free volume to changes in volume. Moreover, the approximate constancy in column III is consistent with the observation that the isothermal–isoaffinity lines for different affinity values, as computed previously for the quasi-equilibrium glass,[5] show pronounced slopes but are nearly parallel. Furthermore, one can anticipate a small variation of free volume with increasing pressure under isochoric–isothermal restraints, at least at moderate pressures, and hence large values in column III. The minor variation in the time span considered here arises from the small variation in $V$ seen in the second column of Table I.

A qualitative rationalization of the slow decay of $\langle \delta\rho^2 \rangle / \rho^2$ is suggested by Cowie. During the initial stages molecular motions should primarily annihilate the large vacancy clusters of the size distribution.[16] Correspondingly, the fraction of smaller multiplets is enhanced. This distortion of the distribution should primarily affect $V$ and $H$, related to molecular packing, whereas density fluctuations depend on the existence of inhomogeneities. According to this argument, the differences in aging rates should be more pronounced in high- than in low-$T_g$ systems, as a consequence of the differences in the width of the distribution.[16]

Thus we have been able to show that comparatively rapid rates of relaxation of $V$ and $H$ are consistent with a very low rate for thermal density fluctuations. The relations used for the computations of the latter were the very same employed successfully for the quasi-equilibrium glass at elevated temperatures.[6] As shown earlier for polystyrene and poly(methyl methacrylate),[6] below about $T_g - 50$, frozen inhomogeneities begin to play the dominant role, and the outcome of aging experiments at low temperatures can be expected, but for different reasons than closer to $T_g$.

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# Origin of Logarithmic Factors in the Four-Dimensional Polymer Chain Expansion Factor

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ABSTRACT: Based on the cluster series for the mean-square end-to-end distance $\langle R^2 \rangle$ of a linear flexible polymer chain in $d$ dimensions, it is shown that the logarithmic dependence of $\langle R^2 \rangle$ on the number of bonds $N$ in four dimensions arises from the counterbalance between the long-range and short-range interactions along the chain contour. The free energy due to segment–segment interactions and the second virial coefficient are also computed and are found to depend on ln $N$ at $d = 4$.

Recently, Chikahisa, Tanaka, Šolc, and Takahashi (CTST)[1] calculated the mean-square end-to-end distance $\langle R^2 \rangle$ of polymer chains in $d$-dimensional space on the basis of the perturbation theory.[2-4] According to these authors, the square expansion factor $\alpha^2$ for a ratio of the mean-square end-to-end distance to its value in unperturbed chains without interactions is a function only of $z$

$$\alpha^2 = 1 + C_1^{(d)}z - C_2^{(d)}z^2 + \ldots \qquad (1)$$

where $C_k^{(d)}$ are numerical constants depending on the dimensionality and $z$ are defined for each dimension as

$$z = (d/2\pi b^2)^{d/2} N^{2-(d/2)}\beta \qquad \text{for } d = 1, 2, 3 \qquad (2)$$

$$z = (2/\pi b^2)^2 (\ln N)\beta \qquad \text{for } d = 4 \qquad (3)$$

$$z = (d/2\pi b^2)^{d/2}\beta \qquad \text{for } d = 5, 6, \ldots \qquad (4)$$

Here $N$ is the number of bonds in a polymer chain, $b$ is the effective bond length, and $\beta$ is the binary cluster integral for a pair of segments.

In 2- and 3-dimension studies[2,5] it is well-known that the power-law dependence of $\alpha$ on $N$ comes from interactions between segments far apart from each other along the chain contour. The scaling theory[6] predicts that $\alpha$ is independent of $N$ for dimensions higher than 4 because the interaction free energy in such cases is negligible compared to the entropic contribution to the free energy. For exactly $d = 4$, the question is less simple. It was considered by CTST[1] that the logarithmic dependence originates largely from the interaction of nearby segments, since $C_1^{(4)}z$ involves an integral

$$I = \int_{1/N}^{1} \mathrm{d}x/x \qquad (5A)$$

where $x$ is a reduced (by $N$) contour length between two

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interacting segments. However, this integral can equally well be written in terms of the unreduced contour length $y = Nx$ as

$$I = \int_1^N \mathrm{d}y/y \tag{5B}$$

and now the logarithmic term seems to reflect long-range interactions! Since eq 5A and 5B are identical, neither interpretation alone can be adequate. We now show that such factors are indeed a consequence of a counterbalance between the long-range and short-range correlations along the chain contour. The free energy due to segment–segment interactions is also computed and is found to be proportional to $\ln N$ at $d = 4$. Further, it is shown that the second virial coefficient $A_2$ is also a function of the same parameters $z$ appearing in $\alpha$, as expected from the two-parameter principle.

