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(38) As to the active sphere radius $r_0'$ for intermolecular electron transfer, there are some arguments. If one assumes a uniform distribution of energy acceptors around an energy donor, the condition that the total transfer efficiency calculated by the active sphere model is the same as that for the exact case, yields,

$$\int_0^{r_0'} 4\pi r^2 \, dr = \int_0^{\infty} \frac{r_0^6}{r_0^6 + r^6} 4\pi r^2 \, dr$$

where $r_0$ denotes the Förster distance. Integration gives $r_0' = 1.16 r_0$. The above equation means the radius of the active sphere should be a little larger than the Förster distance. Jabłoński (A. Jabłoński, *Bull. Acad. Pol. Sci., Ser. Sci. Math., Astron. Phys.*, **6**, 663 (1958)) reported a similar calculation and suggested $r_0' = 1.33 r_0$. On the other hand, in the intramolecular case, the distribution of acceptors cannot be uniform and, strictly speaking, there can be no simple way to define $r_0'$. In fact, a comparison of static transfer efficiency for the active sphere model (broken line in Figure 3) with that for the exact case (solid line, $r_0 = 24$ Å) indicates that $r_0'$ should be smaller than $r_0$ for $n < 12$ but larger than $r_0$ for $n < 12$. However, since the difference between the two lines is not significant, it is sufficient to use the Förster distance as an active sphere radius in our approximate analysis. A small change in the active sphere radius did not change any conclusions in the text. The authors wish to thank the referee for informing us of this point.

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# Phase Transition Behavior of the Isolated Polymer Chain

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ABSTRACT: A mean field theory of chain dimensions is formulated which is very similar to the van der Waals theory of a simple fluid. In the limit of infinite chain length, the chain undergoes a Landau-type second-order phase transition. For finite chains, the transition is pseudo-second-order. At low temperatures, the chain is in a condensed or globular state, and the mean square gyration radius $\langle S^2 \rangle$ varies as $r^{2/3}$ where $r$ is proportional to chain length. At high temperatures, the chain is in a gaslike or coil state where $\langle S^2 \rangle$ varies as $r^{6/5}$. In the globular state, fluctuations in $\langle S^2 \rangle$ are very small, whereas they are very large in the coiled state. A characteristic feature of the theory is that ternary and higher order intramolecular interactions are approximated. At high temperatures, only binary interactions are important, but at low temperatures, many of the higher order terms contribute. An important conclusion of this study is that a polymer chain does not obey ideal chain statistics at the $\Theta$ temperature. Although the second virial coefficient vanishes at $\Theta$, the third virial coefficient does not; its presence is responsible for the perturbation of the chain statistics. For an infinite chain, $\Theta$ and the second-order phase-transition temperature are identical. For finite chains, the pseudo-second-order transition temperature is less than $\Theta$. When generalized to $d$ dimensions, the theory yields at low temperatures $\langle S^2 \rangle^{d/2} \sim r$ for all $d$ and at high temperatures $\langle S^2 \rangle \sim r^{6/(d+2)}$, $d < 4$, and $\langle S^2 \rangle \sim r$, $d > 4$.

## Historical Perspective

Recently, there has been a spate of theoretical papers dealing with the "collapse transition" of a flexible polymer chain in a poor solvent.[1-12] As early as 1960, Stockmayer[13] suggested that "even atatic chain molecules must collapse to a rather dense form if the net attraction between their parts becomes sufficiently large". However, theoretical interest in this subject remained relatively restrained until experiments gave evidence of the transition not only in synthetic polymers,[14-18] but also in biopolymers such as DNA.[19-21] Interest in this subject has also been stimulated by the recent arrival of neutron scattering as an analytical tool for the investigation of chain configurations and dynamics[22,23] and by theoretical advances (renormalization group methods) in treating phase-transition phenomena.

In 1972, in a terse note of less than 500 words, deGennes[24] made the remarkable observation that a correspondence exists between the self-excluded volume problem in polymers and critical point phenomena. He showed that renormalization group methods were applicable to polymers in dilute solution. Later, deGennes[2] also noted that the $\Theta$ point of a polymer solution was probably not an ordinary second-order critical point, but a *tricritical* point. His argument for a tricritical point is somewhat indirect. The evidence is based on the observation that at the $\Theta$ point the third virial coefficient cannot be ignored. This has the theoretical implication that in a Landau free-energy expansion near the $\Theta$ point, terms to sixth order have to be retained because the coefficient of the sixth-order term is proportional to the third virial coefficient.[2] It is this form of the free energy that is capable of yielding a tricritical point.[25,26]

The identification of the $\Theta$ point as a probable tricritical point and the extension of deGennes ideas to the semidilute region by des Cloizeaux[27] has led to the construction of tricritical phase diagrams by Daoud and Jannink.[28,29] Several neutron scattering experiments[30-33] have been directed at checking the theoretical predictions of these new phase diagrams. Some of these predictions differ from those of Edwards who has developed a mean field theory of dilute[34] and concentrated[35] polymer solutions.

The importance of the third virial coefficient at the Θ point has also been emphasized by Oono.[36,37] Oono has obtained two important results which are pertinent to the present work: The first is that at the Θ point a polymer chain does not obey ideal chain statistics because the third virial coefficient perturbs the distribution. The second major result is that the failure of the traditional two-parameter perturbation theory of the excluded volume effect[38-40] is related to the tacit assumption that ternary interactions can be ignored at the Θ point. However, there is not complete unanimity of opinion among theorists concerning the importance of ternary interactions near the Θ point.[41-43]

In the present paper, a primitive mean field theory of a polymer chain with excluded volume and attractive interactions is formulated which is very similar to the van der Waals theory of a simple fluid. As in van der Waals theory, second and all higher order virial coefficients are approximated and retained. Theories which only retain the second virial coefficient can only describe the expanded or *coiled* state. Theories which retain both the second and third virial coefficients are capable of describing both the coil and the collapsed or globular states.[2,12,44] In the latter theories, and under certain conditions, the globule–coil transition resembles a first-order phase transition as suggested by Domb.[1] In the present theory and in the thermodynamic limit of an infinite chain, the transition is second order in agreement with the conclusion of Moore.[6]

Our only excuse for adding this theory to the already large number of existing theories is its simplicity and uniqueness. It is unique in that it is the only theory in which all higher order intramolecular interactions are approximately taken into account.

## Theory

**A. Self-Excluded Volume.** Consider a polymer chain composed of $r$ "mers" that are labeled 1, 2, . . ., $r$. The mers of an *ideal chain* are volumeless and interact neither repulsively nor attractively with one another. A chain configuration can be generated by a random walk (RW) of $r - 1$ steps. At each step, there are $z$ possible directions in which the step can be taken. The number of configurations available to the ideal chain is $z^{r-1}$. A subset of the $z^{r-1}$ configurations, all of which start at a common origin, will terminate in an infinitesimal volume element $\mathrm{d}\mathbf{R}$ at a vector distance $\mathbf{R}$ from the origin (the first mer is always at the origin, and the $r$th mer is at $\mathbf{R}$). If $r$ is large, the number of such chain configurations is given by

$$\omega_0(\mathbf{R})\ \mathrm{d}\mathbf{R} = z^{r-1}P_0(\mathbf{R})\ \mathrm{d}\mathbf{R} \qquad (1)$$

$$P_0(\mathbf{R}) = \left(\frac{3}{2\pi\langle R^2\rangle_0}\right)^{3/2} \exp\left[-\frac{3\mathbf{R}^2}{2\langle R^2\rangle_0}\right] \qquad (2)$$

$$\langle R^2\rangle_0 = \int R^2 P_0(\mathbf{R})\ \mathrm{d}\mathbf{R} \qquad (3)$$

A subscript zero is used here and subsequently to denote properties of the ideal chain.

