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LETTER TO THE EDITOR

Polymers with long-ranged self-repulsion: a variational approach

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Abstract. We use a variational approach to study self interacting polymers with long-ranged repulsion decaying for large distances as $r^{-\lambda}$. For $2 \leqslant \lambda \leqslant 4$ and $\lambda < d$ (where d is the spatial dimension), we find that the exponent for the end-to-end distance of the chain is $\nu = 2/\lambda$ (with logarithmic corrections for $\lambda = 2$ or $\lambda = 4$), in agreement with renormalization group computations and recent numerical simulations. We discuss the entire λ, d plane, using a renormalization group near $\lambda = 4$, $d = 4$.

The variational treatment of path integrals was pioneered by Feynman in his famous treatment of the polaron problem [1] and subsequently used for many other problems, including the problem of polymers with an excluded volume caused by short-ranged self-repulsion [2]. Recently, the variational approach was successfully combined with the replica method in studies of heteropolymers [3] and of directed polymers (or manifolds) in a random medium [4]. For these problems, the variational method has the advantage that it is inherently non-perturbative, and can therefore incorporate the effects of replica symmetry breaking which are crucial for dealing with the presence of many metastable states.

In this letter, we apply a Gaussian variational method to the problem of a homopolymer with long-ranged power-law self-repulsion. For the case of a polymer with short-ranged (delta-function) repulsions [2], the variational result for the critical exponent ν is rather poor, which has perhaps led to a relative neglect of this method for other polymer problems. For our problem with long-ranged repulsion, however, we find results for ν which agree with renormalization group calculations as well as numerical simulations, and which indeed are probably exact. We shall try to explain why the variational approach gives good results for our long-ranged problem even though it gave relatively poor results for the short-ranged problem.

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We consider a closed polymer made of N monomers in a d-dimensional space. The Hamiltonian of the system is chosen to be

$$H=\tfrac{1}{2}\sum_{\tau=1}^{N}(\boldsymbol{x}_{\tau+1}-\boldsymbol{x}_{\tau})^{2}+\sum_{1\leqslant\tau<\tau'\leqslant N}V((\boldsymbol{x}_{\tau'}-\boldsymbol{x}_{\tau})^{2}) \tag{1}$$

where $\boldsymbol{x}_{N+1}=\boldsymbol{x}_1$ and $V(z)\sim gz^{-\lambda/2}$ for large z. We will work in units such that the temperature is equal to 1.

We are particlarly interested in the value of the exponent ν, defined by

$$\lim_{\tau\to\infty}\left[\lim_{N\to\infty}\left\langle\frac{(\boldsymbol{x}_{\tau}-\boldsymbol{x}_{1})^{2}}{\tau^{2\nu}}\right\rangle\right]=C>0. \tag{2}$$

The particular case of the Coulomb interaction between charged monomers ($\lambda=d-2$) has been studied using the renormalization group method by Pfeuty *et al* [5]. They find in that case $\nu=2/\lambda=2/(d-2)$ for $4<d<6$.

Our variational method is based on the following Gaussian trial Hamiltonian

$$H_0=\tfrac{1}{2}\sum_{\tau,\tau'}(G^{-1})_{\tau,\tau'}(\boldsymbol{x}_{\tau}\cdot\boldsymbol{x}'_{\tau}) \tag{3}$$

where $G_{\tau,\tau'}$ is the trial 'propagator' which will be determined variationally. The exact free energy

$$F=-\log Z=-\log\int\prod_{\tau}\mathrm{d}\boldsymbol{x}_{\tau}\,\mathrm{e}^{-H} \tag{4}$$

is approximated by

$$F_0=\langle H-H_0\rangle_0-\log\int\prod_{\tau}\mathrm{d}\boldsymbol{x}_{\tau}\,\mathrm{e}^{-H_0} \tag{5}$$

where $\langle\ldots\rangle_0$ means expectation value with the measure e^{-H_0}:

$$\langle A\rangle_0=\frac{\int\prod_{\tau}\mathrm{d}\boldsymbol{x}_{\rho}\,A(\boldsymbol{x}_{\tau})\,\mathrm{e}^{-H_0}}{\int\prod_{\tau}\mathrm{d}\boldsymbol{x}_{\tau}\,\mathrm{e}^{-H_0}}. \tag{6}$$

F_0 depends on the trial propagator G, and from the convexity inequality for the exponential, one gets $F_0\geqslant F$. We therefore search for the optimal propagator which minimizes F_0.

