Conformation Space Renormalization of Polymers. 4. Equilibrium Properties of the Simple Ring Polymer Using Gell-Mann–Low Type Renormalization Group Theory

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ABSTRACT: The method of Oono, Ohta, and Freed is used to derive static properties of a ring polymer above the Θ point. This method uses the technique of dimensional regularization as formulated in conformational space where monomers are specified by their positions in space and along the chain. The distribution function for an internal vector of a ring polymer is determined by using the renormalization group analysis with an expansion in $d = 4 - \epsilon$ space, d being the spatial dimensionality. The distribution function yields exponents describing the asymptotic, long- and short-range, behavior of polymer rings. These exponents are the same to order ϵ as those for linear chains.

I. Introduction

The simplest picture of a polymer with excluded volume is that of a random walk, generated from the origin, which is constrained to be self-avoiding. That is, the polymer may not cross through itself; the random walk must keep track of where it has been. This is, of course, the direct parallel, by the model, of the real excluded volume effect. The simple random walk, or one with short-range constraints, displays long-range correlations because all the steps are connected. For a long enough walk there is a nonzero probability distribution for having the walk ends separated by some vector **R**. This asymptotic Gaussian distribution depends only on one parameter apart from the walk length and **R**, and the form of the distribution is "universal", being independent of the short-scale behavior of the walk.

The self-avoiding walk, and hence the polymer chain with excluded volume, likewise has long-range correlations which differ substantially from those of the random walk—the polymer becomes swollen in good solvents. We seek for the polymer with excluded volume a simple universal description of the long-range correlations within the chain which is independent of the short length scale properties of the chain apart, perhaps, from the appearance of some parameter(s) characterizing certain average properties.

The two essential characteristics of the presence of long-range correlations and the existence of universal behavior in polymer systems are common features of systems near critical, or second-order phase transition, points. It is, therefore, not surprising that there exists simple formal analogies between the description of long-chain polymer properties and the behavior of spin systems, fluids, etc. near a critical point. Indeed, as is well-known, de Gennes[1] supplied the exact relation between the self-avoiding walk and the n-vector spin model. In the present paper, however, we do not utilize the spin (or magnetic) analogy and develop a method solely in terms of familiar polymer language following the methods of our previous papers.[2]

It is crucial, in approaching this problem, that we distinguish the macroscopic or long-wavelength formulations of polymer properties from those which are microscopic, or "bare".[2] In this paper, what is meant by a macroscopic theory is a phenomenological description, based on experimental bulk measurements. A microscopic theory is one which is built up from an atomistic root, generally, as in our case, from a Hamiltonian. A long-wavelength description of the polymer (ring) system depends, in general, on the molecular size, an excluded volume parameter, and the macroscopic length scale, while the corresponding bare description depends on the polymer contour length, a microscopic excluded volume parameter, and a finite cutoff length reflecting the discrete, atomic nature of matter. These two descriptions are separate in that we expect one particular macroscopic description to be compatible with a large (infinite) number of microscopic models.

This last statement is the cornerstone of our method[2] and the fundamental hypothesis of the renormalization group approach.[3] It pays therefore to dwell on this point momentarily. The macroscopic world does not appear to suggest a minimum size for matter, and as a result it is only within the past 100 years that the atomic theory came to be accepted. This fact strongly suggests that very many microscopic models of matter yield the same "results" in a macroscopic sense. Some of these models may even treat matter to be continuous.

In order to proceed with a macroscopic theory, we choose an appropriate length scale. Later on the length scale is used to convert all quantities of interest to dimensionless form. Most significantly, however, the chosen unit of length is seen to be entirely arbitrary. That it may be chosen in any convenient fashion follows directly from the independence of the macroscopic regime, as discussed earlier,[2] from a particular length scale. This fact is crucial and is exploited in deriving the renormalization group equation from which is determined the general functional form, the scaling law, for the internal distribution function of intersegment separations.

There are two appropriate renormalization group approaches, Kadanoff–Wilson[4] and Gell-Mann–Low.[5] In the former, a transformation is applied to the polymer configuration in a fashion which effectively amounts to a uniform shrinking of the chain followed by a blurring of details.[6,7] The net result is a removal of microscopic features irrelevant to the macroscopic long-wavelength, properties of the system. Throughout this procedure, the microscopic cutoff length never vanishes. Such an approach was first introduced for polymers by de Gennes,[6] who grouped several sequential monomer units together into "blobs". The rigid blob construction, however, only permits use of the model to first order in the small parameter, ϵ. Recently,[7b] two of us elucidated a general, Kadanoff–Wilson procedure for evaluating polymer properties to all orders in ϵ. This method does not lead to the rigid blob interpretation. Rather, the short-range

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excluded volume interactions themselves determine the coarse-graining construction which removes the microscopic details.

The Gell-Mann–Low renormalization group approach takes another, completely equivalent, tack. The philosophy of this approach is straightforward and is described by Oono et al. in paper 3[2] as follows. We are interested in macroscopic properties, invariant to changes in purely microscopic details. In particular, such a macroscopic description must persist even when the microscopic cutoff length, a, tends to zero. Letting a tend to zero may well result in the divergence of quantities in the microscopic theory. But we require that all well-defined macroscopic quantities remain finite for all finite spatial dimensionalities. This requirement of nondiverging macroscopic quantities manifests itself in very specific relations between the sets of macroscopic and microscopic variables. The evaluation of these "macro–micro" relations then allows the calculation of the quantities of interest.

The precise computational mechanism for converting general relations between the macroscopic distribution function and its microscopic counterpart into the final specific form for ring polymers is the modified perturbation expansion of section IV, which is a double series expansion in ϵ and the excluded volume. In the $a \to 0$ limit, the requirement of nondiverging macroscopic quantities uniquely determines the macro–micro relations[2] and consequently fixes the distribution function for intersegment separations.

Finally, appropriate exponents for power law dependencies can be defined and evaluated for the asymptotic regimes of the polymer ring system. These are easily compared with those for linear polymer chains as originally derived by des Cloizeaux.[8]

It should be mentioned that renormalization group methods have been applied, in a wide variety of ways.[9] Our feeling is that the method we have used, involving conformation space renormalization and perturbation expansions about the usual Gaussian chain model, is a more intuitive approach for polymer scientists than other methods and is highly suited to calculation of the kinds of distribution functions of interest.[10]

Section II presents the formula for a simple, but physically sufficient, Hamiltonian which introduces the excluded volume in the form of a δ-function. From the invariance of the microscopic theory to the choice of a macroscopic length scale and from simple dimensional analysis, we derive in section III the general long-wavelength scaling law for the internal intersegment vector of the ring polymer.

