Size of a Polymer Molecule in Solution

Part 1.—Excluded Volume Problem

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A study is made of the probability distribution of the end to end distance R of a polymer of N segments, length $Nl = L$, and of self repulsion ω. A simple method, capable of adoption in more complicated problems, is developed, using the idea of an effective step length.

The mean square value of R^2 is developed as a series which for large L is

$$R^2 = \omega^{2/5} L^{6/5} l^{2/5} (1.12+1.05+1.03+ \dots).$$

The probability distribution is developed in terms of the dimensionless parameter $x = R^2/l^{2/5} \omega^{2/5} L^{6/5}$, and for small x,

$$\log p(x) \sim -x\left(\frac{1}{2.24}+\frac{1}{2.10}+\frac{1}{2.06}+ \dots\right)$$

but for large x a definite asymptotic form is derived

$$\log p(x) = -(\tfrac{3}{5})^{\frac{3}{2}} \pi^{\frac{1}{2}}/3\, x^{\frac{5}{4}}.$$

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1. INTRODUCTION

The excluded volume problem has been a central part of polymer solution theory since Flory's original classic study of 1949.[1] There seems no doubt that the law for the mean square end to end distance is either that of Flory, or something very close to it. Computer simulations, theories based on an interpretation of numerical work by Domb *et al.*,[2] Lax *et al.*[3] or an expansion in dimensionality [4] by de Gennes agree on

$$\langle R^2 \rangle \propto L^{\alpha} \tag{1.1}$$

where $\alpha = \frac{6}{5}$ to within one to two percent. Analytic theories based on self consistent fields give α to be exactly $\frac{6}{5}$ (Edwards,[5] de Gennes [4]) and an extremely thorough development of the s.c.f. method by Kosmas and Freed [6] which includes fluctuations of the s.c.f., confirms this result. A worry remains in that for $4-\varepsilon$ dimensions, the s.c.f. method does not agree with the renormalization group expansion as $\varepsilon \to 0$. However, since the s.c.f. method does not converge in this limit, and there can also reside some doubt due to the asymptotic nature of the ε method, it is not clear whether there is a real disagreement. However, the $\varepsilon \to 0$ argument concerns a region remote from physical reality and, given the extreme accuracy of the s.c.f. result, it suggests that analytic methods should be further developed to the point at which they can make a real contribution to the theory of semi-dilute solutions, gels, and so on. The difficulty with all the papers cited (with the exception of Flory's work, which does not go far enough for the kind of application we have in mind) is that they have reached such a level of mathematical complexity in giving the very simplest results,

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that one is daunted from considering them as the lemma to some really difficult theorem.

In this paper we propose a simple method which permits a rapid and accurate attack on the problem, and in subsequent papers will give applications to semi-dilute and concentrated solutions, and to networks.

The paper is restricted to two things, the shape of the distribution probability, $P(\boldsymbol{R}, L)$, and its moment

$$\langle R^2 \rangle = \int R^2 P(R)\, \mathrm{d}^3 R. \tag{1.2}$$

The entropy of the system is more difficult and the authors hope to study this in a later paper. The chain is given a definite length L for all the papers.

2. FORMULATION

The model used is the simplest possible in which an effective pseudopotential ω replaces the molecular complexity of the real chain. The chain is considered a locus in space $\boldsymbol{r}(s)$, s the arc length, and the random walk constraint is represented by the Wiener measure

$$\exp\left[-\frac{3}{2l}\int_0^L \dot{r}^2(s)\, \mathrm{d}s\right] \tag{2.1}$$

and the interaction

$$\exp\left\{-\omega \int_0^L \int_0^L \delta[r(s)-r(s')]\, \mathrm{d}s\, \mathrm{d}s'\right\}. \tag{2.2}$$

The interaction strength $\omega \propto T-\theta$, where θ is the Flory temperature. We only consider $\omega > 0$. The step length is l, and ω has the dimensions of volume.

If the symbol (δr) denotes integration over all paths, then

$$\langle R^2 \rangle = \frac{\displaystyle\int_{r(0)=0}^{r(L)=R} (\delta r)[r(L)-r(0)]^2 \exp(A)}{\displaystyle\int \mathrm{d}^3 R \int_{r(0)=0}^{r(L)=R} \exp(A)\,(\delta r)}. \tag{2.3}$$

The quantity $\langle R^2 \rangle$ is a single function, a function of l, L and ω. This suggests that if we study $\langle R^2 \rangle$ alone it ought to be possible to find an equation for that quantity, or some similar quantity directly related to it, without the intermediary of some much more complicated quantity like a mean field, which will have to be $\phi(l, L, \omega, \boldsymbol{r})$. Edwards [5] tried to simplify the latter function by letting $L \to \infty$, but this still leaves integro-differential equations, whose fluctuations require a mathematical *tour de force* to give results, although it has indeed been accomplished by Kosmas and Freed.[6]

Instead we argue that an effective step length l_1 be introduced, so that, by definition

$$\langle R^2 \rangle = L\, l_1. \tag{2.4}$$

This would result from

$$\mathrm{e}^{-\frac{3}{2l_1}\int \dot{r}^2 \mathrm{d}s} \quad \text{replacing} \quad \mathrm{e}^{-\frac{3}{2l}\int \dot{r}^2 \mathrm{d}s}$$

for a free chain. We therefore write

$$\frac{3}{2l}\int \dot{r}^2\, \mathrm{d}s + \omega \iint \delta[r(s)-r(s')]\, \mathrm{d}s\, \mathrm{d}s'$$

$$= \frac{3}{2l_1}\int \dot{r}^2\, \mathrm{d}s + \left\{\frac{3}{2}\left(\frac{1}{l}-\frac{1}{l_1}\right)\int \dot{r}^2\, \mathrm{d}s + \omega \iint \delta[r(s)-r(s')]\, \mathrm{d}s\, \mathrm{d}s'\right\} \tag{2.5}$$

$$= \frac{3}{2l_1}\int \dot{r}^2\, \mathrm{d}s + B, \quad \text{say} \tag{2.6}$$

$$= C + B. \tag{2.7}$$

Then

$$\langle R^2 \rangle = \frac{\int [r(L)-r(0)]^2\, \mathrm{e}^{-\frac{3}{2l_1}\int \dot{r}^2\, \mathrm{d}s - B}\, (\delta r)}{\int \mathrm{e}^{-\frac{3}{2l_1}\int \dot{r}^2 - B}\, (\delta r)} \tag{2.8}$$

$$= \frac{\int [r(L)-r(0)]^2\, \mathrm{e}^{-C}\, (\delta r)}{\int \mathrm{e}^{-C}\, (\delta r)} -$$

$$\left[\frac{\int [r(L)-r(0)]^2\, B\, \mathrm{e}^{-C} \int \mathrm{e}^{-C} - \int [r(L)-r(0)]^2\, \mathrm{e}^{-C} \int B\, \mathrm{e}^{-C}}{(\int \mathrm{e}^{-C}\, \delta r)^2}\right] +$$

$$\mathcal{O}(B^2) + \mathcal{O}(B^3) + \ldots \tag{2.9}$$

$$= L\, l_1 + \mathcal{O}(B) + \mathcal{O}(B^2) + \mathcal{O}(B^3) + \ldots \quad . \tag{2.10}$$

At this point we choose l_1 such that

$$\langle R^2 \rangle = L\, l_1 \tag{2.11}$$

so that to first order in B

$$\int [r(L)-r(0)]^2\, B\, \mathrm{e}^{-C}\, \delta r \int \mathrm{e}^{-C}\, \delta r = \int [r(L)-r(0)]^2\, \mathrm{e}^{-C}\, \delta r \int B\, \mathrm{e}^{-C}\, \delta r. \tag{2.12}$$

The evaluation is straightforward and given in Appendix A. It gives the equation

$$L l_1^2\left(\frac{1}{l}-\frac{1}{l_1}\right) = 2\sqrt{\frac{6}{\pi^3}}\, \omega\, \frac{L^{\frac{3}{2}}}{l_1^{\frac{1}{2}}}. \tag{2.13}$$

The solution to this equation clearly subsumes perturbation theory, for if ω is small, $l \cong l_1$,

$$\langle R^2 \rangle = Ll + 2\sqrt{\frac{6}{\pi^3}}\omega L^{\frac{3}{2}} l^{-\frac{1}{2}} \tag{2.14}$$

but for $L^{\frac{1}{2}} > \omega$ one has a Flory type equation with solution

$$l_1 = (2)^{\frac{2}{5}}\left(\frac{6}{\pi^3}\right)^{\frac{1}{5}} \omega^{\frac{2}{5}} l^{\frac{2}{5}} L^{\frac{6}{5}} \tag{2.15}$$

so that

$$\langle R^2 \rangle = (2)^{\frac{2}{5}}\left(\frac{6}{\pi^3}\right)^{\frac{1}{5}} l^{\frac{2}{5}} \omega^{\frac{2}{5}} L^{\frac{6}{5}}. \tag{2.16}$$

The remarkable thing is that if we add in the terms $\mathcal{O}(B^2)$, $\mathcal{O}(B^3)$ . . . one always retains the structure of this equation, only revising the numerical coefficient.