Here we show how logarithmic factors arise in the perturbation theory. Following the standard development,[2,3] we find the first deviation term of $\alpha^2$ from its unperturbed value ($\alpha = 1$) to be

$$C_1 z = \frac{2}{(6-d)(4-d)}\left(\frac{d}{2\pi b^2}\right)^{d/2} N^{2-(d/2)}\beta\left\{2 - (6-d) \times \left(\frac{u}{N}\right)^{2-(d/2)} + (4-d)\left(\frac{u}{N}\right)^{3-(d/2)}\right\} \tag{6}$$

where $u$ is a physical cutoff of order $N^0$. The first term of eq 6 arises from interactions between segments far apart from each other along the chain contour, while the second and third terms come from short-range interations. When $d < 4$, the first term is predominant and the cutoff value $u$ is insignificant. On the other hand, for $d > 4$, $C_1 z$ is influenced mainly by near-neighbor interactions. Such effects depend on the order of short-range correlations, and so on the parameter $u$. The two contributions are of the same order of magnitude at $d = 4$, and the power law given by eq 6 is changed into a logarithmic form:

$$\lim_{d\to 4} C_1 z = (2/\pi b^2)^2 \beta \ln (N/u) \tag{7}$$

The cutoff parameter is irrelevant if $\ln N \gg \ln u$.

Alternatively, it may be instructive to consider the free energy due to segment–segment interactions. The local free energy may be expanded around zero segment volume fraction and the first three terms retained, since the segment density within a polymer molecule is low. The total free energy is a sum of all local free energy contributions. After summation (integration), the first two terms give constants, independent of segment distribution. The third term represents the binary interactions and is consistent with our previous treatment. Its contribution $F$ to the total free energy may be written as[2,7]

$$F/kT = (\beta/2)\int [\rho(\mathbf{r})]^2 \, \mathrm{d}\mathbf{r} \tag{8}$$

where $\rho(\mathbf{r})$ is a segment-density distribution function at an arbitrary point $\mathbf{r}$. If the chain is long enough ($N \gg 1$), $\rho(\mathbf{r})$ may be approximated by a pair correlation function and can be written as[6]

$$\rho(r) = \frac{\Gamma(d/2+1)}{\pi^{d/2} b^2} r^{2-d} \tag{9}$$

Substitution of eq 9 into eq 8 yields

$$F/kT = \frac{d\Gamma(d/2+1)}{2\pi^{d/2} b^d} \, \frac{\beta}{4-d} [N^{2-(d/2)} - \sigma^{4-d}] \tag{10}$$

where the upper and lower limits of $r$ used are the chain size $N^{1/2}b$ and the segment size $\sigma b$, respectively.

**Table I**
**$N$ Dependence of $z$ and Numerical Values of $C_k^{(d)}$ in the Expansion Factor**
$\alpha^2 = 1 + C_1^{(d)} z - C_2^{(d)} z^2 + \ldots$

| $d$ | $N$ dependence of $z$ | $C_1^{(d)}$ | $C_2^{(d)}$ | $C_2^{(d)}/C_1^{(d)}$ |
|---|---|---|---|---|
| 1 | $N^{3/2}$ | $^4/_{15}$ | $^{71}/_{648}\pi - {}^{16}/_{45}$ | $-0.0425$ |
| 2 | $N$ | $^1/_2$ | 0.12154 | 0.243 |
| 3 | $N^{1/2}$ | $^4/_3$ | $^{16}/_3 - {}^{28}/_{27\pi}$ | 1.56 |
| 4 | $\ln N$ | 1 | $^3/_2$ | $^3/_2$ |
| $\geqslant 5$ | $N^0$ | $\dfrac{2}{d-4} u^{(4-d)/2}$ | | |

