August, 1996
LU TP 96-22

Relation between a Screened Polyelectrolyte and a Field Theory

Bo Söderberg

Department of Theoretical Physics
Lund University
Sölvegatan 14
S-223 62 LUND

Abstract

There exists a generic relationship between the thermodynamics of a continuous polymer with a generic self-interaction and the two-point function of an interacting field-theory. In addition, the $(2N)$-point function of the resulting field theory is similarly related to a system of N interacting polymers.

In the present paper, this relation is explored for the special case of a polyelectrolyte, characterized by a screened Coulomb pair potential. The corresponding field theory can be recast in a particularly simple form, corresponding to a quantum-mechanical particle, self-interacting via the emission and absorption of a massive scalar field.

This is particularly useful in a perturbative treatment: perturbative expansions for the polyelectrolyte can be simply derived from the loop expansion for the related field-theoretical two-point function, for which established computational methods exist.

Introduction

Relations between Euclidean field theories and random walks or polymers are well-known [1, 2, 3, 4, 5, 6]. For a non-interacting continuous polymer, equivalent to a random walk, the relation to the propagator of a free field theory is trivial. For the case of a continuous polymer with a delta-function pair interaction, corresponding to a self-avoiding random walk, de Gennes has shown the relation to a ϕ^4 field theory (Landau-Ginsburg model) [2, 3, 4, 5]. A similar relation has been exploited for an unscreened polyelectrolyte [7]. The focus of the present paper is to exploit the generic result for the special case of a screened polyelectrolyte, leading to a specific, very simple field-theory.

The generic interacting polymer

A quite generic self-interacting discrete polymer with N monomers in D-dimensional space is described by the Hamiltonian

$$\begin{aligned} H(\mathbf{x}_1,\ldots,\mathbf{x}_N) &= \frac{1}{2}\sum_{i=1}^{N-1}(\mathbf{x}_{i+1}-\mathbf{x}_i)^2+\sum_{i=1}^{N}\tilde{V}_1(\mathbf{x}_i)+\sum_{i=1}^{N}\sum_{j=i+1}^{N}\tilde{V}_2(\mathbf{x}_i,\mathbf{x}_j) \\ &+ \sum_{i=1}^{N}\sum_{j=i+1}^{N}\sum_{k=j+1}^{N}\tilde{V}_3(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x}_k)+\ldots, \end{aligned}$$

where $\mathbf{x}_i$ denotes the position in $\mathcal{R}^D$ of the ith monomer. The first term represents a harmonic bonding force between nearest-neighbour monomers, while $\tilde{V}_1(\mathbf{x})$ is a generic one-particle potential, $\tilde{V}_2(\mathbf{x},\mathbf{y})$ a ditto pair potential, etc. The interaction is the most general one that depends on positions only and is independent of monomer indices. Thermodynamic averages at temperature T are defined based on the Boltzmann distribution, $P(\mathbf{x}_1,\ldots,\mathbf{x}_N)\propto\exp(-H/T)$.

For the Boltzmann exponent $S\equiv H/T$, we obtain in the continuum approximation, defined by replacing the discrete monomer index i by a continuous chain parameter $\tau=Ti$, such that $\mathbf{x}_i\to\mathbf{x}(Ti)\equiv\mathbf{x}(\tau)$, the following expression:

$$\begin{aligned} S[\mathbf{x}(\tau)] &= \frac{1}{2}\int_0^\mu d\tau\,\dot{\mathbf{x}}^2+\int_0^\mu d\tau\,V_1(\mathbf{x}(\tau))+\frac{1}{2}\int_0^\mu d\tau\int_0^\mu d\tau'\,V_2(\mathbf{x}(\tau),\mathbf{x}(\tau')) \\ &+ \frac{1}{6}\int_0^\mu d\tau\int_0^\mu d\tau'\int_0^\mu d\tau''\,V_3(\mathbf{x}(\tau),\mathbf{x}(\tau'),\mathbf{x}(\tau''))+\ldots, \end{aligned}$$

