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► To cite this version:

G. Jug. Relevance of swelling corrections in a polyelectrolyte chain below six dimensions. Journal de Physique Lettres, 1981, 42 (18), pp.409-412. 10.1051/jphyslet:019810042018040900 . jpa-00231960

HAL Id: jpa-00231960

<https://hal.science/jpa-00231960>

Submitted on 1 Jan 1981

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Classification
Physics Abstracts
 05.70 — 36.20

Relevance of swelling corrections in a polyelectrolyte chain below six dimensions

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(Reçu le 12 juin 1981, accepté le 3 juillet 1981)

Résumé. — L'importance des corrections de gonflement dans la théorie des champs décrivant une chaîne polyélectrolyte isolée sans écrantage est examinée à partir de la théorie de renormalisation des opérateurs composés. On montre que ces corrections deviennent pertinentes en dessous d'une dimension non spécifiée $d^* < 6$, où le résultat exact $\nu = 2/(d - 2)$ perd sa validité, ainsi que sa signification physique, et un nouveau modèle décrit le système.

Abstract. — The importance of swelling corrections in the field-theoretic model describing an isolated, unscreened polyelectrolyte chain below six dimensions is examined using the renormalization theory of higher composite operators. Evidence is given of the relevance of these corrections below an unspecified dimension $d^* < 6$, when the unphysical exact result $\nu = 2/(d - 2)$ breaks down and the system is described by a new model.

1. Introduction and formulation of the problem. — The conformation properties of an isolated unscreened polyelectrolyte chain have been recently investigated using renormalization group (RG) methods [1, 2]. The main result is that, at least near the critical dimension $d_c = 6$, the chain ends' probability distribution function, $G(N; \mathbf{x}_1 - \mathbf{x}_2)$, satisfies, as $N \rightarrow \infty$, a scaling law, and introduces a radius of gyration $R_G \propto lN^\nu$ (l = length of a unit, N = number of units in the chain). Also, the size exponent ν is known to all orders in $\varepsilon = 6 - d$ and is given simply by

$$\nu = 2/(d - 2),$$

at least near $d_c = 6$. As first pointed out in reference [1], this result is unphysical for $d < 4$, as R_G would grow with N faster than the chain's linear length $L = Nl$. In this same paper, the authors have also proposed a simple RG decimation procedure to show that the result for ν breaks down below $d = 4$ as a consequence of the fixed point of the RG transformation becoming unstable for $d < 4$.

In this letter we present an alternative explanation

based upon the breakdown of the equivalence between the polyelectrolyte chain and the corresponding field-theoretic model producing the result

$$\nu = 2/(d - 2).$$

This is due to the fact that corrections associated with the swelling of the polyelectrolyte chain, as d is lowered towards $d = 4$, become relevant at a dimension $d = d^*$, thus providing perturbations to which the original fixed point is unstable.

Consider the exact integral equation satisfied by $G(N; \mathbf{x}_1, \mathbf{x}_2)$ [2, 3] in a d -dimensional space :

$$G(L + l; \mathbf{x}_1, \mathbf{x}_2; V) = \int d\mathbf{x}' \frac{1}{\Omega_d l^{d-1}} \times \\ \times \delta(|\mathbf{x}' - \mathbf{x}_2| - l) \exp[-\beta V(\mathbf{x}_2)] \\ \times G(L; \mathbf{x}_1, \mathbf{x}'; V(\mathbf{x}) + W(\mathbf{x} - \mathbf{x}_2)) \quad (1)$$

where $\Omega_d = \int d\Omega_d = 2 \pi^{d/2} / \Gamma(\frac{1}{2}d)$ is the integral over all angles, $V(\mathbf{x})$ is an external potential acting on each unit (here introduced for mathematical convenience and set equal to zero at the end of the procedure), $\beta = 1/k_B T$ and $W(\mathbf{x}' - \mathbf{x}'')$ is the interaction potential between units.

