The ring polymer model with excluded volume

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Abstract. The many-parameter Gaussian theory of a polymer chain is in the asymptotic region $N \to \infty$ (N is the number of monomer units) equivalent to a one-parameter scaled Gaussian theory. Such theories fulfil the necessary condition of minimum free energy only in a polymer chain without remote interactions along the chain. Therefore they cannot be used as a reliable basis in SCF calculations in polymers.

1. Introduction

In Flory's theory of the excluded volume effect in polymers the mean-square length of a chain $\langle R^2 \rangle$ has the value of $\langle R^2 \rangle \sim N^{2\nu}$ in the asymptotic region $N \to \infty$. Flory determined the value of the 'critical exponent' $\nu = 3/(2 + d)$ for $1 \le d \le 4$ and $\nu = \frac{1}{2}$ for $d > 4$ (d is the space dimension). The most satisfactory and explicitly self-consistent derivation of this result was given by Gillis and Freed (1975). This derivation is based on an uncontrolled approximation which replaces the linear chain by a ring, and the polymer chain is considered as a long segment of this closed cycle. These authors further justify the use of this approximation by the reliability of the results of des Cloizeaux (1970).

The starting point of des Cloizeaux's work is the replacement of the distribution function of a polymer chain by the distribution function of the Gaussian closed ring. The Gaussian interaction potential, involving remote interactions along a chain, was chosen as a stiff chain potential minimising the free energy of the system. The asymptotic value of the 'critical index' ν in this theory was determined as $\frac{2}{3}$.

Fixman's theory (Fixman 1966) also uses the Gaussian interaction potential on a linear chain model. However, this model takes into account only the nearest neighbour interactions along a chain; excluded volume interactions are considered in this potential by means of just one adjustable parameter α which is analogous to the expansion factor of a chain. Fixman gives the value of the 'critical exponent' as $\nu = \frac{3}{5}$.

des Cloizeaux (1970) compares his theory with that of Fixman. He states that the starting point of his theory in determining the Gaussian trial potential is the principle of minimum free energy of a polymer, whereas Fixman describes the expansion of the chain by a more subtle consistency argument.

2. Equivalence of the des Cloizeaux many-parameter approach with the Fixman one-parameter theory

To justify the use of the boson operator method in the treatment of non-equilibrium polymer dynamics, Fixman (1966) applied the same method to the equilibrium

excluded volume problem. The zero approximation to the equilibrium distribution function of the linear polymer chain was chosen as follows:

$$\psi^\alpha = \frac{\exp(-\beta \sum_{i=1}^N S_i^\alpha)}{\int \exp(-\beta \sum_{i=1}^N S_i^\alpha)\,dr}, \qquad dr = dr_2 \ldots dr_{N+1} \tag{1}$$

where $\beta = 1/kT$ and $S_i^\alpha = (3kT/2b^2)|r_i - r_{i+1}|^2$ is the effective Gaussian 'spring' potential between the i'th and $(i+1)$'th links of a chain. The flexibility of the distribution (1) is wholly contained in the parameter b related to the chain 'expansion factor' α by

$$b = b_0\alpha. \tag{2}$$

The parameter α measures in a very crude way the expansion of a chain caused by the excluded volume effect, relative to the reference length b_0. One end of the chain of equation (1) is fixed at the origin, i.e. $r_1 = 0$. Fixman's boson operator method consists of the representation of all functions of coordinates by boson creation and annihilation operators. The distribution function (1) then gives the ground state $|0\rangle$ of the system.

In the des Cloizeaux theory the Gaussian distribution function

$$\psi^G = \frac{\exp(-\beta S^G)}{\int \exp(-\beta S^G)\,dr} \tag{3}$$

corresponds to Fixman's distribution function (1). The Gaussian potential S^G has the form

$$S^G = \frac{3kT}{2b_0^2} \sum_{1 \le i < j \le N+1} G(i-j)r_{ij}^2. \tag{4}$$

All the flexibility of the distribution (4) is now, in contrast to distribution (1), contained in the set of N initial parameters G. These parameters form the set of N variational parameters of the des Cloizeaux theory (1970).