where square brackets [] are used to indicate that S is a functional. The length of the polymer is represented by $\mu=NT$, while $V_k\equiv\tilde{V}_k/T^{k+1}$, for $k=1,2,\ldots$. The dot in $\dot{\mathbf{x}}$ stands for the derivative with respect to τ. The continuum approximation is valid when the nearest-neighbour distances are small in comparison to the range of the interactions. The independence on monomer index is turned into a translation invariance with respect to the chain position τ: V_n depends on $(\tau,\tau',\ldots)$ only via $(\mathbf{x}(\tau),\mathbf{x}(\tau'),\ldots)$.

The continuum formulation will be the starting point for the analysis carried out in the rest of this letter, and $S[\mathbf{x}(\tau)]$ will be referred to as the *action* of the system. To begin with, we will assume fixed B.C., with the endpoints of the chain locked at $\mathbf{x}(0)=\mathbf{a}$, $\mathbf{x}(\mu)=\mathbf{b}$. The main object of interest is the *partition function*, which is given by the functional integral

$$Z(\mu,\mathbf{a},\mathbf{b}) = \int_{\mathbf{x}(0)=\mathbf{a}}^{\mathbf{x}(\mu)=\mathbf{b}} d[\mathbf{x}(\tau)] \exp\left(-S[\mathbf{x}(\tau)]\right).$$

The proper partition function for free boundary conditions is obtained simply by integrating $Z(\mu,\mathbf{a},\mathbf{b})$ over the endpoints $\mathbf{a},\mathbf{b}$.

The relation to a field theory

The generic relation to a field-theory is has been described in the literature (see e.g. [6] and references therein). For the sake of completeness, we will here provide a derivation.

The translation-invariance of the interaction ensures that the interaction part $S_{\rm int}$ of the action be a functional only of the *particle density*, $\rho(\mathbf{y}) = \int_0^\mu d\tau \delta\left(\mathbf{y}-\mathbf{x}(\tau)\right)$, in terms of which it is given by

$$\begin{aligned} S_{\rm int}[\rho] &= \int d\mathbf{x}\rho(\mathbf{x})V_1(\mathbf{x}) + \frac{1}{2}\int d\mathbf{x}\rho(\mathbf{x})\int d\mathbf{y}\rho(\mathbf{y})V_2(\mathbf{x},\mathbf{y}) \\ &+ \frac{1}{6}\int d\mathbf{x}\rho(\mathbf{x})\int d\mathbf{y}\rho(\mathbf{y})\int d\mathbf{z}\rho(\mathbf{z})V_3(\mathbf{x},\mathbf{y},\mathbf{z}) + \ldots \end{aligned}$$

as a functional Taylor expansion. Next, we assume that the corresponding Boltzmann factor, $\exp(-S_{\rm int})$, can be functionally Laplace transformed with respect to the (non-negative) particle density,

$$F[\xi(\mathbf{x})] = \int d[\rho(\mathbf{x})] \exp\left(-\int d\mathbf{x}\xi(\mathbf{x})\rho(\mathbf{x}) - S_{\rm int}[\rho]\right).$$

This is well-defined for any combination of arbitrary one-particle potentials and non-negative many-particle potentials. The functional Laplace transform can be inverted to yield, formally,

$$\exp\left(-S_{\rm int}[\rho]\right) \propto \int d[\xi(\mathbf{x})]F[\xi(\mathbf{x})]\exp\left(\int d\mathbf{x}\xi(\mathbf{x})\rho(\mathbf{x})\right),$$

where each $\xi(\mathbf{x})$ is to be integrated along a complex contour to the right of all singularities. We then obtain for the partition function

$$Z(\mu,\mathbf{a},\mathbf{b}) \propto \int d[\xi(\mathbf{x})]F[\xi(\mathbf{x})] \int_{\mathbf{x}(0)=\mathbf{a}}^{\mathbf{x}(\mu)=\mathbf{b}} d[\mathbf{x}(\tau)]\exp\left(-\frac{1}{2}\int_0^\mu d\tau\, \dot{\mathbf{x}}^2 + \int_0^\mu d\tau\xi(\mathbf{x}(\tau))\right),$$