Now consider a chain where each mer has a volume of $\sigma^3$. For this chain, the number of allowable configurations is considerably smaller than for the corresponding ideal chain. In the ideal chain, configurations involving chain intersections are allowed, whereas they are excluded for a chain that occupies space. For the latter chain, the number of chain ends that terminate within a volume element $\mathrm{d}\mathbf{R}$ centered at a vector distance $\mathbf{R}$ is

$$\omega(\mathbf{R})\ \mathrm{d}\mathbf{R} = \omega_0(\mathbf{R})\prod_{k=1}^{r-1}(1 - P_{\mathrm{k}})\ \mathrm{d}\mathbf{R} \qquad (4)$$

where $1 - P_k$ is the *conditional probability* that the $k$th step does not intersect with any of the previous $k - 1$ steps ($k$ mers); $P_k$ is conditional because the RW must terminate at $\mathbf{R}$.

The exact calculation of $P_k$ is very difficult because it is a nonMarkovian probability. However, we can approximate $P_k$ by calculating $P_k$ for an ideal chain:

$$P_{k-1} \simeq b\sigma^3\sum_{j=1}^{k-1}P_0(O_{jk}|\mathbf{R}) \qquad (5)$$

$$P_0(O_{jk}|\mathbf{R}) = \left[\frac{3}{2\pi\langle R^2\rangle_0\sigma_{jk}{}^2}\right]\exp\left[-\frac{3(k/r)(1 - j/k)^2R^2}{2\langle R^2\rangle_0\sigma_{jk}{}^2}\right] \qquad (6)$$

$$\sigma_{jk}{}^2 = (k/r)(1 - j/k)[1 - (k/r)(1 - j/k)] \qquad (7)$$

where $P_0(O_{jk}|\mathbf{R})$ is the conditional probability density that the $k$th mer overlaps with the $j$th mer given that the end-to-end vector of the ideal chain is $\mathbf{R}^{4/5}$ and $b\sigma^3$ is the volume excluded for a pair of mers.[45] The constant $b$ is as small as 2 if the RW is constrained to a lattice. As will be seen in what follows, the exact value of $b$ becomes unimportant. Converting the sum in eq 5 to an integral and making the following change of variable

$$\frac{j}{k} = \frac{\langle R^2\rangle_0{}^{3/2}}{R^3}x \qquad (8)$$

we find after integrating that $P_k$ becomes

$$P_k = k(\sigma/R)^3g(k/r,R/\langle R^2\rangle_0{}^{1/2}) \qquad (9)$$

where $g$ is a dimensionless function of $k/r$ and $R/\langle R^2\rangle_0{}^{1/2}$. A zeroth approximation for $P_k$ is to set $R = \langle R^2\rangle_0{}^{1/2}$ in $g$ and replace $g(k/r,1)$ by its mean value $\bar{g}$:

$$\bar{g} \equiv \frac{1}{r}\sum_{k=1}^{r}g(k/r,1) \simeq \int_0^1 g(x,1)\ \mathrm{d}x = \text{constant} \qquad (10)$$

and thus

$$P_k = k(\sigma/R)^3\bar{g} \qquad (11)$$

This zeroth approximation is equivalent to the assumption that at the $k$th step the prior $k - 1$ steps were confined to a volume of space proportional to $R^3$. This approximation seriously overestimates $P_k$ for $R/\langle R^2\rangle_0{}^{1/2} \ll 1$ but should be a reasonable approximation for $R/\langle R^2\rangle_0{}^{1/2}$ values of order unity.

The end-to-end distance $R$ is an inferior property to use as a measure of a chain's size or extent. The gyration radius $S$ or the Hollingsworth radius $R_{\mathrm{H}}$ are much better measures. The latter is defined as the radius of the smallest sphere which contains all mers of the chain and is centered at the origin of the RW.[46]

Arguments similar to those given above for the number of configurations having an end-to-end distance $R$ can be repeated for those configurations that have a gyration radius $S$ or a Hollingsworth radius $R_{\mathrm{H}}$. For a chain that occupies space (mers of volume $\sigma^3$), the number of chains that have a gyration radius between $S$ and $S + \mathrm{d}S$ is [cf. eq 1, 4, and 5]

$$\omega(S)\,\mathrm{d}S = \omega_0(S)\prod_{k=1}^{r-1}(1 - P_k)\,\mathrm{d}S \tag{12}$$

$$\omega_0(S) = z^{r-1}P_0(S) \tag{13}$$

$$P_{k-1} \simeq b\sigma^3\sum_{j=1}^{k-1}P_0(O_{jk}|S) \tag{14}$$

where $P_0(S)$ is the probability density of the ideal chain gyration radius and $P_0(O_{jk}|S)$ is the conditional probability density that the $k$th and $j$th mers overlap given that the gyration radius is $S$. The exact functional form of $P_0(O_{jk}|S)$ is not known. However, it is very reasonable to expect that $P_0(O_{jk}|S)$ will have a similar functional dependence on the relevant variables as that of $P_0(O_{jk}|R)$. That is, a change of variables analogous to those in eq 8 followed by integration should yield

$$P_k = k(\sigma/S)^3 f(k/r, S/\langle S^2\rangle_0^{1/2}) \tag{15}$$

where $f$ is an unknown function of $k/r$ and $S/\langle S^2\rangle_0^{1/2}$; $\langle S^2\rangle_0$ is the mean square gyration radius of the ideal chain. Setting $S = \langle S^2\rangle_0^{1/2}$ in $f$ and replacing $f(k/r,1)$ by its mean value $\bar{f}$, we obtain

$$P_k = k(\sigma/S)^3\bar{f} \tag{16a}$$

where $\bar{f}$ is a constant independent of $k$, $S$, and $r$.

To make this zeroth approximation more concrete and physical, let all chains that have a gyration radius $S$ pervade a space of volume $V$ that is proportional to $S^3$. The *fraction of space* $\phi_s$ *occupied by those configurations with a gyration radius* $S$ is

$$\phi_s = \frac{r\sigma^3}{V} \sim r(\sigma/S)^3 \tag{17}$$

Assuming that all $r$ mers are contained in $V$, then eq 16a becomes

$$P_k = (k/r)\phi_s \tag{16b}$$

Equation 16b, crucial to what follows, is physically intuitive. Since $\phi_s$ is the fraction of sites occupied by an $r$ mer of gyration radius $S$, the mean field probability that a lattice site is occupied at the $k$th step is just $k/r$ times $\phi_s$.