In section IV we introduce the method of perturbation analysis and use it subsequently to derive an analytic expression for the distribution function. Once this is accomplished, the probability distribution and radial moments follow straightforwardly.

Throughout this paper we follow closely the work of Oono, Ohta, and Freed presented in part 3 of this series.[2] This is especially true of the theoretical aspects of the Gell-Mann–Low procedure and of section III in particular.

II. The Hamiltonian

We begin with the following microscopic, dimensionless Hamiltonian $H_a(\mathbf{C})$ for the polymer:[11,12]

$$H_a(\mathbf{C}) = (1/2)\int_0^M \dot{\mathbf{C}}(\tau)^2\,\mathrm{d}\tau + (1/2)v_0\int_{|\tau-\tau'|>a}\mathrm{d}\tau\int\mathrm{d}\tau'\;\delta(\mathbf{C}(\tau) - \mathbf{C}(\tau')) \quad \text{(II.1)}$$

Here, $\mathbf{C}(\tau)$ represents the continuous-chain spatial location, parameterized by the contour length, τ (see Figure 1). v_0 is the microscopic excluded volume parameter and $\dot{\mathbf{C}}(\tau) = \mathrm{d}\mathbf{C}(\tau)/\mathrm{d}\tau$. For convenience, microscopic quantities calculated from (II.1) may be referred to as "bare".

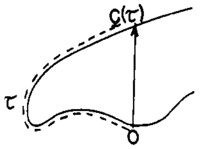

Figure 1. A portion of the polymer ring. τ is a contour length measured in the clockwise direction along the chain from a fixed origin on the chain. The vectorial position of the monomeric unit located at a point along the chain corresponding to the contour length, τ, is denoted $\mathbf{C}(\tau)$.

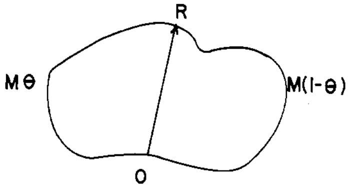

Figure 2. A polymer ring of length M. The internal intersegment vector, $\mathbf{R}$, is fixed by the specification of a given value, between 0 and 1, of the parameter of advancement, θ.

An examination of this Hamiltonian shows it to be composed of a simple entropic free energy contribution and a term which takes into account the constraint of excluded volume. The simple δ-function repulsion assumed here for the latter has been shown to yield the same results as do more realistic potentials for temperatures far above the Θ point.[7]

The cutoff length, a, is naturally present in the excluded volume part of the Hamiltonian and serves to eliminate monomer self-interactions. In the process of carrying out the Gell-Mann–Low procedure and letting a tend to zero, divergences due to self-interactions reappear and must be removed.[2,3,13] This is the function of the macro–micro relations to be introduced in section III. It becomes apparent later in the analysis that $d = 4$ is the "critical dimension" above which the distribution function assumes a Gaussian form for the polymer problem. (The terminology is borrowed from fluid and magnetic systems.) Taking $d = 4 - \epsilon$ to be the spatial dimension, we perform simple (engineering) dimensional analysis on the Hamiltonian. If $[\tau] = X$ are the units of τ, then[13,15]

$$[\tau] = X$$

$$[\mathbf{C}] = X^{1/2}$$

and finally

$$[v_0] = X^{-\epsilon/2} \quad \text{(II.2)}$$

III. Renormalization Group Equation

To derive the renormalization group equation, we follow the procedure of Oono et al.[2] in paper 3 and begin with the macro–micro relations. These relations, which link the macroscopic and bare distribution functions, are sufficiently binding so as to provide us with a very specific form for the distribution function. The bare distribution function for an internal intersegment vector, $\mathbf{R}$ of a ring polymer depends on the cutoff, a, the total contour length, M, the bare excluded volume parameter, v_0, $\mathbf{R}$, and θ, the "parameter of advancement" (see Figure 2). The macroscopic distribution function depends, meanwhile, on the arbitrary macroscopic length, L, the macroscopic polymer size, N, the excluded volume parameter, v, $\mathbf{R}$, and θ. For convenience, we use the coupling parameters in their dimensionless forms, $u_0 = v_0L^{\epsilon/2}$ and $u = vL^{\epsilon/2}$.

Since both N and M must be proportional to the molecular weight, they are proportional to each other, and we write

$$N = Z(u,a/L)M \qquad \text{(III.1)}$$

The excluded volume parameters must also be related, although not necessarily in such a simple way. As u_0 tends to zero, u must also tend to zero, so we write

$$\begin{aligned} u_0 &= u_0(u,a/L) \\ &= u - Du^2 + \ldots \end{aligned} \qquad \text{(III.2)}$$

Additionally, the distribution functions, calculated both macro- and microscopically, must also be proportional since when normalized they must correctly yield the probability. Letting G_b be the bare unnormalized distribution function as calculated from (II.1) and G its macroscopic counterpart, this implies

$$G = Z_q^{-1}(u,a/L)G_b \qquad \text{(III.3)}$$

These three macro–micro relations (III.1) to (III.3) are now formally fixed following paper 3 by the requirement that at $a = 0$ the macroscopic distribution function remains analytic for finite d. Appropriately, this is termed the dimensional regularization requirement.

The above arguments enable us to write

$$G(N^{-1},\mathbf{R},\theta,v;L) = \lim_{a\to 0} Z_q^{-1}G_b(ZN^{-1},\mathbf{R},\theta,v_0;a) \qquad \text{(III.4)}$$

or

$$Z_qG((ZM)^{-1},\mathbf{R},\theta,u;L) = G_b(M^{-1},\mathbf{R},\theta,u_0;a \to 0) \qquad \text{(III.5)}$$

G_b is a bare function which cannot depend on the purely macroscopic length unit, L. Hence $\partial G_b(\cdots)/\partial L$ must vanish, and we may differentiate both sides of this equation with respect to L, yielding the renormalization group equation

$$\left[L\left.\frac{\partial}{\partial L}\right|_{v_0,M,a} Z_qG((ZM^{-1}),\mathbf{R},\theta,u;L) \right] = 0 \qquad \text{(III.6)}$$

which when expanded may be written

$$\left(L\frac{\partial}{\partial L} + L\frac{\partial u}{\partial L}\frac{\partial}{\partial u} + L\frac{\partial \ln Z_q}{\partial L} + L\frac{\partial \ln Z}{\partial L}N\frac{\partial}{\partial N} \right) \times G(N^{-1},\mathbf{R},\theta,u;L) = 0 \qquad \text{(III.7)}$$

The solution of this differential equation yields the general functional form of the macroscopic distribution function. The solution depends explicitly on the excluded volume u, and we now seek to determine a universal long-chain limiting form.

