Polymer Journal, Vol. 10, No. 1, pp 27—36 (1978)

Intramolecular Interactions in a Flexible Polymer Molecule

Harumitsu MIYAKAWA and Nobuhiko SAITÔ

Department of Applied Physics, Waseda University, Nishiokubo 4-170, Shinjuku-ku, Tokyo 160, Japan.

(Received June 28, 1977)

ABSTRACT: The effect of intramolecular interactions on the configration of a flexible polymer molecule is investigated by the method of cluster expansion. Using the first approximation which takes account of the special type of diagrams, expansion parameters for the mean square end-to-end distance and the mean square radius of gyration are calculated near the Θ-temperature. It is shown that both expansion parameters are singular at the Θ-temperature. The expansion parameter for the mean square radius of gyration is a measurable quantity and to find the singularity experimentally it is necessary to measure the mean square radius of gyration at the temperature $|T-\Theta|<1K$ for $N=500$ or $|T-\Theta|<3K$ for $N=100$.

KEY WORDS Intramolecular Interactions / Excluded Volume Effect / Globule-Coil Transition / Diagrams / Expansion Parameter /

The globule-coil transition was first discovered experimentally in the solution of poly(methacrylic acid) by Birshtein, *et al.*,[1] and Ptitsyn, *et al.*[2] The cause of such transitions was attributed to the coexistence of the hydrophobic groups and hydrophilic groups in a macromolecular chain. On the other hand, such a transition phenomena was observed near the Θ-temperature in poly(vinyl acetate) in carbon tetrachloride and poly(*p*-chlorostyrene) in *n*-propylbenzene through dielectric and viscosity measurements and through small angle X-ray scattering by Mashimo, Chiba, and others.[3-5] In these molecules the residues cannot be differentiated into hydrophobic groups and hydrophilic groups. Therefore, the globule-coil transitions seem to be due to the attractive intramolecular interactions.

Repulsive intramolecular interactions bring about the excluded volume effect.[6] Langmuir[7] first suggested that attractive intramolecular interactions give rise to a transition such as the one mentioned above; this transition was also suggested by Stockmayer.[8] Statistical mechanical theories of the transitions were developed by Edwards[9] and by several workers.[10-15] One of the authors[16] has shown in preliminary reports that the globule-coil transition occurs at the Θ-temperature and that the expansion parameter for the mean square end-to-end distance changes abruptly at the Θ-temperature. Theoretically the globule-coil transition should occur at the Θ-temperature in the limit $N\rightarrow\infty$. The reason that the globule-coil transition occurs at the Θ-temperature in finite N in the present theory is due to the Gaussian approximation, which is valid only at the limit $N\rightarrow\infty$. This point will be discussed in a separate paper.

In this paper we calculate the expansion parameters for the mean square end-to-end distance α^2 and for the radius of gyration $\alpha_s{}^2$ below and above the Θ-temperature. Our calculation is based upon the Ursell—Mayer cluster expansion; the first approximation,[17] which takes account of the special type of diagrams, is used. In such a way it can be shown that both expansion parameters, α^2 and $\alpha_s{}^2$, are singular at the Θ-temperature.

PARTITION FUNCTION

The partition function of a polymer molecule with fixed end-to-end distance has been already obtained in the first approximation by the method of a generating function.[16] Here we show that this partition function can also be obtained by the diagramatic method.

We consider a flexible polymer molecule in solution. A polymer in solution is assumed to be represented by a model which is constructed of $N+1$ segments linked by N bonds of length b. The segments are numbered from 0 to N along the chain; the coordinates of the ith segment are denoted by $\boldsymbol{r}_i$ and the interaction energy between the ith and jth segments is assumed to be $u(\boldsymbol{r}_i-\boldsymbol{r}_j)=u(\boldsymbol{r}_{ij})$. Then the partition function with fixed end-to-end distance can be written as

$$Q(\boldsymbol{r}_N-\boldsymbol{r}_0, N)=\int\cdots\int P(\boldsymbol{r}_0\cdots\boldsymbol{r}_N)\times\exp\left[-\beta\sum_{i<j}\sum u(\boldsymbol{r}_{ij})\right]\prod_{i=1}^{N-1}\mathrm{d}\boldsymbol{r}_i \quad (1)$$

where $P(\boldsymbol{r}_0\cdots\boldsymbol{r}_N)$ is assumed gaussian:

$$P(\boldsymbol{r}_0\cdots\boldsymbol{r}_N)=\prod_{i=1}^{N}\left(\frac{3}{2\pi b^2}\right)^{3/2}\exp\left(-\frac{3|\boldsymbol{r}_i-\boldsymbol{r}_{i-1}|^2}{2b^2}\right) \quad (2)$$

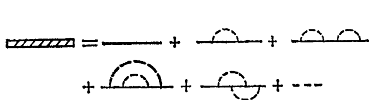
and $1/\beta$ is the absolute temperature multiplied by the Boltzmann constant. We define χ_{ij} by

$$\chi_{ij}=\exp\left[-\beta u(\boldsymbol{r}_{ij})\right]-1 \quad (3)$$

and expand Q in powers of χ's.

$$Q(\boldsymbol{r}_N-\boldsymbol{r}_0, N)=\int\cdots\int P(\boldsymbol{r}_0\cdots\boldsymbol{r}_N)\left(1+\sum_{i<j}\sum\chi_{ij}+\sum_{i<j}\sum\sum_{k<l}\sum\chi_{ij}\chi_{kl}+\cdots\right)\prod_{i=1}^{N-1}\mathrm{d}\boldsymbol{r}_i \quad (4)$$

If we represent Q by , Q_0 by ——, and χ_{ij} by , eq 4 can be written in the diagramatic form:



(5)

