Lagrangian theory for a self-avoiding random chain

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The Lagrangian theory of random chains with excluded volume is used to study $Z_N(\vec{r})$, the number of chains with N links, starting from the origin and arriving at a point $\vec{r}$. Its asymptotic expression $(N \to \infty)$ is $Z_N(r) \simeq N^{\gamma-1-\nu d} F(rN^{-\nu})$, where γ and ν are critical indices. The short- and long-range behaviors of $F(x)$ are calculated in terms of γ and ν. In particular, it is shown that for $x \ll 1$, we have $F(x) \simeq Fx^{\theta}$ with $F = \text{const}$ and $\theta = (\gamma - 1)/\nu$.

I. INTRODUCTION

Recently de Gennes[1] has remarked that the problem of random walks with excluded volume (polymers) in a space of dimension $d = 4 - \epsilon$ is equivalent to a Euclidean field theory defined by a Lagrangian of the form

$$\mathcal{L}(\vec{x}) = \frac{1}{2}\sum_{j=1}^{n}[(\vec{\nabla}\varphi_j)^2 + m_0^2(\varphi_j)^2] + \tfrac{1}{8}g_0\Big(\sum_{j=1}^{n}(\varphi_j)^2\Big)^2, \tag{1.1}$$

where n is the number of components, which in this case must be given the value $n = 0$ by analytic continuation. A weight $W\{\varphi\} = \exp(-\int \mathcal{L}(\vec{x})\, d^d x)$ is associated with this Lagrangian. Green's functions are defined as mean products of fields (with weight W)

$$\mathcal{G}_{j_1 \cdots j_{2q}}(m_0; \vec{r}_1, \ldots, \vec{r}_{2q}) = \langle \varphi_{j_1}(\vec{r}_1) \cdots \varphi_{j_q}(\vec{r}_{2q}) \rangle . \tag{1.2}$$

These quantities can be calculated by expanding $W\{\varphi\}$ with respect to g_0 and each term in the expansion of $\mathcal{G}_{j_1, \ldots, j}(m_0; \vec{r}_1, \ldots, \vec{r}_{2q})$ can be represented by a diagram containing q open lines and a certain number of closed loops (see Fig. 1). Each solid line corresponds to a field index j. Now, we may sum up the loop indices. Thus, we see that a factor n corresponds to each loop in the contribution of the corresponding diagram. In the polymer case, no loop is allowed in the diagrams and this situation corresponds to the case $n = 0$ (field with zero component). Of course, no Lagrangian can be associated with this case but the process has a meaning in perturbation theory.

The connection between the polymer problem and this Lagrangian can be made as follows. First, we remark that the coupling constants g_0 and m_0 have dimensions. Thus, we may introduce a fundamental length l and set

$$g_0 = a\epsilon l^{\epsilon} . \tag{1.3}$$

Here a is an arbitrary pure number. The factor ϵ is introduced for reasons of mathematical convenience, in order to obtain smooth limits when ϵ goes to zero. Similarly, we define the dimensionless constant s by setting

$$s = m_0^2 l^2 . \tag{1.4}$$

Now, consider chains with excluded volume. Let $Z_N(\vec{r})$ be the number of chains made of N links starting from the origin and arriving at $\vec{r}$. The length of a chain is L, and we represent this length by $L = Nl$. For finite N, $Z_N(\vec{r})$ is given by a Boltzmann law, of the form

$$Z_N(\vec{r}) = \sum_{C(\vec{r})} e^{-\beta(U_0 + U_I)}; \tag{1.5}$$

we sum over all configurations of chains starting from the origin and arriving at $\vec{r}$ after N steps. The term U_0 expresses the fact that we are dealing with a chain and U_I describes the interaction, i.e., the fact that the chain is self-avoiding. The factor $\beta = 1/kT$ does not play any role and we may set $\beta = 1$ if we wish.