and $-\xi(\mathbf{x})$ appears as an effective one-particle potential for the polymer. Now the $\mathbf{x}$ integral is recognized as the Euclidean quantum-mechanical path integral for the amplitude $<\mathbf{a}|\exp(-\mu\hat{H})|\mathbf{b}>$ to go from $\mathbf{a}$ to $\mathbf{b}$ in imaginary time μ, with the quantum-mechanical Hamiltonian

$$\hat{H} = -\frac{1}{2}\nabla^2 - \xi(\mathbf{x}) + const..$$

We thus have

$$Z(\mu, \mathbf{a}, \mathbf{b}) \propto \int d[\xi(\mathbf{x})] F[\xi(\mathbf{x})] \left\langle \mathbf{a} \left| \exp\left(-\mu \hat{H}\right) \right| \mathbf{b} \right\rangle .$$

Now, we can make a Laplace transform in μ,

$$W(s, \mathbf{a}, \mathbf{b}) = \int_0^\infty d\mu \exp(-s\mu) Z(\mu, \mathbf{a}, \mathbf{b}),$$

yielding

$$W(s, \mathbf{a}, \mathbf{b}) \propto \int d[\xi(\mathbf{x})] F[\xi(\mathbf{x})] \left\langle \mathbf{a} \left| \left(\hat{H} + s\right)^{-1} \right| \mathbf{b} \right\rangle .$$

The matrix-element can be written as a functional integral over a field $\vec{\phi}(\mathbf{x})$ having $n = 0$ components,

$$\left\langle \mathbf{a} \left| \left(\hat{H} + s\right)^{-1} \right| \mathbf{b} \right\rangle = 2 \int d[\vec{\phi}(\mathbf{x})] \phi_1(\mathbf{a}) \phi_1(\mathbf{b}) \exp\left(- \int d\mathbf{x} \vec{\phi} \left(\hat{H} + s\right) \vec{\phi}\right),$$

and we obtain

$$W(s, \mathbf{a}, \mathbf{b}) \propto \int d[\xi(\mathbf{x})] F[\xi(\mathbf{x})] \int d[\vec{\phi}(\mathbf{x})] \phi_1(\mathbf{a}) \phi_1(\mathbf{b}) \exp\left(- \int d\mathbf{x} \left\{ \frac{1}{2} \left(\nabla \vec{\phi}\right)^2 + s\vec{\phi}^2 - \xi(\mathbf{x}) \vec{\phi}^2 \right\}\right).$$

Now we can do the ξ integral to recover $\exp\left(-S_{\rm int}[\rho(\mathbf{x})]\right)$, but with a modified particle density, $\rho(\mathbf{x}) \to \vec{\phi}(\mathbf{x})^2$. Thus, we finally arrive at the following result:

$$W(s, \mathbf{a}, \mathbf{b}) \propto \int d[\vec{\phi}(\mathbf{x})] \phi_1(\mathbf{a}) \phi_1(\mathbf{b}) \exp\left(-\hat{S}[\phi(\mathbf{x})]\right).$$

The RHS defines the two-point function $G(s, \mathbf{a}, \mathbf{b})$ of an interacting field theory, with an action $\hat{S}$ given by

$$\begin{aligned} \hat{S}[\phi(\mathbf{x})] &= \int d\mathbf{x} \left\{ \frac{1}{2} \left(\nabla \vec{\phi}\right)^2 + s\vec{\phi}^2(\mathbf{x}) + V_1(\mathbf{x}) \vec{\phi}^2(\mathbf{x}) \right\} + \frac{1}{2} \int d\mathbf{x} \int d\mathbf{y}\ V_2(\mathbf{x}, \mathbf{y}) \vec{\phi}^2(\mathbf{x}) \vec{\phi}^2(\mathbf{y}) \\ &+ \frac{1}{6} \int d\mathbf{x} \int d\mathbf{y} \int d\mathbf{z}\ V_3(\mathbf{x}, \mathbf{y}, \mathbf{z}) \vec{\phi}^2(\mathbf{x}) \vec{\phi}^2(\mathbf{y}) \vec{\phi}^2(\mathbf{z}) + \ldots \end{aligned}$$