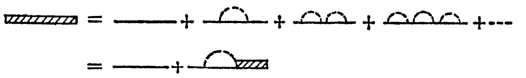
The expression which corresponds to any arbitrary diagram can be written down immediately. For example, the third term of the right hand side of eq 5 is found to correspond to the following expression, after integrating all the coordinates except $\boldsymbol{r}_i$, $\boldsymbol{r}_j$, $\boldsymbol{r}_k$, and $\boldsymbol{r}_l$:

$$\sum_{i<j<k<l}\sum\sum\sum\int\mathrm{d}\boldsymbol{r}_i\,\mathrm{d}\boldsymbol{r}_j\,\mathrm{d}\boldsymbol{r}_k\,\mathrm{d}\boldsymbol{r}_l Q_0(\boldsymbol{r}_i-\boldsymbol{r}_0, i)\times Q_0(\boldsymbol{r}_j-\boldsymbol{r}_i, j-i)Q_0(\boldsymbol{r}_k-\boldsymbol{r}_j, k-j)\times Q_0(\boldsymbol{r}_l-\boldsymbol{r}_k, l-k)Q_0(\boldsymbol{r}_N-\boldsymbol{r}_l, N-l)\chi_{ij}\chi_{kl} \quad (6)$$

where Q_0 is

$$Q_0(\boldsymbol{r}_j-\boldsymbol{r}_i, j-i)=\left(\frac{3}{2\pi(j-i)b^2}\right)^{3/2}\times\exp\left(-\frac{3|\boldsymbol{r}_j-\boldsymbol{r}_i|^2}{2(j-i)b^2}\right) \quad (7)$$

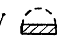
Next we make an approximation which takes account of only the following type of diagrams.[17]



(8)

The second line of eq 8 forms a diagramatic equation and can be written in the form of an integro-difference equation:

$$Q(\boldsymbol{r}_N-\boldsymbol{r}_0, N)=Q_0(\boldsymbol{r}_N-\boldsymbol{r}_0, N)+\sum_{i<j}\sum\int\mathrm{d}\boldsymbol{r}_i\,\mathrm{d}\boldsymbol{r}_j Q_0(\boldsymbol{r}_i-\boldsymbol{r}_0, i)\times Q_0(\boldsymbol{r}_j-\boldsymbol{r}_i, j-i)Q(\boldsymbol{r}_N-\boldsymbol{r}_j, N-j)\chi_{ij} \quad (9)$$

We call this approximation as the first approximation. We shall be able to include such diagrams as the fourth and fifth terms on the right hand side of eq 5 by replacing  by  in eq 8 and by introducing the vertex, respectively. But we shall consider only the first approximation in this paper. To solve eq 9 we make a change of variables:

$$\boldsymbol{r}_N-\boldsymbol{r}_0=\boldsymbol{R}, \quad \boldsymbol{r}_i-\boldsymbol{r}_0=\boldsymbol{R}_1, \quad \boldsymbol{r}_j-\boldsymbol{r}_i=\boldsymbol{R}_2, \quad \boldsymbol{r}_N-\boldsymbol{r}_j=\boldsymbol{R}_3 \quad (10)$$

$$i=n_1, \quad j-i=n_2, \quad N-j=n_3 \quad (11)$$

The following relations hold among the new variables:

$$\boldsymbol{R}_1+\boldsymbol{R}_2+\boldsymbol{R}_3=\boldsymbol{R} \quad (12)$$

$$n_1+n_2+n_3=N \quad (13)$$

Then eq 9 becomes

$$Q(\boldsymbol{R}, N)=Q_0(\boldsymbol{R}, N)+\sum_{n_1,n_2,n_3}{}'\int{}'\mathrm{d}\boldsymbol{R}_1\,\mathrm{d}\boldsymbol{R}_2\,\mathrm{d}\boldsymbol{R}_3\times Q_0(\boldsymbol{R}_1, n_1)Q_0(\boldsymbol{R}_2, n_2)Q(\boldsymbol{R}_3, n_3)\chi(\boldsymbol{R}_2) \quad (14)$$

The prime with the summation sign means that we make the summation under the condition given by eq 13 and the prime with the integration sign means that we carry out the integration under the condition given by eq 12. Let us define the Fourier transformation and generating function of Q, Q_0, and χ by

$$W(\boldsymbol{k}, z)=\sum_{N=0}^{\infty} z^N \int \mathrm{d}\boldsymbol{r}\, \mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}} Q(\boldsymbol{r}, N) \quad (15)$$

$$W_0(\boldsymbol{k}, z)=\sum_{N=0}^{\infty} z^N \int \mathrm{d}\boldsymbol{r}\, \mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}} Q_0(\boldsymbol{r}, N)$$
$$=\left[1-z\exp\left(-\frac{b^2}{6}k^2\right)\right]^{-1} \quad (16)$$

and

$$\tilde{\chi}(\boldsymbol{k})=\int \mathrm{d}\boldsymbol{r}\, \mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \chi(\boldsymbol{r}) \quad (17)$$

Then eq 14 becomes

$$W(\boldsymbol{k}, z)=W_0(\boldsymbol{k}, z)+W_0(\boldsymbol{k}, z)W(\boldsymbol{k}, z) \times \int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3}\tilde{\chi}(\boldsymbol{q})W_0(\boldsymbol{k}-\boldsymbol{q}, z) \quad (18)$$

which yields

$$W(\boldsymbol{k}, z)=\frac{W_0(\boldsymbol{k}, z)}{1-W_0(\boldsymbol{k}, z)\displaystyle\int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3}\tilde{\chi}(\boldsymbol{q})W_0(\boldsymbol{k}-\boldsymbol{q}, z)} \quad (19)$$

Here we assume that

$$\chi(\boldsymbol{r})=-\beta_1\delta(\boldsymbol{r}) \quad (20)$$

namely,

$$\tilde{\chi}(\boldsymbol{q})=-\beta_1 \quad (21)$$

Here β_1 is the excluded volume and is given by

$$\beta_1=\int [1-\mathrm{e}^{-\beta u(r)}]\,\mathrm{d}\boldsymbol{r}=\frac{4\pi a^3}{3}\left(1-\frac{\Theta}{T}\right) \quad (22)$$

where a is a diameter of the segment. Using eq 16 and 21, eq 19 becomes

$$W(\boldsymbol{k}, z)=\left[1-z\exp\left(-\frac{b^2}{6}k^2\right)+\beta_1'\phi\left(z, \frac{3}{2}\right)\right]^{-1} \quad (23)$$

where β_1' is given by

$$\beta_1'=\left(\frac{3}{2\pi b^2}\right)^{3/2}\beta_1 \quad (24)$$

and $\phi(z, s)$ is defined by

$$\phi(z, s)=\sum_{n=1}^{\infty} z^n/n^s \quad (25)$$

MEAN SQUARE END-TO-END DISTANCE

Now we calculate the expansion parameter for the mean square end-to-end distance defined by

$$\alpha^2=\langle r^2\rangle/\langle r^2\rangle_0\,, \qquad \langle r^2\rangle_0=Nb^2 \quad (26)$$