The free energy is proportional to $N^{2-(d/2)}$ for $d < 4$, proportional to $\ln N$ at $d = 4$, and independent of $N$ for $d > 4$. Although eq 9 is the pair correlation function for ideal chains with no interactions, the essential features of the above argument are not altered even if a more legitimate form[6] with an excluded-volume exponent is used:

$$\rho(r) = \frac{\Gamma(d/2+1)}{\pi^{d/2} b^{(d+2)/3}} r^{2(1-d)/3} \tag{11}$$

The exponents of $N$ and $\sigma$ and a numerical constant of eq 10 are modified, but for $d = 4$ the dependence of $F$ on $\ln N$ is again obtained. It is noted that the interaction parameter $z$ is proportional to the free energy $F$ for ideal chains.

According to the two-parameter principle, one may expect that properties other than $\langle R^2 \rangle$ and $F$ should also depend only on $z$. The second virial coefficient furnishes another example. The theory of the second virial coefficient involves two chains, and in general these chains have different lengths. We evaluate $A_2$ between two polymer molecules of unperturbed square sizes $N_1 b^2$ and $N_2 b^2$. It may be written as

$$A_2 = (N_{\mathrm{A}}/2m^2)\beta h(z) \tag{12}$$

where $m$ is the molecular weight of a segment, $N_{\mathrm{A}}$ is the Avogadro number, and a series form of $h$ may be written as

$$h(z) = 1 - C_1 z + C_2 z^2 - \ldots \tag{13}$$

with

$$z \equiv (d/2\pi b^2)^{d/2} N_1^{2-(d/2)} \beta \quad \text{for } d = 1, 2, 3 \tag{14}$$

$$z \equiv (2/\pi b^2)^2 \beta \ln (N_1 N_2)^{1/2} \quad \text{for } d = 4 \tag{15}$$

$$z \equiv (d/2\pi b^2)^{d/2} \beta \quad \text{for } d = 5, 6, \ldots \tag{16}$$

The linear coefficient $C_1$ can be evaluated for arbitrary dimensionality, again by standard methods.[2] If the ratio of the two molecular sizes is defined as

$$\eta = (N_2 b^2)/(N_1 b^2) \tag{17}$$

the results for $C_1$ are

$$C_1 = \frac{16}{(d-2)(d-4)(d-6)}\left\{\eta^{2-(d/2)} + 1 - \frac{2}{8-d} \times [(1+\eta)^{4-(d/2)} - 1 - \eta^{4-(d/2)}]\right\} \quad \text{for } d = 1, 3 \tag{18}$$

$$= \frac{1}{3\eta}[(1+\eta)^3 \ln (1+\eta) - \eta^2(3+\eta) \ln \eta - \eta(1+\eta)] \quad \text{for } d = 2 \tag{19}$$

$$= 2 \quad \text{for } d = 4 \tag{20}$$

$$= \frac{2^{5-(d/2)}}{(d-2)(d-4)} \quad \text{for } d = 5, 6, \ldots \tag{21}$$

Table II
Values of the Exponent $\mu$ in $\alpha^{\mu}$ = (const)$z$

| | $\mu$ | | |
|---|---|---|---|
| $d$ | Pade approximant method[1,2,12] | mean field theory[19,20] | renormalization group theory[10,18] $\epsilon^2$ $\epsilon^3$ |
| 1 | 1.36 | 3 | (3.32, 5.97) |
| 2 | 3.94 | 4 | (4.12, 6.53) |
| 3 | 6.67 | 5 | 5.68 (5.45, 7.19) |
| 4 | 8 | | 8 |

When $N_1 = N_2$, $C_1$ reduces to numerical constants and the parameters $z$ are indentical with the definition given by eq 2–4. The coefficient $C_1$ for $d = 3$ has long been known.[8,9]

Considering that the excluded volume problem is closely related to other many-body problems, such as critical phenomena in magnetic systems, we expect that the logarithmic dependence may arise in those systems too. Actually, logarithmic factors should appear for $m$-body interactions in the $d$-dimensional space, if the following relation is satisfied

$$m\delta = d \tag{22}$$

where it is assumed that the correlation function decays like $r^{-\delta}$. Hence, in a binary interaction approximation, with $\rho$ following eq 9, logarithmic effects appear in four-dimensional systems as seen above, while ternary interactions generate such factors even in three-dimensional systems (for example, a tricritical phase transition[6,10]).