This shows that the partition function for a generic interacting polymer, when Laplace transformed with respect to the chain-length μ, yields the propagator of a zero-component field theory, with a bare mass determined by the corresponding conjugate variable s, and where the interaction appears in terms of a particle density given by the square of the field. Upon collecting the neglected constants of proportionality accumulated in the tranformations, the exact relation is given by

$$2G(s,\mathbf{a},\mathbf{b}) = \int_0^\infty d\mu \exp(-s\mu) \frac{Z(\mu,\mathbf{a},\mathbf{b})}{\int d\mathbf{a} Z_0(\mu,\mathbf{a},\mathbf{0})}$$

where Z_0 denotes the partition function of a non-interacting polymer; the correctness can be verified by considering the case of no interactions, since the constants of proportionality involved do not depend on the interaction.

Several polymers

Having established the relation between the partition function of an interacting polymer and the two-point function of a related field theory, one might wonder what is the relevance of the higher order moments in $\vec{\phi}$. It turns out (the proof is analogous to the one-polymer case) that the four-point function $\langle\phi_1(\mathbf{a})\phi_1(\mathbf{b})\phi_2(\mathbf{c})\phi_2(\mathbf{d})\rangle$ is proportional to the Laplace transform of the partition function for *two polymers*, one with its endpoints in $\mathbf{a}$ and $\mathbf{b}$, the other in $\mathbf{c}$ and $\mathbf{d}$, interacting both internally and with each other, and allowed to exchange monomers with each other: The parameter μ, conjugate to s, merely fixes their *total length.* In addition, the moment $\langle\phi_1(\mathbf{a})\phi_1(\mathbf{b})\phi_1(\mathbf{c})\phi_1(\mathbf{d})\rangle$ corresponds to the sum of the three possible endpoint rearrangements of the two polymers. Similarly, the six-point functions are related to a system of three polymers, etc.

In contrast, a system of N polymers of *fixed lengths* μ_i corresponds to, upon Laplace transforming each length individually, a field theory with distinct squared masses $2s_i$ for N subsets (of zero components each) of the field components.

For dominantly repulsive interactions, the consideration of several polymers will of course make sense only in a finite volume (or finite polymer concentration).

The screened polyelectrolyte

In the physically interesting case of a screened polyelectrolyte in three dimensions [8, 9], having only a pair interaction given by a screened Coulomb potential,

$$V_2(\mathbf{x},\mathbf{y}) = g\exp(-\kappa r)/4\pi r, \text{ with } r = |\mathbf{x}-\mathbf{y}|,$$

we have the resulting action

$$\hat{S}[\phi(\mathbf{x})] = \int d\mathbf{x} \left\{ \frac{1}{2}\left(\nabla\vec{\phi}\right)^2 + s\vec{\phi}^2(\mathbf{x}) \right\} + \frac{g}{2}\int d\mathbf{x}\int d\mathbf{y}\ \frac{\exp(-\kappa|\mathbf{x}-\mathbf{y}|)}{4\pi|\mathbf{x}-\mathbf{y}|}\vec{\phi}^2(\mathbf{x})\vec{\phi}^2(\mathbf{y}).$$