Substitution of eq 16b into eq 12 yields

$$\omega(S) = \omega_0(S)\frac{(\phi_s/r)^r(r/\phi_s)!}{\left(\dfrac{r}{\phi_s} - r\right)!} \tag{18a}$$

or using Sterling's approximation for the factorials

$$\ln\omega = \ln\omega_0 - r[(1 - \phi_s)\ln(1 - \phi_s)/\phi_s + 1] \tag{18b}$$

Notice that

$$\lim_{\phi_s\to 0}\omega = \omega_0 \tag{19}$$

$$\lim_{\phi_s\to 1}\omega = \omega_0 e^{-r} \tag{20}$$

**B. Attractive Interactions.** We now wish to weigh the $k$th step of the RW by an appropriate Boltzmann factor which takes into account the attractive interaction of the $k + 1$ mer with the other $k$ mers. The probability that any of the previous $k$ mers will be at a distance $s$ from the $k + 1$ mer is, in a mean field approximation, equal to the fraction of space occupied by the $k$ mers:

$$\frac{k\sigma^3}{V} \equiv \left(\frac{k}{r}\right)\phi_s \equiv P_k \tag{21}$$

Let $\epsilon(s/\sigma)$ be a spherically symmetric pair potential that characterizes the attractive interaction between mers separated by a reduced distance $s/\sigma$. Then the total interaction energy of the $k + 1$ mer with the other $k$ mers is given by

$$4\pi\int_1^\infty P_k(s/\sigma)^2\epsilon(s/\sigma)\,\mathrm{d}(s/\sigma) = -\epsilon^* P_k \tag{22}$$

As long as $\epsilon(s/\sigma)$ falls off faster than $(s/\sigma)^{-3}$, the above integral converges and $\epsilon^*$ will be a positive constant. Therefore, the proper statistical weight for the $k$th step of a RW of $r - 1$ steps that has a gyration radius of $S$ is

$$(1 - P_k)e^{P_k(\Theta/T)} \tag{23}$$

where $\Theta$ is a characteristic temperature defined by

$$\Theta \equiv \epsilon^*/k_B \tag{24}$$

and $k_B$ is Boltzmann's constant.

The statistical weight $\Omega$ for all RW's of $r - 1$ steps that have a gyration radius between $S$ and $S + \mathrm{d}S$ is

$$\Omega(S) = z^{r-1}P_0(S)\prod_{k=1}^{r-1}(1 - P_k)e^{P_k(\Theta/T)} \tag{25a}$$

The above product is easily evaluated [cf. eq 18]. Taking the logarithm, using Sterling's approximation, and ignoring unity compared to $r$, we obtain

$$\ln\Omega = \ln P_0(S) + rq(\phi_s) \tag{25b}$$

$$q(\phi_s) = \tfrac{1}{2}(\Theta/T)\phi_s - (1 - \phi_s)\ln(1 - \phi_s)/\phi_s + \ln(z/e) \tag{26}$$

As will become more apparent in what follows, the function $rq(\phi_s)$ is a generating function for the virial coefficients.

The probability that a chain will have a gyration radius between $S$ and $S + \mathrm{d}S$ is

$$P(S)\,\mathrm{d}S = Z^{-1}\Omega(S)\,\mathrm{d}S = Z^{-1}P_0(S)\exp[rq(\phi_s)]\,\mathrm{d}S \tag{27}$$

where the normalization constant (partition function) is given by

$$Z = \int_0^\infty \Omega(S)\,\mathrm{d}S \tag{28}$$

**C. Calculation of $\langle S^2\rangle$.** Although the ideal chain distribution function $P_0(S)$ can be expressed as an infinite series,[47] it is not very convenient to use. Alternatively, we can utilize the Gaussian approximation for $P_0(S)$, which only yields the correct second moment, or the improved Flory–Fisk distribution[48]

$$P_0(S) \sim S^6\exp(-mS^2/\langle S^2\rangle_0) \tag{29}$$

which approximates the first four even moments quite well with $m = 7/2$. For the latter, the mean square gyration radius $\langle S^2\rangle$ and the associated expansion factor $\alpha^2$ are given by

$$\alpha^2 \equiv \langle S^2\rangle/\langle S^2\rangle_0 = -\left.\frac{\partial\ln Z}{\partial m}\right|_{m=7/2} \tag{30}$$

1. ***T*/Θ < 1.** As will be shown, the function $q(\phi_s)$, defined by eq 26, has a maximum value at $S^*$ and a corresponding density $\phi_{s^*}$ which lies in the range $0 < \phi_{s^*} < 1$. Under these conditions and for large $r$, we can obtain an adequate approximation for the partition function, eq 28, by expanding $q(\phi_s)$ around $S^*$ and retaining terms only to second order; thus,

$$Z \simeq \exp[rq(\phi_{x^*})]\int_{-\infty}^{\infty}P_0(x)\exp\left[-\frac{r}{2}\left|q''(\phi_{x^*})\right|(x - x^*)^2\right]\mathrm{d}x \tag{31a}$$

$$Z \simeq \left[ \frac{2\pi}{r|q''(\phi_{x^*})|} \right]^{1/2} \exp[rq(\phi_{x^*})]P_0(x^*) \qquad (31b)$$

where

$$x \equiv S/\langle S^2\rangle_0^{1/2} \qquad (32)$$

$$\phi_{x^*} \equiv \phi_{s^*} \equiv \phi_0/(x^*)^3 \qquad (33)$$

$$\phi_0 \sim r\sigma^3/\langle S^2\rangle_0^{3/2} \sim r^{-1/2} \qquad (34)$$

The parameter $\phi_0$ is the *fraction of space occupied by chains whose square gyration radius equals the ideal value of* $\langle S^2\rangle_0$.

The above approximation for $Z$ is valid provided

$$q''(\phi_{x^*}) \equiv \left.\frac{\mathrm{d}^2q}{\mathrm{d}x^2}\right|_{x=x^*} < 0 \qquad (35)$$

and

$$r|q''(\phi_{x^*})| \gg 1 \qquad (36)$$

The maximum value of $q$ is determined by the equation

$$\phi_{x^*}{}^2 \left.\frac{\partial q}{\partial \phi_x}\right|_{\phi_x=\phi_x^*} = \frac{1}{2}(\Theta/T)\phi_{x^*}{}^2 + \ln(1-\phi_{x^*}) + \phi_{x^*} = 0 \qquad (37)$$

Now it is easy to show that

$$q''(x^*) = \left[\left(\frac{\partial\phi_x}{\partial x}\right)^2 \frac{\partial^2 q}{\partial \phi_x{}^2}\right]_{x=x^*} = -9\left(\frac{\phi_{x^*}}{\phi_0}\right)^{2/3}\left\{\frac{1}{3} + \frac{1}{2}\phi_{x^*} + \frac{3}{5}\phi_{x^*}{}^2 + \ldots\right\} \qquad (38)$$

As $\phi_{x^*}$ approaches zero, $q''(\phi_{x^*})$ approaches zero, and condition 36 no longer holds. The behavior of $\phi_{x^*}$ as a function of $T/\Theta$ as determined from eq 37 is shown in Figure 1.