To elucidate this we must draw attention to a remarkable property of the perturbation series which hitherto does not seem to have attracted comments. Yamakawa [7] gives a series in terms of the parameter $z = \omega L^{\frac{1}{2}} l^{-\frac{3}{2}}$ in our notation,

$$\frac{\langle R^2 \rangle}{Ll} = 1+\tfrac{4}{3}z-2.075z^2+6.459z^3+\ldots \quad . \tag{2.17}$$

Now these coefficients are related to the various averages and moments of the interaction, and are thus related to the Feynman diagrams

to order ω

to order ω^2, multiples of order ω and

The structure of integrals appearing in a series in ω alters in dimensionality, and logarithms arise at second order. One could therefore expect

$$1+az+bz^2+cz^2\log z+dz^3+ez^3\log z+fz^3(\log z)^2+\ldots ; \tag{2.18}$$

for the entropy, such terms do indeed arise.

There is probably some deep reason why they do not arise in eqn (2.17), but we do not know what it is. However, we took the precaution of checking this property of Yamakawa's calculation, and it is indeed correct.* This absence of logarithms leads to a stability of the index which could not in general terms be predicted.

To establish the stability of the index α against higher approximations, we write $\langle R^2 \rangle$ as follows

$$\langle R^2 \rangle = Ll+\frac{A\omega L^{\frac{3}{2}}}{l^{\frac{1}{2}}}+\frac{B\omega^2 L^2}{l^2}+\frac{C\omega^3 L^{\frac{5}{2}}}{l^{\frac{7}{2}}} \tag{2.19}$$

where A, B and C are numbers.[7] Now we introduce the effective step length l such that

$$\frac{1}{l} = \frac{1}{l_1}+\frac{1}{l}-\frac{1}{l_1}$$

$$= \frac{1}{l_1}\left[1+l_1\left(\frac{1}{l}-\frac{1}{l_1}\right)\right]$$

$$l = l_1\left[1-l_1\left(\frac{1}{l}-\frac{1}{l_1}\right)+l_1^2\left(\frac{1}{l}-\frac{1}{l_1}\right)^2\ldots\right]; \tag{2.20}$$

using eqn (2.20) in (2.19) we get to 3rd order in ω

$$\langle R^2 \rangle = Ll_1-Ll_1^2\left(\frac{1}{l}-\frac{1}{l_1}\right)+Ll_1^3\left(\frac{1}{l}-\frac{1}{l_1}\right)^2+\frac{A\omega L^{\frac{3}{2}}}{l_1^{\frac{1}{2}}}+$$
$$\frac{A}{2}\omega L^{\frac{3}{2}} l_1^{\frac{1}{2}}\left(\frac{1}{l}-\frac{1}{l_1}\right)+\frac{B\omega^2 L}{l_1^2}+2B\omega^2\frac{l^2}{l_1}\left(\frac{1}{l}-\frac{1}{l_1}\right)+\frac{C\omega^3 L^{\frac{5}{2}}}{l_1^{\frac{7}{2}}} \tag{2.21}$$

* Prof. Domb of King's College, London informs us that he too has noticed this fact and checked it in detail. He also finds an error in the z^3 coefficient, but it does not materially affect our results.

so the first order approximation gives

$$L l_1^2\left(\frac{1}{l}-\frac{1}{l_1}\right) = \frac{A\omega L^{\frac{3}{2}}}{l_1^{\frac{1}{2}}} \tag{2.22}$$

$$\alpha^5-\alpha^3 = A\omega L^{\frac{1}{2}}/l^{\frac{3}{2}}$$

where

$$\alpha^2 = l_1/l. \tag{2.23}$$

For $L \to \infty$ and $l_1 \gg l$

$$\alpha^5 = (A\omega L^{\frac{1}{2}}/l^{\frac{3}{2}})$$

with

$$A = \tfrac{4}{3},\ \alpha = (\tfrac{4}{3})^{\frac{1}{5}}\,\omega^{\frac{1}{5}}\,L^{(1/10)}\,l^{-(3/10)}$$

$$\alpha = 1.059\,\omega^{\frac{1}{5}}\,L^{(1/10)}\,l^{-(3/10)} \tag{2.24}$$

Since

$$\langle R^2\rangle \sim \alpha^2 \simeq L l_1 = 1.12\,\omega^{\frac{2}{5}}L^{\frac{6}{5}}l^{\frac{2}{5}}.$$

Now to the 2nd order we have

$$L l_1^3\left(\frac{1}{l}-\frac{1}{l_1}\right)^2+\frac{A\omega L^{\frac{1}{2}}}{2l^{\frac{3}{2}}}l_1^{\frac{1}{2}}\left(\frac{1}{l}-\frac{1}{l_1}\right)+\frac{B\omega^2L^2}{l_1^2} = 0.$$

which can be written in the following form

$$(\alpha^5-\alpha^3)^2+\frac{A\omega L^{\frac{1}{2}}}{2l^{\frac{3}{2}}}(\alpha^5-\alpha^3)+\frac{B\omega^2L^2}{l^3} = 0. \tag{2.25}$$

For $L \to \infty$, $l_1 \gg l$

$$\alpha^{10}+\frac{A\omega L^{\frac{1}{2}}}{2l^{\frac{3}{2}}}\alpha^5+\frac{B\omega^2L^2}{l^3} = 0$$

which for $B = -2.075$ has the following solution

$$\alpha = 1.025\,\omega^{\frac{1}{5}}L^{(1/10)}l^{-(3/10)}. \tag{2.26}$$

$\langle R^2\rangle$ still retains the form $\sim\omega^{\frac{2}{5}}L^{\frac{6}{5}}l^{\frac{2}{5}}$. Now to the 3rd order we have the following

$$-L l_1^4\left(\frac{1}{l}-\frac{1}{l_1}\right)^3-\frac{A\omega}{8}L^{\frac{3}{2}}l_1^{\frac{3}{2}}\left(\frac{1}{l}-\frac{1}{l_1}\right)^2+\frac{2B\omega^2L^2}{l_1}\left(\frac{1}{l}-\frac{1}{l_1}\right)+\frac{C\omega^3L^{\frac{5}{2}}}{l_1^{\frac{7}{2}}} = 0 \tag{2.27}$$

which can be written as follows

$$(\alpha^5-\alpha^3)^3+\frac{A\omega L^{\frac{1}{2}}}{8l^{\frac{3}{2}}}(\alpha^5-\alpha^3)^2-\frac{2B}{l^3}\omega^2L(\alpha^5-\alpha^3)+\frac{C\omega^3L^{\frac{3}{2}}}{l^{\frac{9}{2}}} = 0.$$

For $L \to \infty$, $l_1 \gg l$ this becomes

$$\alpha^{15}+\frac{A\omega L^{\frac{1}{2}}}{8l^{\frac{3}{2}}}\alpha^{10}-\frac{2B\omega^2}{l^3}L\alpha^5+\frac{C\omega^2L^{\frac{3}{2}}}{l^{\frac{9}{2}}} = 0$$

which can be solved for $C = 6.459$ to give

$$\alpha = 1.015\,\omega^{\frac{1}{5}}L^{(1/10)}l^{-(3/10)}$$

$$\langle R^2\rangle \sim \alpha^2 = 1.03\,\omega^{\frac{2}{5}}L^{\frac{6}{5}}l^{\frac{2}{5}}. \tag{2.28}$$

It is clear from eqn (2.24), (2.26) and (2.28) that the index α stays near unity and is stable against higher order approximations. In the light of the above one may, however, be tempted to remark that since $\langle R^2\rangle$ is a ratio of two seemingly divergent quantities, their ratio might be stable. But in the absence of proof, we refrain from making such a statement about the stability of the index in general. If the correct results were

$$\begin{aligned}\langle R^2\rangle &= L^{\frac{6}{5}+\eta}\\ &= L^{\frac{6}{5}}(1+\eta\log L+\ldots)\end{aligned} \tag{2.29}$$

it would turn out that a symptom of this would have been logarithms in the perturbation series, even though our method and answers are remote from perturbation theory.