At this point, it is important to recognize that all the terms beginning $L(\mathrm{d}/\mathrm{d}L)$ in the renormalization group equation are dimensionless. Thus they can only depend on u in the $a \to 0$ limit. We proceed by defining three functions of u

$$\begin{aligned} A(u) &= L(\partial \ln Z_q/\partial L)_{v_0,M,a} \\ B(u) &= L(\partial \ln Z/\partial L)_{v_0,M,a} \\ C(u) &= L(\partial u/\partial L)_{v_0,M,a} \end{aligned} \qquad \text{(III.8)}$$

To solve the renormalization group equation it is necessary to first solve for D in (III.2). This involves lengthy calculations; the details follow as in paper 3.[2] The final result[2] is

$$u_0 = u + (2/\epsilon\pi^2)u^2 + \ldots \qquad \text{(III.9)}$$

From the chain rule (and recalling that $u_0 = v_0L^{\epsilon/2}$) it is easy to solve for $C(u)$:

$$C(u) = (1/\pi^2)u(u^* - u) + \ldots \qquad \text{(III.10)}$$

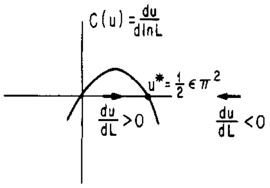

Figure 3. A graph vs. u, the microscopic coupling parameter, of $C(u)$, a measure of the change in u for increasing L in d (<4) space. As L increases, corresponding to the approach to the macroscopic, long-wavelength limit, the value of u approaches u^*. u^* is a stable fixed point.

where $u^* = {}^1/_2\epsilon\pi^2$.

It follows (Figure 3) that in d (<4) space, u^* is a stable fixed point for all $u > 0$. Letting L grow corresponds to the approach to the macroscopic limit. In this limit, $u = u^*$ is a stationary fixed point. We may also note that for $d > 4$, i.e., $\epsilon < 0$, the macroscopic limit corresponds to $u = 0$; the chain behaves purely Gaussian.

The renormalization group equation simplifies for $u = u^*$ to

$$\left(L\frac{\partial}{\partial L} + A + BN\frac{\partial}{\partial N} \right)G(N^{-1},\mathbf{R},\theta,u^*;L) = 0 \qquad \text{(III.11)}$$

where $A = A(u^*)$ and $B = B(u^*)$. Following paper 3[2] the general solution of this equation is

$$G(N^{-1},\mathbf{R},\theta,u^*;L) = L^{-A}F(\mathbf{R},\theta,LN^{-1/B}) \qquad \text{(III.12)}$$

With the help of some additional dimensional analysis, it is possible to refine the functional form of G. From (II.1), and recalling the notation of Figure 2, the bare distribution function can be written

$$G_b(M^{-1},\mathbf{R},\theta,v_0;a) = \int_{\mathbf{C}(0)=0}^{\mathbf{C}(M)=0} \mathcal{D}[\mathbf{C}]\delta[\mathbf{C}(M\theta) - \mathbf{R}] \exp[-H_a(\mathbf{C})] \qquad \text{(III.13)}$$

$\mathcal{D}$ is the appropriate weighting factor.[11] Dimensional analysis now yields

$$\begin{aligned} [N] &= X \\ [G] &= X^{-d} \\ [L] &= X \\ [\theta] &= X^0 \end{aligned} \qquad \text{(III.14)}$$

Likewise, as in paper 3,[2] it follows from simple dimensional analysis that for any real number $s > 0$

$$G(N^{-1},\mathbf{R},\theta,u^*;L) = s^{-d}G(s/N,s^{-1/2}\mathbf{R},\theta,u^*;s^{-1}L) \qquad \text{(III.15)}$$

Using (III.12) further simplifies the form of the distribution function:

$$\begin{aligned} G(N^{-1},\mathbf{R},\theta,u^*;L) &= s^{-d}(Ls^{-1})^{-A}F(s^{-1/2}\mathbf{R},\theta,s^{-1}L(N/s)^{-1/B}) \\ &= s^{-d+A}L^{-A}F(s^{-1/2}\mathbf{R},\theta,LN^{-1/B}s^{-1+(1/B)}) \end{aligned} \qquad \text{(III.16)}$$

Finally, with the choice for s

$$LN^{-1/B}s^{-1+(1/B)} = 1 \qquad \text{(III.17)}$$

a more comprehensive form for G is found:

$$\begin{aligned} G(N^{-1},\mathbf{R},\theta,u^*;L) &= \\ L^{-B(d-A)/(B-1)}N^{(d-A)/(B-1)}f(\mathbf{R}/N^{1/(2-2B)},\theta,L^{-B/(2-2B)}) &= \\ N^{(d-A)/(B-1)}f(\mathbf{R}/N^{1/2(1-B)},\theta) \qquad (L = 1)& \end{aligned} \qquad \text{(III.18)}$$

The new f should again be a well-behaved function of the argument given.

A and B have simple physical interpretations as explained in paper 3.[2] The mean-square value for the internal vector **R** is simply given by

$$\langle \mathbf{R}^2 \rangle_{u^*} = \int \mathrm{d}\mathbf{R}\, |\mathbf{R}|^2 G \Big/ \int \mathrm{d}\mathbf{R}\, G \propto N^{2\nu} \qquad \text{(III.19)}$$

From (III.18) and (III.19) it is found that

$$2\nu = 1/(1 - B)$$

$$B \equiv L \left.\frac{\partial \ln Z}{\partial L}\right|_{u=u^*} = \frac{2\nu - 1}{2\nu} \qquad \text{(III.20)}$$

Similarly, the total number of allowed configurations, U_N, is related to the exponent α by

$$U_N = \int \mathrm{d}\mathbf{R}\, G \sim N^{\alpha-2}\mu^N \qquad \text{(III.21)}$$