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Introducing the Laplace transform $G(s; \mathbf{x}_1, \mathbf{x}_2; V)$ with respect to L/l and expanding the corresponding

equation in the $l \rightarrow 0$, $N \rightarrow \infty$, $V \rightarrow 0$ limits, equation (1) becomes :

$$\left[s + \beta V(\mathbf{x}_2) - \int d\mathbf{x} W(\mathbf{x} - \mathbf{x}_2) \frac{\delta}{\delta V(\mathbf{x})} - \sum_{m=1}^{\infty} \frac{l^{2m}}{(2m)!} \times \right. \\ \left. \times \sum_{\alpha_1, \dots, \alpha_{2m}=1}^d I_{\alpha_1, \dots, \alpha_{2m}} \frac{\partial^{2m}}{\partial x_{2\alpha_1} \dots \partial x_{2\alpha_{2m}}} \right] G(s; \mathbf{x}_1, \mathbf{x}_2; V) = l \delta(\mathbf{x}_1 - \mathbf{x}_2) \quad (2)$$

where $I_{\alpha_1, \dots, \alpha_{2m}} = \Omega_d^{-1} \int d\mathbf{x} \delta(|\mathbf{x}| - 1) x_{\alpha_1} \dots x_{\alpha_{2m}}$ is a symmetric tensor and the integral is over a d -dimensional unitary sphere. If the chain is sufficiently coiled up on itself, equation (2) can be simplified by keeping only the first term in the development and neglecting higher order derivatives of G . The problem is then mapped into the zero component limit of the conventional field theory with Lagrangian [2] :

$$\mathcal{L} = \int d\mathbf{x} \left[\frac{1}{2} [r_0 + \Lambda(\mathbf{x})] \varphi^2(\mathbf{x}) + \frac{1}{2} (\nabla \varphi(\mathbf{x}))^2 \right] + \\ + \frac{1}{4!} \int d\mathbf{x} d\mathbf{x}' \varphi^2(\mathbf{x}) u(\mathbf{x} - \mathbf{x}') \varphi^2(\mathbf{x}') \quad (3)$$

where $r_0 = 2 d s l^{-2}$, $\Lambda = 2 d \beta V l^{-2}$ and

$$u = 12 d^2 \beta W l^{-4}.$$

However, if the chain is very swollen, higher order terms in equation (2) might become important. The first correction term, for instance, modifies the model Lagrangian (3) into the new Lagrangian :

$$\mathcal{L}' = \mathcal{L} + \frac{1}{2!} b_0 \int d\mathbf{x} [\nabla^2 \varphi(\mathbf{x})]^2 \quad (4)$$

where $b_0 = l^2/4(d+2)$ is a small coupling constant.

We have investigated the relevance of the corrections introduced by the lowest swelling operator in equation (4) both in the case of a neutral, excluded-volume chain below $d_c = 4$ and in the case of a polyelectrolyte chain below $d_c = 6$.

2. Case of the neutral, excluded volume chain. — The interaction is in this case

$$u(\mathbf{x}' - \mathbf{x}'') = \lambda_0 \delta(\mathbf{x}' - \mathbf{x}''),$$

$\lambda_0 = u_0 \kappa^\varepsilon$, $\varepsilon = 4 - d$, κ = arbitrary momentum scale. The model Lagrangian (3) then becomes, for $\Lambda = 0$:

$$\mathcal{L} = \int d\mathbf{x} \left[\frac{1}{2} r_0 \varphi^2(\mathbf{x}) + \frac{1}{2} (\nabla \varphi(\mathbf{x}))^2 + \frac{\lambda_0}{4!} (\varphi^2(\mathbf{x}))^2 \right], \quad (5)$$

showing that the size exponent ν is given by the $n = 0$ limit of the correlation length's exponent of the n -vector model. The relevance of the perturbation introduced by the operator $(\nabla^2 \varphi)^2$ into this model is studied to first order by making use of renormalized perturbation theory. The theory of renormalization of higher composite operators is well established [4, 5, 6, 7, 8]. The initial composite operator is mixed by the renormalization procedure with all composite operators $A_i(x)$ having the same naive dimensions and the same internal symmetry group ($0(n)$ in this case) of the Lagrangian (3). Lower order operators are eliminated from the calculation by dimensional regularization [8]. The renormalized vertex functions with one insertion $A_i(p)$ satisfy a RG equation containing a matrix $\gamma_{ij}(u)$ [7, 8]. (Here, $A_i(p)$ is the momentum representation of $A_i(\mathbf{x})$ and u is the renormalized coupling constant). At the fixed point, $\gamma_{ij}(u^*)$ defines through its left eigenvectors a set of eigenoperators $\{\hat{A}_\alpha(p)\}$ which are linear combinations of the $A_i(p)$'s. The eigenvalues of $\gamma_{ij}(u^*)$, λ_α represent the anomalous dimensions of the operators $A_\alpha(p)$. The condition for irrelevance of any of the composite operators $A_i(p)$ is, then, that the total dimensions of the eigenoperators $\hat{A}_\alpha(p)$, i.e. :

$$d_{\hat{A}_\alpha} = 2 + \lambda_\alpha, \quad (6)$$

must all be positive [7, 8].