If we know the Fourier transformation and the generating function $W(\boldsymbol{k}, z)$ of the partition function with fixed end-to-end distance, we can calculate the mean square end-to-end distance from $W(\boldsymbol{k}, z)$ in the following way:

$$\langle r^2\rangle=b^2I_N/Z_N \quad (27)$$

where

$$Z_N=\frac{1}{2\pi i}\oint \frac{\mathrm{d}z}{z^{N+1}}W(0, z) \quad (28)$$

and

$$b^2I_N=\frac{1}{2\pi i}\oint \frac{\mathrm{d}z}{z^{N+1}}[-\nabla_k{}^2W(\boldsymbol{k}, z)]_{k=0} \quad (29)$$

From eq 26 and 27, the expansion parameter can be written as

$$\alpha^2=\frac{1}{N}\frac{I_N}{Z_N} \quad (30)$$

Since the first approximation $W(\boldsymbol{k}, z)$ is given by eq 23, Z_N and I_N have the following forms:

$$Z_N=\frac{1}{2\pi i}\oint \frac{\mathrm{d}z}{z^{N+1}}\frac{1}{1-z+\beta_1'\phi\left(z, \frac{3}{2}\right)} \quad (31)$$

$$I_N=\frac{1}{2\pi i}\oint \frac{\mathrm{d}z}{z^{N+1}}\frac{z}{\left[1-z+\beta_1'\phi\left(z, \frac{3}{2}\right)\right]^2} \quad (32)$$

For $\beta_1'<0$ the integrals eq 31 and 32 are evaluated from the residues at the pole $z=z_0$ for large N and, when $z_0<1$

$$Z_N'\simeq-\frac{1}{z_0{}^N\left[-z_0+\beta_1'\phi\left(z_0, \frac{1}{2}\right)\right]} \quad (33)$$

$$I_N'\simeq\frac{N}{z_0{}^{N-1}\left[-z_0+\beta_1'\phi\left(z_0, \frac{1}{2}\right)\right]^2} \times\left[1+\frac{\beta_1'}{N}\frac{\phi\left(z_0, -\frac{1}{2}\right)-\phi\left(z_0, \frac{1}{2}\right)}{-z_0+\beta_1'\phi\left(z_0, \frac{1}{2}\right)}\right] \quad (34)$$

Consequently,

$$\alpha^2 = \frac{z_0}{z_0 - \beta_1'\phi\left(z_0, \frac{1}{2}\right)} \times \left[1 + \frac{\beta_1'}{N} \frac{\phi\left(z_0, -\frac{1}{2}\right) - \phi\left(z_0, \frac{1}{2}\right)}{-z_0 + \beta_1'\phi\left(z_0, \frac{1}{2}\right)}\right] \quad (35)$$

where

$$1 - z_0 + \beta_1'\phi\left(z_0, \frac{3}{2}\right) = 0 \quad (36)$$

As shown in Appendix A, we have for $\beta_1' \rightarrow 0-$, and thus $z_0 \rightarrow 1-$,

$$-\beta_1'\phi\left(z_0, \frac{1}{2}\right) \rightarrow \sqrt{-\beta_1'}\sqrt{\pi}\,\zeta\left(\frac{3}{2}\right)^{-1/2} \quad (37)$$

and

$$-\beta_1'\phi\left(z_0, -\frac{1}{2}\right) \rightarrow \frac{1}{\sqrt{-\beta_1'}} \frac{\sqrt{\pi}}{2} \zeta\left(\frac{3}{2}\right)^{-3/2} \quad (38)$$

Accordingly we obtain for small β_1',

$$Z_N' \rightarrow 1 - \sqrt{-\beta_1'}\sqrt{\pi}\,\zeta\left(\frac{3}{2}\right)^{-1/2} \quad (39)$$

$$I_N' \rightarrow N\left(1 - 2\sqrt{-\beta_1'}\sqrt{\pi}\,\zeta\left(\frac{3}{2}\right)^{-1/2}\right) + \frac{1}{\sqrt{-\beta_1'}} \frac{\sqrt{\pi}}{2} \zeta\left(\frac{3}{2}\right)^{-3/2} \quad (40)$$

which means that I_N' given by eq 34 diverges for small β_1'. In this case we have to take account of the contributions from the contour integrals around the branch cut which are given in Appendix A. The divergent term in eq 40 can be shown to be cancelled, and we have (see eq A-13)

$$\alpha^2 = 1 - 2\sqrt{-\beta_1'}\sqrt{\pi}\,\zeta\left(\frac{3}{2}\right)^{-1/2} \quad (41)$$

For $\beta_1' > 0$ the integrands of eq 31 and 32 have no real pole inside the unit circle and the two poles nearest to the origin are determined by the equation:

$$1 - z + \beta_1'\phi_\pm\left(z, \frac{3}{2}\right) = 0 \quad (42)$$

where ϕ_+ and ϕ_- are the values of $\phi(z, 3/2)$ just above and below the real axis, respectively, and are expanded as

$$\phi_\pm\left(z, \frac{3}{2}\right) = \zeta\left(\frac{3}{2}\right) \pm 2\sqrt{\pi}\, i\sqrt{z-1} + \zeta\left(\frac{1}{2}\right)(z-1) + \cdots \quad (43)$$

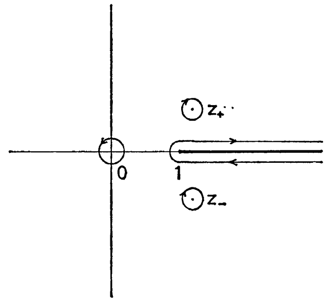


Figure 1. Path of integration for calculating Z_N and I_N for $\beta_1' > 0$.

