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The statistical mechanics of polymers with excluded volume

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Abstract. The probability distribution of the configurations of a polymer consisting of freely hinged links of length l and excluded volume v is studied. It is shown that the interaction of the polymer with itself can be represented by considering the polymer under the influence of a self-consistent field which reduces the problem to an equation like the Hartree equation for an atom. This can be solved asymptotically, giving the probability of the nth link of the polymer passing through the point r to be

$$\mathcal{N}(L)\exp\left[-27\left\{r-\left(\frac{5}{3}\right)^{3/5}\left(\frac{v}{3\pi l}\right)^{1/5}L^{3/5}\right\}^2\frac{1}{20Ll}\right]$$

where $L = nl$ is the length along the polymer and $\mathcal{N}(L)$ the normalization. Thus the mean square of r, $\langle r^2\rangle$, is

$$\left(\frac{5}{3}\right)^{6/5}\left(\frac{v}{3\pi l}\right)^{2/5}L^{6/5}.$$

The theory is extended to polymers of finite length, to the excluded random walk problem and to n dimensions.

1. Introduction

The effect of finite thickness on the configurational statistical mechanics of polymers is an important problem in polymer science and biophysics, since it has long been believed that the probability of finding the nth link at r in such a polymer (assumed for the present to consist of freely hinged links of length l) will not be the random walk distribution

$$\left(\frac{8}{3}\pi nl^2\right)^{-3/2}\exp\left(-\frac{3r^2}{4nl^2}\right)$$

but a broader distribution. This will have the effect of making the mean of r^2 greater than the Einstein value nl^2, and important physical results stem from the failure of the Einstein law. This problem has been extensively studied in the model in which the links of the chain are restricted to joining neighbouring points of a perfect lattice. Though it was for some time believed that the asymptotic form of $\langle r^2\rangle$ would depend upon the type of lattice studied, recent work by Domb (1963) rules this out. Domb has done calculations on finite chains and finds that all lattices give similar behaviour. His results tend towards the relation $\langle r^2\rangle \sim n^{6/5}$ and numerical experiments by Wall and Erpenbeck (1959) agree with this, giving $\langle r^2\rangle \sim n^{\gamma}$ where $0{\cdot}22 > \gamma > 0{\cdot}18$. Phenomenological arguments implying this law are also given by Flory (1953).

This paper will give a general derivation of this law and the probability distribution from which it stems. The basic fact which the analysis relies on is as follows. Consider

the probability of finding the polymer at the point $\mathbf{r}$ knowing only that it starts at the origin. Use the Gaussian distribution for a start and consider the polymer of infinite length. Since the probability that the nth link lands at $\mathbf{r}$ is

$$p_{\mathrm{E}} = \left(\frac{8}{3}\pi Ll\right)^{-3/2} \exp\left(-\frac{3r^2}{4Ll}\right) \tag{1.1}$$

where $L = nl$ is the length along the chain, the probability required is

$$\tilde{p}_{\mathrm{E}}(r) = \int_0^\infty \left(\frac{8}{3}\pi Ll\right)^{-3/2} \exp\left(-\frac{3r^2}{4Ll}\right) dL \tag{1.2}$$

$$= \frac{3}{4\pi rl}. \tag{1.3}$$

Compare this with a rigid polymer pointing in an arbitrary direction. Since the surface of a sphere is $4\pi r^2$ one has

$$\tilde{p}_{\mathrm{rigid}}(r) = \frac{1}{4\pi r^2}. \tag{1.4}$$

One can expect that a real polymer with excluded volume will have a law lying between these extremes, and it is found that the realistic answer tends to

$$\tilde{p}(r) = \frac{1}{4}\left(\frac{3l}{\pi^2 v}\right)^{1/3} \frac{1}{r^{4/3}} \tag{1.5}$$

where v is the excluded volume, defined by

$$v = \int_0^\infty (1 - \mathrm{e}^{-U/\kappa T}) d^3r \tag{1.6}$$

where U is the potential between two segments separated by a distance r. For a discussion of the excluded volume see Flory (1953) and Volkenstein (1963).