For $T < \Theta$, $\phi_{x^*}$ is finite, and the approximation, eq 31, holds for sufficiently large $r$. Under these conditions, eq 30 yields

$$\alpha^2 \simeq (x^*)^2 = (\phi_0/\phi_{x^*})^{2/3} = cr^{-1/3} \qquad (39)$$

or

$$\langle S^2\rangle \simeq dr^{2/3} \qquad (40)$$

where $c$ and $d$ are functions of $T/\Theta$ only.

Equations 39 and 40 indicate that the chain has collapsed. Fluctuations in $\alpha$ are of order $[r|q''(\phi_{x^*})|]^{-1/2}$ and thus are very small. The distribution of $x$ for large $r$ is similar to a delta function centered at $x^*$.

**2. $T/\Theta > 1$.** When $T > \Theta$, $q(\phi_x)$ decreases monotonically with $\phi_x$. For this case we write

$$\Omega(x) \sim x^6 \exp[h(x)] \qquad (41)$$

$$h(x) = -mx^2 + rq(\phi_x) \qquad (42)$$

Since $h(x)$ is composed of two terms, one increasing with $x$ and the other decreasing with $x$, it will have a well-defined minimum at $x = x^*$. To obtain an approximation to the partition function $Z$, we expand $h(x)$ around $x^*$ and retain terms only to second order:

$$Z = \int_0^\infty \Omega(x)\,\mathrm{d}x \simeq \int_{-\infty}^\infty x^6 \exp[h(x^*) - \tfrac{1}{2}h''(x^*)(x-x^*)^2]\,\mathrm{d}x \qquad (43)$$

where $x^*$ is now the solution to

$$\partial h(x)/\partial x = 0 \qquad (44)$$

For large $r$, eq 44 yields

$$(x^*)^5 = \frac{3r\phi_0}{4m}(1-\Theta/T) \sim r^{1/2}(1-\Theta/T) \qquad (45)$$

and

$$h''(x^*) \equiv \left.\frac{\partial^2 h}{\partial x^2}\right|_{x=x^*} = 2m \qquad (46)$$

Substituting eq 45 and 46 into eq 43 and integrating, we obtain ($r$ is assumed to be large):

$$Z \simeq (x^*)^6(2\pi/m)^{1/2}\exp[-m(x^*)^2 + rq(\phi_{x^*})] \qquad (47)$$

and

$$\alpha^2 = -\left.\frac{\partial \ln Z}{\partial m}\right|_{m=7/2} = (x^*)^2 + 1/7 \qquad (48)$$

Equations 45 and 48 indicate that the chain is expanded (coil state) and that we have obtained the well-known Flory result[49] that

$$\alpha^2 \sim r^{1/5} \text{ or } \langle S^2\rangle \sim r^{6/5} \qquad (49)$$

Notice that since $h''(x^*) = 2m$ is of order unity, fluctuations in $x^*$ or $\alpha$ are of order unity. Thus, unlike the situation for $T/\Theta < 1$, fluctuations in chain dimensions for $T/\Theta > 1$ are very large. A significant property of the $\Theta$ temperature is that it separates the regimes of small and large fluctuations.

**3. Hermans–Overbeek Approximation.** In the Hermans–Overbeek (HO) approximation[45,50]

$$\alpha^2 \simeq x_{\max}{}^2 \qquad (50)$$

where $x_{\max}$ is the solution of the following equation:

$$\frac{\partial \ln[x\Omega(x)]}{\partial x} = 0 \qquad (51)$$

The basis for this approximation is that $\Omega(x)$ is slightly skewed to high $x$ values so that the second moment, $\langle x^2\rangle$, approximately coincides with the maximum in $x\Omega(x)$. This leads to

$$\frac{7\phi_\alpha}{3r}(1-\alpha^2) = \phi_\alpha{}^2\frac{\partial q}{\partial \phi_\alpha} = \frac{1}{2}(\Theta/T)\phi_\alpha{}^2 + \ln(1-\phi_\alpha) + \phi_\alpha \qquad (52a)$$

where

$$\phi_\alpha \equiv \phi_0/\alpha^3 \simeq \phi_0/x_{\max}{}^3 \qquad (53)$$

As $r \to \infty$, the left-hand side of eq 52a approaches zero ($0 \le \phi_\alpha \le 1$ for all $r$). Therefore, if eq 52 has a solution as $r \to \infty$, the right-hand side of eq 52a must also approach zero for large $r$. The right-hand side always has a zero if $T/\Theta < 1$ as is illustrated in Figure 1 [cf. eq 37]. The HO approximation also suggests, as did our previous approximation, eq 31 and 39, that the chain collapses for $T/\Theta < 1$ and $r \to \infty$.

It is easy to show, by expanding $\ln(1-\phi_\alpha)$, that the right-hand side of eq 52a is always negative if $T/\Theta > 1$. Therefore, for eq 52a to have a solution for $T/\Theta > 1$ requires the left-hand side to be negative or

$$\alpha^2 > 1 \qquad (54)$$

Under these conditions, $\phi_a$ is very small and eq 52a can be rewritten as [expand $\ln(1-\phi_\alpha)$]:

$$\alpha^5 - \alpha^3 = \frac{3r\phi_0}{14}(1-\Theta/T) + \frac{r\phi_0{}^2}{7\alpha^3} + \ldots \qquad (52b)$$

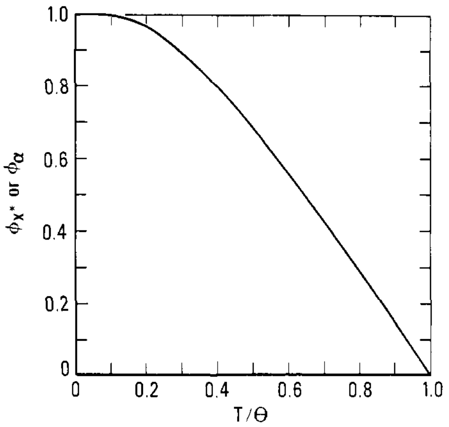

**Figure 1.** The values of $\phi_x$ that maximize eq 26 are given by the transcendental eq 37 and are denoted by $\phi_{x^*}$ or $\phi_\alpha$. Numerical solutions to eq 37 are shown as a function of $T/\Theta$.

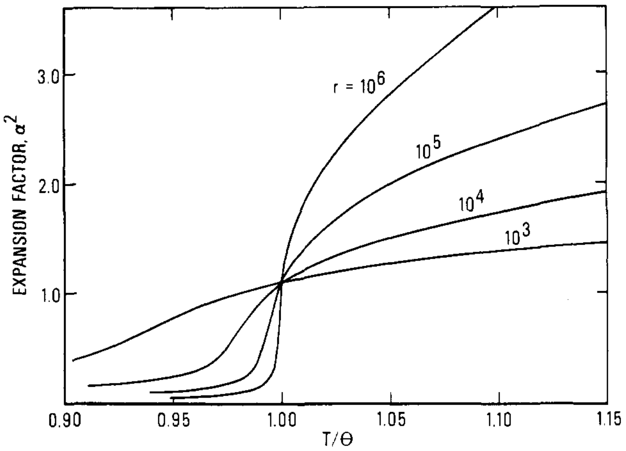

**Figure 2.** The expansion factor $\alpha^2$ as calculated from the Hermans–Overbeek approximation, eq 52, is shown as a function of chain length ($r$) and $T/\Theta$. The quantity $\phi_0$ is determined via eq 61.