Introducing eq 43 into eq 42 and ignoring the higher order terms of eq 43, the solutions of eq 42 are given as

$$z_\pm = 1 + \beta_1'\left[\zeta\left(\frac{3}{2}\right) - 2\pi\beta_1'\right] \pm i2\sqrt{\pi}\,\beta_1'^{3/2}\sqrt{\zeta\left(\frac{3}{2}\right) - \pi\beta_1'} \quad (44)$$

Besides the poles, the integrands of eq 31 and 32 have a branch cut on the real axis ($1 < z < \infty$). The integrals of eq 31 and 32 are replaced by the sum of the residues of the pole $z_\pm$ and the contour integral around the branch cut. (see Figure 1) Then we can write

$$Z_N = Z_N' + Z_N'' \quad (45)$$

$$I_N = I_N' + I_N'' \quad (46)$$

where Z_N', Z_N'', I_N', and I_N'' are given by

$$Z_N' = -\frac{1}{z_+^N\left[-z_+ + \beta_1'\phi_+\left(z_+, \frac{1}{2}\right)\right]} + \text{c.c.} \quad (47)$$

$$Z_N'' = \frac{1}{2\pi i}\int_1^\infty \frac{d\xi}{\xi^{N+1}}\left(\frac{1}{1-\xi+\beta_1'\phi_+} - \frac{1}{1-\xi+\beta_1'\phi_-}\right) \quad (48)$$

$$I_N' = \frac{N}{z_+^{N-1}\left[-z_+ + \beta_1'\phi\left(z_+, \frac{1}{2}\right)\right]^2} \times \left[1 + \frac{\beta_1'}{N} \frac{\phi\left(z_+, -\frac{1}{2}\right) - \phi\left(z_+, \frac{1}{2}\right)}{-z_+ + \beta_1'\phi_+\left(z_+, \frac{1}{2}\right)}\right] + \text{c.c.} \quad (49)$$

$$I_N''=\frac{1}{2\pi i}\int_1^\infty \frac{d\xi}{\xi^N}\left[\frac{1}{(1-\xi+\beta_1'\phi_+)^2}-\frac{1}{(1-\xi+\beta_1'\phi_-)^2}\right] \quad (50)$$

Z_N'' and I_N'' are calculated in Appendix B; they yield for the case $\beta_1'N \ll 1$

$$Z_N''=-\exp\left[N\beta_1'\left(2\pi\beta_1'-\zeta\left(\frac{3}{2}\right)\right)\right](1+2\pi N\beta_1'^2+\cdots) \quad (51)$$

$$I_N''=-N\exp\left[N\beta_1'\left(2\pi\beta_1'-\zeta\left(\frac{3}{2}\right)\right)\right](1+4\pi N\beta_1'^2+\cdots) \quad (52)$$

Introducing eq 44 into eq 47 and 49 and regarding β_1' as small, Z_N' and I_N' can be calculated as

$$Z_N'=2\exp\left[N\beta_1'\left(2\pi\beta_1'-\zeta\left(\frac{3}{2}\right)\right)\right](1+2\pi N\beta_1'^2+\cdots) \quad (53)$$

$$I_N'=2N\exp\left[N\beta_1'\left(2\pi\beta_1'-\zeta\left(\frac{3}{2}\right)\right)\right](1+4\pi N\beta_1'^2+\cdots) \quad (54)$$

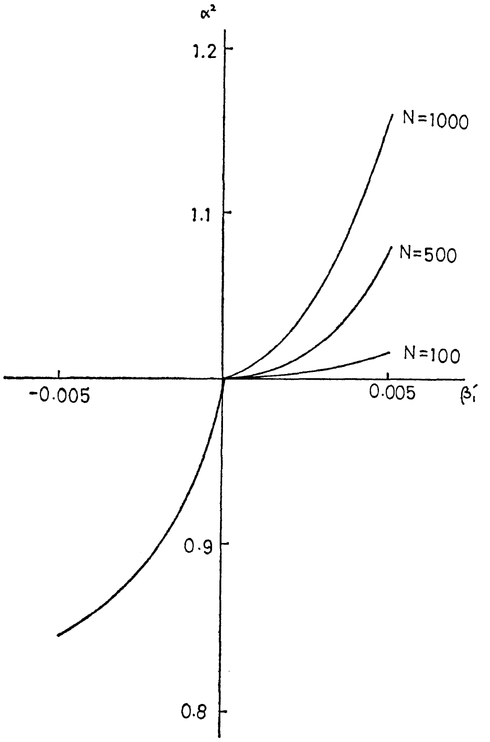


Figure 2. Expansion parameter α^2 as a function of β_1'.

From eq 51—54, Z_N and I_N become

$$Z_N=Z_N'+Z_N''=\exp\left[N\beta_1'\left(2\pi\beta_1'-\zeta\left(\frac{3}{2}\right)\right)\right](1+2\pi N\beta_1'^2+\cdots) \quad (55)$$

$$I_N=I_N'+I_N''=N\exp\left[N\beta_1'\left(2\pi\beta_1'-\zeta\left(\frac{3}{2}\right)\right)\right](1+4\pi N\beta_1'^2+\cdots) \quad (56)$$

Introducing eq 55 and 56 into eq 30, we obtain

$$\alpha^2=1+2\pi N\beta_1'^2+0(N^2\beta_1'^3) \quad (57)$$

From eq 41 and 57 it turns out that $\beta_1'=0$ ($T=\Theta$) is a singular point of α^2. (see Figure 2)

MEAN SQUARE RADIUS OF GYRATION

In this section we calculate the mean square radius of gyration, defined by

$$\langle s^2\rangle=\frac{1}{(N+1)^2}\sum_{i<j}\sum\langle r_{ij}^2\rangle \quad (58)$$

where $\langle r_{ij}^2\rangle$ is

$$\langle r_{ij}^2\rangle=\int r_{ij}^2 P(\boldsymbol{r}_0\cdots\boldsymbol{r}_N)\exp\left[-\beta\sum_{i<j}\sum u(r_{ij})\right]\prod_{i=0}^N d\boldsymbol{r}_i \times\left\{\int P(\boldsymbol{r}_0\cdots\boldsymbol{r}_N)\exp\left[-\beta\sum_{i<j}\sum u(r_{ij})\right]\times\prod_{i=0}^N d\boldsymbol{r}_i\right\}^{-1} \quad (59)$$

