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Statistical Mechanics of Charged Manifolds.

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Abstract. – We study the behavior of D-dimensional manifolds, embedded in d-dimensional space, in which the repulsive interaction between charges decays as $1/r^{d-\alpha}$. Tethered manifolds can be «crumpled», or «flat». In the crumpled regime the exponent ν is calculated exactly, and γ is obtained to $O(\varepsilon)$. In the flat regimes we discuss the coupling of phonons and undulations, and the scaling of transverse fluctuations. For liquid manifolds with screening we obtain the dependence of the effective bending energy, and the resulting persistence length, on the screening length.

There is currently great interest in understanding the behavior of surfaces, interfaces, and membranes [1]. In view of recent experiments on charged bilayer films [2], it is natural to inquire about the effects of long-range (*e.g.*, Coulomb) interactions. One may generalize the theory of polyelectrolytes [3], by considering charged D-dimensional ($D = 1$ for polymers, $D = 2$ for surfaces, etc.) tethered surfaces [4, 5] in which the constituent particles are permanently bonded to form a fixed network, moving in an external d-dimensional space. We find that at high dimensions the surfaces are crumpled and the radius of gyration R scales with the linear size L as $R \sim L^{\nu}$. As indicated in fig. 1 for $d > d_u$ interactions are irrelevant, while for $d_l < d < d_u$ the manifold becomes stretched and flat ($R \sim L$). In the flat regime we investigate the extent of transverse fluctuations, and find several qualitatively different behaviors.

Configurations of a tethered manifold are described by $\{\vec{r}(\boldsymbol{x})\}$ where $\boldsymbol{x}$ is a D-dimensional vector denoting the position of a monomer in *internal* space, while $\vec{r}(\boldsymbol{x})$ is the actual location of the particle in the *external* d-dimensional embedding space [5]. Subject to long-range repulsive interactions that fall off as $1/r^{d-\alpha}$, a continuum Hamiltonian for the manifold is

$$H = (K/2)\int \mathrm{d}^D\boldsymbol{x}\,(\nabla\vec{r})^2 + (\sigma^2/2)\int \mathrm{d}^D\boldsymbol{x}\,\mathrm{d}^D\boldsymbol{x}'\,|\vec{r}(\boldsymbol{x}) - \vec{r}(\boldsymbol{x}')|^{\alpha-d}, \tag{1}$$

with $(\nabla\vec{r})^2 = \sum_{i=1}^{D}(\partial\vec{r}/\partial x_i)^2$. The first term is an entropic elasticity with a force constant K

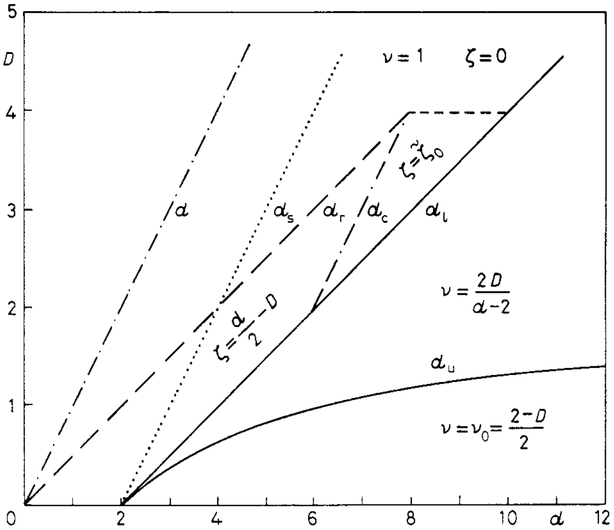

Fig. 1. – Behaviors of charged ($\alpha = 2$) D-dimensional manifolds embedded in d-dimensions. The different regimes are described in the text.

(proportional to $k_B T$) representing the gain in entropy of the manifold upon crumpling [4]. The long-range interactions of the second term describe Coulomb potentials for $\alpha = 2$ due to a density σ of immobile charges on the manifold. Implicit in eq. (1) is a lower cut-off a, representing the minimum separation of monomers. A realistic description of the manifold should also include the excluded volume (self-avoiding, steric) interaction $v/2 \int \mathrm{d}^D \boldsymbol{x} \mathrm{d}^D \boldsymbol{x}' \, \delta^d (\vec{r}(\boldsymbol{x}) - \vec{r}(\boldsymbol{x}'))$. This term, however, will be irrelevant in the determination of scaling behavior in all the different regimes.

