decide between different models for galactic confinement of cosmic rays.[2]

Measurements have been performed in a magnetic spectrometer of Carstensen *et al.*[3] and Carstensen.[4] The mean maximum momentum $\bar{p}_{\max}$ defined by $p\psi = \bar{p}_{\max}\sigma_\psi$ (with ψ the angular deflection, σ_ψ the angular resolution, and p the momentum)[5] amounts to 750 GeV/c. The original charge ratio R_μ at muon productions is modified for low- and high-energy muons: Because the viewing direction is towards east [75 ± 7° zenith angle and 288 ± 20° azimuth angle], low-energy positive muons run a longer path in the atmosphere than the negative muons by geomagnetic

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