Performing the integral with respect to all the coordinates except $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$, eq 59 can be written as

$$\langle r_{ij}^2\rangle=\frac{1}{Z_N}\int r_{ij}^2 F(r_{ij}, j-i)\, d\boldsymbol{r}_{ij} \quad (60)$$

where Z_N is a normalization constant and is identical with eq 28 and $F(r_{ij}, j-i)$ is a partition function with fixed r_{ij} and is defined by

$$F(r_{ij}, j-i)=\int P(\boldsymbol{r}_0\cdots\boldsymbol{r}_N)\exp\left[-\beta\sum_{i<j}\sum u(r_{ij})\right]\times\prod_{k\neq i,j} d\boldsymbol{r}_k \quad (61)$$

If we know the Fourier transformation of $F(r_{ij}, j-i)$, which is defined by

$$\tilde{F}(\boldsymbol{k}, j-i)=\int d\boldsymbol{r}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}F(\boldsymbol{r}, j-i) \quad (62)$$

$\langle r_{ij}^2\rangle$ can be calculated from $\tilde{F}$ as follows:

$$\langle r_{ij}^2\rangle=Z_N^{-1}[-\nabla_k^2\tilde{F}(\boldsymbol{k}, j-i)]_{\boldsymbol{k}=0} \quad (63)$$

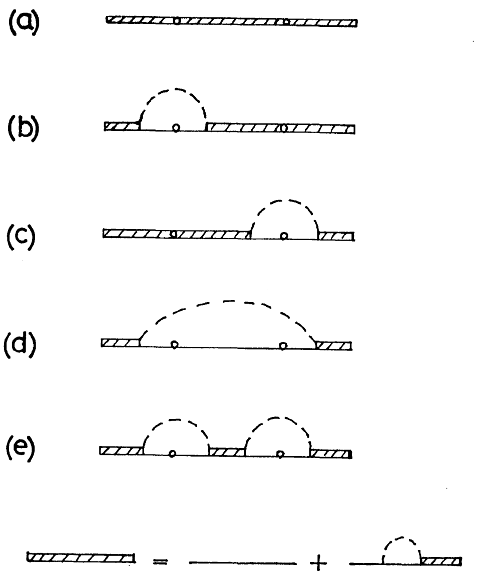


Figure 3. Diagrams necessary for calculating the mean sguare radius of gyration in the first approximation.

In the first approximation we must consider the five diagrams shown in Figure 3. Correspondingly the partition function with fixed r_{ij} can be written as

$$F(r_{ij}, j-i)=F^{(a)}(r_{ij}, j-i)+F^{(b)}(r_{ij}, j-i) +F^{(c)}(r_{ij}, j-i)+F^{(d)}(r_{ij}, j-i) +F^{(e)}(r_{ij}, j-i) \tag{64}$$

The expression which corrsponds to the diagram shown in Figure 3-a is

$$F^{(a)}(r_{ij}, j-i)=\int d\boldsymbol{r}_0\, d\boldsymbol{r}_N Q(\boldsymbol{r}_i-\boldsymbol{r}_0, i)Q(\boldsymbol{r}_j-\boldsymbol{r}_i, j-i) \times Q(\boldsymbol{r}_N-\boldsymbol{r}_j, N-j) \tag{65}$$

where Q is defined by eq 9. The Fourier transformation of eq 65 becomes

$$\tilde{F}^{(a)}(\boldsymbol{k}, j-i)=Z_i Z_{N-j}\frac{1}{2\pi i}\oint \frac{dz}{z^{j-i+1}}W(\boldsymbol{k}, z) \tag{66}$$

where Z_i and $W(\boldsymbol{k}, z)$ are given by eq 31 and eq 23, respectively. Introducing eq 66 into eq 63, we obtain

$$\langle r_{ij}^2\rangle^{(a)}=b^2 Z_N^{-1} Z_i Z_{N-j} I_{j-i} \tag{67}$$

where I_{j-i} is given by eq 29. The partition function with fixed r_{ij} which corresponds to Figure 3-b can be written as

$$F^{(b)}(r_{ij}, j-i)=\sum_{l=0}^{i}\sum_{m=i}^{j}\int d\boldsymbol{r}_0\, d\boldsymbol{r}_l\, d\boldsymbol{r}_m\, d\boldsymbol{r}_N Q(\boldsymbol{r}_l-\boldsymbol{r}_0, l) \times Q_0(\boldsymbol{r}_i-\boldsymbol{r}_l, i-l)Q_0(\boldsymbol{r}_m-\boldsymbol{r}_i, m-i) \times Q(\boldsymbol{r}_j-\boldsymbol{r}_m, j-m)Q(\boldsymbol{r}_N-\boldsymbol{r}_j, N-j) \times \chi(\boldsymbol{r}_m-\boldsymbol{r}_l) \tag{68}$$

The Fourier transformation of eq 68 becomes

$$\tilde{F}^{(b)}(\boldsymbol{k}, j-i)=\sum_{l=0}^{l}\sum_{m=i}^{j} Z_l Z_{N-j}\tilde{Q}(\boldsymbol{k}, j-m) \times \int \frac{d\boldsymbol{q}}{(2\pi)^3}\tilde{\chi}(\boldsymbol{q})\tilde{Q}_0(\boldsymbol{q}, i-l) \times \tilde{Q}_0(\boldsymbol{q}-\boldsymbol{k}, m-i) \tag{69}$$

where $\tilde{Q}$ and $\tilde{Q}_0$ are defined by

$$\tilde{Q}(\boldsymbol{k}, j-m)=\frac{1}{2\pi i}\oint \frac{dz}{z^{j-m+1}}W(\boldsymbol{k}, z) \tag{70}$$

and

$$\tilde{Q}_0(\boldsymbol{k}, i-l)=\frac{1}{2\pi i}\oint \frac{dt}{z^{i-l+1}}W_0(\boldsymbol{k}, z) = \exp\left(-\frac{(i-l)b^2}{b}k^2\right) \tag{71}$$

After integrating over $\boldsymbol{q}$, eq 69 becomes

$$\tilde{F}^{(b)}(\boldsymbol{k}, j-i)=\sum_{l=0}^{i}\sum_{m=i}^{j} Z_l Z_{N-j}\tilde{Q}(\boldsymbol{k}, j-m)\frac{-\beta_1'}{(m-l)^{3/2}} \times \exp\left[-\frac{b^2(m-i)(i-l)}{6(m-l)}k^2\right] \tag{72}$$