Under the change of variabiles $\boldsymbol{x} \to \lambda \boldsymbol{x}$ and $\vec{r} \to \lambda^{\nu} \vec{r}$, the elastic and repulsive terms scale as $K \to \lambda^{y_K} K$ and $\sigma^2 \to \lambda^{y_{\sigma^2}} \sigma^2$, with $y_K = D - 2 + 2\nu$ and $y_{\sigma^2} = 2D - (d - \alpha)\nu$. In the free «Gaussian» theory the elastic term is scale invariant and $\nu = \nu_0 = (2 - D)/2$. Such behavior is valid if $y^0_{\sigma^2} < 0$ (when the repulsive term is irrelevant), *i.e.* for $d > d_u \equiv \alpha + 4D/(2 - D)$. (Note that d_u is simply shifted by α compared to the self-avoiding case [5].) For $d < d_u$ the interaction term is relevant and a renormalization-group (RG) analysis has to be performed. The procedure is similar to the corresponding polymer calculation [3] and easily generalized to D-dimensional manifolds [5]. A perturbative calculation in $g \sim \sigma^2 K^{(d-\alpha)/2}$ is divergent in $d < d_u$, and is reorganized into an RG by first integrating over separations $a < |\boldsymbol{x} - \boldsymbol{y}| < a(1 + \delta)$, followed by a rescaling by $\lambda = (1 + \delta)$ as above. For the elastic energy we find $K \to K\lambda^{y_K - Bg}$, where the constant B can be obtained by manipulations similar to the self-avoiding case [5]. Perturbatively there is no correction to the long-range interaction, but rather a short-range (self-avoiding) term ($v \sim g^2$) is generated [3]. This is quite a general feature of RG with long-range interactions, and in fact to *all orders* in perturbation theory $\sigma^2 \to \sigma^2 \lambda^{y_{\sigma^2}}$. A fixed point is obtained for $y_{\sigma^2} = 0$, leading to the *exact exponent* $\nu = 2D/(d - \alpha)$. This is valid so long as the newly generated self-avoiding interactions are irrelevant, and holds for $\alpha > 0$. For $\alpha < 0$, the self-avoiding term dominates and long-range interactions are irrelevant. Note that at the fixed point the elastic coefficient K, and the self-avoiding interaction v, are kept constant by the proper choice of g^* and v^*. These fixed-point values can be calculated perturbatively in an $\varepsilon = (d_u - d)(2 - D)$ expansion. We can also define in analogy to polymers an exponent γ for the anomalous scaling of the manifold partition function [5], *i.e.* $Z \sim L^{\gamma-1}$, where L is the linear dimension. This exponent in the lowest order is given by $\gamma(\alpha) = 1 + [d^* A(D^*)/D^*(d^* - \alpha)]\,\varepsilon$, where (d^*, D^*) is the expansion point on the upper critical line ($d = d_{\mathrm{u}}$ in fig. 1). The constant $A(D^*)$ is the coefficient of a logarithmic divergence in $I_D = \int \mathrm{d}^D\boldsymbol{x}\,\mathrm{d}^D\boldsymbol{x}'\, 1/|\boldsymbol{x} - \boldsymbol{x}'|^{2D}$ and is independent of d and α! This constant has been discussed in detail elsewhere [5] and in general depends on the shape of the manifold [5, 6]. For the case of linear polymers $A(1) = 1/4$ and $\gamma(\alpha)$ generalizes previous results for polymers [3] to arbitrary α.