In the case of the neutral, excluded-volume chain, the mixing operators are listed below :

$$A_1 = \frac{1}{2!} (\nabla^2 \varphi)^2, \quad A_2 = \varphi \nabla^4 \varphi, \quad A_3 = \nabla^2 (\varphi \nabla^2 \varphi), \quad A_4 = \frac{1}{2!} \nabla^4 (\varphi^2), \\ A_5 = \frac{\kappa^\varepsilon}{3!} S_{i_1 \dots i_4} \varphi_{i_1} \varphi_{i_2} \varphi_{i_3} \nabla^2 \varphi_{i_4}, \quad A_6 = \frac{\kappa^\varepsilon}{4!} S_{i_1 \dots i_4} \nabla^2 (\varphi_{i_1} \dots \varphi_{i_4}) = \frac{\kappa^\varepsilon}{4!} \nabla^2 (\varphi^2)^2, \\ A_7 = \frac{\kappa^{2\varepsilon}}{6!} S_{ii_1 i_2 i_3} S_{ii_4 i_5 i_6} \varphi_{i_1} \dots \varphi_{i_6},$$

where

$$S_{i_1 i_2 i_3 i_4} = \frac{1}{3}(\delta_{i_1 i_2} \delta_{i_3 i_4} + \delta_{i_1 i_3} \delta_{i_2 i_4} + \delta_{i_1 i_4} \delta_{i_2 i_3}).$$

Apart from a shift of 2ε in their naive dimensions and the complication of the n -vector model, these operators are the same as those used in reference [8] to show the irrelevance of φ^6 -corrections for the scalar φ^4 -model. Generalization to the n -vector model is straightforward, and, to order ε , we find the eigenvalues :

$$\lambda_\alpha = \left\{ 0; 0; -\eta = 0 + 0(\varepsilon^2); 2 - \nu^{-1} = \frac{n+2}{n+8}\varepsilon + 0(\varepsilon^2); \omega = \varepsilon + 0(\varepsilon^2); 0 + 0(\varepsilon^2); 3\varepsilon + 0(\varepsilon^2) \right\}$$

$\alpha = 1, \dots, 7$

where ω is the fixed point stability exponent and where results given in closed form follow, to all orders in ε , from the use of renormalized equations of motion [5, 6, 8].

Insertion of the λ_α 's into equation (6) shows that all d_{A_α} 's remain, or are very likely to remain, positive as d is lowered from 4 to 3. In fact, since, at $d = 3$, $\frac{1}{2} \leq \nu < 1$, the chain appears to be only slightly swollen and corrections introduced by A_1 are expected to be irrelevant.

3. Case of the unscreened polyelectrolyte chain. —

The interaction between units is

$$u(\mathbf{x}' - \mathbf{x}'') = \lambda_0 |\mathbf{x}' - \mathbf{x}''|^{2-d},$$

$\lambda_0 = u_0 \kappa^\varepsilon$, $\varepsilon = 6 - d$. The model Lagrangian equivalent to (3) is [2] :

$$\mathcal{L} = \int d\mathbf{x} \left[\frac{1}{2} r_0 \varphi^2(\mathbf{x}) + \frac{1}{2} (\nabla \varphi(\mathbf{x}))^2 + \frac{1}{2} (\nabla \psi(\mathbf{x}))^2 + \frac{1}{2!} g_0 \varphi^2(\mathbf{x}) \psi(\mathbf{x}) \right] \quad (7)$$

where $g_0^2 = -\frac{1}{3} \lambda_0 = w_0^2 \kappa^\varepsilon$ and where $\psi(\mathbf{x})$ is a scalar Coulomb field. The operators $A_i(p)$ having naive dimensions $d_{A_i}^0 = 2$ and mixing with

$$A_1 = (\nabla^2 \varphi)^2 / 2!$$

in the renormalization procedure are listed below :