Now, the conventional normal-coordinate transformation diagonalises the form (4). The orthogonal transformation (Fixman 1966)

$$r_i = \sum_{k=0}^N Q_{i,k} q_k, \qquad q_k = \sum_{i=1}^{N+1} Q_{k,i} r_i \tag{5}$$

where

$$Q_{i,k} = \left(\frac{2 - \delta_{k10}}{N}\right)^{1/2} \cos\left(\frac{ik\pi}{N}\right) \tag{6}$$

defines the system of normal coordinates q and converts the quadratic form (4) to the following:

$$S^G = \frac{3kT}{2b_0^2} \sum_{l=1}^N |q_l|^2 \sum_{p=1}^N G(p)\phi_{p,l}, \tag{7}$$

where

$$\phi_{p,l} = \sum_{i=1}^{N-p+1} (Q_{i+p,l} - Q_{i,l})^2. \tag{8}$$

The function ϕ in equation (8) can be written explicitly (Gradsteyn and Ryzhik 1963) as

$$\phi_{p,l} = 4\sin^2\frac{pl\pi}{2N}\left\{1 - \frac{1}{N}\left[p - 1 + \frac{\sin[1-(p-1/N)]l\pi \cos(1+(2/N))l\pi}{\sin(l\pi/N)}\right]\right\}. \tag{9}$$

If $p = 1$ and $G(1) = \alpha^{-2}$ are substituted into the quadratic form (7) it is transformed, using $\phi_{1,l}$ from equation (9), into the relation

$$S^{\alpha} = \frac{6kT}{b^2} \sum_{l=1}^{N} |q_l|^2 \sin^2 \frac{l\pi}{2N} \tag{10}$$

which is identical with the potential $S^{\alpha} = \Sigma_{i=1}^{N} S_i^{\alpha}$ used in equation (1), transformed into normal coordinates.

We now construct the basis of boson operators, not as in Fixman's theory by the weight function defined by equation (1), but by that from equation (3). In this way the distribution function ψ^G is given to the basic state $|0\rangle$ of a system. It will now be shown that in the asymptotic region $N \to \infty$ this distribution function does not change any of the fundamental relations in Fixman's theory.

In agreement with Fixman (1966) we define the potential V as follows:

$$V = \beta \left[S - S^G + kTX \sum_{i<j}^{N+1} \delta(r_i - r_j) \right] \tag{11}$$

where $S = \alpha^2 S^{\alpha}$, X is Fixman's binary cluster integral and $\delta(r)$ is a three-dimensional Dirac δ function. If we write equation (11) using three-dimensional Bose destructors and constructors in the basis of Hermite polynomial functions with the weight function ψ^G, we obtain

$$\hat{V} = \frac{1}{2} \sum_{k=1}^{N} \sum_{l=1}^{N} G_{k,l}(b_k + b_k^+) \cdot (b_l + b_l^+). \tag{12}$$

The coefficients $G_{k,l}$ in equation (12) are given by

$$G_{k,l} = \frac{\sigma_k \sigma_l}{\gamma_k \gamma_l} \delta_{k,l} - \frac{X}{16\pi^{3/2}} \sum_{i<j}^{N+1} (c_{i,j})^{-5/2} f_k f_l \tag{13}$$

where

$$\sigma_l^2 = \frac{6}{b_0^2} \sin^2 \frac{\pi l}{2N} - \gamma_l^2 \tag{14}$$

and

$$\gamma_l^2 = \frac{3}{2b_0^2} \sum_{p=1}^{N} G(p)\phi_{p,l}. \tag{15}$$

The coefficients $c_{i,j}$ and f_l, also appearing in equation (12), are given by

$$c_{i,j} = \frac{1}{4} \sum_{l=1}^{N} \gamma_l^{-2} (Q_{l,j} - Q_{l,i})^2 \tag{16}$$

$$(f_l)_{i,j} = (Q_{l,j} - Q_{l,i})/\gamma_l 2^{1/2} \tag{17}$$

with a factor γ_l instead of the factor $\alpha_l = (6^{1/2}/b) \sin(l\pi/2N)$ in Fixman's work (1966).