For $\alpha > 1$, all terms except the first on the RHS of eq 52b can be ignored ($r\phi_0 \sim r^{1/2}$), and we obtain the well-known Flory form[49] for the expansion factor.

In Figure 2, $\alpha^2$ as calculated from the HO approximation is plotted against $T/\Theta$ for several values of $r$. In Figure 3, Slagowski's[14,17] experimental values of $\alpha^2$ for a very high molecular weight polystyrene in cyclohexane are compared with theory values. The value of $r$ chosen to calculate the theoretical curve via the HO approximation was determined by dividing the polymer molecular weight ($4.4 \times 10^7$) by the monomer molecular weight (104); as will be discussed in the next section, $\phi_0$ is determined from eq 61.

In summary, the chain is in a globular state for $T/\Theta < 1$ and in a coiled state for $T/\Theta > 1$. As $r \rightarrow \infty$, the coil–globule transition will become very sharp as illustrated in Figure 2. In the globular state, $\alpha^2 \sim r^{-1/3}$, and fluctuations in $\alpha$ are very small (of order $r^{-1/2}$). In the coil state, $\alpha^2 \sim r^{1/5}$, and fluctuations in $\alpha$ are very large (or order unity).

**D. Transition Behavior.** The abrupt change in $\alpha^2$ near $T/\Theta = 1$ is indicative of a phase transition. However, to characterize the phase transition it is better to use $\phi_\alpha$ rather than $\alpha^2$ as an order parameter because it is bounded for infinite $r$. In the globular state ($T/\Theta < 1$), $\phi_\alpha$ is a function of $T/\Theta$ only; its value can be determined from Figure 1 for $r \rightarrow \infty$. In the coiled state ($T/\Theta > 1$), $\phi_\alpha$ is very small and varies as $r^{-4/5}$; as $r \rightarrow \infty$, $\phi_\alpha \rightarrow 0$. In a first-order-phase transition, an order parameter jumps discontinuously at the transition temperature. The analysis presented above for $\alpha^2$ suggests that $\phi_\alpha$ is continuous through the transition region. However, as $r \rightarrow \infty$, the temperature derivative of $\phi_\alpha$ becomes discontinuous at $T = \Theta$. The latter behavior is characteristic of a second-order-phase transition in the Landau theory of phase transitions.[25,26]

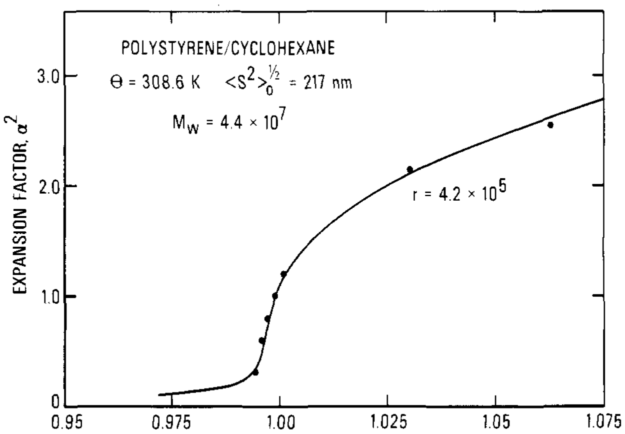

**Figure 3.** A comparison of theoretical (solid line) and experimental (solid circles) values of the expansion factor $\alpha^2$. Data were taken from ref 14 (raw data). Theoretical line calculated from eq 52 and 61. The value of $r$ was set equal to the degree of polymerization.

In the Landau theory, the "ordered" phase is characterized by a finite value of the order parameter $\phi$ while the "disordered" phase has $\phi = 0$. At the critical temperature $T_c$ that separates the two phases, $\phi$ is continuous but $\mathrm{d}\phi/\mathrm{d}T$ is not. An isolated critical point is defined by

$$\frac{\partial^2 A(\phi)}{\partial \phi^2} = \frac{\partial^3 A(\phi)}{\partial \phi^3} = 0; \qquad \frac{\partial^4 A(\phi)}{\partial \phi^4} > 0 \tag{55}$$

That is, the second and third derivatives of the free energy $A$ are zero at the critical point (the first derivative of $A$ is also zero at the critical point and at all other temperatures because this is the condition that minimizes $A$). The condition that the fourth derivative be positive not only guarantees that the critical point corresponds to a minimum in $A$ but also implies that $A(\phi)$ is analytic at the critical point—a feature characteristic of mean field theories.

The free energy for chain configurations with a gyration radius $S$ or a mer density $\phi_s$ is equal to $-k_B T \ln \Omega(S)$ and

$$\Omega(S) \sim \left(\frac{\phi_0}{\phi_s}\right)^2 \exp\left[-m\left(\frac{\phi_0}{\phi_s}\right)^{2/3} + rq(\phi_s)\right] \tag{56}$$

The condition that the second and third derivatives of $A$ equal zero at the critical point yields, with $m = 7/2$

$$r\phi_c\left[\frac{\Theta}{T_c} - \frac{1}{1-\phi_c}\right] + \frac{7}{9}x_c^2 - 2 = 0 \tag{57}$$

$$(x_c^3 - \phi_0)^2\left(1 - \frac{35}{54}x_c^2\right) = \frac{1}{2}r\phi_0^2 = \text{constant} \tag{58}$$

where $T_c$ and $x_c$ are the critical values of $T$ and $x$ and

$$\phi_c \equiv \phi_0/x_c^3 \tag{59}$$

Equation 58 implies that

$$x_c^2 < 54/35 \tag{60}$$

Since $\phi_0 \rightarrow 0$ as $r \rightarrow \infty$, we can arbitrarily let $x_c \rightarrow 1$ as $r \rightarrow \infty$ to obtain from eq 58:

$$\tfrac{1}{2}r\phi_0^2 = 19/54 \text{ or } \phi_0 = (19/27)^{1/2}r^{-1/2} \tag{61}$$

The value of the constant $r\phi_0^2$, which we have arbitrarily fixed, can also be related to the intrinsic flexibility of the chain.[2,12]

If we treat $x_c$ as a function of $\phi_0$, we can obtain an approximate solution to eq 58 for finite $r$ by expanding $x_c$:

$$x_c = 1 + \left.\frac{\partial x_c}{\partial \phi_0}\right|_{\phi_0=0} \phi_0 + ... \tag{62b}$$

$$x_c = 1 + {}^{19}\!/_{22}\phi_0 + ... \tag{62a}$$

Since $\phi_c$ varies as $r^{-1/2}$, eq 62 and 57 imply that

$$r^{1/2}(\Theta/T_c - 1) = \text{positive constant} \tag{63}$$

For the infinite chain, $T_c = \Theta$, and the transition is truly second order in the Landau sense. For finite chains, $T_c < \Theta$, and the transition is pseudo-second-order because $\mathrm{d}\phi_\alpha/\mathrm{d}T$ remains finite through the transition. Moore[6] has also concluded that the transition is second order in the thermodynamic limit of an infinite chain.