μ is a constant which we do not consider here. From (III.18), (III.20), and (III.21) it follows that

$$A \equiv L \left.\frac{\partial \ln Z_{\mathrm{q}}}{\partial L}\right|_{u=u^*} = \frac{\nu d + \alpha - 2}{2\nu} \qquad \text{(III.22)}$$

Finally, (III.18), (III.20), and (III.22) combine to yield the simple formula,[17] for $L \equiv 1$,

$$G(N^{-1},\mathbf{R},\theta;u^*) = N^{\alpha-2-\nu d} f(\mathbf{R}/N^{\nu}) \qquad \text{(III.23)}$$

Equation III.23 is a general result which we have obtained simply from the assumed renormalizability of the system, that is, the existence of the macro–micro constants, i.e., Z, Z_{q}, and the relation $u(u_0)$, general scaling considerations, and the trivial but important requirement that G_{b} be L independent. Furthermore, eq III.23 is valid to all orders in ϵ since we assume no ϵ expansion in our derivation.[18,19]

IV. Perturbation Theory

The practical means by which the constants A and B are evaluated, and through which the specific distribution function for the vector **R** is determined, is the perturbation theory which follows. It would be desirable to be able to obtain A and B in closed form; however, there is no known method which makes this possible. Nevertheless, the perturbation series approach, in principle, allows for the calculation of the constants and G to arbitrary order in ϵ as described by Oono et al.[2]

Because we expect many microscopic descriptions to be compatible with the observed macroscopic details, it should be possible to find regimes in which the coupling parameter, u_0, is small. Then it makes sense to expand the quantities appearing in the macro–micro relations in powers of the coupling parameters.

Consider a series expansion for the distribution function (or any other macroscopic observable) in powers of the bare excluded volume parameter:

$$G_{\mathrm{b}} = \sum_{m=0}^{\infty} G_{\mathrm{b}}^{(m)} v_0^{\,m} \qquad \text{(IV.1)}$$

The dimensions $[v_0] = X^{-\epsilon/2}$ and $[M] = X$ imply that $[v_0 M^{\epsilon/2}] = X^0$. Thus, the true expansion parameter, as is well-known, is $v_0 M^{\epsilon/2}$, and

$$G_{\mathrm{b}} = \sum_{m=0}^{\infty} \tilde{G}_{\mathrm{b}}(m) v_0^{\,m} M^{m\epsilon/2} \qquad \text{(IV.2)}$$

However, the series is not proper, since M gets very large in the macroscopic limit. To circumvent this difficulty, we can perform the series expansion about 4-space where v_0 is dimensionless and write the double summation

$$G_{\mathrm{b}} = \sum_{m,n} G^0{}_{mn} v_0^{\,m} \epsilon^n \qquad \text{(IV.3)}$$

Although (IV.3) is well-defined (at least as an asymptotic series) for small $\epsilon \neq 0$, in the limit $a \to 0$ the series is divergent in 4-dimensions where negative powers of ϵ blow up. These negative powers of ϵ correspond to the presence originally of terms in powers of ln a which diverge as a tends to zero.

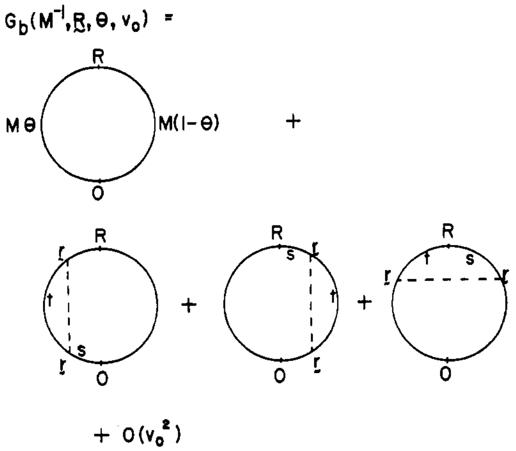

Figure 4. Pictorial representation of the perturbative expansion of G_{b}, the bare distribution function, to first order in the coupling parameter, v_0. The analytic interpretation of these and similar polymer diagrams is given in Appendix I.

In order to deal with these singularities it is necessary to reexamine the consequences of the dimensional regularization requirement that the macroscopically calculated properties of the polymer system be well-defined, even in the continuous-chain limit.[2]

The macroscopic distribution function can likewise be expanded as

$$G = \sum_{m,n} G_{mn} v^m \epsilon^n \qquad \text{(IV.4)}$$

where again the double expansion is required to make the series well-defined. However, here the dimensional regularization assumption removes all negative powers of ϵ from the expansion as explained in paper 3:[2]

$$G = Z_{\mathrm{q}}^{-1} \sum_{m,n=0}^{\infty} G^0{}_{mn} v_0^{\,m}(v) \epsilon^n \qquad \text{(IV.5)}$$

This approach is now clarified by the specific evaluation of the internal distribution function, $G(N^{-1},\mathbf{R},\theta,u^*;L)$, for intersegment separations.

V. Distribution Function for the Internal Vector R

The bare distribution function, $G_{\mathrm{b}}(M^{-1},\mathbf{R},\theta,v_0;a)$, can be expanded in a perturbation series, order by order, in powers of the coupling constant, v_0. From (III.13), and letting a tend to zero, we obtain

$$\begin{aligned} G_{\mathrm{b}} = \lim_{a\to 0} \int_{\mathbf{C}(0)=\mathbf{0}}^{\mathbf{C}(M)=\mathbf{0}} \mathcal{D}[\mathbf{C}]\delta[\mathbf{C}(M\theta) - \mathbf{R}] \times \\ \exp[-H_a(\mathbf{C})] = G_0(\mathbf{R},\mathbf{M}\theta)G_0(\mathbf{R},M(1-\theta)) - \\ v_0 \int_0^{M\theta} \mathrm{d}t \int_0^{M\theta-t} \mathrm{d}s \int \mathrm{d}\mathbf{r}\, G_0(\mathbf{r},s)G_0(\mathbf{0},t)G_0(\mathbf{R} - \\ \mathbf{r},M\theta - s - t)G_0(\mathbf{R},M(1-\theta)) - \\ v_0 \int_0^{M(1-\theta)} \mathrm{d}t \int_0^{M(1-\theta)-t} \mathrm{d}s \int \mathrm{d}\mathbf{r}\, G_0(\mathbf{R} - \\ \mathbf{r},\mathrm{s})G_0(\mathbf{0},t)G_0(\mathbf{r},M(1-\theta) - s - t)G_0(\mathbf{R},M\theta) - \\ v_0 \int_0^{M\theta} \mathrm{d}t \int_0^{M(1-\theta)} \mathrm{d}s \int \mathrm{d}\mathbf{r}\, G_0(\mathbf{r},M\theta - \\ t)G_0(\mathbf{R}-\mathbf{r},t)G_0(\mathbf{R}-\mathbf{r},s)G_0(\mathbf{r},M(1-\theta) - s) + O(v_0^{\,2}) \end{aligned} \qquad \text{(V.1)}$$

where

$$G_0(\mathbf{R},T) = \exp[-(\mathbf{R}^2/2T)]/(2\pi T)^{d/2} \qquad \text{(V.2)}$$

Using the "Diagrammar" (Appendix 1), one can express this series in a simpler fashion, pictorially (Figure 4).