We shall prove the following statement: The set of N initial variational parameters $G(p)$, defined by equation (7), when put into the matrix $G_{k,l}$ defined by equation (13), reduces in the asymptotic region $N \to \infty$ to a single parameter α. This statement is true for both diagonal and non-diagonal elements of the matrix $G_{k,l}$.

To prove this statement it is sufficient to treat the asymptotic value of the function ϕ from equation (9) for only one instance, that is $p \ll N$, $l \ll N$, $N \to \infty$. Then

$$\phi_{p,l} \sim p^2 l^2 \pi^2 / N^2. \tag{18}$$

The requirements leading to equation (18) follow from the definition of the sums of the infinite double and single series (see e.g. Fichtengolc (1969)). Using equation (9) we obtain for the asymptotic value of the parameter γ_l, as given by equation (15), the relation

$$\gamma_i^2 = \frac{3l^2\pi^2}{2b_0^2N^2} \sum_{p=1}^{N} p^2 G(p). \tag{19}$$

If we put $\sum_{p=1}^{\infty} p^2 G(p) \equiv \alpha^{-2}$ in this relation, then in equation (12) the diagonal and non-diagonal elements of matrix $G_{k,l}$ in the expansion of the operator $\hat{V}$ in terms of boson operators are reduced to the same form as Fixman's relations (1969). Equation (19) is then identical with the asymptotic value of the factor α_l for $l \ll N$, $N \to \infty$.

Thus the many-parameter Gaussian theory considered by des Cloizeaux (1970) is reduced to the one-parameter scaled Gaussian theory, developed by Fixman (1966). Fixman's basic approximation, that non-diagonal elements of the matrix $G_{k,l}$ with k and l differing by more than one vanish for $N \to \infty$, is also valid in des Cloizeaux's theory.

3. The principle of minimum free energy

We proved in § 2 that for $N \to \infty$ the assumption of the many parameter distribution (3) is equivalent to the assumption (1) of Gaussian scaling theory. We shall further prove that such a theory cannot fulfil the necessary condition of minimum free energy. The free energy of a polymer chain can be written (des Cloizeaux 1970) as

$$\beta F = \langle V \rangle - \ln \int \exp(-\beta S^\alpha)\, d\boldsymbol{r} \tag{20}$$

where the mean value is taken according to the one-parameter distribution (1). The necessary condition for minimum free energy, $\partial F/\partial \alpha = 0$, gives the relation

$$\sum_{i=1}^{N} \left[\int S_i^\alpha \exp(-\beta S^\alpha)\, d\boldsymbol{r} \int V \exp(-\beta S^\alpha)\, d\boldsymbol{r} \right.$$

$$\left. - \int \exp(-\beta S^\alpha)\, d\boldsymbol{r} \int S_i^\alpha V \exp(-\beta S^\alpha)\, d\boldsymbol{r} \right] = 0 \tag{21}$$

which reduces to

$$\int r_{k,k+1}^2 V \exp\left[-(3/2b^2) \sum_{i=1}^{N} r_{i,i+1}^2 \right] d\boldsymbol{r}$$

$$- b^2 \int V \exp\left[-(3/2b^2) \sum_{i=1}^{N} r_{i,i+1}^2 \right] d\boldsymbol{r} = 0, \qquad k = 1, 2, \ldots, N. \tag{22}$$

We assume in equation (22) that $\alpha \neq 0$. The case $\alpha = 0$ is physically unreal. We shall now determine the α satisfying equation (22). To this end we consider the expression

$$-\frac{\partial}{\partial \lambda_k} \int V \exp\left[-\sum_{i=1}^{N} \lambda_i r_{i,i+1}^2 \right] d\boldsymbol{r} - b^2 \int V \exp\left[-\sum_{i=1}^{N} \lambda_i r_{i,i+1}^2 \right] d\boldsymbol{r}. \tag{23}$$