Introducing eq 72 into eq 63, the contribution of the diagram shown in Figure 3-b to $\langle r_{ij}^2\rangle$ is

$$\langle r_{ij}^2\rangle^{(b)}=-\beta_1' b^2 Z_N^{-1}\sum_{l=0}^{i}\sum_{m=i}^{j}\frac{Z_l Z_{N-j}}{(m-l)^{3/2}} \times\left[\frac{(m-i)(i-l)}{m-l}Z_{j-m}+I_{j-m}\right] \tag{73}$$

In a similar way, the contributions of the diagrams shown in Figure 3-c, 3-d, and 3-e to $\langle r_{ij}^2\rangle$ become

$$\langle r_{ij}^2\rangle^{(c)}=-\beta_1' b^2 Z_N^{-1}\sum_{l=i}^{i}\sum_{m=j}^{j}\frac{Z_i Z_{N-m}}{(m-l)^{3/2}} \times\left[\frac{(j-l)(m-j)}{m-l}Z_{l+i}+I_{l+i}\right] \tag{74}$$

$$\langle r_{ij}^2\rangle^{(d)}=-\beta_1' b^2 Z_N^{-1}\sum_{l=0}^{i}\sum_{m=j}^{j} Z_l Z_{N-m} \times\frac{(j-i)(m-j+i-l)}{(m-l)^{5/2}} \tag{75}$$

$$\langle r_{ij}^2\rangle^{(e)}=\beta_1'^2 b^2 Z_N^{-1} \times \sum_{l=0}^{i}\sum_{m<l'}\sum_{m'=j}^{N} \frac{Z_l Z_{N-m'}}{(m-l)^{3/2}(m'-l')^{3/2}} \times\left[\frac{(m-i)(i-l)}{m-l}+\frac{(m'-j)(j-l')}{m'-l'} \times Z_{l'-m}+I_{l'-m}\right] \quad (76)$$

Since Z and I have already been calculated in eq 55 and 56, we can calculate the contributions of the five diagrams shown in Figure 3 to $\langle r_{ij}^2\rangle$ and therefore to $\langle s^2\rangle$. In this way we can write:

$$\langle s^2\rangle=\langle s^2\rangle^{(a)}+\langle s^2\rangle^{(b)}+\langle s^2\rangle^{(c)}+\langle s^2\rangle^{(d)}+\langle s^2\rangle^{(e)} \quad (77)$$

where

$$\langle s^2\rangle^{(a)}=\frac{Nb^2}{6}(1+\pi N\beta_1'^2+\cdots) \quad (78)$$

$$\langle s^2\rangle^{(b)}=-\frac{52}{315}\beta_1' b^2 N^{3/2}-\frac{2\zeta\left(\frac{3}{2}\right)}{105}\beta_1'^2 b^2 N^{5/2} \quad (79)$$

$$\langle s^2\rangle^{(c)}=\langle s^2\rangle^{(b)} \quad (80)$$

$$\langle s^2\rangle^{(d)}=-\frac{1}{105}\beta_1' b^2 N^{3/2}-\frac{\zeta\left(\frac{3}{2}\right)}{189}\beta_1'^2 b^2 N^{5/2} \quad (81)$$

$$\langle s^2\rangle^{(e)}=\frac{6485}{864}\pi\beta_1'^2 b^2 N^2 \quad (82)$$

Then the expansion parameter for the mean square radius of gyration α_s^2, which is defined by

$$\alpha_s^2=\langle s^2\rangle/\langle s^2\rangle_0\,, \qquad \langle s^2\rangle_0=\frac{Nb^2}{6} \quad (83)$$

becomes

$$\alpha_s^2=1+\frac{6629\pi}{144}\beta_1'^2 N-\frac{214}{105}\beta_1' N^{1/2}-\frac{82\zeta\left(\frac{3}{2}\right)}{315}\beta_1'^2 N^{3/2}+0(N^2\beta_1'^3)$$

$$=1+144.62\beta_1'^2 N-2.04\beta_1' N^{1/2}-0.68\beta_1'^2 N^{3/2}+0(N^2\beta_1'^3) \quad (84)$$

For $\beta_1'\lesssim 0$, Z_N and I_N/N are calculated and found to be independent of N. Therefore, the expansion parameter for $\beta_1'\lesssim 0$ become

$$\alpha_s^2=1-2\sqrt{-\beta_1'}\sqrt{\pi}\,\zeta\left(\frac{3}{2}\right)^{-1/2} \quad (85)$$

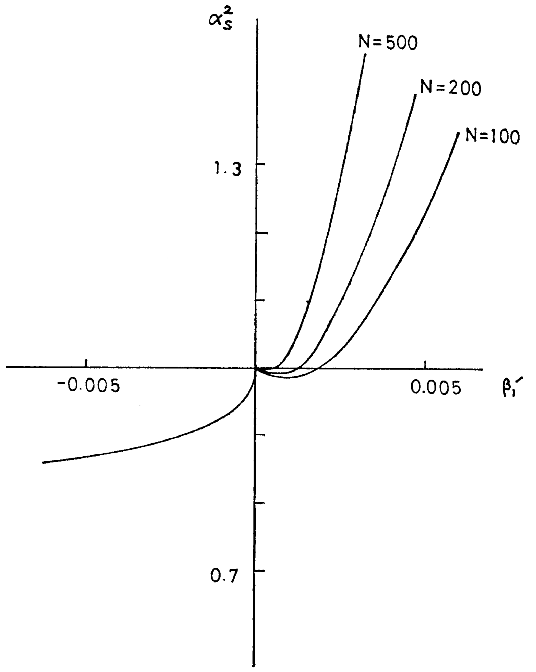


Figure 4. Expansion parameter α_s^2 as a function of β_1'.

The graphs of α_s^2 *vs.* β_1' are shown in Figure 4; α_s^2 is singular at $\beta_1=0$ ($T=\Theta$), just like α^2.

CONCLUSION

Using a method of cluster expansion we have calculated the expansion parameters α^2 and α_s^2 for $|\beta_1'|\ll 1$ in the first approximation. We have shown that the expansion parameter α^2 is equal to 1 at the Θ-temperature, it decreases with infinite slope for $T<\Theta$, and it increases with zero slope for $T>\Theta$. Furthermore, we have also shown that α_s^2 is equal to 1 at the Θ-temperature and it decreases with infinite slope for $T<\Theta$. In contrast to this, for $T>\Theta$, α_s^2 first decreases with finite slope and then increases. Although α^2 and α_s^2 are independent of molecular weight below the Θ-temperature, they are molecular weight dependent above the Θ-temperature. Figure 4 suggests that the singularity is difficult to find experimentally. For a short chain it is easier to find the singularity. If one wants to observe the singularity, one must measure the radius of gyration in the temperature range $|T-\Theta|<1$ K for $N=500$ or $|T-\Theta|<3$ K for $N=100$.