The variational free energy F_0 can be computed easily within the Gaussian ansatz. The only term which deserves some special attention is the expectation value of the potential energy. For a given pair of monomers τ, τ' ($\tau\neq\tau'$), we compute $\langle V((\boldsymbol{x}_{\tau'}-\boldsymbol{x}_{\tau})^{2})\rangle_0$ by noticing that within the Gaussian ansatz, $\boldsymbol{u}=\boldsymbol{x}_{\tau'}-\boldsymbol{x}_{\tau}$ is a Gaussian variable of mean $\boldsymbol{0}$ and width $\langle\boldsymbol{u}^2\rangle_0=\mathrm{d}B_{\tau,\tau'}$, where

$$B_{\tau,\tau'}=G_{\tau,\tau}+G_{\tau',\tau'}-2G_{\tau,\tau'}. \tag{7}$$

Therefore

$$\langle V((\boldsymbol{x}_{\tau'}-\boldsymbol{x}_{\tau})^{2})\rangle_0=\int\frac{\mathrm{d}^{d}\boldsymbol{u}}{(2\pi B_{\tau,\tau'})^{d/2}}\,V(\boldsymbol{u}^{2})\,\mathrm{e}^{-\boldsymbol{u}^{2}/2B_{\tau,\tau'}} \tag{8}$$

$$=\frac{1}{\Gamma(d/2)}\int_{0}^{\infty}\mathrm{d}r\,r^{(d/2)-1}\,\mathrm{e}^{-r}\,V(2B_{\tau,\tau'}r)\equiv\hat{V}(B_{\tau,\tau'}). \tag{9}$$

If $V(z) \sim g z^{-\lambda/2}$ for large z, we get

$$\hat{V}(z) \sim \left[2^{-\lambda/2} g \frac{\Gamma((d-\lambda)/2)}{\Gamma(d/2)} \right] z^{-\lambda/2} \tag{10}$$

if $\lambda < d$, and

$$\hat{V}(z) \sim \left[\frac{2^{d/2}}{\Gamma(d/2)} \int_0^\infty \mathrm{d}y\, y^{d/2-1}\, \mathrm{e}^{-y}\, V(y) \right] z^{-d/2} \tag{11}$$

if $\lambda > d$.

Within this variational method, the asymptotic behaviour of $\hat{V}$ at large arguments will determine the ν exponent. Therefore, all the 'short range' potentials falling off faster than r^{-d} will have the same ν exponent. This is, however, not true for the exact solution (see below and figure 1).

Using (9), we find that the total variational free energy is equal to

$$F_0 = \frac{d}{2} \sum_{\tau=1,N} B_{\tau,\tau+1} + \sum_{1 \leq \tau < \tau' \leq N} \hat{V}(B_{\tau,\tau'}) - \frac{d}{2} \operatorname{Tr} \log G - Nd[1 + \log(2\pi)]. \tag{12}$$

For a ring polymer with $x_{N+1} = x_1$, translational invariance implies that $G_{\tau,\tau'} = G(\tau - \tau')$, where $G(\tau)$ is an even function of τ which satisfies $G(N+1-\tau) = G(\tau)$. The same properties hold for $B(\tau) = 2(G(0) - G(\tau))$. In order to find the optimum function $G(\tau)$, it is convenient to introduce its Fourier transform $\tilde{G}(\omega)$. Taking the $N \to \infty$ limit, $G(\tau)$ becomes an even function defined on the integers. One has then

$$\tilde{G}(\omega) = \sum_{\tau=0}^{\infty} G(\tau)\, \mathrm{e}^{\mathrm{i}\omega\tau} \tag{13}$$

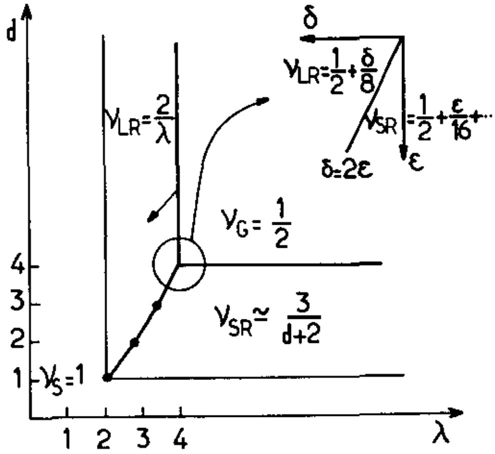

Figure 1. Summary of the different regions in the λ, d plane. The value of ν is given in each region. SR refers to short range, LR to long range, S to 'stretched', and G to Gaussian. The line separating SR from LR is given by: $\lambda \nu_{SR} = 2$. The insert shows the result of a renormalization group calculation done to first order in $\delta = 4 - \lambda$ and $\varepsilon = 4 - d$. The arrow indicates where Pfeuty *et al* [5] performed their renormalization group calculation. The 'super-stretched' regime $\lambda < 1$ is not shown, since it is strongly model-dependent. On the lattice, for example, $\nu = 1$ in this region.