We obtain the left-hand side of equation (22) from expression (23), since

$$\lambda_1 = \ldots = \lambda_N = \lambda = 3/2b^2. \tag{24}$$

To evaluate expression (23) we use the values of two well-known integrals

$$\int \exp\left[-\sum_{i=1}^{N} \lambda_i r_{i,i+1}^2\right] d\boldsymbol{r} = \frac{\pi^{3N/2}}{(\lambda_1 \dots \lambda_N)^{3/2}} \tag{25}$$

$$\int \delta(r_i - r_j) \exp\left[-\sum_{i=1}^{N} \lambda_i r_{i,i+1}^2\right] d\boldsymbol{r} = \frac{\pi^{3(N-1)/2}}{[\sum_{p=i}^{j-1}(\lambda_1 \dots \lambda_N)/\lambda_p]^{3/2}}, \qquad i < j. \tag{26}$$

After the necessary calculations equation (22) takes the form

$$\alpha^2 - 1 - \alpha^3 z h_k, \qquad k = 1, \dots, N, \tag{27}$$

where

$$z = N^{1/2}\left(\frac{3}{2\pi b_0^2}\right)^{3/2} \tag{28}$$

and

$$h_k = \frac{1}{N^{1/2}}\left[\sum_{i=1}^{N}\sum_{j=i+1}^{N+1}\frac{1}{(j-1)^{3/2}} - \sum_{i=k+1}^{N}\sum_{j=i+1}^{N+1}\frac{1}{(j-i)^{3/2}}\right.$$
$$- \sum_{i=1}^{k-1}\sum_{j=i+1}^{k}\frac{1}{(j-i)^{3/2}} - \sum_{i=1}^{k}\sum_{j=k+1}^{N+1}\frac{1}{(j-i)^{3/2}}$$
$$\left. + \sum_{i=1}^{k}\sum_{j=k+1}^{N+1}\frac{1}{(j-i)^{5/2}}\right] = \frac{1}{N^{1/2}}\sum_{i=1}^{k}\sum_{j=k+1}^{N+1}\frac{1}{(j-i)^{5/2}}. \tag{29}$$

The form of equation (27) is identical to Fixman's expression (73), (Fixman 1966). It is easy to see that for $N \to \infty$ and finite k the equation (27) does not have a solution $\alpha \neq \pm 1$ because formula (29) is asymptotically equal to zero in this case. Neither des Cloizeaux's many-parameter Gaussian theory nor Fixman's one-parameter scaling theory satisfy the necessary condition of minimum free energy of a polymer for $N \to \infty$. Furthermore, Fixman's theory derives only from a linear approximation to the potential $X \sum_{i<j} \delta(r_{ij})$ in the normal δ function expansion in the boson operator representation. It therefore violates the variational principle even more strongly. This can be easily shown in the following way.

In the boson operator representation the free energy of a polymer has the following form:

$$\beta F = \langle \hat{V} \rangle - \ln \int \exp(-\beta S^\alpha) \, d\boldsymbol{r} = \langle 0 | \hat{V} | \rho \rangle - \ln\left(\frac{2\pi b^2}{3}\right)^{3N/2}. \tag{30}$$

We express the operator $\hat{V}$ according to equation (12) and for the vector $|\rho\rangle$ we use the linear approximation of Fixman's expression (92) (Fixman 1966):

$$\rho \sim \exp(-\hat{V})|0\rangle = \exp\left[-\frac{1}{2}\sum_{l=1}^{N} G_l(1+G_l)^{-1}b_l^+ \cdot b_l^+\right]|0\rangle$$
$$\sim \left[1 - \frac{1}{2}\sum_{l=1}^{N} G_l(1+G_l)^{-1}b_l^+ \cdot b_l^+\right]|0\rangle. \tag{31}$$

Here $G_l = G_{l,l}$ is a diagonal element of the matrix $G_{l,k}$ as defined by equation (12). After some calculation we obtain

$$\beta F = \frac{3}{2}\sum_{l=1}^{N} G_l(1+G_l)^{-1} - \ln\left(\frac{2\pi b^2}{3}\right)^{3N/2}. \tag{32}$$

The condition $\partial F/\partial \alpha = 0$ gives

$$\sum_{l=1}^{N} \left[\frac{\mathrm{d}G_l/\mathrm{d}\alpha}{2(1+G_l)^2} - \frac{1}{\alpha} \right] = 0. \tag{33}$$