Following our prescription and details paralleling those given by Oono et al.,[2] each of the first-order diagrams is now further expanded in powers of ϵ. The resulting expression is

$$\begin{aligned}
&G_b(M^{-1},\mathbf{R},\theta,\upsilon_0;a) = \\
&\frac{G_0(\mathbf{R},M\theta(1-\theta))}{(2\pi M)^{d/2}}[1 - \upsilon_0\frac{(2\pi M)^{\epsilon/2}}{(2\pi)^2}\{(1-\theta)^{\epsilon/2} \times \\
&\Bigg[\left(\frac{2}{\epsilon} - \hat{\gamma} - \ln\frac{\mathbf{R}^2}{2M(1-\theta)}\right)\left(1 - \frac{\mathbf{R}^2}{2M(1-\theta)}\right) - \\
&\left(2 + \frac{\mathbf{R}^2}{2M(1-\theta)}\right)\Bigg] + \theta^{\epsilon/2}\Bigg[\left(\frac{2}{\epsilon} - \hat{\gamma} - \ln\frac{\mathbf{R}^2}{2M\theta}\right) \times \\
&\left(1 - \frac{\mathbf{R}^2}{2M\theta}\right) - \left(2 + \frac{\mathbf{R}^2}{2M\theta}\right)\Bigg] + \\
&\frac{4}{\epsilon} + 2 + 2\ln(1-\theta) + 2\ln\theta + \\
&\int_0^\theta \mathrm{d}\mu \int_0^{1-\theta}\mathrm{d}\nu \Bigg[\Bigg[\exp\Bigg\{\frac{-\mathbf{R}^2}{2M\theta(1-\theta)} \times \\
&\left[\frac{(\mu(1-\theta) - \upsilon\theta)^2}{(\theta-\mu)(1-\theta-\nu)(\mu+\nu) + \mu\nu(1-\mu-\nu)}\right]\Bigg\} \times \\
&[\theta(1-\theta)]^2/[(\theta-\mu)(1-\theta-\nu)(\mu+\nu) + \\
&(1-\mu-\nu)\mu\nu]^2\Bigg] - \frac{1}{(\mu+\nu)^2} - \frac{1}{(1-\mu-\nu)^2}\Bigg]\} + \ldots] \qquad \text{(V.3)}
\end{aligned}$$

where $\hat{\gamma} \simeq 0.5772$ is Euler's constant.

With the simple substitutions, $u = \upsilon L^{\epsilon/2}$ and $u_0 = \upsilon_0 L^{\epsilon/2}$, eq III.4 can be rewritten

$$G(N^{-1},\mathbf{R},\theta,u;L) = Z_q^{-1}(u)G_b(Z(u)N^{-1},\mathbf{R},\theta,u_0(u);0) \qquad \text{(V.4)}$$

Expanding Z, Z_q, and υ_0 in powers of u

$$\begin{aligned}
Z &= 1 + B'u + O(u^2) \\
Z_q &= 1 + A'u + O(u^2) \qquad \text{(V.5)} \\
\upsilon_0 &= u_0 L^{-\epsilon/2} = uL^{-\epsilon/2} + O(u^2)
\end{aligned}$$

and substituting these into (V.4) and (V.3) yield

$$\begin{aligned}
&G(N^{-1},\mathbf{R},\theta,u;L) = (1 - A'u + \ldots)\frac{G_0(\mathbf{R},N\theta(1-\theta))}{(2\pi N)^{d/2}} \times \\
&\Bigg\{1 - B'u\left[\epsilon + \frac{\mathbf{R}^2}{2N\theta(1-\theta)} - 4\right] - \\
&uK^{-\epsilon/2}(2\pi N)^{\epsilon/2}(2\pi)^{-2}\Bigg[2/\epsilon\Bigg(2 + \left(1 - \frac{\mathbf{R}^2}{2N\theta}\right) + \\
&\left(1 - \frac{\mathbf{R}^2}{2N(1-\theta)}\right)\Bigg) + \ldots\Bigg]\Bigg\} \qquad \text{(V.6)}
\end{aligned}$$

A' and B' are determined uniquely by the dimensional regularization requirement that all singular terms (in this case terms of order $1/\epsilon$) vanish. For this requirement to be satisfied, it must be that

$$\begin{aligned}
&-A' + 4B' - B'\frac{\mathbf{R}^2}{2N\theta(1-\theta)} - \\
&(2\pi)^{-2}(2/\epsilon)\left(4 - \frac{\mathbf{R}^2}{2N\theta(1-\theta)}\right) = 0 \qquad \text{(V.7)}
\end{aligned}$$

or since (V.7) is an identity for all $\mathbf{R}^2/N\theta(1-\theta)$

$$\begin{aligned}
A' &= 0 \\
B' &= (2\pi^2\epsilon)^{-1} \qquad \text{(V.8)}
\end{aligned}$$

With A' and B' determined, it is possible to evaluate the exponents ν and α by means of (III.8). Using the chain rule

$$L(\partial/\partial L)_{u=u^*} = L(\partial u/\partial L)_{u=u^*}(\partial/\partial u)_{u=u^*} \qquad \text{(V.9)}$$

and employing (III.8), (III.9), (V.5), and (V.8), we obtain

$$\begin{aligned}
A &= 0 \\
B &= (1/2)u^*B' = (1/8)\epsilon \qquad \text{(V.10)}
\end{aligned}$$

Substituting (V.10) into (III.20) and (III.22) gives

$$\begin{aligned}
\nu &= 1/2 + (1/16)\epsilon + O(\epsilon^2) \\
\alpha &= (1/4)\epsilon + O(\epsilon^2) \qquad \text{(V.11)}
\end{aligned}$$