All these functions decrease quite fast, but it will turn out that $\tilde{p}$ will play the role of a potential in subsequent calculations, and it will be recalled that there is a great difference between potentials of $1/r$ and $1/r^2$, the former being rather pathological in spite of its familiarity, whilst the latter is rather harmless. The realistic function $r^{-4/3}$ needs to be treated with care but is not as bad as r^{-1}. Since this probability is decreasing fast the following physical picture is proposed. The polymer starts at the origin and the point L moves slowly outwards as L increases, so that an 'average view' from far outside gives a 'polymer density' of $\tilde{p}(r)$. Think of this as established, and now again move out along the polymer from the origin. The current point at L will be deflected from the random walk path by encounters with parts of the polymer having an L' quite different from the current point, and one can think of this current point being deflected by the 'polymer density'. So one may argue that the motion will be like a random walk in the presence of a potential, and this potential will have to be calculated from the complete solution itself. Here is a strong similarity to Hartree's treatment of the atomic problem. Hartree replaced the many-electron problem by the problem of solving the motion of one electron in a certain self-consistent field. From this solution Hartree then went back and calculated the self-consistent field itself. That problem is impossible analytically, but it turns out that in the polymer problem the asymptotic forms can be obtained, though the complete solution is a problem comparable with the atomic problem.

This self-consistent field approximation will be derived in the next section by a straightforward argument; that it is rigorously correct is shown in the appendix. The equation will be solved in § 3 and some generalizations offered in § 4.

2. The self-consistent approximation

Consider briefly the Einstein case. One may argue that the entire problem is described by the probability that the point, a distance L from the origin along the polymer, is at the point $\mathbf{r}$ in space, $p_{\mathrm{E}}(r, L)$. Starting at $\mathbf{r}$, L, consider the probability of finding the polymer at $\mathbf{r}$, $L+l$. This will stem from adding the contributions from all the points $\mathbf{r}+\delta\mathbf{r}$, L, where clearly $\delta\mathbf{r}$ is $l\mathbf{i}$, $\mathbf{i}$ being a unit vector. Thus

$$p_{\mathrm{E}}(\mathbf{r}, L+l) = \frac{1}{4\pi}\int p_{\mathrm{E}}(\mathbf{r}+l\mathbf{i}, L)d\mathbf{i} \tag{2.1}$$

and expanding

$$p_{\mathrm{E}}(\mathbf{r}, L)+l\frac{\partial p_{\mathrm{E}}}{\partial L} = p_{\mathrm{E}}(\mathbf{r}, L)+l^2\nabla^2 p_{\mathrm{E}}\left(\int \tfrac{1}{3}\mathbf{i}^2\, d\mathbf{i}\right) \tag{2.2}$$

or

$$\frac{\partial p_{\mathrm{E}}}{\partial L} = \tfrac{1}{6}l\nabla^2 p_{\mathrm{E}}. \tag{2.3}$$

This is, of course, a completely standard problem, and has the solution (1.1). This has the property of a Markov process, that one can always break up the interval $(\mathbf{o}, \mathbf{r})$, $(0, L)$ in as many places as one likes:

$$(\mathbf{o}, \mathbf{R}_1)(0, L_1),\ (\mathbf{R}_1\mathbf{R}_2)(L_1L_2), \ldots (\mathbf{R}_n\mathbf{r})(L_nL)\ (0 < L_1 < L_2 \ldots < L_n < L)$$

and write

$$p_{\mathrm{E}}(\mathbf{r}, \mathbf{o}; L, 0) = \int p_{\mathrm{E}}(\mathbf{r}, \mathbf{R}_n; L, L_n)p_{\mathrm{E}}(\mathbf{R}_n, \mathbf{R}_{n-1}; L_n, L_{n-1})\ldots$$

$$\ldots p_{\mathrm{E}}(\mathbf{r}_1, 0; L_1, 0)\, d^3R_1\, d^3R_2 \ldots d^3R_n. \tag{2.4}$$

If one takes the ends of all the links of the chain as the R_i, one can write down the probability of the entire configuration

$$P_{\mathrm{E}}(\mathbf{r}, \mathbf{R}_n, \mathbf{R}_{n-1} \ldots, 0) = \Pi p_{\mathrm{E}}(\mathbf{R}_i, l) \tag{2.5}$$

$$= P_{\mathrm{E}}([R])\ \text{say}. \tag{2.6}$$

(The L_i labels now need not appear since $L_i - L_{i+1} = l$.) Now consider the effect of an interaction potential V between points of the chain (V is Ul^{-2} of 1·6) labelled as $R(L)$. It will have the effect of multiplying P_{E}, which expresses just the length of the links, by a Boltzmann factor which for an infinite chain will be

$$\exp\left[-\frac{1}{2\kappa T}\int_0^\infty \int_0^\infty V\{\mathbf{R}(L')-\mathbf{R}(L'')\}\, dL'\, dL''\right]$$

i.e.