Passing to the continuous limit, we may define $Z_N(\vec{r})$ by the classical functional integral

$$Z_N(\vec{r}) = \int_{C(\vec{r})} d\omega[\vec{r}(\lambda)] \exp\left[-\frac{1}{4l}\int_0^L d\lambda \Big(\frac{\partial}{\partial\lambda}\vec{r}(\lambda)\Big)^2 - \frac{g_0 l^2}{2}\int_0^L d\lambda \int_0^L d\lambda'\, \delta(\vec{r}(\lambda) - \vec{r}(\lambda'))\right], \tag{1.6}$$

where $C(\vec{r})$ is the set of functions $\vec{r}(\lambda)$, such that $\vec{r}(0) = 0$, $\vec{r}(L) = \vec{r}$, and $L = Nl$. Note that this passage to the continuous limit introduces a divergence but it can be removed by a simple renormalization in perturbation theory. The Fourier transform of $Z_N(\vec{r})$ is by definition

$$\tilde{Z}_N(\vec{k}) = \int d^d r\ e^{i\vec{k}\cdot\vec{r}} Z_N(\vec{r}), \tag{1.7}$$

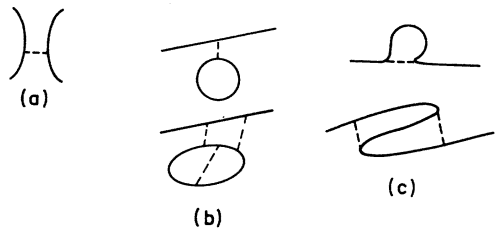

FIG. 1. (a) Interaction vertex. The dashed line indicates the interaction. Each solid line corresponds to a definite component of the field. (b) Diagrams vanishing for $n=0$. (c) Diagrams contributing for $n=0$.

and $Z_N \equiv \tilde{Z}_N(0)$ is the total number of chains starting from the origin.

Following de Gennes[1] and Fisher[2], we introduce an equivalence relation by writing

$$G_U(s,\vec{k}) = l^2 \sum_{N=0}^{\infty} e^{-Ns}\tilde{Z}_N(\vec{k}), \tag{1.8}$$

where the unrenormalized Green's function $G_U(s,\vec{k})$ is the Fourier transform of $\mathcal{G}_{jj}(m_0; 0, \vec{r})$. The equivalence can be established without difficulty by expanding both sides of Eq. (1.8) with respect to g_0 and by comparing term by term.

In order to obtain finite results, a cutoff must be introduced in principle, but in practice, for $\epsilon > 0$, a simple mass renormalization is sufficient (as can be seen by power counting) to ensure the convergence of all the integrals which appear in the expansion. Thus, the Lagrangian theory can be used to calculate interesting physical quantities, and, in particular, our aim is to study the probability

$$P_N(\vec{r}) = Z_N(\vec{r})/Z_N, \tag{1.9}$$

for values of $\vec{r}$, which are either small or large with respect to the mean-square length of $\vec{r}$.

Some years ago, asymptotic properties of $P_N(r)$ were derived by Fisher,[2] and other properties of $P_N(r)$ or $Z_N(r)$ for large and small r have been determined empirically by McKenzie and Moore.[3] My results agree with those of Fisher and McKenzie and Moore. However, the usefulness of the present approach must be emphasized. The reader should realize that until now there did not exist any realistic theory[4] of a chain with excluded volume. Thus, for the first time, the crucial remark of de Gennes and the recent advances made in Lagrangian field theory[5,6] provide the framework of a complete theory of the excluded-volume problem. Thus, all the previous results can be derived by using this method. Some previously assumed properties are now established more rigorously. Finally, a direct application of the theory gives, for the excluded-volume problem, a new relation between the critical indices. These critical indices γ and ν can be defined in terms of the number of walks Z_N and of the mean-square size $\langle r_N^2 \rangle$ by the asymptotic expressions $(N \to \infty)$

$$\begin{aligned} &Z_N \simeq Z N^{\gamma-1}\mu^N, \quad (Z, \mu \text{ constants}), \\ &\langle r_N^2 \rangle \simeq B N^{2\nu}, \quad (B \text{ a constant}). \end{aligned} \tag{1.10}$$