These are the standard results to order ϵ for the polymer excluded volume problem for linear chains.[1]

One immediate consequence of these results is that the general function, f, of (III.18), may be determined. By introducing the reduced variable

$$X = \frac{\mathbf{R}^2}{2N\theta(1-\theta)}\left(\frac{2\pi N}{L}\right)^{-\epsilon/8} \qquad \text{(V.12)}$$

G may be put in the scaling form of eq (III.23). Letting $u = u^*$, the complete distribution function is then

$$\begin{aligned}
&G(N^{-1},\mathbf{R},\theta,u^*;L) = (2\pi N)^{-4+\epsilon/2}[\theta(1-\theta)]^{-2+\epsilon/2}L^{\epsilon/2}e^{-X} \times \\
&\exp(-\epsilon\{1/4 + 1/8[(1-\theta X)\ln(1-\theta)] + \\
&[1 - (1-\theta)X]\ln\theta - (\hat{\gamma} + \ln[(1-\theta)X]) \times \\
&(1 - (1-\theta)X) - (\hat{\gamma} + \ln(\theta X))(1 - \theta X) - (X + 4) + \\
&2 + 2\ln(1-\theta) + 2\ln\theta + \int_0^\theta \mathrm{d}\mu\int_0^{1-\theta}\mathrm{d}\nu \\
&\Bigg[\Bigg\{[\theta(1-\theta)]^2 \times \\
&\frac{\exp\left(-X\left[\dfrac{(\mu(1-\theta) - \nu\theta)^2}{(\theta-\mu)(1-\theta-\nu)(\mu+\nu) + \mu\nu(1-\mu-\nu)}\right]\right)\Bigg\}}{[(\theta-\mu)(1-\theta-\nu)(\mu+\nu) + \mu\nu(1-\mu-\nu)]^2} \\
&\qquad - \frac{1}{(1-\mu-\nu)^2} - \frac{1}{(\mu+\nu)^2}\Bigg]]\}) \qquad \text{(V.13)}
\end{aligned}$$

It is interesting to consider the asymptotic form of the distribution function in the limit $X \to 0$. Although the presence of an integral in the expression complicates the mathematics, it is possible to show that

$$G \sim X^{\epsilon/2} \quad \text{as } X \to 0 \qquad \text{(V.14)}$$

independent of θ. This result is, to first order in ϵ, the same as the determined by des Cloizeaux[10] for the linear polymer chain (see discussion below).

The long-range behavior of G is more complicated and depends in a weak way on θ. However, the dominant contribution to G, in the $X \to \infty$ limit is given by

$$G \approx \exp(-X^{1+\epsilon/8}) \quad \text{as } X \to \infty \qquad \text{(V.15)}$$

This term was also the dominant part of the asymptotic, long-range behavior of the linear chain, as determined by des Cloizeaux originally.[10]

des Cloizeaux discusses three types of contact exponents for linear chains[20] (see Figure 5). The three diagrams

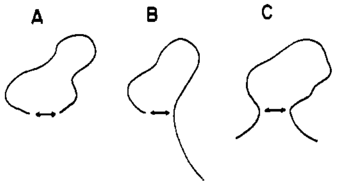

Figure 5. The three contact environments discussed by des Cloizeaux.[20] All relevant contour distances are large. In A, the ends of the infinitely long polymer chain are proximate. In B, one end of the polymer chain approaches an arbitrary point along the chain, very far from both end points. In C, both points are far from each other (contourwise) and far from the end points of the chain, yet proximate in space.

describe (A) the asymptotic approach to contact of the distribution function for the end points of a linear chain, (B) one end point and an internal point far removed from the end points by contour length, and (C) two such internal points. Case C most closely resembles that of the ring polymer (indeed cases A and B have no parallel for rings). To first order in the small parameter, ϵ, the distribution functions for the point–point distances in linear polymer go as X to the power $\epsilon/8$, $\epsilon/4$, $\epsilon/2$. Thus, to first order in ϵ, the contact coefficient for the ring equals that for case C in the chain. This provides strong support for the supposition by des Cloizeaux[21] and later by Gillis and Freed[22] that it is possible to calculate the exponent ν for a linear polymer from the mean-square intersegment separation in a very long ring polymer. The explicit distribution functions for the vector connecting two internal and/or end points will be given in paper 6 of the present series.

VI. Density Distribution Function and $\langle \mathbf{R}^2 \rangle$

For the purposes of this section, it is advantageous to mask the highly complex functional form of the exponential portion of the distribution function and to write

$$G(N^{-1},\mathbf{R},\theta;L) = c_1 \exp[-J(X,\theta)] \qquad \text{(VI.1)}$$

where

$$c_1 = (2\pi N)^{-4}[\theta(1-\theta)]^{-2}[2\pi N\theta(1-\theta)/L]^{\epsilon/2}L \qquad \text{(VI.2)}$$

The parameter X can also be written in a way which singles out the $\mathbf{R}$ dependence. Recalling (IV.12), define the variables

$$X = c_2\mathbf{R}^2 \qquad \text{(VI.3)}$$

and

$$c_2 = [2\pi N\theta(1-\theta)]^{-1}(2\pi N/L)^{-\epsilon/8} \qquad \text{(VI.4)}$$

The probability distribution function, $P(N^{-1},\mathbf{R},\theta;L)$, is the properly normalized form of the distribution function, G. In terms of the present notation

$$P(N^{-1},\mathbf{R},\theta;L) = (2c_2^{2-\epsilon/2}S_d^{-1})I_1^{-1} \exp[-J(X,\theta)] \qquad \text{(VI.5)}$$

where

$$I_n \equiv \int X^{n-\epsilon/2} \exp[-J(X,\theta)]\ \mathrm{d}X \qquad \text{(VI.6)}$$

and S_d is the surface area of a unit sphere in d-space. For $d = 3$, S_d has the value 4π.

A close examination of (VI.5) shows that the probability distribution function varies as $(N/L)^{1+\epsilon/8}L$. N or N/L must be proportional to the molecular weight of the polymer; however, it is impossible to know the proportionality factor. In other words, there exists an arbitrariness to our solution. This is not surprising since we have set out to derive the distribution function by exploiting the universal character of the polymer systems, noting that there exist many different microscopic models consistent with a given macroscopic description. Arbitrariness of this sort is exactly analogous to that involving unknown critical temperatures, or for the polymer excluded volume, the Θ temperature, which varies from species to species.