$$A_1 = \frac{1}{2!} (\nabla^2 \varphi)^2, \quad A_2 = \varphi \nabla^4 \varphi, \quad A_3 = \frac{1}{2!} (\nabla^2 \psi)^2, \quad A_4 = \psi \nabla^4 \psi, \quad A_5 = \frac{\kappa^{\varepsilon/2}}{2!} \varphi^2 \nabla^2 \psi,$$

$$A_6 = \kappa^{\varepsilon/2} \psi \varphi \nabla^2 \varphi, \quad A_7 = \frac{\kappa^{\varepsilon/2}}{2!} \psi^2 \nabla^2 \psi, \quad A_8 = \frac{\kappa^\varepsilon}{4!} (\varphi^2)^2, \quad A_9 = \frac{\kappa^\varepsilon}{(2!)^2} \varphi^2 \psi^2, \quad A_{10} = \frac{\kappa^\varepsilon}{4!} \psi^4,$$

where seven other operators which are total derivatives of lower composite operators have been omitted [7, 8]. The situation is, in some respects, similar to the one in reference [7], where the relevance of φ^4 corrections in the φ^3 -dominated Potts model is discussed. A proper use of renormalized equations of motion linking some of the above operators and a one-loop minimal subtraction calculation lead us to the following eigenvalues, for $n = 0$:

$$\lambda_\alpha = \left\{ 0; 0; 0; -\eta_\varphi = \frac{1}{4}\varepsilon + 0(\varepsilon^2); \frac{3}{2}\varepsilon + 0(\varepsilon^2); -\varepsilon + 0(\varepsilon^2); -\frac{1}{2}\varepsilon + 0(\varepsilon^2); -\frac{1}{2}\varepsilon + 0(\varepsilon^2); -\frac{1}{2}\varepsilon + 0(\varepsilon^2); 3\varepsilon + 0(\varepsilon^2) \right\} \quad \alpha = 1, \dots, 10.$$

The new important feature is the appearance of negative anomalous dimensions for some of the eigenoperators as d is lowered below $d_c = 6(\varepsilon > 0)$. Inserted into equation (6), these negative λ_α 's give evidence that one or more eigenoperators become relevant for $d < d^*$, where $d^* = 6 - \varepsilon^*$ and $2 + \lambda_\alpha(\varepsilon^*) = 0$. The one loop calculation is too poor to localize d^* exactly, but it is evident that it must be : $4 \leq d^* < 6$ (the lower limit coming from physical considerations on the result $\nu = 2/(d-2)$). As we can show that A_1 must enter into the linear combinations defining two of these eigenoperators with negative anomalous dimensions, although this is strictly evident only to

order two loops, we conclude that A_1 itself must become relevant for $d < d^*$.

The stability of the fixed point w^* of the model (7) is controlled by the positive sign of the exponent ω . As $\omega = \varepsilon + 0(\varepsilon^2)$ [2], we argue that the model Lagrangian (7), for which $\nu = 2/(d-2)$, might cease to describe the properties of the polyelectrolyte chain, as a consequence of the relevance of the correction in equation (4), before its fixed point becomes unstable (i.e. $\omega < 0$). The new model, equation (4), would still have a stable fixed point, but its critical behaviour should be described by new exponents, thus providing a new description of the chain's configuration.

Incidentally, observe that the present calculation provides a way to show that the Coulomb interaction dominates above a possible excluded-volume correction. In fact, excluded-volume corrections to model Lagrangian (7) are represented by the operator A_8 which, in the $n = 0$ limit, does not couple to any of the other operators. Therefore, A_8 is itself an eigenoperator, with anomalous dimension given by

$$\gamma_{88}(w^*) = 3\varepsilon + O(\varepsilon^2),$$

indicating that $d_{A_8} = 2 + 3\varepsilon + O(\varepsilon^2)$ is likely to stay positive as d is lowered below $d_c = 6$.

4. Conclusion. — The use of renormalization theory of higher composite operators denotes the appearance

of relevant corrections, associated with the swelling of the unscreened polyelectrolyte chain, to be included in the model Lagrangian describing the system near $d_c = 6$. These corrections would modify the unphysical result $\nu = 2/(d - 2)$ below the marginality dimension d^* .

Details of the present calculation will be presented elsewhere.

Acknowledgements. — The author is grateful to Profs. G. Rickayzen, D. J. Amit and D. J. Wallace for enlightening discussions and to the University of Kent for financial support.

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