II. LAGRANGIAN FORMALISM

In the critical region $0 < (s - s_c) \ll 1$, the renormalized Green's function[5] has the form

$$G_R(m,k) = m^{-2} f(k/m). \tag{2.1}$$

Renormalization conditions must be chosen: they amount to the condition

$$[f(y)]^{-1} = 1 + y^2 + \cdots. \tag{2.2}$$

The renormalization constants of the fields φ and φ^2 can be defined by

$$z_1(s) \equiv \varphi/\varphi_R, \quad z_2(s) = m^2/(m_0^2 - m_{0c}^2), \tag{2.3}$$

where m_{0c} is the unrenormalized critical mass, $\varphi(x)$ is the unrenormalized field, and $\varphi_R(\vec{x})$ the renormalized field. Accordingly, we have

$$G_U(s,k) = z_1^2(s) G_R(m,k). \tag{2.4}$$

The Lagrangian theory[6] says that the renormalization constants become infinite at the critical point (i.e., when $s \to s_c$) as a power of $s - s_c$. Thus, we may write

$$\begin{aligned} &z_1(s) = b(s)(s - s_c)^{(2\nu-\gamma)/2}, \\ &z_2(s) = c(s)(s - s_c)^{2\nu-1}, \end{aligned} \tag{2.5}$$

where $b(s)$ and $c(s)$ have finite limits b and c (depending on ϵ) when $s \to s_c$. The critical indices γ and ν are defined as usual. Using the preceding expressions and Eq. (2.3) we find

$$ml = c^{-1/2}(s - s_c)^{\nu}, \tag{2.6}$$

and from Eqs. (2.4) and (2.1), we deduce

$$G_U(s,\vec{k}) = b^2 l^2 (s - s_c)^{-\gamma} f(c^{-1/2} k l (s - s_c)^{-\nu}). \tag{2.7}$$

In four dimensions, the behavior of the chain is Brownian and therefore $m \to m_0$ when $\epsilon \to 0$. Accordingly, it is possible to show that for $0 < \epsilon \ll 1$

$$c \simeq (a/2\pi^2)^{1/4} \tag{2.8}$$

[see Eq. (1.3)]. We note that this limit exists because a factor ϵ has been introduced for reasons of convenience in the right-hand side of Eq. (1.3). Thus logarithmic singularities are avoided.

For other values of ϵ, we deduce from Eqs. (1.6)–(1.8) the following expressions:

$$\begin{aligned} &Z_N \equiv \tilde{Z}_N(0) = Z N^{\gamma-1} e^{Ns_c}, \\ &P_N(r) = l^{-d} N^{-\nu d} F(r l^{-1} N^{-\nu}). \end{aligned} \tag{2.9}$$

The normalization conditions are

$$\int d^d x\, F(x) = 1, \quad \int d^d x\, x^2 F(x) = \frac{2c^{-1} d\,(\gamma - 1)!}{(\gamma + 2\nu - 1)!}, \tag{2.10}$$

where the indices have the usual meaning. The first condition expresses the fact that $P_N(r)$ is a probability. The second condition is also an exact relation and is a direct consequence of the normalization equation (2.2) (the coefficient of y^2 has been chosen equal to 1). It is obtained by expanding Eq. (1.6) to first order with respect to k^2.

III. BEHAVIOR OF $P_N(r)$ FOR $r \ll N^\nu l$

In Lagrangian theory, the derivatives of the energy with respect to m_0^2 (i.e., with respect to the temperature T in most applications) can be written

$$l^{-2j} \frac{\partial^j E}{(\partial m_0^2)^j} \equiv \int d^d k \frac{\partial^j}{(\partial s)^j} G_U(s, k) \propto l^{-2d} (s - s_c)^{1-\alpha-j} \tag{3.1}$$

and such a relation defines the index α. For $j = 0$, the equation is meaningless because the integral diverges. Thus the relation

$$\langle \varphi^2(0) \rangle = \int d^d k\, G_U(s, k) \tag{3.2}$$

is only formal but the composite field $\varphi^2(\vec{x})$ acquires a meaning in more complicated convergent Green's functions. However, the index α can be derived by dimensional analysis of formal expressions like (3.2). Thus using Eq. (2.2), we may write

$$\langle \varphi_R^2(0) \rangle = \int d^d k\, G_R(m, k) \propto m^{d-2} \propto l^{d-2} (s - s_c)^{\nu(d-2)} . \tag{3.3}$$