$$P^{(\infty)}([R]) = CP_{\mathrm{E}}{}^{\infty}([R])\exp\left[-\frac{1}{2\kappa T}\int_0^\infty \int_0^\infty V\{\mathbf{R}(L')-\mathbf{R}(L'')\}\, dL'\, dL''\right]. \tag{2.7}$$

The constant C allows for the change in normalization caused by the Boltzmann factor.

This factor will include the case of hard rods of radius a, but in the following analysis V will be considered soft and the appropriate generalization made in due course. Clearly $P([R])$ cannot be broken up as was P_E in (2.5). But let us now make the self-consistent field approximation and argue that one may replace the configuration $R(L'')$ by the probability distribution $p(\mathbf{r}, L'')$, i.e. let us write

$$\int_0^\infty \int_0^\infty V\{\mathbf{R}(L') - \mathbf{R}(L'')\}\, dL'\, dL'' \simeq \int\int_0^\infty dL' V\{\mathbf{R}(L') - \mathbf{s}\} \int_0^\infty p(\mathbf{s}, L'')\, dL''\, d^3s \tag{2.8}$$

where p is to be determined. It is now possible to break up P into a Markov chain, for writing

$$W\{R(L)\} = \frac{1}{2\kappa T} \int_0^\infty dL' \int d^3s V\{R(L) - \mathbf{s}\} p(\mathbf{s}, L') \tag{2.9}$$

one can split

$$\int_0^\infty W\{R(L')\}\, dL' = \int_0^L W\{R(L')\}\, dL' + \int_L^\infty W\{R(L')\}\, dL'. \tag{2.10}$$

Hence it follows that if P_1 is the probability of finding a configuration in the presence of the potential W instead of V, the approximation (2.8) gives

$$P([R]) = \int P_1([R]; \mathbf{r}, L) P_1([R]; \mathbf{r}, L; \mathbf{r}_\infty, L_\infty)\, d^3r C(L) \tag{2.11}$$

where $P_1([R], \mathbf{r}, L)$ is the probability of finding a chain $[R]$ starting at $\mathbf{o}$ length 0, ending at $\mathbf{r}$ length L, and $P_1([R]; \mathbf{r}, L; \mathbf{r}_\infty, L_\infty)$ is the probability of finding a chain $[R]$ starting at $\mathbf{r}$ length L and ending at $\mathbf{r}_\infty$, L_∞, and $C(L)$ is inserted because again normalization will be required. Having made the approximation one can split up P_1 into a set of p_1, just as in (2.4):

$$P_1([R], r, L) = p_1(\mathbf{r}, R_n; L, L_n) p_1(\mathbf{R}_n \mathbf{R}_{n-1}, L_n L_{n-1}) \tag{2.12}$$

$$p_1(\mathbf{r}, L) = C(L) \int P_1 \prod_1^n d^3R_i \tag{2.13}$$

and now the p_1 satisfy a differential equation. For consider again the derivation (2.1, 2.3). When one allows a change in the weight factor between L and $L+l$ of

$$\exp\{-lW(r)\} \simeq 1 - lW(r)$$

and a change of normalization, one finds

$$p_1(\mathbf{r}, L+l) = p_1(\mathbf{r}, L) + l\frac{\partial p_1}{\partial L} + lW(r)p_1(r) + \frac{l}{C(L)}\frac{\partial C(L)}{\partial L} p_1. \tag{2.14}$$

As before, this must equal $p_1 - \frac{1}{2}l^2 \nabla^2 p_1$, so that

$$\left\{\frac{\partial}{\partial L} - \frac{l}{3}\nabla^2 + W(r) - \frac{C'(L)}{C(L)}\right\} p_1(\mathbf{r}, L) = 0. \tag{2.15}$$

Returning to the definition of W, since V is short range one may write

$$W = \frac{1}{2\kappa T}\int_0^\infty p(\mathbf{r}, L)\, dL \int d^3s V(s). \tag{2.16}$$