At a lower critical dimension $d_{\mathrm{l}} \equiv 2D + \alpha$, the exponent ν equals one. Below this dimension the manifold ceases to be crumpled and becomes asymptotically flat and stretched. (To the lowest order in $\vec{r}$ and its derivatives, the continuum Hamiltonian will still have the form in eq. (1). However, the value of the constant K may now be related to the specific form of the bond potential.) The typical size of the manifold in this regime can be estimated by setting $\vec{r}(\boldsymbol{x}) = m x_\alpha \vec{e}_\alpha$ ($\{\vec{e}_\alpha\}$ are D orthonormal «in plane» vectors indicating the directions in d space for stretching of the manifold) in eq. (1). Minimizing the energy with respect to m yields $m = m_0 \equiv \{[(d-\alpha)\,\sigma^2/(2DK)\int \mathrm{d}^D\boldsymbol{x}\,|\boldsymbol{x}|^{\alpha-d}\}^{1/(d+\alpha+2)}$, where the integral involves lower and upper cut-offs of a and L, respectively. For $d > d_{\mathrm{s}} \equiv D + \alpha$ the integral is dominated by short distances and m is finite. We denote this interval «elastically flat», as the manifold size is set by the competition between harmonic elastic and long-range repulsive forces. For $d \leqslant d_{\mathrm{s}}$ the integral diverges at large L indicating a total repulsive energy increasing faster than the volume of the manifold; m_0 will increase with L indicating that the repulsion term will tear apart any surface with «soft» intermonomeric potentials. The manifold will maintain its integrity only if the monomer bonding potential has a rigid «stretchability limit». This interval is denoted «rigidly flat». For linear $(D = 1)$ polyelectrolytes $(\alpha = 2)$ $d_{\mathrm{s}} = 3$; and closer examination indicates that in the borderline dimensionality of $d = 3$, the polyelectrolyte is actually «rigidly flat».

The flat phases are characterized by broken rotational symmetry (due to the choice of $\{\vec{e}_\alpha\}$). This leads to a complicated coupling of undulations (out-of-plane fluctuations) and phonons [7] (in-plane fluctuations). To examine these modes in the «elastic flat» regime we set [8] $\vec{r}(\boldsymbol{x}) = m_0[((x_\alpha + u_\alpha(\boldsymbol{x}))\,\vec{e}_\alpha + h_i(\boldsymbol{x})\,\vec{f}_i]$. Undulations h_i are along the $(d - D)$ orthonormal vectors $\{\vec{f}_i\}$ which are orthogonal to the D vectors $\vec{e}_\alpha$. Substituting this $\vec{r}(\boldsymbol{x})$ in (1), we obtain after some manipulations $H = \bar{H} + H_0 + H_i$, where $\bar{H}$ is the electrostatic energy of the uniformly flat phase. For small fluctuations the normal modes $\vec{u}(\boldsymbol{q})$ and $\vec{h}(\boldsymbol{q})$ have energy costs $H_0 = \int \mathrm{d}^D q \cdot \varkappa(q) \cdot q^4(|h(\boldsymbol{q})|^2 + |u(\boldsymbol{q})|^2)/[2(2\pi)^D]$, with $\varkappa(q) = [(d-\alpha)\,\sigma^2/(2m_0^{d-\alpha})] \cdot \cdot \int \mathrm{d}^D\rho(2\cos(\boldsymbol{q}\cdot\rho) - 2 - q^2\rho^2/D)/(q^4\rho^{d-\alpha+2})$. Note that $q^2\varkappa(q) \to 0$ as $q \to 0$, which is a consequence of the rotational symmetry of the initial Hamiltonian. The coupling between phonons and undulations come from an interaction term

$$H_i = [(d-\alpha)(d-\alpha+2)\,\sigma^2/4m^{d-\alpha}] \int \mathrm{d}^D\boldsymbol{x}\,\mathrm{d}^D\boldsymbol{x}'/|\boldsymbol{x} - \boldsymbol{x}'|^{d-\alpha+4} \cdot \\ \cdot \{(x - x') \cdot [\vec{u}(x) - \vec{u}(x)'] + [\vec{h}(x) - \vec{h}(x')]^2/2\}^2 .$$

The joint sum of (δu) and $(\delta h)^2$ terms in the above expression is similar to the appearance of the modified strain [7, 8] $\tilde{u}_{\alpha\beta} = [\partial_\alpha \vec{u}_\beta + \partial_\beta u_\alpha + \partial_\alpha \vec{h}_\alpha \partial_\beta \vec{h}]/2$ in short-range models, and is another consequence of rotational symmetry. In fact, although not explicitly included in eq. (1), a strain energy $H_i' = \Sigma\, \mathrm{d}^D\boldsymbol{x}\,[\tilde{\mu}\,(\tilde{u}_{\alpha\beta})^2 + \tilde{\lambda}/2\,(\tilde{u}_{\alpha\alpha})^2]$, is consistent with symmetries and will be present [7-9].