We have used the first approximation and neglected many diagrams, but the expansion parameters α^2 and α_s^2 may still be singular at the Θ-temperature.

APPENDIX A

First we notice the properties of the analytic continuation of the function $\phi(z, s)$ for $|\log z|<2\pi$:

$$\phi(z, s)=\Gamma(1-s)(-\log z)^{s-1}+\sum_{n=0}^{\infty}\zeta(s-n)\frac{(\log z)^n}{n!} \quad \text{(A-1)}$$

where $\zeta(s)$ is the Riemann's ζ-function. Since eq A-1 is valid for $z=z_0<1$ given by eq 36, we have for $\beta_1'(<0)\rightarrow 0$

$$-\beta_1'\phi\left(z_0, \frac{1}{2}\right)\rightarrow-\beta_1'\Gamma\left(\frac{1}{2}\right)\left(-\beta_1'\zeta\left(\frac{3}{2}\right)\right)^{-1/2}\rightarrow 0 \quad \text{(A-2)}$$

$$-\beta_1'\phi\left(z_0, -\frac{1}{2}\right)\rightarrow-\beta_1'\Gamma\left(\frac{3}{2}\right)\times\left(-\beta_1'\zeta\left(\frac{3}{2}\right)\right)^{-3/2}\rightarrow\infty \quad \text{(A-3)}$$

The integrals of eq 31 and 32 are given respectively as

$$Z_N=Z_N'+Z_N'' \quad \text{(A-4)}$$

$$Z_N''=\frac{1}{2\pi i}\int_1^{\infty}\frac{\mathrm{d}\xi}{\xi^{N+1}}\left(\frac{1}{1-\xi+\beta_1'\phi_+}-\frac{1}{1-\xi+\beta_1'\phi_-}\right) \quad \text{(A-5)}$$

and

$$I_N=I_N'+I_N'' \quad \text{(A-6)}$$

$$I_N''=\frac{1}{2\pi i}\int_1^{\infty}\frac{\mathrm{d}\xi}{\xi^N}\times\left[\frac{1}{(1-\xi+\beta_1'\phi_+)^2}-\frac{1}{(1-\xi+\beta_1'\phi_-)^2}\right] \quad \text{(A-7)}$$

where ϕ_+ and ϕ_- stand respectively for the values just above and below the branch cut of the function $\phi(z, 3/2)$. Putting $\xi=1+x$, we have

$$\phi_\pm\left(\xi, \frac{3}{2}\right)=\xi\left(\frac{3}{2}\right)\mp\Gamma\left(-\frac{1}{2}\right)i\sqrt{x}+\zeta\left(\frac{1}{2}\right)x+\cdots \quad \text{(A-8)}$$

Equation A-5 is then

$$Z_N''=\frac{\beta_1'\Gamma\left(-\frac{1}{2}\right)}{\pi}\times\int_0^{\infty}\frac{\sqrt{x}\,\mathrm{d}x}{(1+x)^{N+1}(x-\beta_1'\phi_+)(x-\beta_1'\phi_-)} \quad \text{(A-9)}$$

which is transformed, through the change of variable $x=(-\beta_1')s$, into

$$Z_N''=-\frac{\Gamma\left(-\frac{1}{2}\right)}{\pi}\sqrt{-\beta_1'}\times\int_0^{\infty}\frac{\sqrt{s}\,\mathrm{d}s}{(s+\phi_+(s))(s+\phi_-(s))}\cdot\frac{1}{(1-\beta_1's)^{N+1}} \quad \text{(A-10)}$$

The integral in eq A-10 converges irrespective of the value β_1'. Thus when $-\beta_1'$ is small, we obtain

$$Z_N''=-\frac{\Gamma\left(-\frac{1}{2}\right)\sqrt{-\beta_1'}}{\pi}\int_0^{\infty}\frac{\sqrt{s}\,\mathrm{d}s}{\left(s+\zeta\left(\frac{3}{2}\right)\right)^2}=\sqrt{-\beta_1'}\sqrt{\pi}\,\zeta\left(\frac{3}{2}\right)^{-1/2} \quad \text{(A-11)}$$

In the same way we obtain

$$I_N''=-\frac{1}{\sqrt{-\beta_1'}}\frac{\sqrt{\pi}}{2}\zeta\left(\frac{3}{2}\right)^{-3/2} \quad \text{(A-12)}$$

which cancels the second term of eq 40. Accordingly we finally obtain

$$\alpha^2=1-2\sqrt{-\beta_1'}\sqrt{\pi}\,\zeta\left(\frac{3}{2}\right)^{-1/2} \quad \text{(A-13)}$$

APPENDIX B

If we put $\xi=1+\beta_1's$ in eq 48, Z_N'' is transformed into

$$Z_N''=-\frac{2\sqrt{\beta_1'}}{\sqrt{\pi}}\int_0^{\infty}\frac{1}{(1+\beta_1's)^{N+1}}\times\frac{\sqrt{s}\,\mathrm{d}s}{\left(s-\zeta\left(\frac{3}{2}\right)\right)^2+4\pi\beta_1's} \quad \text{(B-1)}$$

Since for $N\gg 1$ $(1+\beta_1's)^{-(N+1)}$ is appproximated by $\mathrm{e}^{-\beta_1'Ns}$, Z_N'' is approximated as

$$Z_N''=-\frac{2\sqrt{\beta_1'}}{\sqrt{\pi}}\int_0^\infty \mathrm{e}^{-\beta_1'Ns}\frac{\sqrt{s}\,\mathrm{d}s}{\left(s-\zeta\left(\frac{3}{2}\right)\right)^2+4\pi\beta_1's} \tag{B-2}$$