With this introduction we state the result to order B^2 (derived in Appendix A):

$$\left[Ll_1^2\left(\frac{1}{l}-\frac{1}{l_1}\right)-A\frac{\omega L^{\frac{3}{2}}}{l_1^{\frac{1}{2}}}\right]+\left[Ll_1^3\left(\frac{1}{l}-\frac{1}{l_1}\right)+\frac{A}{2}\omega L^{\frac{3}{2}}\left(\frac{1}{l}-\frac{1}{l_1}\right)l_1^{\frac{3}{2}}+\frac{B\omega^2L^2}{l_1^2}\right]=0 \tag{2.30}$$

The first bracket is order B, and in the second bracket are terms like the square of this term, but also new terms of the same order. The peculiar feature is that, just as the solution of the first order gives

$$l_1 \propto L^{\frac{1}{5}}+\mathcal{O}(1)+\mathcal{O}(L^{-\frac{1}{5}})+\ldots \tag{2.31}$$

the second order bracket is of order $L^{\frac{1}{5}}$ higher than the first but still gives $l_1 \propto L^{\frac{1}{5}}$. Thus in a symbolic way we can typify the series by

$$\begin{aligned}&(l_1-a_0L^{\frac{1}{5}}+b_0-c_0L^{-\frac{1}{5}})+L^{\frac{1}{5}}(l_1-a_1L^{\frac{1}{5}}+b_1-c_1L^{-\frac{1}{5}})+\\ &\qquad L^{\frac{2}{5}}(l_1-a_2L^{\frac{1}{5}}+b_2-c_2L^{-\frac{1}{5}})+\ldots\end{aligned} \tag{2.32}$$

where

$$\begin{aligned}a_1 &= a_0+a^{(1)}\\ a_2 &= a_0+a^{(1)}+a^{(2)}\end{aligned} \tag{2.33}$$

and so on, the $a^{(1)}$, $a^{(2)}$ being pure numbers reflecting terms of new complexity in the series, a kind of dimensionless cluster expansion. We find

$$\begin{aligned}a_0 &= 1.12\\ a^{(1)} &= 1.05\\ a^{(2)} &= 1.03.\end{aligned} \tag{2.34}$$

This finally can be expressed in a series for $\langle R^2\rangle$, the additions coming from the order of expansion

$$\langle R^2\rangle = \omega^{\frac{2}{5}}L^{\frac{6}{5}}l^{\frac{2}{5}}(1.12+1.05+1.03+\ldots). \tag{2.35}$$

3. PROBABILITY DISTRIBUTION

The success of the preceding section suggests that one may be more ambitious and derive the probability distribution function:

$$P(\boldsymbol{R}, L) = \frac{\int \delta[\boldsymbol{R}-r(L)-r(0)]\,\mathrm{e}^{-A}\,\delta r}{\int \mathrm{d}^3R'\,\mathrm{e}^{-A'}\,(\delta r')} \qquad (3.1$$

which in Fourier transform is

$$P(\boldsymbol{k}, L) = \int \mathrm{e}^{\mathrm{i}\boldsymbol{k}\int_0^L \dot{r}(s)\,\mathrm{d}s-A}\Big/\int \mathrm{e}^{-A'}. \tag{3.2}$$

An alternative is to argue that if one has all the moments $\langle R^{2N}\rangle$ that is as good as the probability distribution and can be derived from the derivatives of

$$\int e^{\lambda\int_0^L \dot{\boldsymbol{r}}\, ds - A} \Big/ \int e^{-A'}. \tag{3.3}$$

It turns out to be very important that one studies the real form because then many integrals converge. Moreover, even for the $\boldsymbol{k}$ form, the final calculation is done by a steepest descent evaluation about a point on the imaginary axis, *i.e.*, $\boldsymbol{k}$ pure imaginary. In the subsequent analysis therefore we shall study the case of $\boldsymbol{k}$ pure imaginary, and derive a final answer in the form $Q(\lambda)$ where

$$P(\lambda) = Q(i\lambda). \tag{3.4}$$

Under certain conditions

$$Q(\lambda) = e^{|\lambda|^2\phi_1} \tag{3.5}$$

and under others

$$Q(\lambda) = e^{|\lambda|^{\frac{5}{3}}\phi_2} \tag{3.6}$$

so that the final integrals are

$$\int e^{(i|\boldsymbol{k}|)^{\frac{5}{3}}\phi_2 - (i\boldsymbol{k})\cdot\boldsymbol{R}}\, d^3k \tag{3.7}$$

and

$$\int e^{-k^2\phi_1 - (i\boldsymbol{k})\cdot\boldsymbol{R}}\, d^3k. \tag{3.8}$$

The procedure is just as before, but now

$$l_1 \text{ will be } l_1(\lambda, L, \omega, l).$$

To first order one has (Appendix B)

$$\lambda^2 \frac{l_1^2}{6}\left(\frac{1}{l} - \frac{1}{l_1}\right) = \frac{1}{8}\left(\frac{6}{\pi}\right)^{\frac{3}{2}} \omega L^{\frac{1}{2}} \int_0^L \left(1 - e^{-\frac{\lambda^2 s l_1}{6}}\right) \frac{ds}{s^{\frac{3}{2}} l_1^{\frac{3}{2}}}. \tag{3.9}$$

If one introduces the dimensionless parameters

$$x = \lambda^2 L l_1$$

$$y = \omega\left(\frac{L}{l^3}\right)^{\frac{1}{2}} \quad \text{and} \quad s = L\sigma \tag{3.10}$$

then

$$\frac{x}{6}\left(\frac{l_1}{l}\right) = \frac{1}{8}\left(\frac{6}{\pi}\right)^{\frac{3}{2}} y \int_0^1 \left(1 - e^{-\frac{x\sigma}{6}}\right) \frac{d\sigma}{\sigma^{\frac{3}{2}}}. \tag{3.11}$$

x will be of the structure of $R^2/L^{\frac{6}{5}}$ and y an effective interaction parameter. In all cases of interest to this paper, $l_1 \gg l$ so the equation reduces to

$$x \simeq 2\left(\frac{6}{\pi^3}\right)^{\frac{1}{2}} \frac{l}{l_1} xy \tag{3.12}$$

when the right hand side is expanded in x, *i.e.*, for x small, and

$$x = \left(\frac{9}{\pi}\right)\frac{l}{l_1} y\sqrt{x} \tag{3.13}$$

when x is large. The first gives

$$y = \sqrt{\frac{\pi^3}{6}}\left(\frac{l_1}{2l}\right)$$

and is indeed simply the same calculation as the preceding section, since a second derivative with respect to λ converts this problem into the preceding one, and both sides of the equation contain λ^2. For large λ, however,

$$x = \left(\frac{9}{\pi}\right)^2 \frac{l^2}{l_1^2} y^2 \tag{3.14}$$

i.e.,

$$\lambda^2 l_1^2 = \left(\frac{9}{\pi}\right)\frac{\omega\lambda l}{l_1}$$

$$l_1 = \left(\frac{9}{\pi}\right)^{\frac{1}{3}} \left(\frac{\omega}{\lambda}\right)^{\frac{1}{3}} \tag{3.15}$$