One may recognize in $(1/2\kappa T)\int V(s)d^3s$ the virial coefficient in the soft potential approximation. It is well known that for hard potentials one should replace this by the excluded volume

$$v = \int \left[1 - \exp\left\{-\frac{U(r)}{\kappa T}\right\}\right] d^3r \tag{2.17}$$

$$\left(\text{where } U = l^2 V \quad \text{so that} \quad \sum_{n,m} U(\mathbf{r}_n - \mathbf{r}_m) \to \int\int dL\, dL' V\{\mathbf{R}(L) - \mathbf{R}(L')\}\right).$$

This replacement will be assumed here, further details being given by Volkenstein (1963). Thus one may write $v\tilde{p}(r)l^{-2}$ for W, and also one may define $v\hat{p}(L)l^{-2} = C'/C$, so that finally

$$\left[\frac{\partial}{\partial L} - \frac{l}{3}\nabla^2 + \frac{v}{l^2}\{\tilde{p}(r) - \hat{p}(L)\}\right] p_1(r, L) = 0. \tag{2.18}$$

This is the basic self-consistent field equation which will be solved in the next section. It will be assumed from now on that v is positive; the solution for v negative is quite different and it is hoped to discuss this in another paper.

3. The solution

The term $\hat{p}(L)$ can be removed from the differential equation by extracting a term $\exp(\int_0^L v\hat{p}l^{-2}dL')$, and this should be done, leaving the question of normalization right to the end. Strictly speaking, (2.18) should have a source on the right, since as L tends to zero p_1 and p should tend to $\delta(\mathbf{r})$. One can expect a solution of the type $p_1 = Q(r, L)/r$, where

$$\left\{\frac{\partial}{\partial L} - \frac{l}{3}\frac{\partial^2}{\partial r^2} + \frac{v}{l^2}\tilde{p}(r)\right\} Q = 0. \tag{3.1}$$

Let us introduce the Fourier transform

$$q(r, E) = \frac{1}{2\pi}\int e^{iEL} Q(r, L)\, dL \tag{3.2}$$

and write

$$q(r, E) = \exp\{\phi(r, E)\}.$$

This gives

$$\left\{iE + \frac{v}{l^2}\tilde{p} - \frac{l}{3}\left(\frac{\partial\phi}{\partial r}\right)^2 - \frac{l}{3}\left(\frac{\partial^2\phi}{\partial r^2}\right)\right\} = 0. \tag{3.3}$$

This will be solved in the WBKJ approximation (Jeffreys and Jeffreys 1961) which expands about the solution

$$\phi \simeq \int_0^r \left(\frac{3}{l}\right)^{1/2}\left(iE + \frac{v}{l^2}\tilde{p}\right)^{1/2} ds. \tag{3.4}$$

It can be verified from the solution which will be produced that the $\partial^2\phi/\partial r^2$ term is

negligible in the asymptotic region. Moreover, since p_1 is in fact a Green function it can always be written in terms of the eigenfunctions of the differential equation, which will exist in pairs

$$\psi_n(r)\exp(E_nL),\ \psi_n{}^+(r)\exp(E_nL)$$

$$Q = \sum_n \psi_n{}^+(r)\psi_n(0)\exp(-E_nL). \tag{3.5}$$

As L tends to infinity this sum will be dominated by $E_n \sim 0$, which suggests that a valid further approximation will be to expand ϕ in E:

$$\phi \simeq \left(\frac{3}{l}\right)^{1/2}\int_0^r \left(\frac{v\tilde{p}}{l^2}\right)^{1/2} + iE\left(\frac{3}{l}\right)^{1/2}\frac{1}{2}\int_0^r (v\tilde{p}l^{-2})^{-1/2}\,ds$$
$$-\frac{E^2}{8}\left(\frac{3}{l}\right)^{1/2}\int_0^r (v\tilde{p}l^{-2})^{-3/2}\,ds. \tag{3.6}$$

At this point one should recall that p differs from p_1 by the function $p_1(\mathbf{r}, \mathbf{r}_\infty; L, L_\infty)$. Clearly the only survivor in the sum (3.5) will be $E_n = 0$, and within multiplicative functions of L to the order of (3.6) this is just

$$\exp\left\{\left(\frac{3}{l}\right)^{1/2}\int_r^{r_\infty} (v\tilde{p}l^{-2})^{1/2}\,ds\right\}. \tag{3.7}$$