We now use Fixman's expression for G_l, as given by his equation (73) (1966)

$$G_l = \alpha^2 - 1 - \frac{z}{\alpha^3} g_l, \tag{34}$$

where the g_l are numbers independent of N for large N. Fixman assumed the vector of basic state $|0\rangle$ in equation (31) to be as close to $|\rho\rangle$ as may be achieved by the scaled Gaussian basic set. In the ideal case, unattainable by the one parameter distribution (1), G_l would be zero for all the $l = 1, 2, \ldots, N$. Then from equation (33) and (34) we obtain

$$\alpha^2 - 1 + (3z/2\alpha^3)g_l = 0. \tag{35}$$

With the above assumptions, equation (35) indicates that values of α which are given by putting $G_l = 0$ in equation (34), do not fulfil the minimum free-energy condition. Because the same value of α is not a zero of equation (34) for all the G_l, Fixman chose the condition $G_1 = 0$ and thus made all the values $G_l(1 + G_l)^{-1}$ for $l = 2, \ldots$, finite. Equation (34) leads to further values of α, violating the requirement of equation (33). In the trivial case, $\alpha = 1$ is the minimum free energy condition (27) identically fulfilled in the same way as the condition (33) for $g_1 = 0$. Thus one-parameter Gaussian theories of a polymer fulfil the free energy principle only for $\alpha = 1$ in the absence of remote interactions along the chain.

4. Discussion

Edwards' SCF theory is criticised in the work of des Cloizeaux (1970). It is shown that Edwards' spherically symmetric random SCF potential $V(r)$ completely destroys the symmetry which should exist between the ends of a polymer chain. To remedy this des Cloizeaux uses a trial Gaussian many-parameter potential and in this way the isotropy of space is restored. To simplify the calculation he uses the infinite polymer chain, the cyclic invariance of which allows simplification of the equations. This approximation was also the starting point in the work of Gillis and Freed (1975), where Flory's value of the 'critical exponent' ν in the relation for the mean-square length of a polymer chain was verified.

   Our work has shown that in the asymptotic region $N \to \infty$ des Cloizeaux's many-parameter Gaussian distribution is identical with Fixman's scaled Gaussian theory. In spite of des Cloizeaux's statement that his theory starts from the principle of minimum chain free energy, it has been shown that for $N \to \infty$, one-parameter scaled Gaussian theories do not fulfil the variational principle.

   The real problem with the theory of des Cloizeaux and Fixman is that the methods use a variational trial potential which is much too simple. The failure of these theories does not necessarily imply that the ring polymer approximation is either a good or a bad one. It remains to be tested whether this ring polymer approximation is reasonable and this is indeed difficult.

   The weakest point of all present excluded-volume theories of polymers is the fact that up to now insurmountable mathematical difficulties force us to use approximations

whose effect on the final result is unknown. None of these theories can therefore confirm the validity of the ring polymer approximation. This is a further reason for the inadmissibility of Gaussian one-parameter theories.

Acknowledgments

Note added in proof. After this paper was submitted for publication, the work of Kosmas and Freed (1978) appeared. In this work a new SCF hierarchy was constructed and Flory's value of the 'critical' exponent ν for a linear polymer verified. SCF's in this hierarchy are defined as a dominant contribution to an integral which gives the mean value for the even moments of the end-to-end distance of a polymer chain. This dominant contribution emerges as spherically symmetric, thus verifying Edwards' SCF guess. However, SCF's constructed in such a way differ from those obtained as a dominant contribution to the closure approximation of integrodifferential hierarchies in polymers. The first of these systems gives Edwards' SCF, the second Reiss's SCF etc. The distinguishing feature of SCF's so obtained is elliptic symmetry which has made the problem mathematically intractable until now. In the determination of SCF's using the mean value of even moments of the end-to-vector, as used by work of Kosmas and Freed (1978), less information is involved than in the definition, stemming from dominant contributions to the closure approximations of the Green functions of the integrodifferential systems mentioned above. The work of Kosmas and Freed (1978) cannot therefore hold as a justification of the use of the ring polymer model.

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