and

$$Q(\lambda) \quad \text{is} \quad e^{-L|\lambda|^{\frac{5}{3}}(9/\pi)^{\frac{1}{3}}(\omega l)^{\frac{1}{3}}}$$

or

$$P(k) \quad \text{is} \quad e^{(ik)^{\frac{5}{3}}(9/\pi)^{\frac{1}{3}}L(\omega l)^{\frac{1}{3}}}$$

and

$$P(\boldsymbol{R}, L) = \int d^3k \, e^{(ik)^{\frac{5}{3}}(9/\pi)^{\frac{1}{3}}L(\omega l)^{\frac{1}{3}} - i\hat{k}\,.\,\boldsymbol{R}} \tag{3.16}$$

i.e.,

$$P(\boldsymbol{R}, L) \sim e^{-(R^2/L^{\frac{6}{5}})^{\frac{5}{4}}} \tag{3.17}$$

$$\text{as } \frac{R^2}{L^{\frac{6}{5}}} \to \infty \tag{3.18}$$

This function has been found by Domb *et al.*[2] in numerical simulations of the problem on a lattice and has also been discussed theoretically by Fisher.[8]

At this point one again studies whether higher order terms introduce corrections. For small x, the series is simply x times the results of the preceding section (2), and therefore one gets a revision of the coefficient g in the equation

$$y = g$$

at each order.

But for large x, the higher order terms are repetitions of the first, Thus one gets

$$(x - y\sqrt{x}) + \{(x - y\sqrt{x})^2 + \mathcal{O}(1)y^2 + \mathcal{O}(\log x)y^2\} \tag{3.19}$$

and so on. As $x \to \infty$, to all orders $x \cong y\sqrt{x}$. Details are given in Appendix B. We have therefore found a method of expansion which, for one point $x \to \infty$, gives a complete answer to the problem.

4. CONCLUSION

We have restricted ourselves in this paper to consideration of the relationship between the end to end vector $\boldsymbol{R}$ of a polymer with excluded volume ω, and its contour length L. A direct evaluation of this quantity by relation to itself gives simple equations yielding valuable information. Any such method is more or less bound to give asymptotic expansion, but it has been possible to derive an answer whose functional form is stable against higher approximations, only numerical coefficients changing. Even these seem surprisingly accurately given by the first approximation.

The method is sufficiently simple to provide a basis for a detailed theory of many chain solutions, and this is presented in a subsequent paper.

There are many aspects of the single chain theory which remain unanswered, in particular the probability distribution of interior points

$$\langle[r(s_1)-r(s_2)]^2\rangle$$
$$(0 < s_1 < s_2 < L)$$

or $\langle[r(s_1)-r(s_2)]^2\rangle$ for points s_1, s_2 on an infinite chain. Thus our present theory will not give the X-ray or neutron diffraction of a single chain. The other property is the entropy, where the key character of the present calculations—that they are calculations of a ratio of two rather ill behaved quantities—is not available.

It is hoped to return to these two problems in a later paper.

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APPENDIX A

DERIVATION OF EQN (2.10) AND (2.13)

By definition

$$\frac{\int_0^L [r(L)-r(0)]^2\, e^{-\frac{3}{2l_1}\int_0^L \dot{r}^2\,ds}\,\delta r}{\int_0^L e^{-\frac{3}{2l_1}\int_0^L \dot{r}^2\,ds}\,\delta r} = Ll_1 \quad . \tag{A1}$$

Now let us consider the following integral

$$\int [r(L)-r(0)]^2 B\, e^{-C} \int e^{-C}\,\delta r$$

where B and C are given by eqn (2.6) and (2.7). Since B consists of two parts, the above integral can be decomposed into two integrals. The first integral can be evaluated as follows

$$\frac{3}{2}\left(\frac{1}{l}-\frac{1}{l_1}\right)\int [r(L)-r(0)]^2 \int \dot{r}^2\, e^{-\frac{3}{2l_1}\int \dot{r}^2\,ds}\,\delta r$$
$$= \frac{3}{2}\left(\frac{1}{l}-\frac{1}{l_1}\right)\left[\frac{\partial}{\partial x}\bigg|_{x=-\frac{3}{2l_1}} \frac{\int (\delta r) r^2\, e^{x\int \dot{r}^2\,ds}}{\int (\delta r)\, e^{x\int \dot{r}^2\,ds}} + \frac{\left[\int (\delta r)\, e^{-\frac{3}{2l_1}\int \dot{r}^2\,ds}\, r^2\right]}{\left[\int (\delta r)\, e^{-\frac{3}{2l_1}\int \dot{r}^2\,ds}\right]^2}\times\right.$$
$$\left.\left(\int \delta r\, e^{-\frac{3}{2l_1}\int \dot{r}^2\,ds}\int \dot{r}^2\,ds\right)\right] \tag{A2}$$

$$= \frac{3}{2}\left(\frac{1}{l}-\frac{1}{l_1}\right)\frac{\partial}{\partial x}\left(-\frac{3L}{2x}\right)\Bigg|_{x=-\frac{3}{2l_1}} + \langle R_1^2\rangle \int \delta r\, \mathrm{e}^{-\frac{3}{2l_1}\int \dot{r}^2} B_1 \tag{A3}$$

$$= Ll_1^2\left(\frac{1}{l}-\frac{2}{l_1}\right)+\langle R_1^2\rangle\langle B_1\rangle \tag{A4}$$

where

$$B_1 = \frac{3}{2}\left(\frac{1}{l}-\frac{1}{l_1}\right)\int \dot{r}^2\, \mathrm{d}s. \tag{A5}$$

Let us now calculate the other integral containing ω

$$\omega \int [r(L)-r(0)]^2\, \mathrm{e}^{-\frac{3}{2l_1}\int \dot{r}^2\, \mathrm{d}s}\, \delta[r(s)-r(s')]\, \mathrm{d}s\, \mathrm{d}s'.$$

Using Fourier transformation of the δ function we have

$$= \frac{\omega}{(2\pi)^3}\iiint r^2\, \mathrm{e}^{-\frac{3}{2l_1}\int \dot{r}^2\, \mathrm{d}s+\mathrm{i}k[r(s)-r(s')]}\, \mathrm{d}^3k\, \mathrm{d}s\, \mathrm{d}s'. \tag{A6}$$

Completing the square in this exponent and changing the variable to $R\to r-\mathrm{i}kl_1\sigma/3$ we can write the above as follows

$$= \frac{\omega}{2\pi^2}\iiint k^2\, \mathrm{d}k\, \mathrm{d}s\, \mathrm{d}s'\, \mathrm{e}^{-\frac{k^2 l_1|s-s'|}{6}}\langle R_1^2\rangle - \frac{\omega l_1^2}{18\pi^2}\iiint k^4\, \mathrm{d}k\, \mathrm{d}s\, \mathrm{d}s'\, \mathrm{e}^{-\frac{k^2 l_1|s-s'|}{6}}. \tag{A7}$$

The second term of the above can be written by changing the variable

$$s\to Ls,\ s'\to Ls' \quad \text{and} \quad \frac{k^2 l_1 L}{6}\equiv k^2,$$

when we obtain

$$-\frac{\omega}{\pi^2}\sqrt{\frac{6}{l_1}}\,L^{\frac{3}{2}}\iiint k^4\, \mathrm{d}k\, \mathrm{d}s\, \mathrm{d}s'\, \mathrm{e}^{-k^2|s-s'|}\,|s-s'|^2. \tag{A8}$$

k and s integrations can be easily done to yield

$$= -2\omega\sqrt{\frac{6}{\pi^3}}\frac{L^{\frac{3}{2}}}{l_1^{\frac{1}{2}}}. \tag{A9}$$