Thus

$$p(r, L) = \int \frac{f(L)}{r}\exp\left\{\int_0^{r_\infty}\left(\frac{3}{l}\right)^{1/2}(v\tilde{p}l^{-2})^{-1/2}\,ds - iEL + iE\left(\frac{3}{l}\right)^{1/2}\frac{1}{2}\int_0^r (v\tilde{p}l^{-2})^{-1/2}\,ds\right.$$
$$\left.-\frac{E^2}{8}\left(\frac{3}{l}\right)^{1/2}\int_0^r (v\tilde{p}l^{-2})^{-3/2}\,ds\right\}dE \tag{3.8}$$

where $f(L)$ is the normalization.

This now yields, putting in normalization, and ignoring factors like r^{-1} which are effectively constant in the asymptotic region relative to the distribution below,

$$p(r, L) = \exp\left[-\frac{\{L - A(r)\}^2}{B(r)}\right] \Big/ \int \exp\left[-\frac{\{L - A(s)\}^2}{B(s)}\right] d^3s \tag{3.9}$$

where

$$A = \left(\frac{3}{l}\right)^{1/2}\frac{1}{2}\int_0^r (v\tilde{p}l^{-2})^{-1/2}\,ds \tag{3.10}$$

and

$$B = \frac{1}{2}\left(\frac{3}{l}\right)^{1/2}\int_0^r (v\tilde{p}l^{-2})^{-3/2}\,ds. \tag{3.11}$$

Now it will be argued that this distribution is completely dominated by the region

$$L = A(r) \tag{3.12}$$

$$r = A^{-1}(L) \tag{3.13}$$

so that effectively, for the purpose of calculating $\tilde{p}$,

$$p = \frac{1}{4\pi r^2}\delta\{r - A^{-1}(L)\} \tag{3.14}$$

and

$$\tilde{p} = \int \frac{dL}{4\pi r^2} \delta\{r - A^{-1}(L)\}. \tag{3.15}$$

Putting

$$\begin{aligned} A^{-1}(L) &= s, \\ L = A(s), \qquad dL &= dsA' \end{aligned} \tag{3.16}$$

then

$$\tilde{p} = \frac{A'(r)}{4\pi r^2}. \tag{3.17}$$

Hence

$$4\pi r^2 \tilde{p} = \left(\frac{3}{l}\right)^{1/2} \left(\frac{v}{l^2}\right)^{-1/2} \frac{1}{2} \tilde{p}^{-1/2} \tag{3.18}$$

or

$$\tilde{p} = \left(\frac{\sqrt{3}}{8\pi} \frac{l^{1/2}}{v^{1/2}}\right)^{2/3} \frac{1}{r^{4/3}} \tag{3.19}$$

so that

$$L = A = \frac{3}{5} \left(\frac{3\pi l}{v}\right)^{1/3} r^{5/3} \tag{3.20}$$

$$r = \left(\frac{5}{3}\right)^{3/5} \left(\frac{v}{3\pi l}\right)^{1/5} L^{3/5} \tag{3.21}$$

and

$$B = \frac{4\pi}{3} r^3 l^2 v^{-1}. \tag{3.22}$$

It is convenient to rewrite this as a distribution around r, i.e. to put

$$r = \left(\frac{5}{3}\right)^{3/5} \left(\frac{v}{3\pi l}\right)^{1/5} L^{3/5} + r' \tag{3.23}$$

when in terms of r', to the same accuracy as has been used so far,

$$p(r, L) = \frac{\exp(-27r'^2/20lL)}{\int d^3s \exp(-27s'^2/20lL)}. \tag{3.24}$$

This gives

$$\langle r^2 \rangle = \left(\frac{5}{3}\right)^{6/5} \left(\frac{v}{3\pi L}\right)^{2/5} L^{6/5} + \alpha v^{1/5} l^{3/10} L^{11/10} + \beta L l + \ldots \tag{3.25}$$

where α, β are coefficients which are not accurate since corrections of the same order come from the approximations in (3.4), (3.6), (3.19); and the transition from (3.9) to (3.24) also gives corrections of the same order. The serious expansion of the whole method is in fact the parameter $L^{-1/10} v^{-1/5} l^{7/10}$ and the condition for the present analysis to be valid is that

$$L^{-1/10} v^{-1/5} l^{7/10} \ll 1$$

or

$$L \gg l^7/v^2.$$

To put in another way, for chains whose total length is less than $O(l^7/v^2)$, the Einstein law $\langle r^2 \rangle = Ll$ should be valid, but for chains longer than $O(l^7/v^2)$ the law (3.25) should hold. The present numerical data on lattices are insufficient to comment upon this criterion.