The perturbation series is useful for estimation of the expansion factor at larger $z$, and we may consider our results in this connection. Stockmayer,[11] for example, pointed out that for $d = 3$, the Padé approximant for $\alpha$, based on the first three coefficients $C_k^{(3)}$, gives fairly good values over a wide range of $z$. In further studies[12] it has been shown that an approximant based only on $C_1^{(d)}$ and $C_2^{(d)}$ corresponds to the second-order approximation of the Yamakawa–Tanaka theory.[13] Approximants of this type are given in the CTST paper.[1] However, in the latter work the coefficients $C_k^{(d)}$ contain some errors. The corrected numerical values $C_k^{(d)}$ are summarized in Table I. The coefficients $C_1^{(3)}$, $C_2^{(3)}$, and $C_1^{(2)}$ are due to Teramoto et al.,[14] Fixman,[3] and Kurata and Stockmayer,[5] respectively. The first-order perturbation calculations by von Frankenberg and Hughes[15] are correct for $d = 2$ and 3, if their parameter $\beta/b^3$ is replaced by $\beta/b^d$. Recent results for $C_k^{(4)}$ ($k = 1$, 2) by Kosmas[16] agree with ours, if his parameter $u$ (our $\beta$) is replaced by $u/2$. The factor of $^1/_2$ is due to his counting the same interactions twice. The numerical value $C_2^{(3)} = (11/12)\pi - 4/5$ by Chikahisa[4] is incorrect. It is noted that $C_2^{(1)}$ is negative and that the ratios $C_2^{(d)}/C_1^{(d)}$ decrease with decreasing $d$ (see Table I). Corresponding to the $C_k^{(d)}$ in Table I, the Padê approximants read

$$\alpha^{1.36} = 1 + 0.182z \quad \text{for } d = 1 \tag{23}$$

$$\alpha^{3.94} = 1 + 0.986z \quad \text{for } d = 2 \tag{24}$$

$$\alpha^{6.67} = 1 + 4.45z \quad \text{for } d = 3 \tag{25}$$

$$\alpha^{8} = 1 + 4z \quad \text{for } d = 4 \tag{26}$$

Equation 25 has been reported previously.[2,12] Our recent result[1] of $\alpha$ for $d = 1$ is incorrect and should be replaced by eq 23. These equations are the lowest order approximation of the Padê method[12] and the second lowest in the Yamakawa–Tanaka theory.[13] Higher order results may be preferable in order to obtain more accurate values of $\alpha$. This is especially clear for $d = 1$, where the exact value of the exponent $\alpha$ is 3.

Much recent work[17,18] is mainly concerned with the asymptotic exponent $\mu$, defined by

$$\lim_{z\to\infty} \alpha^{\mu}/z = \text{const} \tag{27}$$

In Table II, $\mu$'s of eq 27 for different dimensions estimated from $C_1^{(d)}$ and $C_2^{(d)}$ are compared with those from the mean field theory[19,20] and the renormalization group theory.[17,18] Since precise values[18] of $\mu$ from the renormalization group theory are available only for $d = 3$, we have calculated $\mu$ from the known formula[21] of the Wilson–Fisher $\epsilon$ ($=4 - d$) expansion to the order $\epsilon^2$ and $\epsilon^3$. The results are included in parentheses in column 4. It should be noted that the $\epsilon$ expansion is valid only for positive $\epsilon$, i.e., $d < 4$. The figure 8 in the fourth column for $d = 4$ is obtained[10] if the exponent $\eta$,[23] which governs the long-distance behavior of the spin–spin correlation function of the Ising model, vanishes. (We are not sure whether or not logarithmic corrections appear in $\eta$ at $d = 4$.)

Our results for $\mu$ involve an irrational number $\pi$ for $d \neq 4$, but only an integer at $d = 4$. This agrees with the prediction[10] that $\alpha$ is a fractional power of a logarithm. The value 8 is also in good agreement with our preliminary data[24] for self-avoiding walks in four dimensions. The value $\mu = 5.68$[18] for $d = 3$, which is believed to be most accurate, is between the second and third truncation values of the $\epsilon$ expansion. The question whether this also occurs for $d = 1$ and 2 has not been answered yet and lies outside the scope of the present investigation.

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