Let us now evaluate the following integral

$$\int B\, \mathrm{e}^{-C}\, \delta r = \int (B_1+B_2)\, \mathrm{e}^{-\frac{3}{2l_1}\int \dot{r}^2\, \mathrm{d}s}\, \delta r$$

$$= \langle B_1\rangle + \frac{\omega}{2\pi^2}\iiint k^2\, \mathrm{d}k\, \mathrm{e}^{\mathrm{i}k[r(s)-r(s')]-\frac{3}{2l_1}\int \dot{r}_2\, \mathrm{d}s}\, \mathrm{d}s\, \mathrm{d}s'.$$

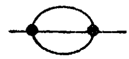
Again by completing the square in the exponent and changing the variable we can have

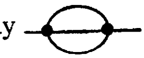
$$= \langle B_1\rangle + \frac{\omega}{2\pi^2}\iiint k^2\, \mathrm{d}k\, \mathrm{d}s\, \mathrm{d}s'\, \mathrm{e}^{-\frac{k^2 l_1|s-s'|}{6}}. \tag{A10}$$

From eqn (A4), (A9), (A10) and (2.10) we get $\langle R^2\rangle$ to first order in B

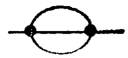
$$\langle R^2\rangle = Ll_1 - Ll_1^2\left(\frac{1}{l}-\frac{1}{l_1}\right)+2\sqrt{\frac{6}{\pi^3}}\frac{\omega L^{\frac{3}{2}}}{l_1^{\frac{1}{2}}}. \tag{A11}$$

Now to find $\langle R^2\rangle$ to $\mathcal{O}(B^2)$ we have to include the contributions from the following diagrams

 ,  and  .

To find the contribution from a typical diagram, say , we use the following identity

$$\langle[r(L)-r(0)]^2\rangle = \frac{\int r^2 G(r, L)\,\mathrm{d}^3r}{\int G(R, L)\,\mathrm{d}^3R} = \frac{\int \left(\frac{\partial^2}{\partial k^2} G(k, E)\right)_{k=0} \mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E}{\int G(0, E)\,\mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E}. \tag{A12}$$

The contribution to $\langle R^2\rangle$ from the diagram  can be obtained from

$$\frac{\int \frac{\partial^2}{\partial k^2}\left(\frac{1}{\mathrm{i}E+\frac{1}{6}lk^2+\Sigma(k, E)}\right)_{k=0} \mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E}{\int \frac{\mathrm{e}^{\mathrm{i}EL}}{\mathrm{i}E+\Sigma(0, E)}\,\mathrm{d}E} \tag{A13a}$$

where

$$\Sigma(k, E) = \left(\frac{6}{4\pi l}\right)^3 \omega^2 \iiint \mathrm{e}^{\mathrm{i}k.r-3\sqrt{\frac{6E}{l}}r}\frac{\mathrm{d}^3r}{r^3}. \tag{A13b}$$

Eqn (A13*a*) can be expressed as

$$\frac{l\int \frac{\mathrm{e}^{\mathrm{i}EL}}{E^2}\,\mathrm{d}E + \int \frac{\Sigma''(0, E)}{E^2}\,\mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E - \frac{2l}{\mathrm{i}}\int \frac{\Sigma(0, E)}{E^3}\,\mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E}{\int \frac{\mathrm{e}^{\mathrm{i}EL}}{\mathrm{i}E}\,\mathrm{d}E - \int \frac{\Sigma(0, E)}{\mathrm{i}^2E^2}\,\mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E} \tag{A14}$$

$$= -l\frac{\partial}{\partial\alpha}\log\int \frac{\mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E}{\mathrm{i}E-\alpha+\Sigma(0, E)}\bigg|_{\alpha=0} + \frac{\int \frac{\Sigma''(0, E)}{E^2}\,\mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E}{\int \frac{\mathrm{e}^{\mathrm{i}EL}}{\mathrm{i}E}\,\mathrm{d}E + \int \frac{\Sigma(0, E)}{E^2}\,\mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E}$$

$$= l\int \mathrm{i}\,\frac{\partial\Sigma(0, E)}{\partial E}\,\frac{\mathrm{e}^{\mathrm{i}EL}}{E^2}\,\mathrm{d}E + \frac{\int \frac{\Sigma''(0, E)}{E^2}\,\mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E}{\int \frac{\mathrm{e}^{\mathrm{i}EL}}{\mathrm{i}E}\,\mathrm{d}E} \tag{A15}$$

where

$$\Sigma''(0, E) \equiv \frac{\partial^2}{\partial k^2}\Sigma(k, E)\,|_{k=0} = -\left(\frac{4\pi}{3}\right)\left(\frac{6}{4\pi l}\right)^3 \omega^2 \int_0^\infty r\,\mathrm{e}^{-3\sqrt{\frac{6E}{l}}r}\,\mathrm{d}r \tag{A16}$$

which can be evaluated to give

$$\Sigma''(0, E) = -\frac{\omega^2}{12\pi^2 l^2 E}$$

and

$$\frac{\partial \Sigma}{\partial E}(0, E) = -6\pi\left(\frac{6}{4\pi l}\right)^3 \sqrt{\frac{6}{l}} \frac{1}{\sqrt{E}} \int_0^\infty e^{-3\sqrt{\frac{6E}{l}}\, r} \, dr \tag{A17}$$

$$= -\frac{27}{4\pi^2 l^3 E}. \tag{A18}$$

Using eqn (A16)-(A18) we finally get to order ω^2

$$= -\left(\frac{27}{4\pi^2 l^2}\right) i \int \frac{e^{iEL}}{E^3} \, dE - \frac{25^2}{12\pi^2 l^2} \int \frac{e^{iEL}}{E^3} \, dE \Big/ \int \frac{e^{iEL}}{iE} \, dE. \tag{A19}$$

Introducing

$$\chi_0 = i\oint \frac{e^{iE}}{E^3} \, dE \quad \text{and} \quad \oint \frac{e^{iE}}{iE} \, dE = 2\pi$$

we get

$$-\frac{L^2\omega^2}{12\pi^2 l^2}\left(81 + \frac{1}{2\pi}\right)\chi_0. \tag{A20}$$

The contribution to $\langle R^2 \rangle$ from the diagram  can be easily obtained as it is a repetition of  . It is

$$\frac{\int \frac{\partial \Sigma_0}{\partial E}\left(\frac{1}{iE+\Sigma_0}\right)^2 e^{iEL} \, dt}{\int \frac{e^{iEL}}{iE+\Sigma_0} \, dE} \tag{A21}$$

where Σ_0 is the self energy correction arising from  and is given by

$$\Sigma_0 = -2\pi^2 \omega \left(\frac{6}{l_1}\right)^{\frac{3}{2}} i^{\frac{1}{2}} \sqrt{E} = a\sqrt{E} \tag{A22}$$

so the contribution to $\langle R^2 \rangle$ comes out to be of the form

$$\sim -a\chi_1 L^{\frac{3}{2}} + a^2 \chi_1 \chi_2 + 2a^2 L^2 \chi_0 \tag{A23}$$

where

$$\chi_1 = \sqrt{i} \int \frac{e^{iE}}{E^{\frac{5}{2}}} \, dE, \qquad \chi_2 = \sqrt{i} \int \frac{e^{iE}}{E^{\frac{3}{2}}} \, dE. \tag{A24}$$

In the spirit of the above, the contribution of  to $\langle R^2 \rangle$ can be obtained by putting Σ_0 into itself, *i.e.*,

$$\frac{\int \frac{\partial^2}{\partial k^2}\left(\frac{1}{\mathrm{i}E+\frac{1}{6}lk^2+a\sqrt{E}}\right)_{k=0} \mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E}{\int \left(\frac{\mathrm{e}^{\mathrm{i}EL}}{\mathrm{i}E+aE^{\frac{1}{2}}}\right)\mathrm{d}E}$$

which gives

$$-2a^2lL^2\chi_1\chi_2-2alL^{\frac{3}{2}}\chi_1. \tag{A25}$$

From eqn (A11), (A19), (A23) and (A25) we finally have

$$\langle R^2\rangle = Ll_1-Ll_1^2\left(\frac{1}{l}-\frac{1}{l_1}\right)+A\frac{\omega L^{\frac{3}{2}}}{l_1^{\frac{1}{2}}}+\frac{A}{2}\omega L^{\frac{3}{2}}\left(\frac{1}{l}-\frac{1}{l_1}\right)+\frac{B\omega^2L^2}{l_1^2}+\ldots . \tag{A26}$$