4. Some generalizations

The discussion above concerns the probability that a polymer of infinite length starting at the origin will pass through the point **r**, at length L. One obvious generalization is to consider a polymer of finite length L_1. This leads to a straightforward change, replacing $\tilde{p}(r)$ by $\tilde{p}(r, L_1)$ where

$$\tilde{p}^{(1)}(r, L_1) = \int_0^{L_1} p(r, L')\, dL' \tag{4.1}$$

and

$$\hat{p}^{(1)}(L, L_1) = \int p(r, L)\tilde{p}^{(1)}(r, L_1)\, d^3r. \tag{4.2}$$

Clearly

$$\tilde{p}^{(1)}(r, \infty) = \tilde{p}(r)$$

and

$$\hat{p}^{(1)}(L, \infty) = \hat{p}(L). \tag{4.3}$$

As functions of r and L respectively, $\tilde{p}^{(1)}$ and $\hat{p}^{(1)}$ are more complicated than $\tilde{p}$ and $\hat{p}$ and a solution has not been attempted, though it would be a comparatively easy matter to give an expansion of $\tilde{p}^{(1)}$, $\hat{p}^{(1)}$ in terms of ${L_1}^{-1}$, and, since it has been argued that p is effectively a δ function anyway, this should converge rapidly.

Another obvious generalization is to the random walk with excluded volume. This problem is equivalent to the polymer at **r**, L only seeing that part of the polymer of length less than L. This is equivalent to replacing $\tilde{p}$, $\hat{p}$ by $\tilde{p}^{(2)}$, $\hat{p}^{(2)}$ where

$$\tilde{p}^{(2)}(r, L) = \int_0^{L} p(r, L')\, dL' \tag{4.4}$$

$$\hat{p}^{(2)}(L) = \int_0^{L} \tilde{p}^{(2)}(r, L)p(r, L)\, d^3r. \tag{4.5}$$

The integro-differential equation now becomes much more difficult, the only obvious comment being that as L tends to infinity $\tilde{p}^{(2)}$, $\hat{p}^{(2)}$ will tend to $\tilde{p}$ and $\hat{p}$.

5. Conclusion

The self-consistent field approach has been shown to give the law $\langle r^2 \rangle \sim L^{6/5}$. The number of dimensions in which the problem resides is essential to this answer. The value of $\tilde{p}_E$ comes out to be r^{-1} in three dimensions, r^{-2} in four dimensions, and, in general, r^{2-n} in n dimensions ($n \geqslant 3$). In two dimensions $\tilde{p}_E$ does not exist. Now one can treat r^{-2}, r^{-3} etc. by perturbation theory. It follows that there is only a coefficient change in the Einstein law $\langle r^2 \rangle \propto L$ in four dimensions, and not even that in five and higher. In two dimensions, although $\tilde{p}_E$ does not exist, one may still calculate the self-consistent field and $\tilde{p}$ becomes $r^{-2/3}$, the final law being $\langle r^2 \rangle \sim L^{3/2}$. In one dimension,

obviously $\langle r^2 \rangle \sim L^2$ when there is volume exclusion, so for

$$n \leqslant 3, \qquad \langle r^2 \rangle \sim L^{6/(n+2)}$$

for

$$n > 3, \qquad \langle r^2 \rangle \sim L. \tag{5.1}$$

It is a property of the self-consistent field for atoms that, although the first approximation is straightforward though involving heavy computing, the higher approximations are virtually impossible. The author suspects the same situation here. It should be possible to evaluate the full self-consistent field of (2.19) numerically, but to improve (2.19) is probably very hard.

Another interesting and indeed much more drastic change from the Einstein law appears when v is negative, for the possibility then arises that the polymer can collapse under suitable circumstances. It is hoped to discuss this in detail in a subsequent publication.