Noting that

$$\frac{\exp(-\kappa|\mathbf{x}-\mathbf{y}|)}{4\pi|\mathbf{x}-\mathbf{y}|} = \left(-\nabla^2+\kappa^2\right)^{-1}(\mathbf{x},\mathbf{y}),$$

we can make a further simplification by introducing an additional scalar field, the exchange of which mediates the interaction. This gives

$$W(s,\mathbf{a},\mathbf{b}) \propto \int d[\vec{\phi}(\mathbf{x})] \int d[\psi(\mathbf{x})] \phi_1(\mathbf{a})\phi_1(\mathbf{b}) \exp\left(-\tilde{S}[\phi(\mathbf{x}),\psi(\mathbf{x})]\right),$$

with a *local* combined action $\tilde{S}$ given by

$$\tilde{S}[\phi(\mathbf{x}),\psi(\mathbf{x})] = \int d\mathbf{x} \left\{ \frac{1}{2}\left(\nabla\vec{\phi}\right)^2 + s\vec{\phi}^2 + \frac{1}{2}\left(\nabla\psi\right)^2 + \frac{1}{2}\kappa^2\psi^2 + i\sqrt{g}\vec{\phi}^2\psi \right\}.$$

The variable s, conjugate to the chain length μ, appears only in the (bare) $\vec{\phi}$ mass, while the inverse range κ of the interaction potential appears as the ψ mass; for the case of an unscreened potential, the ψ-field will be massless.

Now we can modify the boundary conditions; noting that the polymer is translationally and rotationally invariant, the partition function $Z(\mu,\mathbf{a},\mathbf{b})$ can depend only on $R \equiv |\mathbf{a}-\mathbf{b}|$. Integrating also over $\mathbf{R}$ would yield the relevant partition function for the case of free boundary conditions. However, it adds no complication to include a factor $\exp(i\mathbf{P}\cdot\mathbf{R})$ in the integral, yielding

$$\begin{aligned} W(s,\mathbf{P}) &= \int d\mathbf{R} \int_0^\infty d\mu\ \exp(-s\mu + i\mathbf{P}\cdot\mathbf{R}) Z(\mu,0,\mathbf{R}) \\ &= \int_0^\infty d\mu \exp(-s\mu)\tilde{Z}(\mu,\mathbf{P}) \propto \int d\mathbf{R} \exp(i\mathbf{P}\cdot\mathbf{R}) G(0,\mathbf{R}) \equiv \tilde{G}(\mathbf{P}). \end{aligned}$$

This yields the two-point function in momentum space, at momentum $\mathbf{P}$, for the $\vec{\phi}$ field. It contains all relevant information on the distribution of the end-to-end distance $\mathbf{R}$ of the polymer. Thus, eg., the average end-to-end distance squared, $\langle R^2 \rangle$, can be obtained from

$$\frac{Z(\mu,\mathbf{P})}{Z(\mu,0)} = 1 - \frac{P^2\langle R^2\rangle}{6} + \mathcal{O}(P^4).$$

Relation in terms of perturbation theory

A perturbative (in the coupling g) expansion for the polyelectrolyte is obtained by applying an inverse Laplace transform to the loop expansion for the resulting local field theory, the latter amounting to the well-known computation of Feynman graphs. In three dimensions, no ultraviolet divergences will appear, as can be seen from a simple dimensional analysis.

The Feynman rules for computing $\tilde{G}(\mathbf{P})$ are simple: On a single ϕ line add lines of emitted and re-absorbed ψ lines joining the first line in vertices. A ϕ propagator carries a factor $1/(q^2+2s)$ and a ψ propagator a factor $1/(k^2+\kappa^2)$. For every vertex add a factor $-2i\sqrt{g}$. The external ϕ momentum is given by $\mathbf{P}$, and momentum is conserved at every vertex. For every loop, add a momentum integral $\int d^3p/(2\pi)^3$. It is easy to see from dimensional counting, that in three dimensions the result will be ultra-violet finite for all graphs. Note that no ϕ-loops are allowed (due to $n=0$);

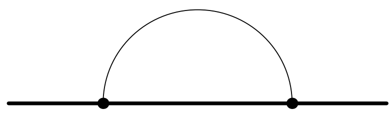

Figure 1: The only graph contributing to first order in the perturbation series for $\tilde{G}(\mathbf{P})$.

this can be interpreted as the ϕ-field corresponding to a quantum-mechanical particle that is not second-quantized; thus, there can be no creation or annihilation of the corresponding particles.