**E. Behavior in *d* Dimensions.** To investigate the behavior in $d$ dimensions, we found it convenient to use the Gaussian approximation for $P_0(S)$

$$P_0(S) \sim x^{d-1} \exp(-dx^2/2) \tag{64}$$

where as before

$$x^2 = S^2/\langle S^2\rangle_0 \tag{65}$$

For an ideal RW, $\langle S^2\rangle_0 \sim r$ in all dimensions. The fraction of occupied space is given by

$$\phi_x \sim r\sigma^d/S^d = \phi_0/x^d \tag{66}$$

where

$$\phi_0 \sim r\sigma^d/\langle S^2\rangle_0^{d/2} \sim r^{1-d/2} \tag{67}$$

For $T/\Theta < 1$ and sufficiently large $r$, we can approximate the partition function as before [cf. eq 31 and 39]:

$$\alpha^2 \sim \phi_0^{2/d} \sim r^{(2-d)/d} \text{ or } \langle S^2\rangle^{d/2} \sim r \tag{68}$$

This result shows that the chain is always in the globular state for $T/\Theta < 1$ and $d \geq 2$. Unlike Moore,[6] we predict chain collapse even for $d > 4$. In one dimension, it is impossible for the chain to collapse; notice that eq 68 yields $\langle S^2\rangle \sim r^2$ in one dimension as it should.

For $T/\Theta > 1$, we look for the maximum term in $x\Omega$ (Hermans–Overbeek approximation). Let $\alpha$ equal the value of $x$ that yields the maximum term; then

$$\partial \ln [x\Omega(x)]/\partial x = 0 \tag{69a}$$

yields

$$1 - \alpha^2 = r\phi_\alpha \frac{\partial q}{\partial \phi_\alpha} \tag{69b}$$

The RHS of eq 69b is always negative for $T/\Theta > 1$ which implies that $\alpha^2 > 1$ [see discussion following eq 53]. Expanding the RHS of eq 69b [see eq 37], we obtain

$$\alpha^2 = 1 + r\phi_\alpha\{{}^1\!/_2(1 - \Theta/T) + {}^1\!/_3\phi_\alpha + ...\} \tag{69c}$$

Since $r\phi_\alpha \sim r^{(4-d)/2}/\alpha^d$, this term dominates the RHS of eq 69c for $d < 4$. Thus, for very large $r$ and $T/\Theta > 1$, we have

$$\alpha^2 \sim r^{(4-d)/(2+d)} \text{ or } \langle S^2\rangle \sim r^{6/(d+2)} \tag{70}$$

For $d > 4$ and $T/\Theta > 1$, unity is larger than all other terms on the RHS of eq 69c, and thus

$$\alpha^2 = 1 + O(r^{-(d-4)/2}) \text{ or } \langle S^2\rangle \sim r \tag{71}$$

Equations 70 and 71 are in agreement with those results obtained from scaling arguments.[51]

**F. Relationship to Other Theories.** If we make the approximation,

$$1 - P_k \simeq e^{-P_k} \tag{72}$$

which should always be valid for the low-density coiled state, then from eq 4

$$\omega(\mathbf{R}) \simeq \omega_0(\mathbf{R}) \exp[-\sum_{k=1}^{r-1} P_k] = \omega_0(\mathbf{R}) \exp\left[-\frac{V(\mathbf{R})}{k_\mathrm{B}T}\right] \tag{73}$$

where $V(\mathbf{R})$ is defined as the potential of mean force. Now instead of eq 5, let[45]

$$P_{k-1} = \sum_{j=1}^{k-1} \int_0^\beta P(O_{jk}|\mathbf{R})\, \mathrm{d}\beta' \tag{74}$$

where $\beta$ is the well-known binary-cluster integral. The conditional probability in eq 74 is to be evaluated in the intermediate "perturbed" state $\beta'$. The potential of mean force becomes

$$\frac{V(\mathbf{R})}{k_\mathrm{B}T} = \sum_{k=1}^{r-1} P_k = \sum\sum_{j<k} \int_0^\beta P(O_{jk}|\mathbf{R})\, \mathrm{d}\beta' \tag{75}$$

Equations 73 and 75 were first obtained by Fujita, Okita, and Norisuye.[52] Equation 75 and its equivalent for $V(S)$ are considered to be formally exact within the framework of the two-parameter theory of excluded volume. They are the starting point for several approximate theories of the excluded volume effect.[45]

In the simplest approximation, $P(O_{jk}|\mathbf{R})$ is replaced by $P_0(O_{jk}|\mathbf{R})$, and eq 74 becomes

$$P_{k-1} = \beta\sum_{j=1}^{k-1} P_0(O_{jk}|\mathbf{R}) \tag{76}$$

For nonattractive mers, $\beta = b\sigma^3$, and we obtain eq 5.

Thus, we see two important differences between the present theory and the traditional two-parameter theories of excluded volume. First, we never make the approximation given by eq 72, and second, attractive interactions are not included via the introduction of a binary cluster integral. Approximation 72, although valid for the coil state ($P_k \ll 1$), is invalid for the globular state where $P_k$ values can be of order unity.

The present theory is more closely related to the van der Waals theory of fluids. To see this more clearly, we consider the classical configurational partition function $Q$ for a system of $N$ hard spheres, each of diameter $d_0$ in a cubical box of volume $V$

$$Q = \frac{1}{N!}\int_V ... \int_V \prod_{i<j} H(|\mathbf{R}_i - \mathbf{R}_j|)\, \mathrm{d}\mathbf{R}_1\, \mathrm{d}\mathbf{R}_2 ... \mathrm{d}\mathbf{R}_N \tag{77}$$

where the $\mathbf{R}_i$ are position vectors and $H(X)$ is the unit step function. If $|\mathbf{R}_i - \mathbf{R}_j| \equiv R_{ij}$, then

$$H(R_{ij}) = 0,\ R_{ij} \leq d_0$$

$$H(R_{ij}) = 1,\ R_{ij} > d_0 \tag{78}$$

The above partition function cannot be evaluated, except approximately. In the dilute limit where

$$V \gg Nv_0; \qquad v_0 = 4\pi d_0^3/3 \tag{79}$$

we can ignore the effects of multiple overlapping and obtain (the excluded volume per pair of spheres is 8 times the volume of one of the spheres or $v_0$)

$$Q \simeq \frac{1}{N!}V(V - v_0)(V - 2v_0)...[V - (N - 1)v_0] \tag{80a}$$

$$Q = \frac{V^{N}}{N!}\prod_{k=1}^{N-1}\left[1 - \frac{k}{N}\phi\right] \tag{80b}$$

where

$$\phi = Nv_0/V \tag{81}$$

At this point, eq 80b should be compared with eq 12 with $P_k$ defined by eq 16b. The factor $V^N/N!$ is the configurational partition function of an ideal gas which is "corrected" for the effects of excluded volume by the product over $k$. Similarly, the ideal number of chain configurations in eq 12 is "corrected" for the effects of self-excluded volume by a similar product over $k$.

To obtain the van der Waals equation in the absence of attractive interactions, we replace the factor $1 - (k/N)\phi$ by its average value $1 - \phi/2$, and eq 80b then becomes

$$Q \simeq \frac{V^N}{N!}(1 - \phi/2)^N = \frac{(V - b)^N}{N!} \tag{82}$$

where $b = Nv_0/2$ is the van der Waals excluded volume parameter.