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Appendix

A formal assessment of the problem

In this section the chain will be taken as continuous. The problem is to evaluate

$$p(r, L) = \mathcal{N} \int \exp\Big[-\frac{4l}{3} \int_0^\infty \Big(\frac{\partial R}{\partial L}\Big)^2 - \frac{1}{2\kappa T} \int_0^\infty \int_0^\infty V\{R(L_1) - R(L_2)\}\, dL_1\, dL_2 \Big]\, d(\text{path}) \tag{A1}$$

taken over all paths which go through $R(0) = 0$ and $R(L) = r$. (These path integrals are discussed, for example, by Gel'fand and Yaglom (1960) as are the χ integrals below.) The functional integral can be parameterized by writing

$$\exp\Big[-\frac{1}{2\kappa T} \int_0^\infty \int_0^\infty V\{R(L_1) - R(L_2)\}\, dL_1\, dL_2 \Big] = \mathcal{N} \int \exp\Big[i \int_0^\infty \chi\{R(L)\}\, dL - \frac{\kappa T}{2} \int\int \chi(r) V^{-1}(r-s) \chi(s)\, d^3r\, d^3s \Big] \delta\chi$$

$$\Big(\mathcal{N} = \int \delta\chi \exp\Big(-\frac{\kappa T}{2} \int\int \chi V^{-1} \chi \Big) \Big) \tag{A2}$$

where V^{-1} is the inverse operator to V (assumed positive definite for simplicity) and the integral is taken over all functions χ. The identity is proved by completing the square

$$\chi(r) \to \chi'(r) + i \frac{1}{\kappa T} \int V\{r - R(L)\}\, dL. \tag{A3}$$

Since V is always short range one may replace $\kappa TV^{-1}(r-s)$ by $v^{-1}\delta(\mathbf{r}-\mathbf{s})$, and this will also work when the excluded volume stems from a hard potential rather than a soft, in the usual way. Thus

$$p(r,L) = \int \mathcal{N} \int_{R(0)=0}^{R(L)=r} \exp\left[-\frac{4l}{3}\int_0^L \left(\frac{\partial R}{\partial L'}\right)^2 dL' - i\int_0^L \chi\{R(L')\}\,dL'\right] d(\text{path})$$
$$\times \int d^3 r_\infty \int_{R(L)=r}^{R(\infty)=r_\infty} \exp\left[-\frac{4l}{3}\int_L^\infty \left(\frac{\partial R}{\partial L'}\right)^2 dL' - i\int_L^\infty \chi\{R(L')\}\,dL'\right] d(\text{path})$$
$$\times \exp\left\{-\frac{1}{2v}\int \chi^2(\mathbf{s})\,ds\right\}\delta\chi. \tag{A4}$$

(The symbol $\mathcal{N}$ will always be used for the various normalizations.)

Now one has rigorously obtained the Markov type process under the χ integral sign. It follows now that

$$p(r,L) = \mathcal{N}\int G(r,L,[\chi])G(r,r_\infty;L-L_\infty,[\chi])\exp\left(-\frac{1}{2v}\int \chi^2\,d^3s\right)\delta\chi \tag{A5}$$

where

$$\left\{\frac{\partial}{\partial L} - \frac{l}{3}\nabla^2 + i\chi(r)\right\}G(r,r';L-L') = \delta(r-r')\delta(L-L') \tag{A6}$$

or

$$\left\{-\frac{l}{3}\nabla^2 + i(\chi(r)+E)\right\}G(r,r';E) = \delta(r-r'). \tag{A7}$$

This Green function must have sets of solutions $\psi_n(\gamma)\exp(E_nL)$ and $\psi_n{}^+(r)\exp(-E_nL)$ (ψ, ψ^+ are the (at most) two solutions for given E; in Hermitian systems they are complex conjugates, but cannot be so identified since χ is a variable of integration):

$$G(r,r_\infty;L-L_\infty) = \sum \psi_n{}^+(r)\psi_n(r_\infty)\exp\{-E_n(L_\infty - L)\}. \tag{A8}$$

Clearly as L_∞ tends to infinity only $E_n = 0$ will survive, i.e.

$$G(r,r_\infty;L-L_\infty) \to \psi_0{}^+(r)\psi_0(r_\infty). \tag{A9}$$

Now G will be obtained by the method of steepest descent, writing

$$G = \mathrm{e}^\phi/r \tag{A10}$$

$$\nabla^2\phi + \left(\frac{\partial\phi}{\partial r}\right)^2 = \left(\frac{3}{l}\right)i(E+\chi) \tag{A11}$$

$$\phi \simeq \int_0^r \left(\frac{3}{l}\right)^{1/2} i^{1/2}(E+\chi)^{1/2}\,ds. \tag{A12}$$