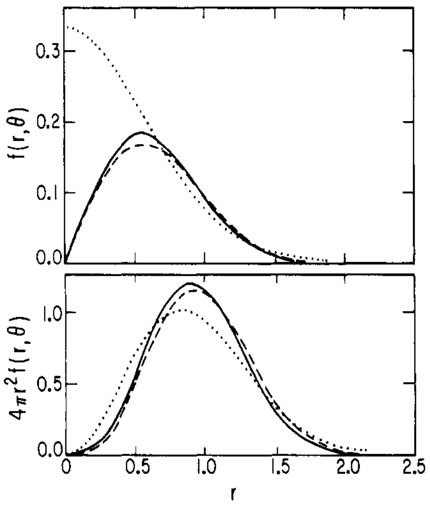

Figure 6. Plot of the density distribution function, $f(\mathbf{r},\theta)$, vs. radial distance in three dimensions for two values of the parameter, $\theta = 0.1$ (---) and $\theta = 0.25$ (—). The unperturbed Gaussian distribution (no excluded volume) is also plotted (···). (Computational evaluation of the integrals appearing in (V.13) yields results for this diagram accurate to within roughly 2%.)

To fix the probability distribution function in a specific case, it is necessary to perrform an experiment. One example is the measuring of $\langle \mathbf{R}^2 \rangle$. In the shorthand notation of this section, the mean-square distance, $\langle \mathbf{R}^2 \rangle$, is given by the integral

$$\begin{aligned} \langle \mathbf{R}^2 \rangle &= \int \mathbf{R}^2 P(N^{-1},\mathbf{R},\theta;L)\ \mathrm{d}\mathbf{R} \\ &= (I_2/I_1)c_2^{-1} \qquad \text{(VI.7)} \end{aligned}$$

With this expression, it is possible to eliminate all of the occurrences of N and L. We define the density distribution function $f(\mathbf{r},\theta)$ for the reduced distance $\mathbf{r} = (\mathbf{R}^2/\langle \mathbf{R}^2 \rangle)^{1/2}$ by

$$f(\mathbf{r},\theta)\ \mathrm{d}\mathbf{r} = P(N^{-1},\mathbf{R},\theta;L)\ \mathrm{d}\mathbf{R} \qquad \text{(VI.8)}$$

This ultimately leads to

$$f(\mathbf{r},\theta)\ \mathrm{d}\mathbf{r} = (2/S_d)I_2^{2-\epsilon/2}I_1^{-3+\epsilon/2} \exp[-J(\mathbf{r}^2 I_2/I_1,\theta)]\ \mathrm{d}\mathbf{r} \qquad \text{(VI.9)}$$

f can then be compared directly with experiment.

Although an analytic solution to even the ring problem seems impossible, the integrals I_1 and I_2 can be performed numerically. The results of such a calculation are used to derive the density distribution functions and the individual (true) distribution functions as illustrated in Figures 6 and 7. The density distribution function for the ring internal vector is seen to be slightly dependent on θ at intermediate distances. However, the individual distribution functions are clearly highly dependent on θ (Figure 7), as expected. For small values of θ, monomeric units are expected to be nearer the origin than for larger values of θ. There is also a larger spread of possible values for $\mathbf{r}$ as θ increases—again, something to be expected.

VII. Discussion

Here we illustrate the chain conformation space renormalization group methods of paper 3[2] by applying them to the case of a simple ring polymer. These theoretical

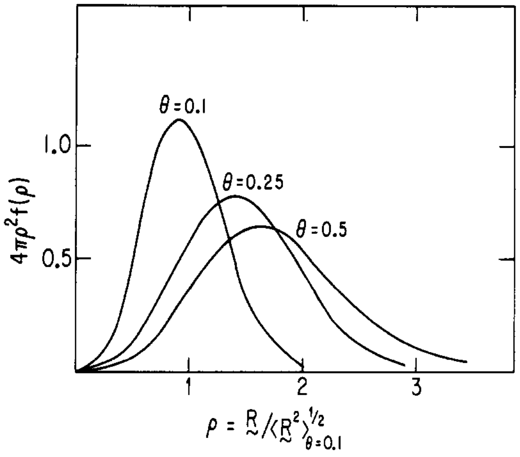

Figure 7. The (true) density distribution functions for three values of the advancement parameter, θ. Here, the root-mean-square distance for $\theta = 0.1$ is chosen to coincide with that of the self-avoiding random walk, as in Figure 6. Using eq VI.6 the distribution functions for all values of θ may be determined.

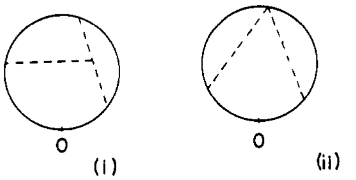

Figure 8. Forbidden diagrams. These diagrams cannot appear in the perturbation expansion of the bare distribution function.

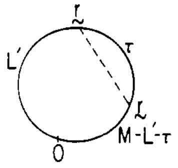

Figure 9. A sample diagram.

methods provide very general means of evaluating polymer distribution functions to arbitrary order in ϵ.[23]

In order to accomplish this task, we make a distinction between the microscopic structural descriptions of polymers and the corresponding phenomenological description at long wavelength. Philosophically, it is important to grasp the notion that the size of the monomer unit is immaterial to the macroscopic, universal properties of the polymer (ring) system, provided the size of the polymer is very large. In the ideal limit of infinite length, which we call the macroscopic limit, microscopic details become completely washed out.

In order to implement the renormalization group approach, "bare" perturbation theory is employed. In the long-chain limit the dimensionless expansion parameter becomes too large, and it becomes necessary to use a double expansion in v_0 and ϵ. The technical details involve, first, an expansion of the partition function G for fixed intersegment vector $\mathbf{R}$ perturbatively in powers of v_0 and then a subsequent expansion in ϵ with all the poles removed.

A final note concerns the choice of the ring polymer for this paper. To the best of our knowledge, the precise distribution function, as well as the asymptotic limiting forms and exponents, has never been calculated for ring polymers with excluded volume. However, it has been argued that the *locally similar* nature of the rings to chains should lead to identical exponents. At least to first order in ϵ, we have shown this to be the case.

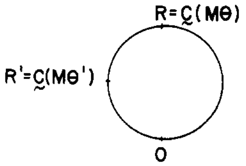

Figure 10. A polymer ring with *two* fixed points used for the calculation of the constant D in the relation $u = u(u^*)$.