and

$$G(\tau)=\int_{-\pi}^{\pi}\frac{\mathrm{d}\omega}{2\pi}\,\tilde{G}(\omega)\,\mathrm{e}^{-\mathrm{i}\omega\tau}. \tag{14}$$

The functional minimization with respect to $\tilde{G}(\omega)$ leads to the following set of saddle point equations:

$$\frac{1}{\tilde{G}(\omega)}=2(1-\cos\omega)+\tfrac{1}{2}\sum_{\tau=1}^{\infty}(1-\cos\omega\tau)\,\hat{V}'\left[\int_{-\pi}^{\pi}\frac{\mathrm{d}\omega'}{2\pi}\,\tilde{G}(\omega')2(1-\cos\omega'\tau)\right]. \tag{15}$$

The scaling behaviour with an exponent ν corresponds to the following behaviour:

$$B(\tau)\simeq C\tau^{2\nu} \tag{16}$$

for large τ and

$$\tilde{G}(\omega)\simeq\omega^{-(1+2\nu)} \tag{17}$$

for small ω. In order to find the value of ν, we must analyse and match the small ω behaviour of the different terms of (15). In this small ω regime, the only important feature of $\hat{V}$ is its asymptotic shape at large distances, given by (10), (11). In fact, exactly the same function equation (15), with $\hat{V}$ behaving as a power law ($\hat{V}(z)\simeq z^{-d/2}$), has been obtained by des Cloizeaux [2] in his analysis of the polymer with short range (delta-function) interactions. The analysis of (15) is quite subtle, and has been very carefully done in [2]. The results are as follows:

For $2<\lambda<4$, $\nu=2/\lambda$.

For $\lambda=2$, one finds logarithmic corrections to 'ballistic' behaviour:

$$\lim_{N\to\infty}\langle(x_\tau-x_1)^2\rangle\sim\frac{\tau^2}{\log\tau} \tag{18}$$

for large τ

For $\lambda=4$, one finds logarithmic corrections to 'diffusive' behaviour:

$$\lim_{N\to\infty}\langle(x_\tau-x_1)^2\rangle\sim\tau\log^{1/2}\tau \tag{19}$$

for large τ.

The result $\nu=2/\lambda$ which differs from the naive Flory estimate $\nu_{\mathrm{F}}=3/(\lambda+2)$ has been checked recently by a careful numerical simulation ([6]) in $d=3$, for $\lambda=2$ or 2.5. In particular, for $\lambda=2$, the presence of logarithmic corrections predicted by (15) is very clear, although the exact power of the logarithm cannot be determined with good precision. On the other hand, this result must break down when λ is large enough. Indeed for purely short range potentials, $(V(x_\tau-x_{\tau'})=\delta(x_\tau-x_{\tau'}))$, the variational approach done by des Cloizeaux [2] leads to $\nu=2/d$ for $2<d<4$, which is a rather poor result compared with the values $\nu_{\mathrm{SR}}(d=2)=\frac{3}{4}$ and $\nu_{\mathrm{SR}}(d=3)\simeq0.586$. It does not agree with the $\varepsilon=4-d$ expansion to leading order and is much worse than the usual Flory result $\nu_{\mathrm{F}}=3/(d+2)$.

In order to check the result $\nu=2/\lambda$ and to establish its range of validity, we have performed a renormalization group calculation for a $\phi^4_{m=0}$ theory with both long range and short range interactions in the ϕ^4 term. The expansion must be made simultaneously in $\varepsilon = 4 - d$ and $\delta = 4 - \lambda$. Transposing very similar calculations by Weinrib and Halperin [7] on a different problem[†], one finds, to first order in ε and δ, the following results: if $\varepsilon < 2\delta$, a 'long range' fixed point of the renormalisation flow exists, and gives $\nu_{\mathrm{LR}} = \frac{1}{2} + \frac{\delta}{8} + \ldots$, while for $\varepsilon > 2\delta$, one finds the standard short range fixed point, with $\nu_{\mathrm{SR}} = \frac{1}{2} + \varepsilon/16 + \ldots$. Let us notice that the value of ν_{LR} is the expansion of $2/\lambda$ for λ close to 4. One may argue that the absence of higher order corrections in δ to $2/\lambda$ in the long range case is related to conservation of 'charge' under renormalisation [8].