The fourth term is the cross term which can be seen to arise if we write symbolically

$$(\int \dot{r}^2)^2+\{\omega \iint \delta[r(s)-r(s)]\}+(\int \dot{r}^2)^2+(\int \dot{r}^2)\{\omega \iint \delta[r(s)-r(s')]\}+$$
$$\{\omega \iint \delta[r(s)-r(s')]\}^2.$$

Alternatively one could write

$$\frac{1}{a} = \frac{1}{l_1}+\frac{1}{l}-\frac{1}{l_1}$$
$$a = l_1\left[1-l_1\left(\frac{1}{l}-\frac{1}{l_1}\right)+l_1^2\left(\frac{1}{l}-\frac{1}{l_1}\right)^2+\ldots\right] \tag{A27}$$

with this

$$\langle R^2\rangle = \frac{\int R^2\,\mathrm{e}^{-\frac{3}{2a}\int \dot{r}^2\,\mathrm{d}s-\omega\iint \delta[r(s)-r(s)]\,\mathrm{d}s\,\mathrm{d}s'}\,\delta r}{\int \mathrm{e}^{-\frac{3}{2a}\int \dot{r}^2\,\mathrm{d}s-\omega\iint \delta[r(s)-r(s')]\,\mathrm{d}s\,\mathrm{d}s'}\,\delta r}$$
$$= La+2\omega\sqrt{\frac{6}{\pi^3}}\frac{L^{\frac{3}{2}}}{a^{\frac{1}{2}}}+\mathcal{O}(A^2)+\ldots \tag{A28}$$

Using eqn (A27) in (A28) gives

$$\langle R^2\rangle = Ll_1-Ll_1^2\left(\frac{1}{l}-\frac{1}{l_1}\right)+Ll_1^3\left(\frac{1}{l}-\frac{1}{l_1}\right)^2+A\omega\frac{L^{\frac{3}{2}}}{l_1^{\frac{1}{2}}}+$$
$$\frac{A}{2}\omega L^{\frac{3}{2}}l_1^{\frac{1}{2}}\left(\frac{1}{l}-\frac{1}{l_1}\right)+B\frac{\omega^2L^2}{l_1^2}+\ldots . \tag{A29}$$

APPENDIX B

DERIVATION OF THE PROBABILITY DISTRIBUTION FUNCTION $P(\boldsymbol{R}, L)$

Let us consider the average of exp ($\lambda \int \dot{r}\,\mathrm{d}s$) in general *i.e.*,

$$\frac{\int \mathrm{e}^{\lambda\int \dot{r}\,\mathrm{d}s-\frac{3}{2l}\int \dot{r}^2\,\mathrm{d}s-\omega\iint \delta[r(s)-r(s')]\,\mathrm{d}s\,\mathrm{d}s'}\,\delta r}{\int \mathrm{e}^{-\frac{3}{2l}\int \dot{r}^2\,\mathrm{d}s-\omega\iint \delta[r(s)-r(s')]\,\mathrm{d}s\,\mathrm{d}s'}\,\delta r} \tag{B1}$$

$$= \frac{\int e^{-\frac{3}{2l}\int \dot{r}^2 + \lambda \int \dot{r}\, ds} (1+B)\, \delta r}{\int e^{-\frac{3}{2l}\int \dot{r}^2\, ds} (1+B)} \tag{B2}$$

where $B = -\omega \int\int \delta[r(s)-r(s')] ds\, ds'$ and we have retained terms to order B only The above can be written as

$$\frac{\langle e^{\lambda \int \dot{r}\, ds} \rangle + \langle e^{\lambda \int \dot{r}} B \rangle}{1+\langle B \rangle} \tag{B3}$$

where

$$\langle e^{\lambda \int \dot{r}} \rangle = \int e^{-\frac{3}{2l}\int \dot{r}^2 + \lambda \int \dot{r}}\, \delta r$$

and we have to order B

$$\frac{\langle e^{\lambda \int \dot{r}} \rangle}{\int e^{-C}\, \delta r} + \left[\frac{\langle e^{\lambda \int \dot{r}} B \rangle}{\int e^{-C}} - \frac{\langle e^{\lambda \int \dot{r}} \rangle \langle B \rangle}{(\int e^{-C})^2} \right] + \mathcal{O}(B^2) + \ldots . \tag{B4}$$

Consider the first term

$$\frac{\int e^{-\frac{3}{2l}\int \dot{r}^2\, ds + \lambda \int \dot{r}\, ds}\, \delta r}{\int e^{-\frac{3}{2l}\int \dot{r}^2\, ds}\, \delta r}.$$

We can complete the square in the numerator

$$\int e^{-\frac{3}{2l}\int (\dot{r} - \frac{\lambda l}{3})^2}\, e^{\frac{\lambda^2 l L}{6}}\, \delta r; \tag{B5}$$

changing the variables to $R \to r - i\lambda l\sigma/3$ we finally get $e^{\frac{\lambda^2 l L}{6}}$.

Now let us consider the first integral of the second term in the bracket.

$$\int e^{-\frac{3}{2l}\int \dot{r}^2 + \lambda \int \dot{r}} B\, \delta r$$

$$= -\frac{\omega}{(2\pi)^3} \int e^{-\frac{3}{2l}\int \dot{r}^2 + \lambda \int \dot{r} + ik[r(s)-r(s')]}\, ds\, ds'\, d^3k\, \delta r$$

$$= -\left(\frac{\omega}{2\pi^2}\right) \int e^{\frac{\lambda^2 Ll}{6}} \int e^{-\frac{3}{2l}\int R^2 - \frac{l}{6}|s-s'|(k-i\lambda)^2 - \frac{\lambda^2 l|s-s'|}{6}}\, \delta R k^2\, dk\, ds\, ds'$$

$$= -\left(\frac{\omega}{2\pi^2}\right) \int e^{-k^2 \frac{l}{6}|s-s'| - \frac{\lambda^2 l|s-s'|}{6}}\, e^{\frac{\lambda^2 Ll}{6}}\, k^2\, dk\, ds\, ds'. \tag{B6}$$

Performing the k integration yields

$$-\frac{\omega L^{\frac{1}{2}}}{8 l^{\frac{3}{2}}} \left(\frac{6}{\pi}\right)^{\frac{3}{2}} e^{\lambda^2 \frac{Ll}{6}} \int\int_0^L \frac{e^{-\frac{\lambda^2 l|s-s'|}{6}}}{|s-s'|^{\frac{3}{2}}}\, ds\, ds'. \tag{B7}$$

The second term of the square bracket in eqn (2.4) gives

$$-\frac{\omega}{8 l^{\frac{3}{2}}} \left(\frac{6}{\pi}\right)^{\frac{3}{2}} L^{\frac{1}{2}}\, e^{\lambda^2 \frac{Ll}{6}}. \tag{B8}$$

From eqn (B4), (B7) and (B8) we have

$$\left[-\lambda^2\,\frac{Ll_1^2}{6}\left(\frac{1}{l}-\frac{1}{l_1}\right)+\frac{1}{8}\left(\frac{6}{\pi}\right)^{\frac{3}{2}}\left(\frac{\omega L^{\frac{1}{2}}}{l_1^{\frac{3}{2}}}\right)\int_0^L \frac{\left(1-\mathrm{e}^{-\frac{\lambda^2 L l_1 \sigma}{6}}\right)}{\sigma^{\frac{3}{2}}}\,\mathrm{d}\sigma\right]=0 \tag{B9}$$

which in terms of x reduces to

$$\frac{x}{6}l_1\left(\frac{1}{l}-\frac{2}{l_1}\right)=\left(\frac{3}{4}\right)\sqrt{\frac{6}{\pi^3}}\left(\frac{\omega L^{\frac{1}{2}}}{l_1^{\frac{3}{2}}}\right)\int_0^1 \frac{\left(1-\mathrm{e}^{-\frac{x\sigma}{6}}\right)}{\sigma^{\frac{3}{2}}}\,\mathrm{d}\sigma. \tag{B10}$$

Here two cases are of interest to us.