But, by definition

$$\langle \varphi^2(0) \rangle = Z_2(s) \langle \varphi_R^2(0) \rangle , \tag{3.4}$$

since $Z_2(s)$ is the renormalization constant of the composite field $\varphi^2(\vec{x})$. Thus, using Eq. (2.3), we find the formal result

$$\langle \varphi^2(0) \rangle \equiv \int d^d k\, G(s, k) \propto l^{d-2} (s - s_c)^{\nu d - 1} . \tag{3.5}$$

By comparing Eqs. (3.1) and (3.5), we determine α, which satisfies the usual scaling relation[7]

$$\alpha = 2 - \nu d . \tag{3.6}$$

Equations (1.8) and (3.1) give the order of magnitude of the number of chains returning to the origin

$$Z_N(0) \propto l^{-d} N^{\alpha - 2} e^{N s_c} . \tag{3.7}$$

On the other hand, we may try to calculate $Z_N(0)$ by writing

$$Z_N(r) = Z_N P_N(r) , \tag{3.8}$$

and by replacing Z_N and $P_N(r)$ by their asymptotic expressions (scaling laws) Eq. (2.9). The result is

$$Z_N(r) = Z N^{\gamma - \nu d - 1} e^{N s_c} F(r l^{-1} N^{-\nu}) . \tag{3.9}$$

In general, $\gamma - 1 > 0$ and $\alpha = 2 - \nu d$; therefore in order to avoid inconsistencies between Eqs. (3.3) and (3.5), we have to assume that

$$F(0) = 0 . \tag{3.10}$$

This interesting result is in agreement with the computer calculations of Renardy[8] and McKenzie.[9] It is a direct and rather subtle consequence of the renormalization theory.[10]

Let us now study the behavior of $F(x)$ for small values of x. For $0 < x \ll 1$, we write

$$F(x) \approx F_0 x^\theta , \tag{3.11}$$

and we may express θ in terms of α as was shown by McKenzie and Moore.[3] Indeed, since Eq. (3.9) is only valid for $1 \ll r l^{-1} \ll N^\nu$, there is a cutoff at $r = l$ and we guess that

$$Z_N(0) \simeq Z_N(l) = F_0 Z N^{\gamma - \nu d - \nu\theta - 1} . \tag{3.12}$$

Comparing with Eq. (3.7), we find

$$\theta = (\gamma + \nu d - \alpha + 1)/\nu , \tag{3.13}$$

a relation previously obtained by McKenzie. Finally, using Eq. (3.6), we find

$$\theta = (\gamma - 1)/\nu , \tag{3.14}$$

which is our main result. We may also write

$$\theta = d_{a2} - 2d_{a1} , \tag{3.15}$$

where d_{a2} and d_{a1} are the anomalous dimensions of the respective φ^2 and φ ($d_{a2} = d - 1/\nu$, $2d_{a1} = d - \gamma/\nu$, the canonical dimensions being $d_{c2} = 2d_{c1} = d - 2$).

The value of θ in Eq. (3.14) has been derived in a heuristic way, but it is possible to obtain it directly by more sophisticated methods. The behavior of $F(x)$ for small x is related to the asymptotic behavior[11] of $f(y)$ for large y,

$$[f(y)]^{-1} \approx y^{\gamma/\nu} [A + B y^{-1/\nu} + C y^{-(d-1/\nu)}] . \tag{3.16}$$

By inverting Eq. (1.7), we can express the difference $F(x) - F(0)$ in terms of $(\partial/\partial s) G(s, k)$ and therefore in terms of $f(y)$. Thus, using Eq. (3.16), we can confirm the results given in Eqs. (3.11), and (3.14) and find explicitly that

$$F_0 = -\frac{A^{-2} C}{(4\pi)^{(d-1)/2}} \frac{(\gamma - 1)!(-\theta - 1)!}{(-\nu d)!\,(-\frac{1}{2}\theta - \frac{1}{2})(\frac{1}{2}\theta + \frac{1}{2}d - 1)!} \tag{3.17}$$