If we take attractive interactions into account in a mean field approximation, we obtain a potential energy that is proportional to $N^2/2V$. The contribution to the partition function is therefore approximately $e^{a/Vk_BT}$ where $a \sim N^2/2$ is the van der Waals attraction constant. From $P = k_BT\ \partial \ln Q/\partial V$, the van der Waals equation of state follows.

For the present theory, the total attractive part of the potential energy of a chain is given by

$$-k_B\Theta\sum_{k=1}^{r-1} P_k = -\tfrac{1}{2}rk_B\Theta\phi_s \sim V^{-1} \tag{83}$$

which is a van der Waals type energy (inversely proportional to the volume of the system).

Although eq 80 is a good approximation at low densities, it becomes increasingly less exact at higher densities. The same can be said about eq 18. Extension of eq 80 or 18 to high densities in effect yields approximate higher virial coefficients.

The high-density limit corresponds to a RW which visits every lattice point only once (a completely filled lattice). A RW of this type is called a Halmilton walk. The entropy of a Halmilton walk is much smaller than an ideal RW. Monte-Carlo and analytical studies of Halmilton walks in two dimensions have shown that the entropy reduction is somewhat less than $k_B$ per mer;[53] the exact entropy reduction depends on the details of the "traffic regulations" used to generate the RW. From eq 20, we see that our approximate calculation of the entropy reduction in the high-density limit is $k_B$ per mer. This result suggests that eq 18 overestimates the excluded volume effect at high densities.

## Discussion

An aspect of the present theory which distinguishes it from all other theories of the excluded volume effect is that ternary and higher-order interactions are approximately taken into account. In the mean field approximation employed, $\phi_s$ is equal to the probability of finding a mer at a given lattice site for all chain configurations that have a gyration radius $S$. The number of binary mer interactions for these chains is proportional to $r\phi_s$, and the number of $n$-tuple mer interactions is proportional to $r\phi_s^{n-1}$. The function $rq(\phi_s)$, defined by eq 26, is the generating function for the virial coefficients of these $n$-tuple interactions.

At the Θ temperature, the second virial coefficient, which is the only temperature-dependent one, vanishes. An important result is that ternary interactions cannot be ignored at the Θ temperature.[54] Since the chain expansion factor $\alpha^2$ is of order unity at Θ, the number of $n$-tuple interactions at $T = \Theta$ is of order $r^{(3-n)/2}$. Thus, for large $r$, the third-order term is of order unity, and all higher ones are negligible by comparison. The effect of the third virial coefficient on the probability distribution at $T = \Theta$ is graphically shown in Figure 4. Some of the theoretical ramifications of this result have already been explored by deGennes[2] and Oono;[36,37] the most important of these is that *ideal chain statistics are not obtained at* Θ *or at any other temperature.*

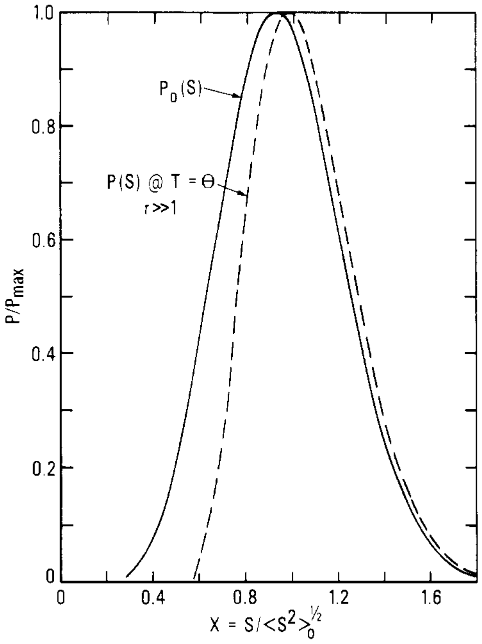

**Figure 4.** A comparison of the probability distributions (relative to their maximum values) for the gyration radius $S$; $P_0(S)$ (solid line) is the *ideal* distribution given by eq 29, and $P(S)$ (dashed line) is the distribution of a chain with excluded volume, eq 27, at $T = \Theta$. The two distributions are not identical because of ternary interactions (see text).

In two dimensions, the deviation from ideal chain statistics at the Θ temperature is more severe. Unlike a three-dimensional chain, the mer density $\phi_0$ of an ideal two-dimensional chain is independent of $r$ [see eq 67]. Thus, even for the infinite two-dimensional ideal chain, $\phi_0$ remains finite. For $T > \Theta$, the mer density $\Theta_\alpha$ varies as $r^{-1/2}$. For $T < \Theta$, $\phi_\alpha$ is finite just as it is for an ideal chain. At some unique temperature below Θ, say $T_0$, $\phi_\alpha = \phi_0$. For example, if $\phi_0 = 0.5$, then from Figure 1 $T_0/\Theta \simeq 0.65$. At this temperature, the chain dimensions would be the same as those of the ideal chain ($\alpha = 1$). However, the probability distribution $P(S)$ for the gyration radius would resemble a delta function and not a two-dimensional Gaussian. For temperatures in the range $T_0 < T < \Theta$, the gyration radius would be expanded above its ideal value ($\alpha > 1$), but $P(S)$ would still resemble a delta function. As $T$ approaches Θ, the distribution broadens and signals the onset of large fluctuations in the gyration radius. Within the context of the present theory, *a significant property of the* Θ *temperature is that it separates the regimes of small and large fluctuations.*

In the traditional two-parameter theories of the excluded volume effect, only binary interactions are considered, and the expansion factor can be expressed as a function of a single variable $z$:[45]

$$\alpha^2 = f(z) \tag{84}$$

$$z \equiv \left( \frac{3}{2\pi \langle R^2 \rangle_0} \right)^{3/2} r^2 \beta \qquad (85)$$

In contrast, the present theory for $\alpha^2$ cannot be expressed as a function of $z$ only except at temperatures above the $\Theta$ temperature where it reduces to the classical Flory theory.[49] At temperatures well above $\Theta$, binary interactions are the only important ones. At temperatures well below $\Theta$ where $\alpha^2 \sim r^{-1/3}$, the number of $n$-tuple interactions becomes proportional to $r$. Thus, many of the higher-order interaction terms contribute significantly when $T/\Theta < 1$.

Chain dimensions change rapidly near the $\Theta$ temperature as shown in Figure 2; the longer the chain, the more rapid the change in chain dimensions near $\Theta$. These curves look remarkably similar to those obtained by McCrackin, Mazur, and Guttman[55] and Clark and Lal[56] by computer simulation. Excellent agreement between theory and experiment has been obtained for a very high molecular weight polystyrene as shown in Figure 3.

As the chain length $r$ becomes very large, the globule–coil transition takes on the character of a Landau-type, second-order phase transition.[25,26] The mer density $\phi_\alpha$ is continuous through the transition, but $\mathrm{d}\phi_\alpha/\mathrm{d}T$ becomes discontinuous as $r \rightarrow \infty$ (see Figure 1). The transition temperature $T_c$ for a finite chain, which is only pseudo-second-order, is always less than $\Theta$, but $T_c \rightarrow \Theta$ as $r$ becomes large. Therefore, for the infinite chain, $T_c$ becomes coincident with the $\Theta$ temperature.