CASE I:

$$x=\lambda^2 L l_1 \text{ small yields,}$$

with

$$y=\frac{\omega L^{\frac{1}{2}}}{l_1^{\frac{3}{2}}}\quad\text{and}\quad l_1 \gg l$$

$$x\left(\frac{l_1}{l}\right)\cong 2\sqrt{\frac{6}{\pi^3}}\,xy$$

whose solution gives

$$l_1 \cong (2)^{\frac{2}{5}}\left(\frac{6}{\pi^3}\right)^{\frac{1}{5}}\omega^{\frac{2}{5}}l^{\frac{2}{5}}L^{\frac{1}{5}}, \tag{B11}$$

which is our previous result.

CASE II: x large. This gives with a change of variable

$$\frac{x}{6}\left(\frac{l_1}{l}\right)=\left(\frac{3}{2}\right)\frac{\sqrt{x}}{\pi^{\frac{3}{2}}}y\int_0^\infty\left(1-\mathrm{e}^{-t^2}\right)\frac{\mathrm{d}t}{t^2}. \tag{B12}$$

The integral can be evaluated and is equal to $\sqrt{\pi}$. With this we have

$$\sqrt{x}=\left(\frac{9}{\pi}\right)\left(\frac{l}{l_1}\right)y$$

$$l_1^3=\left(\frac{9}{\pi}\right)\left(\frac{\omega l}{\lambda}\right)$$

which yields

$$l_1=\left(\frac{9}{\pi}\right)^{\frac{1}{3}}\left(\frac{\omega l}{\lambda}\right)^{\frac{1}{3}}. \tag{B13}$$

With this

$$Q(\lambda)\sim \mathrm{e}^{(9/\pi)^{\frac{1}{3}}\lambda^{\frac{5}{3}}L(\omega L)^{\frac{1}{3}}}$$

and

$$P(\boldsymbol{k})=\mathrm{e}^{(\mathrm{i}k)^{\frac{5}{3}}(9/\pi)^{\frac{1}{3}}L(\omega l)^{\frac{1}{3}}} \tag{B14}$$

and

$$P(\boldsymbol{R},L)\sim\int \mathrm{e}^{(\mathrm{i}k)^{\frac{5}{3}}(9/\pi)^{\frac{1}{3}}\omega^{\frac{1}{3}}l^{\frac{1}{3}}L-\mathrm{i}\boldsymbol{k}.\boldsymbol{R}}\,\mathrm{d}^3k. \tag{B15}$$

At this stage the evaluation of the integral is done by steepest descent which requires

$$\left(\frac{5}{3}\right)\left(\frac{9}{\pi}\right)^{\frac{1}{3}} \mathrm{i}^{\frac{5}{3}} k^{\frac{2}{3}} \omega^{\frac{1}{3}} l^{\frac{1}{3}} L = \mathrm{i}R$$

i.e.,

$$k^{\frac{2}{3}} = \left(\frac{3}{5}\right)\frac{R}{\mathrm{i}^{\frac{2}{3}}(9/\pi)^{\frac{1}{3}}\omega^{\frac{1}{3}} l^{\frac{1}{3}} L}$$

or

$$k = \left(\frac{3}{5}\right)^{\frac{3}{2}} \frac{R^{\frac{3}{2}}}{\mathrm{i}(9/\pi)^{\frac{1}{2}}(\omega l)^{\frac{1}{2}} L^{\frac{3}{2}}}. \tag{B17}$$

With this, the probability distribution becomes

$$P(\boldsymbol{R}, L) \sim \mathrm{e}^{-\left(\frac{3}{5}\right)^{\frac{3}{2}} \frac{\sqrt{\pi}}{3}\left[\frac{R^2}{L^{\frac{6}{5}}\omega^{\frac{2}{5}} l^{\frac{2}{5}}}\right]^{\frac{5}{4}}}. \tag{B18}$$

The probability distribution $P(\boldsymbol{R}, L)$ can also be similarly found for the case when x is small. In this case

$$Q(\lambda) \sim \mathrm{e}^{\lambda^2 L l_1}$$
$$= \mathrm{e}^{\lambda^2 L^{\frac{6}{5}}(2)^{\frac{2}{5}}(6/\pi_3)^{\frac{1}{5}}\omega^{\frac{2}{5}} l^{\frac{2}{5}}}$$

and

$$P(\boldsymbol{k}) \cong \mathrm{e}^{(2)^{\frac{2}{5}}(6/\pi_3)^{\frac{1}{5}}(\mathrm{i}k)^2(\omega l)^{\frac{2}{5}} L^{\frac{6}{5}}}$$

and

$$P(\boldsymbol{R}, L) \sim \int \mathrm{e}^{-(2)^{\frac{2}{5}}(6/\pi_3)^{\frac{1}{5}} k^2 (\omega l)^{\frac{2}{5}} L^{\frac{6}{5}} - \mathrm{i}\boldsymbol{k}.\boldsymbol{R}}\, \mathrm{d}^3 k. \tag{B19}$$

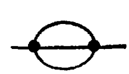
Doing the integration again by steepest descent yields

$$P(\boldsymbol{R}, L) \sim \exp\left[-\frac{1}{2(2)^{\frac{2}{5}}}\left(\frac{\pi^3}{6}\right)^{\frac{1}{5}} \frac{R^2}{L^{\frac{6}{5}}\omega^{\frac{2}{5}} l^{\frac{2}{5}}}\right]. \tag{B20}$$

Since $x = k^2 L l_1$ is small in our previous calculation, it is not difficult to see that higher orders add corrections to $P(\boldsymbol{R}, L)$ in the form [use eqn (2.24), (2.26) and (2.28)]

$$\log p(\boldsymbol{R}, L) \simeq -\left[\frac{1}{2.24} + \frac{1}{2.10} + \frac{1}{2.06} + \dots\right] \frac{R^2}{L^{\frac{6}{5}}\omega^{\frac{2}{5}} l^{\frac{2}{5}}}. \tag{B21}$$

At this point it is of interest to examine if higher order terms affect the probability distribution for x large. For this we again have to find the contributions from the following diagrams

 ,  and  .

It is found that the contribution from  can be written as follows

$$\frac{1}{2\pi}\int \frac{\mathrm{e}^{\mathrm{i}EL}\,\mathrm{d}E}{(\mathrm{i}E + \frac{1}{6}lk^2)^3}\left\{\frac{1}{(2\pi)^3}\int \frac{\mathrm{d}^3 j}{(\mathrm{i}E + \frac{1}{6}lj^2)}\right\}^2 -$$
$$\frac{1}{2\pi}\int \frac{\mathrm{e}^{\mathrm{i}EL}}{(\mathrm{i}E)^3}\,\mathrm{d}E \left\{\frac{1}{(2\pi)^3}\int \frac{\mathrm{d}^3 j}{(\mathrm{i}E - \frac{1}{6}lj^2)}\right\}^2 \mathrm{e}^{-\frac{k^2 L l}{6}} \tag{B22}$$

which we write as $C'-D'$ where

$$C' = \frac{27}{4\pi^3}\left(\frac{\omega^2}{l^3}\right)\int \frac{e^{iEL}\, iE\, dE}{(iE+\frac{1}{6}lk^2)^3}.$$

Putting $iE+l/6\, k^2 = iF$ we get

$$C' = -\frac{27}{4\pi^3}\left(\frac{\omega^2}{l^3}\right) e^{-k^2\frac{Ll}{6}}\left[\int \frac{e^{iFL}}{F^2}\, dF - \frac{x}{6L}\int \frac{e^{iFL}}{iF^3}\, dF\right]$$

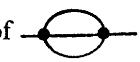
$$= -\frac{27}{4\pi^3}\left(\frac{L\omega^2}{l^3}\right) e^{-k^2\frac{Ll}{6}}\left[\int \frac{e^{iE}}{E^2}\, dE - \frac{x}{6}\int \frac{e^{iE}}{iE^3}\, dR\right]. \tag{B23}$$