We would like to calculate the exponent ζ controlling transverse fluctuations via $\langle|\delta h|\rangle \sim L^\zeta$. Under a rescaling $\boldsymbol{x} \to \lambda\boldsymbol{x}$, and $h \to \lambda^\zeta h$ ($u \to \lambda^{2\zeta-1}u$, due to rotational symmetry) the interaction terms in H_i and H_i' scale as $H \to \lambda^y H$ with $y_i = 2D - d + \alpha - 4 + 4\zeta$ and $y_i' = D - 4 + 4\zeta$, respectively. Since $y_i' = y_i + d - D - \alpha$, the short-range interactions always dominate in the elastic flat regime. The scale of long-wavelength fluctuations is set by the $q \to 0$ limit of $\varkappa(q)$. For $d > d_c = D + \alpha + 2$ (dot-dashed line in fig. 1), $\cos(\boldsymbol{q} \cdot \varrho)$ can be expanded in powers of q leading to a constant $\varkappa(q)$ which is characteristic of bending energies in short-range models. This term is made scale invariant by the choice of $\zeta = \zeta_0 = (4 - D)/2$. However, at such a fixed point the interaction term becomes relevant for $D - 4$ ($y_l' > 0$) and has to be treated by a perturbative RG [9]. Indeed in the regime $d > d_c$ and $D < 4$ the exponent ζ equals $\tilde{\zeta}_0$ calculated for short-range models [9], while for $D > 4$ $\zeta = 0$.

For $d < d_c$ (however, still in the «elastic flat» regime) we can no longer expand $\cos(\boldsymbol{q} \cdot \varrho)$ analytically in powers of q in $\varkappa(q)$, and indeed as $q \to 0$, $\varkappa(q) \sim q^{d-\alpha-D-2}$. Such a «bending constant» leads to transverse fluctuations scaling with an exponent

$$\zeta = 1 - D + (d - \alpha)/2 . \tag{2}$$

However, again at such a fixed point H_l' grows with an exponent $y_l' = 2(d - \alpha) > 0$, and an RG analysis [9] is necessary. We speculate that H_l' does not generate corrections to the nonanalytic bending constant. This would be similar to nonrenormalization of the interaction term in the crumpled regime which lead to the exact expression for ν. We similarly conjecture that eq. (2) gives the exact value of the exponent ζ, but this statement should be checked by more explicit RG analysis. Note that $\zeta = 0$ for $d < d_r \equiv 2D + \alpha - 2$ (dashed line in fig. 1) which connects to the line $d = d_c$ at $D = 4$ (see fig. 1).

In the «rigid flat» regime ($d < d_s$), we can no longer use eq. (1) as a basis for calculations. The bonds are stretched by the long-range forces to their limit and the surface becomes incompressible and isometric. We attempt to evaluate fluctuations by estimating the energy to deflect a manifold of linear size L by a height h along a particular direction. This energy is easily seen to scale as $\sigma^2 h^2 L^{2D-d+\alpha-2}$, which equated to a thermal energy of $k_B T$ gives $h \sim L^{\zeta}$ with ζ as in eq. (2). Note, however, that interference from fluctuations in other directions may indeed increase this bending energy and reduce the exponent ζ. A similar reasoning would indeed fail with short-range forces only, but we have currently no better argument to offer than possible «freezing» of phonon modes for «rigid flat» manifolds. If eq. (2) is correct, then the exponent ζ is continuous at $d = d_s$. Polyelectrolytes and charged surfaces for $d = 3$ both fall in this regime. For surfaces $\zeta = 0$ (superflat), while for polymers $\zeta = 1/2$, *i.e.* as if the polyelectrolyte performs a random walk in the transverse direction.