Thus, to lowest order $\tilde{G}(\mathbf{P})$ is given by the bare propagator

$$\tilde{G}^{(0)}(\mathbf{P}) = \frac{1}{P^2 + 2s}.$$

which is indeed half of the Laplace transform of $\exp(-\mu P^2/2)$, reflecting the distribution of $\mathbf{R}$ for a free polymer being proportional to $\exp(-\mathbf{R}^2/2\mu)$. To first order in g, corresponding to one loop, there is only one graph contributing, displayed in Fig. 1, yielding

$$\begin{aligned}\tilde{G}^{(1)}(\mathbf{P}) &= \frac{-4g}{(P^2+2s)^2} \int \frac{d^3\mathbf{q}}{(2\pi)^3} \frac{1}{(q^2+\kappa^2)((\mathbf{P}-\mathbf{q})^2+2s)} \\ &= \frac{-4g}{(P^2+2s)^2} \frac{1}{4\pi P} \arctan\left(\frac{P}{\sqrt{2s}+\kappa}\right).\end{aligned}$$

To second order there are three distinct graphs, displayed in Fig. 2.

To compute the partition function Z, and related entities like $\langle S_{\mathrm{int}} \rangle$, it is enough to consider $\mathbf{P} = 0$, while for $\langle R^2 \rangle$, the leading small P^2 corrections must be taken into account. Work on perturbative calculations for the polyelectrolyte relying on the above analysis is in progress, and will be presented elsewhere [10].

In a similar way, any pair-potential that only depends on the relative position, $V_2(\mathbf{x}, \mathbf{x}') = U(\mathbf{x}-\mathbf{x}')$, can be perturbatively treated; provided the ψ propagator is replaced by the Fourier transform of the potential, $\tilde{U}(\mathbf{q}) = \int d\mathbf{x} \exp(i\mathbf{q}\cdot\mathbf{x}) U(\mathbf{x})$.

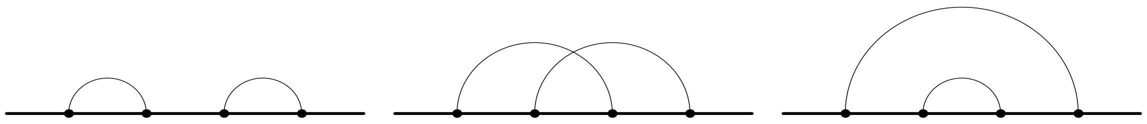

Figure 2: The three graphs contributing to second order in the perturbation series for $\tilde{G}(\mathbf{P})$.

References

[1] K. Symanzik, *Euclidean Quantum Field Theory*, in *Local Quantum Theory, Proc. International School of Physics "Enrico Fermi"* XLV, Ed. L. Jost (Academic Press, New York 1969), p. 152.

[2] P.G. de Gennes, Phys. Lett. **38 A**, 339 (1972).

[3] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca 1979), chpt. X.

[4] G. Parisi, *Statistical Field Theory* (Addison-Wesley, Urbana 1988), chpt. 16.

[5] C. Itzykson and J.-M. Drouffe, *Statistical Field Theory* (Cambridge Univ. Press, New York 1989), vol. 1, chpt. 1.

[6] J. des Cloizeaux and G. Jannink, *Polymers in Solution* (Clarendon Press, Oxford 1990), chpt. 11.

[7] P. Pfeuty, R.M. Velasco and P.G. de Gennes, J. de Physique **38**, L-5 (1977).

[8] C. Peterson, O. Sommelius and B. Söderberg, Phys. Rev. Lett. **76**, 1079 (1996).

[9] C. Peterson, O. Sommelius and B. Söderberg, Lund Univ. preprint LU TP 95-25 (To appear in J. Chem. Phys.)

[10] B. Söderberg, work in progress.