To first order in ε, δ, we thus find that the borderline between the two regimes occurs for $\varepsilon = 2\delta$. More generally, this borderline should be given by the equation $\lambda\nu_{\mathrm{SR}} = 2$. This can be understood by a simple scaling argument, treating the long range part of the interaction perturbatively. Upon rescaling the 'time' τ as $b\tau$ and the distances as $b^{\nu_{\mathrm{SR}}}$, one finds that the long range part of the interaction is multiplied by $b^{2-\lambda\nu_{\mathrm{SR}}}$, and hence decays to zero on large length scales if $2 - \lambda\nu_{\mathrm{SR}} < 0$. Note that the exponent ν is thus continuous across this line. We thus find that $\nu = \min(2/\lambda, \nu_{\mathrm{SR}})$ in the region $\lambda > 2$.

The region $\lambda < 2$ is less interesting. For $1 < \lambda < 2$, one must write $x_t = vt + \delta x_t$: the walk is 'stretched' and similar to a straight line. A variational computation can be one to evaluate v and the fluctuations δx_t[‡]. For $\lambda < 1$, one finds that the energy density becomes infinite in the limit of infinite chains. The walk becomes 'super-stretched', since one finds that $\nu = 3/(2+\lambda) > 1$. Each spring has thus a length which diverges with the number of monomers. Note that in this last regime ν is given by the Flory formula.

Figure 1 summarizes our expectations for the different values of ν in the whole plane λ, d. The three methods (renormalization group, variational and numerical) agree with $\nu = 2/\lambda$ in the domain $2 < \lambda < 4$, $\lambda < 2/\nu_{\mathrm{SR}}$, which is probably an exact result.

The reason why the variational method is very reasonable for long range interactions but bad for short range potentials is the following. Let $P(r, \tau)$ be the probability that $|\boldsymbol{x}_{1+r} - \boldsymbol{x}_1| = r$ (in the $N \to \infty$ limit). From scaling, it is clear that $P(r, \tau) = \tau^{-\nu d} f(r/\tau^{\nu})$. For the ususal short range self-avoiding polymer, it is well known (see e.g. [8]) that $f(x)$ goes to zero at small x, as $x^{(\gamma-1)/\nu}$, where γ is the susceptibility exponent. This reflect the difficulty for the chain to 'loop'. In the variational ansatz, however, $f_{\mathrm{var}}(x)$ is a Gaussian which is maximum for small separations! The potential energy is thus very much overestimated in this calculation and in response the chain 'overswells', giving too large a value for ν. For the long range case, on the other hand, the part of $f(x)$ near $x = 0$ is negligible in our overall estimate of the potential energy, and thus the error made is of no importance as far as the exponent ν is concerned.

Returning to the short-range case, it is perhaps interesting to notice that the Flory value for the ν exponent can be recovered by the following heuristic argument: a value of γ greater than 1 can be thought of as an enhancement of the effective space dimensionality, since

$$P(r = a, \tau) \sim \tau^{-\nu d} \tau^{-(\gamma-1)} \sim \tau^{-\nu \hat{d}}$$

where a is some short distance cut-off (the size of a hard core) and $\hat{d} \equiv d + (\gamma - 1)/\nu$. A naive extension of des Cloizeaux's result then leads to $\nu = 2/\hat{d}$ or $\nu = (3-\gamma)/d$,

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[†] One should set the number m of components of the spins and the inter-replica interaction to zero in their calculation.

[‡] Here rotational invariance is broken and one must distinguish between longitudinal and transverse fluctuations.

which is much better than $2/d$. In fact, the choice $\gamma = 2\nu$ (advocated in [8], [9]) leads back to the Flory formula, $\nu = 3/(d+2)$.

More generally, one may study along similar lines the case where the interaction between two monomers τ apart decreases as $\tau^{-\alpha}$. (The above paragraph corresponds to $\alpha = \gamma - 1$.) One finds in this case that

$$\nu = \max\left(\tfrac{1}{2}, \frac{2-\alpha}{d}\right) \tag{20}$$

instead of

$$\nu_F = \max\left(\tfrac{1}{2}, \frac{3-\alpha}{2+d}\right) \tag{21}$$

which would be the result obtained following a Flory type argument.

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