Similarly D' can be evaluated to give

$$D' = -\left(\frac{27}{4\pi^3}\right)\left(\frac{L\omega^2}{l^3}\right) e^{-k^2\frac{Ll}{6}}\int \frac{e^{iE}}{E^2}\, dE. \tag{B24}$$

Therefore $C'-D'$ becomes

$$= \frac{9}{8\pi^3}\left(\frac{\omega^2 L}{l^3}\right) x\, e^{-k^2\frac{Ll}{6}}\, i\int \frac{e^{iE}}{E^3}\, dE. \tag{B25}$$

Now to find the contribution of  we have to evaluate the following integrals

$$\frac{\omega^2\alpha}{2\pi l^3}\left[\int \frac{e^{iEL}}{(iE+\frac{1}{6}lk^2)^2}\, e^{ik.r-\beta\sqrt{\frac{E}{l}}r}\, \frac{d^3r}{r^3}\, dE - \int \frac{e^{iEL}}{(iE)^2}\, e^{-\beta\sqrt{\frac{E}{l}}r}\, \frac{d^3r}{r^3}\, dE\, e^{-k^2\frac{Ll}{6}}\right] \tag{B26}$$

i.e., $A'-B'$ where

$$A' = -\frac{\omega^2}{l^3}\alpha\int_{-1}^{1} dh\, e^{-k^2\frac{Ll}{6}}\int e^{iFL+ikrh-\beta'\sqrt{F+i\frac{lk^2}{6}}}\, dF\, \frac{dr}{r}$$

where

$$\beta' = \frac{\beta}{\sqrt{l}} = 3\sqrt{\frac{6}{l}} \quad \text{and} \quad \alpha = \left(\frac{6}{4\pi}\right)^3.$$

Similarly we can write for B'

$$B' = -\frac{\omega^2\alpha}{l^3}\int_{-1}^{1} dh\, e^{-k^2\frac{Ll}{6}}\int \frac{e^{iFL}}{F^2}\, dF\, \frac{dr}{r}$$

and

$$A'-B' = \omega^2\alpha\, e^{-k^2\frac{Ll}{6}}\int_{-1}^{1} dh\int \frac{e^{iFL}}{F^2}\, dF\left[(e^{-\beta'+\sqrt{F}r} - e^{ikrh-\beta'\sqrt{F+i\frac{lk^2}{6}}r})\, \frac{dr}{r}\right] \tag{B27}$$

using the following identity

$$\int (e^{-ar}-e^{-br})\frac{dr}{r} = \log\frac{b}{a}.$$

We can write

$$A'-B' = \omega^2\alpha\, e^{-k^2\frac{Ll}{6}} \int_{-1}^{1} dh \int \frac{e^{iFL}}{F^2}\, dF \log\left\{\frac{\beta'\sqrt{F+\frac{ilk^2}{6}-ikh}}{\beta'\sqrt{F}}\right\}. \tag{B28}$$

The logarithmic term can be written for x small

$$\log\left\{1+i\left(\frac{x}{12LF}-\frac{x^{\frac12}h}{\beta\sqrt{FL}}\right)\right\}$$

which can be expanded

$$i\left(\frac{x}{12FL}-\frac{x^{\frac12}h}{\beta\sqrt{FL}}\right)+\frac{1}{2}\left(\frac{x}{12FL}-\frac{x^{\frac12}h}{\beta\sqrt{FL}}\right)^2$$

$$= -i\frac{x^{\frac12}h}{\beta\sqrt{FL}}+\left(\frac{i}{12FL}+\frac{h^2}{2\beta^2FL}\right)x-\frac{x^{\frac32}h}{24\beta L^{\frac32}F^{\frac32}}+\frac{x^2}{2(144)F^2L^2}+\ldots. \tag{B29}$$

All the terms containing odd powders of h will drop upon integration, therefore we will finally have retaining only first power in x

$$A'-B' = 2\alpha\, e^{-k^2\frac{Ll}{6}}\omega^2 x\left[\int \frac{e^{iFL}}{F^2}\left(\frac{i}{12FL}-\frac{1}{6\beta^2FL}\right)dF\right]$$

$$= 2\alpha\omega^2 xL\, e^{-k^2\frac{Ll}{6}}\left[i\int\frac{e^{iE}}{E^3}\,dE-\frac{1}{6\beta^2}\int\frac{e^{iE}}{E^3}\,dE\right]$$

$$\cong 2\alpha\omega^2 xL\, e^{-k^2\frac{Ll}{6}}\chi_0. \tag{B30}$$

For x large the major contribution to the integral can be written as follows

$$A'-B' \simeq 2\alpha\frac{\omega^2L}{l^3}\log x\int\frac{e^{iE}}{E^2}\,dE = 2\alpha\frac{\omega^2L}{l^3}(\log x)\chi_0'. \tag{B31}$$

The contribution of the diagram  can be obtained from the following

$$\frac{1}{2\pi}\int\frac{e^{iEL}dE}{(iE+\frac16lk^2)^2}\left\{\frac{1}{(2\pi)^3}\int\frac{d^3j}{(iE+\frac16lj^2)^2}\right\}\left\{\frac{1}{(2\pi)^3}\int\frac{d^3j'}{(iE+\frac16lj'^2)}\right\}-$$

$$\frac{1}{2\pi}\int\frac{e^{iEL}}{(iE)^2}\,dE\left\{\frac{1}{(2\pi)^3}\int\frac{d^3j}{(iE+\frac16lj^2)^2}\right\}\frac{1}{(2\pi)^3}\int\left(\frac{d^3j'}{(iE+\frac16lj'^2)}\right)e^{-k^2\frac{Ll}{6}}. \tag{B32}$$

We need evaluate integrals of the following type

$$\int\frac{d^3j}{(iE+\frac16lj^2)}\quad\text{which can be expressed as}\quad = C-2\pi^2\omega\left(\frac{6}{l}\right)^{\frac32}\sqrt{iE}$$

where C is the divergent term. But the divergence has to do with the shape of ω and can be thrown. The above integrations are straightforward and give zero. We omit their exact evaluation and quote the result finally to second order in ω

$$\frac{x}{6}\left(\frac{l_1}{l}\right)^2+\frac{x^2}{72}\left(\frac{l_1}{l}\right)^2 \simeq +\left(\frac{27}{4\pi^3}\right)\chi_0\left(\frac{\omega^2L}{l_1^3}\right)\frac{x}{6}-$$

$$(\log x)\, 2\alpha\left(\frac{\omega^2L}{l^3}\right)\chi_0'+\mathcal{O}(1)\left(\frac{\omega^2L}{l^3}\right)+\text{cross terms}\ldots. \tag{B33}$$

The important thing is that for x small we still retain the structure of the equation for $l_1 > l$, *i.e.*,

$$l_1 \simeq l^{\frac{2}{5}}\omega^{\frac{2}{5}}L^{\frac{1}{5}}$$

so that there is only the change of the coefficient, as noticed in the previous calculation.

For x large we have

$$\frac{x}{6}\left(\frac{l_1}{l}\right)^2 + \frac{x^2}{72}\left(\frac{l_1}{l}\right)^2 - \left(\frac{27x}{24\pi^3}\right)\left(\frac{\omega^2 L}{l_1^3}\right)\chi_0 + 2\alpha\chi_0' \frac{\omega^2 L}{l_1^3}(\log x) - \mathcal{O}(1)\left(\frac{\omega^2 L}{l_1^3}\right) - \text{cross terms} + \ldots = 0. \tag{B34}$$

To evaluate χ_0 and χ_0' we employ the following

$$\frac{1}{2\pi \mathrm{i}} \oint \frac{\mathrm{e}^{\mathrm{i}E}}{E^n}\, \mathrm{d}E = \frac{1}{(n-1)!}\frac{\partial^{n-1}}{\partial E^{n-1}}(\mathrm{e}^{\mathrm{i}E})_{E=0} \tag{B35}$$

and get

$$\chi_0 = \pi$$
$$\chi_0' = -2\pi \tag{B36}$$

with these eqn (B34) and (B12) can be recast into eqn (3.19) with the cross term as $\sim \omega k(1/l - 1/l_1)L$.