The discussion so far omits the important effects of screening by counter charges. Treating these charges consistently, even for polymers, is quite cumbersome, and may for example lead to a nonuniform charge density $\sigma(\boldsymbol{x})$. Instead we shall briefly discuss a model potential with a screening length λ, *i.e.* a two-body potential $V(r) \sim \sigma^2 \exp[-\pi/\lambda]/r^{d-\sigma}$. Within this model our previous results are valid only if $\lambda \gg R$. Otherwise, on length scales larger than λ there is an effective «self-avoiding» interaction and a crossover to short-range behavior. However, on length scales less than λ the exponential cut-off can be ignored, and bending a unit of size l by h costs an energy $\sigma^2 h^2 l^{2D-d+\alpha-2}$ as before. Since typical bending energy ($\varkappa \int d^D \boldsymbol{x} (\nabla^2 h)^2$) scales as $\varkappa h^2 l^{D-4}$, there is a scale-dependent bending constant $\varkappa(l) \sim \sigma^2 l^{D+\alpha+2-d}$. Therefore, upon coarse-graning to the screening length there is an effective bending rigidity of $\varkappa_e = \sigma^2 \lambda^{D+\alpha+2-d}$. If the internal dimension D of a tethered manifold is sufficiently large it can still support a flat phase [8, 10], even in the absence of interactions, for $\varkappa_e$ greater than some critical $\varkappa_c$. It should therefore be possible to induce such a transition in $D = 2$ and $d = 3$ by simply changing the screening length.

Since the above calculation of the bending energy induced by screened charges only assumes a fixed charge density, it can also be applied to liquid surfaces, such as soapy bilayers [2]. Indeed the estimate is more likely to be correct due to the absence of the coupling between bending modes, present in tethered surfaces. Given the bending energy $\varkappa_e$, the persistence length ξ for orientational order is estimated as follows: due to thermal excitation of bending modes, typical orientational fluctuations over a distance ξ scale as

$$\langle (\nabla h)^2 \rangle\, \xi \sim \int_{\xi-1} [\mathrm{d}^D \boldsymbol{q}/(2\pi)^D] \cdot k_B T q^2/(\varkappa_e q^4) \sim k_B T \xi^{2-D}/\varkappa_e .$$

Since on the scale of a persistence length these fluctuations are of the order unity, $\xi \sim (\varkappa_e/k_B T)^{1/(2-D)}$. Combined with the scaling of $\varkappa_e$ calculated in the previous paragraph, we obtain $\xi \sim (\sigma^2/k_B T)^{1/(2-D)} \lambda^{(D+\alpha+2-d)/(2-D)}$, while for the special case of $D=2$, $\xi \sim \sim \exp \cdot [c\sigma^2 \lambda^{4+\alpha-d}/k_B T]$. Note the persistence length ξ is typically much larger than the Debye screening length λ. This is indeed known for polymers, where ξ is the «Odijk length» [11], and our result can be regarded as a generalization of this result to arbitrary manifolds. For charged surfaces in $d=3$, the persistence length is $\zeta \sim \exp[c\sigma^2 \lambda^3/k_B T]$; where the numerical constant c is of the order of unity [12]. Once $\sigma^2 \lambda^3$ exceeds $k_B T$, this length becomes very large, and can quickly exceed the system size. The effects of the effective bending constant $\bar{\varkappa} = \varkappa_0 + \sigma^2 \lambda^3$ should therefore by very pronounced in experiments.

Finally we note that the usual Flory theory in the crumpled regime, obtained be equating «typical» elastic and interaction energies (*i.e.* $y_K = y_{\sigma^2}$) predicts $\nu_F = (D+2)/(d+2-\alpha)$ which clearly disagrees with the exact result. The manifold is always less crumpled than predicted by ν_F. This may be a consequence of the charges being fixed on the network skeleton. If we instead introduce a model of «conducting manifolds» in which the charge density is allowed to vary along the surface (again a possible consequence of counter charges), the dominant configurations may be closer to those described by Flory theory. Indeed if all the charges migrate to the boundary of an object of size R, there will be a repulsive energy of $\sigma^2 L^{2D}/R^{d-\alpha}$. Balancing this repulsion with the elastic attraction $R^2 L^{2-D}$, from the purely Gaussian manifold in the charge-free internal region, leads to $R \sim L^{\nu_F}$ with the Flory exponent given above.

The above, rather condensed, discussion indicates some of the interesting problems that arise in charged manifolds. For polyelectrolytes in $d = 3$ transverse fluctuations still scale as $L^{1/2}$, while there are no such fluctuations for tethered surfaces. Indeed the most experimentally useful aspect of the discussion may be the dependence of the bending energy (and the persistence length) on the Debye screening length. Further experimental verification and theoretical analysis will be valuable.

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