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Appendix I. The Diagrammar

A diagram for the ring problem consists of a solid ring, containing a fixed origin and any number of other fixed vertices (denoted by an X). In addition, a diagram may also contain any *even* number of unfixed vertices; these are located on the ring and are connected, in pairs, by dotted bonds. Pairs of unfixed vertices connected by a bond occupy the same point in conformation space.

A solid line, running from vertex A at $\mathbf{R}_A$ to vertex B at $\mathbf{R}_B$ with contour length separation L' and without passing through any other vertex, has the value $[2\pi L']^{-d/2}\cdot\exp[-(\mathbf{R}_B - \mathbf{R}_A)^2/2L']$, where $d = 4 - \epsilon$ is the spatial dimension. Bonds between pairs of vertices contribute a factor of $-v_0$, and all unfixed vertices are integrated over. In addition, the contour lengths of all solid lines terminating at an unfixed vertex are to be integrated over.

It should be noted that this definition excludes the two diagrams in Figure 8, the first because a vertex occurs, not on the solid ring but on a bond, the second because there are an odd number of unfixed vertices. Although the first of these two diagrams is unphysical, it is possible to assign a meaning to the second diagram in terms of three-body interactions.[7] These interactions only become significant, however, at temperatures near the Θ point;[24,14,7] for this reason we have no need of the second type of diagram.

As an example of the use of this Diagrammar, consider the diagram in Figure 9. Its value is given by

$$\int_0^M d\tau \int_0^{M-\tau} dL' \int d\mathbf{r}\, \frac{\exp[-\mathbf{r}^2/2L']}{[2\pi L']^{d/2}} \frac{1}{[2\pi\tau]^{d/2}} \times \frac{\exp[-\mathbf{r}^2/2(M - L' - \tau)]}{[2\pi(M - L - \tau)]^{d/2}}$$

Appendix II

The derivation of an expansion for u_0 in terms of u is rather complex; one can exactly follow the method outlined in paper 3 by using the distribution function $G'(M^{-1}, M\theta', \mathbf{R}', M\theta, \mathbf{R}, u; L)$ for a ring with two fixed points $\mathbf{R}',\theta'$ and $\mathbf{R},\theta$ (Figure 10). However, since the singularity arises from "small" bond loops, the global form of the polymer is irrelevant. Therefore we can safely adopt the result which follows for the linear chain in paper 3;[2] $D = -2/\epsilon\pi^2$.

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(10) We stress again that our method involves direct renormalization along the polymer chain. We do not depend on the magnetic analogy or field theoretical formulations as given by Schäfer and Witten (Schäfer, L.; Witten, T. A. *J. Phys.* (*Orsay, Fr.*) **1980**, *41*, 459). Recent work by des Cloizeaux (des Cloizeaux, J. *J. Phys., Lett.* (*Orsay, Fr.*) **1980**, *41*, L151) has made use of direct renormalization as well. des Cloizeaux introduces spatial Fourier transforms and applies renormalization to various vertex functions. Previous work involving conformation space renormalization[6] had encountered difficulties inherent in the block renormalization (blob model). Reference 7a and, subsequently, ref 7b provide a correct coarse-graining approach which suffers from none of these difficulties and which may be extended to all orders. Our present treatment does not utilize this "block" renormalization procedure.

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(16) First introduced by t'Hooft: t'Hooft, G.; Veltman, M. *Nucl. Phys. B* **1972**, *B44*, 189.

(17) Those familiar with the polymer–magnet analogy may suspect that $A = 0$ from the hyperscaling relation $\alpha - 2 = \nu d$. We show this to be true. Then the distribution function has an even simpler form $\sim N^{-2\nu d}$. However, our work is independent of the magnet analogue.

(18) It is interesting to note that the same analysis may be carried through with u not equal to u^*. It is found[19] that (III.12) takes the more general form

$$G = \exp\left[-\int_{u_1}^{u}\frac{A(u)}{L\dfrac{\partial u}{\partial L}}\,\mathrm{d}u\right]\times F\left(L\exp\left[-\int_{u_1}^{u}\frac{\mathrm{d}u}{L\dfrac{\partial u}{\partial L}}\right], N\times \exp\left[-\int_{u_1}^{u}\frac{\mathrm{d}u}{L\dfrac{\partial u}{\partial L}}\right], \mathbf{R}, \theta\right)$$

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Simple and Complex Relaxations

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ABSTRACT: Viscoelastic relaxations are considered to be simple or complex depending on their activation entropies. Simple relaxations have activation entropies near zero and reflect the motion of small molecular fragments without much cooperative involvement. Complex relaxations have large positive activation entropies and involve cooperative motions of neighboring groups or molecules. By these tests, alkyl group relaxations and relaxations due to the motion of small absorbed molecules are simple. Many main-chain local mode relaxations are complex, but some which are restricted due to crystallinity or hydrogen bonding are simple. Relaxations associated with the motion of polar groups may be either simple or complex. Glass transitions have large activation entropies. In some cases, however, they may consist of a spectrum of relaxations in which the individual components are simple.

Introduction

A puzzling aspect of viscoelastic relaxations in polymers is the large magnitude for the activation energies derived from Arrhenius plots. For glass transitions, it is not unusual to find activation energies of 50–100 kcal/mol, greater than the energy of a primary chemical bond. Clearly, such large activation energies indicate that there is a high degree of complexity in the motion associated with the relaxations. This impression of complexity is confirmed by large activation entropies for many of these relaxations. Moreover, this behavior is not limited to polymers.

In 1942 Kauzmann of Westinghouse published a survey on the application of absolute rate theory to relaxations in low molecular weight solids and liquids as well as polymers.[1] Chloropentamethylbenzene is one of several related compounds which exhibit relaxations in the solid state having small activation energies and zero or small activation entropies. The behavior of cyclopentanol, cyclohexanol,[2] and 2,3-dimethylbutane[2] is similar. Clearly, these relaxations involve very simple motions within the solids. In contrast with this, benzophenone has a dielectric relaxation in the solid with an activation energy of 45 kcal/mol and an activation entropy of 103 eu. This must be a much more complex relaxation.

Similar contrasts occur among low molecular weight liquids. Ethyl alcohol has a relaxation with an activation energy of only 4.7 kcal/mol and an activation entropy of 6 eu whereas supercooled propylene glycol has a relaxation with an activation energy of 20 kcal/mol and an activation

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