In three dimensions, the product $r\phi_0{}^2$ is a constant independent of chain length. deGennes[2] and Zimm and Post[12] have emphasized that this constant is proportional to chain flexibility. We have arbitrarily set $r\phi_0{}^2 = 19/27$ so that in the thermodynamic limit $\alpha \rightarrow 1$ as $T \rightarrow T_c$. For smaller values of this constant (corresponding to relatively stiff polymer chains) and *finite* values of $r$, it is possible for the free-energy function, eq 56, to have double maxima over a limited temperature range. This suggests the possibility of a discontinuous or first-order phase transition. Qualitatively similar behavior is observed in the theories of deGennes[2] and Zimm and Post.[12] However, we tend to discount the possibility of a first-order phase transition, since it disappears in the thermodynamic limit. As $r \rightarrow \infty$, the double maxima merge into one irrespective of the value chosen for $r\phi_0{}^2$. In the thermodynamic limit, only a second-order phase transition is possible.

The behavior of the transition temperature with $r$ is similar to the behavior of the critical temperature of real chain fluids. The $\Theta$ temperature is analogous to the Boyle temperature $T_B$ of a real fluid, and the transition temperature $T_c$ is analogous to the gas–liquid critical temperature $T_c$. In a van der Waals fluid, $T_B$ is well above $T_c$ ($T_B/T_c = 27/8$). For real chain liquids, such as the $n$-alkanes, the ratio $T_B/T_c$ is smaller and decreases with increasing chain length. There is also theoretical evidence that $T_B/T_c \rightarrow 1$ as $r \rightarrow \infty$ for chain fluids.[57]

Experimentally, it is known that in both dilute[58] and concentrated[59] polymer solutions, chain dimensions can pass through a maximum as a function of temperature. At temperatures that approach the *lower critical solution temperature* of a polymer solution, the chain begins to collapse in a manner quite similar to that observed near $\Theta$. Since the LCST of a polymer solution is intimately associated with the compressible nature of the solvent,[60] it is believed that a correct theory of chain dimensions must treat the solvent as a compressible fluid. If the solvent is treated as an incompressible fluid, the present theory can be easily generalized to include solvent effects. However, the theory remains basically unchanged [$\chi \leftrightarrow {}^1/_2(\Theta/T)$] and thus incapable of describing chain dimensions near an LCST. If the solvent is treated as a compressible fluid, the generalization of the theory is nontrivial and we postpone its development to a subsequent paper.

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# Pyrolysis Gas Chromatographic Characterization of Highly Alternating Copolymers Containing Styrene and Tetracyanoquinodimethan, Methyl Acrylate, Acrylonitrile, or Methyl Methacrylate Units

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ABSTRACT: A method of characterizing configurational microstructures of highly alternating copolymers was proposed using pyrolysis gas chromatography with a high-resolution glass capillary column. By this method, almost perfectly ordered microstructures of styrene (St)–tetracyanoquinodimethan (TCNQ) alternating copolymer were confirmed, and the degree of disordered configuration was estimated for various highly alternating copolymers such as St–methyl methacrylate (MA), St–acrylonitrile (AN), and St–methyl methacrylate (MMA) copolymers.

It is well known that highly alternating copolymers are obtained through copolymerization of electron-donor type monomers (unsaturated hydrocarbons, vinylamines, vinyl ethers, etc.) and electron-acceptor type monomers (acrylates, methacrylates, unsaturated nitriles, etc.) in the presence of monomer complexing Lewis acids such as $ZnCl_2$, $SnCl_4$, $AlEtCl_2$, etc. The copolymerization often proceeds spontaneously and yields highly alternating copolymers regardless of the monomer feed ratios. On the other hand, recently, Iwatsuki et al.[1] reported that tetracyanoquinodimethan (TCNQ), one of the most strong electron-acceptor reagents, copolymerized with styrene (St) spontaneously even at room temperature to yield an alternating copolymer without using any additional complexing reagents.

There have been many arguments about the polymerization mechanisms of the highly alternating copolymers. However, it is usually difficult to decide which view is definitely correct without knowing the detailed configurational microstructures of the resulting copolymers. So far, $^1$H NMR and $^{13}$C NMR were most frequently utilized for characterizing these microstructures.[1-8] The characteristic resonance peaks reflecting the disordered configurations, however, are often not so easy to assign positively, even if they are reasonably resolved among the strong cluster peaks reflecting the ordered configurations since the amount of the disordered configurations should be less than a few percent or so at most. Nevertheless, using high-resolution $^1$H NMR (100, 220, or 300 MHz), Suzuki et al.[4] and Harwood et al.[5,6] suggested the existence of the disordered configurations to some extent in some so-called alternating copolymers.

In this work, therefore, a unique method of characterizing the microstructures of highly alternating copolymers was developed using pyrolysis gas chromatography (pyrolysis GC) with a high-resolution glass capillary column. By this method, the configurational microstructures of P(St-*alt*-TCNQ) were investigated, and the degree of disordered configurations was estimated for various highly alternating copolymers such as P(St-*alt*-MA), P(St-*alt*-AN), and P(St-*alt*-MMA).

## Experimental Section

**Materials.** P(St-*alt*-TCNQ), which was synthesized in acetonitrile solution of St and TCNQ without using any additional complexing reagents at 40 °C,[1] was kindly supplied by Dr. S. Iwatsuki, Nagoya University. P(St-*alt*-MA), P(St-*alt*-AN), and P(St-*alt*-MMA), which were synthesized in the presence of a complexing reagent, $AlEt_{1.5}Cl_{1.5}$,[9] were kindly offered from Dr. M. Hirooka, Sumitomo Chemical Co. The associated homopolymers and random copolymers synthesized by the usual radical polymerization were also used as reference materials. Among them, a series of low conversion P(St-*co*-MA) samples[10] were kindly supplied by Dr. Y. Yamashita, Nagoya University.

**Pyrolysis Gas Chromatographic Conditions.** A vertical microfurnace type pyrolyzer, which was designed by the authors to attain instantaneous and specific thermal degradation of polymer samples,[11,12] was directly attached to a gas chromatograph, Shimadzu 7-AG, with a high-resolution glass capillary column (o.d. 0.9 mm × i.d. 0.3 mm × 50 m long) suspension-coated with OV-101 and Silanox (325 mesh) from Shimadzu. In order to get high resolution even for relatively polar components, the active sites of the inner surface of the glass capillary column were treated with a dilute solution of PEG-20M, baked out at 250 °C for 30 h by passing nitrogen carrier gas, and washed by chloroform prior to the final dynamic coating with OV-101. The column temperature was programmed from 50 to 250 °C at a rate of 4 °C/min; 55 mL/min of nitrogen flow at the pyrolyzer was reduced to 1.0 mL/min at the capillary column through a splitter (55:1). The dead volume of the splitter was packed with 5% of OV-101 on Diasolid H (80–100 mesh) of which temperature was maintained at 250 °C. Here, the packing in the splitter plays an important role for preventing column contamination by tarry components

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