Expansions of γ, ν, A, B, and C with respect to d have been calculated by several authors[11] and for $0<\epsilon\ll 1$ we have

$$A\simeq 1,\quad B\simeq \tfrac{3}{2},\quad C=-\tfrac{1}{2},$$

$$(\gamma-1)/\nu=\tfrac{1}{4}\epsilon+\tfrac{9}{128}\epsilon^2,\quad F_0=(16\pi^2)^{-1}\delta. \tag{3.18}$$

IV. BEHAVIOR OF $P_N(r)$ FOR $r\gg N^\nu l$

If the Lagrangian theory is a genuine field theory, the Green's function $G_R(m,k)$ has a pole at $k^2=-M^2=-h^2m^2$ ($h=$const) and a cut starting at $k^2=-9M^2$. Thus, we may assume that the singularities of $f(y)$ nearest to the real axis are simple poles at $y=\pm ih$, where h can be calculated by perturbation theory. The behavior of $Z_N(\vec{r})$ for $r\gg lN^\nu$ is directly related to the existence of these poles. Thus, by taking the Fourier transform $\mathcal{G}_U(s,\vec{r})$ of $G_U(s,\vec{k})$, we find for large r

$$\mathcal{G}_U(s,r)=G(s-s_c)^{-\gamma+\nu(d+1)/2}(rl^{-1})^{1-d/2}\times\exp[-hc^{1/2}rl^{-1}(s-s_c)^\nu], \tag{4.1}$$

where the right-hand side is the dominant contribution of the poles. From the Fourier transform of Eq. (1.7)

$$\mathcal{G}_U(s,r)=l^2\sum_0^\infty e^{-Ns}Z_N(x), \tag{4.2}$$

we obtain, by means of an inverse Laplace transformation, in accordance with Fisher's predictions,[2] the expression

$$F(x)\simeq F_1x^\sigma\exp[-(Gx)^\tau], \tag{4.3}$$

where

$$\tau=\frac{1}{1-\nu},\quad \sigma=\frac{1-\gamma+\nu d-\frac{1}{2}d}{1-\nu},\qquad G=hc^{1/2}\nu^{-1}\left(\frac{1-\nu}{\nu}\right)^{2-\nu}, \tag{4.4}$$

in agreement with the results which have been derived by McKenzie and Moore[3] from slightly different assumptions.

For $0<\epsilon<1$, we have

$$h=1,\quad F_1=(4\pi)^{-2}c^2. \tag{4.5}$$

V. CONCLUSION

The present theory explains all the known characteristics of the behavior of a single chain with excluded volume. One of them is the fact, established by computer calculations, that the asymptotic form of the probability $P_N(r)$ vanishes at the origin. To our knowledge, the present theory is the only one which predicts this subtle result. Nevertheless, the predictions of the theory cannot be compared in detail with all the results obtained by computer calculations, for several reasons. For instance, the values of γ and ν are known only for small values of ϵ. Apparently the expansions obtained in ϵ do not converge[6] and they may be only asymptotic. In particular, the estimates are better for $\epsilon=1$ than for $\epsilon=2$.

On the other hand, the best results obtained by computer experiments correspond to the two-dimensional case ($\epsilon=2$). For short chains, we have exact results but different treatments of these may lead to rather different estimates for γ and ν. For long chains, the Monte Carlo method gives more precise results but they do not strictly apply to the random-chain problem: the chains are the same, but the Monte Carlo statistical weight is different for each chain.[8] However, we may hope for some progress in testing the theory In particular, the index θ of Sec. III can be measured directly and this gives a relation between γ and ν. In experiments on real polymers, ν can be measured but until now there was no way of measuring γ. Now, we see that in principle θ can be measured and experimental values of γ deduced from the relation $\gamma=1+\nu\theta$.

On the other hand, the present approach is not completely satisfactory because we need a theory with a larger range of validity in ϵ, and a good starting point might be the group-renormalization method of Wilson.[12]

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