This integral is easily calculated by using the change of variable $s=y^2$:

$$\begin{aligned}Z_N''&=-\frac{2\sqrt{\beta_1'}}{\sqrt{\pi}}\int_{-\infty}^\infty \frac{\mathrm{e}^{-N\beta_1'y^2}y^2}{\left(y^2-\zeta\left(\frac{3}{2}\right)\right)^2+4\pi\beta_1'y^2}\mathrm{d}y\\
&=-\exp\left[N\beta_1'\left(2\pi\beta_1'-\zeta\left(\frac{3}{2}\right)\right)\right]\\
&\times\left\{\sqrt{\frac{\pi\beta_1'}{\zeta\left(\frac{3}{2}\right)-\pi\beta_1'}}\right.\\
&\times\sin\left[2N\beta_1'\sqrt{\pi\beta_1'\left(\zeta\left(\frac{3}{2}\right)-\pi\beta_1'\right)}\right]\\
&\left.+\cos\left[2N\beta_1'\sqrt{\pi\beta_1'\left(\zeta\left(\frac{3}{2}\right)-\pi\beta_1'\right)}\right]\right\}\end{aligned} \tag{B-3}$$

By expanding sin and cos in eq B-3 and neglecting higher order terms of β_1', we obtain eq 51. In a similar manner I_N'' is calculated. If we put $\xi=1+\beta_1's$ in eq 50, we obtain

$$\begin{aligned}I_N''=&\frac{4}{\sqrt{\pi}\sqrt{\beta_1'}}\int_0^\infty \frac{\mathrm{d}s}{(1+\beta_1's)^N}\\
&\times\frac{s\sqrt{s}-\zeta\left(\frac{3}{2}\right)\sqrt{s}}{\left[\left(s-\zeta\left(\frac{3}{2}\right)\right)^2+4\pi\beta_1's\right]^2}\end{aligned} \tag{B-4}$$

which is transformed, through the change of variable $s=y^2$, into

$$I_N''=\frac{4}{\sqrt{\pi}\sqrt{\beta_1'}}\int_{-\infty}^\infty \frac{\mathrm{e}^{-N\beta_1'y^2}\left(y^4-\zeta\left(\frac{3}{2}\right)y^2\right)}{\left[\left(y^2-\zeta\left(\frac{3}{2}\right)\right)^2+4\pi\beta_1'y^2\right]^2}\mathrm{d}y \tag{B-5}$$

This integral is calculated easily and becomes

$$\begin{aligned}I_N''=&-2\exp\left[N\beta_1'\left(2\pi\beta_1'-\zeta\left(\frac{3}{2}\right)\right)\right]\\
&\times\left\{\sqrt{\frac{\pi\beta_1'}{\zeta\left(\frac{3}{2}\right)-\pi\beta_1'}}\right.\\
&\times\sin\left[2N\beta_1'\sqrt{\pi\beta_1'\left(\zeta\left(\frac{3}{2}\right)-\pi\beta_1'\right)}\right]\\
&+\frac{1}{2}\frac{\zeta\left(\frac{3}{2}\right)-2\pi\beta_1'}{\zeta\left(\frac{3}{2}\right)-\pi\beta_1'}\\
&\times\cos\left[2N\beta_1'\sqrt{\pi\beta_1'\left(\zeta\left(\frac{3}{2}\right)-\pi\beta_1'\right)}\right]\\
&-\frac{\sqrt{\pi}}{2N}\frac{1}{\sqrt{\beta_1'}}\frac{1}{\left(\zeta\left(\frac{3}{2}\right)-\pi\beta_1'\right)^{3/2}}\\
&\left.\times\sin\left[2N\beta_1'\sqrt{\pi\beta_1'\left(\zeta\left(\frac{3}{2}\right)-\pi\beta_1'\right)}\right]\right\}\end{aligned} \tag{B-6}$$

which, by expanding sin and cos and regarding β_1' small, reduces to eq 52.

Acknowledgment. This work was supported in part by a research grant from the Ministry of Education.

REFERENCES

1. T. M. Birshtein, Ye. V. Anufrigeva, T. N. Nekrasova, O. B. Ptitsyn, and T. V. Sheveleva, *Vysokomol. Soedin.*, **7**, No. 2, 372 (1965).
2. O. B. Ptitsyn, A. K. Kron, and Yu. Ye Eizuer, *J. Polym. Sci., Part C*, No. 16, 3509 (1968).
3. S. Mashimo and K. Shinohara, *J. Phys. Soc. Jpn.*, **64**, 1141 (1973).
4. A. Chiba, S. Uzawa, M. Uda, and S. Doi, *Rep. Prog. Polym. Phys. Jpn.*, **17**, 105 (1974).
5. Y. Iwasa, S. Mashimo, A. Chiba, and K. Shinohara, *ibid.*, **17**, 95 (1974).
6. H. Yamakawa, "Modern Theory of Polymer Solutions," Harper & Row, N.Y., 1971.
7. I. Langmuir, D. Sc., "Colloid Chemistry," J. Alexander, Chemical Catalog Co., N.Y., 1926, p 525.
8. W. H. Stockmayer, *Macromol. Chem.*, **35**, 54 (1960).
9. S. F. Edwards, "Critical Phenomena," M. S. Green and J. V. Sengen Ed., NBS Publishers, 273, 1966, p 225.
10. A. K. Kron, *Vysokomol. Soedin.*, **7**, 1228 (1965); A. K. Kron and O. B. Ptitsyn, *ibid.*, **7**, 1235 (1965).
11. Y. Oono, *J. Phys. Soc. Jpn.*, **39**, 25 (1975).
12. I. M. Lifschitz, *Soviet Phys. JETP.*, **28**, 1280 (1969).

13. C. Domb, *Polymer*, **15**, 259 (1974).
14. Yu. Ye. Eizner, *Vysokomol. Soedin., Ser. A*, *14*, 1512 (1972). Yu. Ye. Eizner, *ibid., Ser. A*, *11*, 364 (1969).
15. P. G. de Gennes, *J. de Physique Lett.*, **46**, L55 (1975).
16. N. Saitô and M. Inoue, *Rep. Prog. Polym. Phys. Jpn.*, **17**, 17 (1974); N. Saitô, Symposium for High Polymer Physics Center for Theore tical Physics & Chemistry, Seoul, Korea, (1975), p 31.
17. T. Kato, *J. Phys. Soc. Jpn.*, **30**, 675 (1971); Y. Chikahisa, *J. Chem. Phys.*, **52**, 206 (1970).