The next terms in the series for ϕ, due to $\nabla^2\phi$, have been investigated by Jeffreys and Jeffreys (1961) who give a systematic expansion, but attention here will be restricted to the leading terms only. Thus

$$G = \frac{1}{r}\exp\left\{\int_0^r \left(\frac{3}{l}\right)^{1/2} i^{3/2}(E+\chi)^{1/2}\,ds\right\} \tag{A13}$$

and

$$\psi_0 = \exp \int_r^{r_\infty} \left(\frac{3}{l}\right)^{1/2} i^{3/2}\chi^{1/2}\, ds \tag{A14}$$

and

$$p = \int dE \int \delta\chi\, \mathscr{N} \int d^3 r_\infty \exp\Big[-\frac{1}{2v}\int \chi^2\, ds + \int_0^{r_1} \left(\frac{3}{l}\right)^{1/2} i^{3/2}\chi^{1/2}\, ds + \left(\frac{3}{l}\right)^{1/2} i^{3/2} \int_0^r \{(E+\chi)^{1/2} - \chi^{1/2}\}\, ds - iEL\Big]. \tag{A15}$$

As has been noted, large L corresponds to small E, so one may expand in E to give

$$(E+\chi)^{1/2} = \chi^{1/2} - \tfrac{1}{2}E\chi^{-1/2} - \tfrac{1}{8}E^2\chi^{-3/2} \ldots \tag{A16}$$

whereupon

$$p = \int d^3 r_\infty \int \delta\chi r^{-1} \Big(\int_0^r \chi^{-3/2}\, ds\Big)^{-1/2} \times \exp\Big\{-\frac{1}{2v}\int \chi^2\, ds + \int_0^{r_\infty} \left(\frac{3}{il}\right)^{1/2} \chi^{1/2}\, ds\Big\} \exp\Big[-\frac{2\{L + \frac{1}{2}(3/il)^{1/2}\int_0^r \chi^{-1/2}\, ds\}^2}{(3/li)^{1/2}\int_0^r \chi^{-3/2}\, ds}\Big]. \tag{A17}$$

Now one has the χ integration to perform, and this also is done by steepest descent. The function of steepest descent χ_s is dominated by the first two terms of the exponent, since the third vanishes at the maximum of the function. Thus one finds since

$$\frac{\delta}{\delta\chi(r)} \int \chi^2(s)\, d^3 s = 2\chi(r) \tag{A18}$$

$$\frac{\delta}{\delta\chi} \int \chi^{1/2}\, ds = \frac{\delta}{\delta\chi} \int \frac{\chi^{1/2}}{4\pi s^2}\, d^3 s = (8\pi s^2)^{-1}\chi^{-1/2} \tag{A19}$$

$$i\chi_s(r) = \left\{\left(\frac{3}{l}\right)^{1/2} \frac{v}{8\pi}\right\}^{2/3} r^{-4/3} \tag{A20}$$

which is real and is indeed $v\tilde{p}l^{-2}$ of (3.17). As before, one can now write p in the forms (3.9) and (3.24).

The other cases are obtained by considering

$$\int_0^L \int_0^L V\{R(L_1) - R(L_2)\}\, dL_1\, dL_2 \tag{A21}$$

for the finite chain, giving just G, but the random walk problem

$$\int_0^L dL_1 \int_0^{L_1} dL_2 V\{R(L_1) - R(L_2)\} \tag{A22}$$

appears to have no simple parameterization.

The functional integral (A5) cannot be evaluated more generally. Further terms can be taken in the solution of G, and the steepest descent equation can be studied in the

exact form

$$L = \left(\frac{3}{l}\right)^{1/2} \int_0^r \frac{ds}{(E+\chi)^{1/2}} \tag{A23}$$

$$\chi(s) = \left(\frac{3}{l}\right)^{1/2} i^{3/2}\chi^{-1/2}(s) + \left\{\frac{1}{(E+\chi)^{1/2}} - \frac{1}{\chi^{1/2}}\right\}\Theta \tag{A24}$$

$$(\Theta = 0, \qquad s > r)$$

but it appears these are beyond analytic treatment.

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