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Reduced Third Virial Coefficient for Linear Flexible Polymers in Good Solvents

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ABSTRACT: Effects of chain stiffness and three-segment interactions on the reduced third virial coefficient g ($\equiv A_3/A_2^2M$) for linear flexible chains in good solvents are theoretically investigated to explain the recent experimental finding that, in contrast to the two-parameter theory prediction, g remains positive when the radius expansion factor α_S approaches unity by lowering the polymer molecular weight M in a given good solvent. Here, A_2 and A_3 are the second and third virial coefficients, respectively. The stiffness effect on g is evaluated in the binary cluster approximation first by applying perturbatively Yamakawa and Stockmayer's wormlike bead model and then by combining the first-order result with the Stockmayer–Casassa theory of g for flexible chains. The excluded-volume parameter is transformed to α_S^3 using the combination of the Yamakawa–Stockmayer–Shimada theory and the Domb–Barrett equation for α_S. Finally, the effect of three-segment interactions is incorporated in a first-order perturbation approximation. The theoretical g thus calculated as a function of α_S^3 is found to agree satisfactorily with the published data for polystyrene and polyisobutylene in good solvents for α_S down to near unity.

Introduction

According to the two-parameter theory[1] for linear flexible chains, the reduced third virial coefficient g defined by A_3/A_2^2M is a universal function of the radius expansion factor α_S and vanishes at $\alpha_S = 1$. Here, A_2 and A_3 are the second and third virial coefficients, respectively, M is the polymer molecular weight, and α_S is defined by $\alpha_S^2 = \langle S^2\rangle/\langle S^2\rangle_0$, with $\langle S^2\rangle$ and $\langle S^2\rangle_0$ being the perturbed and unperturbed mean-square radii of gyration, respectively. In our recent work, it was shown that data of g for polystyrene[2] and polyisobutylene[3] in good solvents, when plotted against α_S^3, are approximately superimposed on a single curve and explained almost quantitatively by the early two-parameter theory of Stockmayer and Casassa[4] for g (combined with the original Flory equation[5] for α_S) in the region of α_S^3 above 2. However, when α_S^3 approached unity, the experimental g stayed far above zero, in contrast to the two-parameter theory prediction mentioned above. The purpose of the present study is to explain this discrepancy theoretically.

A similar discrepancy[6] between two-parameter theory and experiment is known for the interpenetration function Ψ [$\equiv A_2M^2/(4\pi^{3/2}N_A\langle S^2\rangle^{3/2})$, with N_A the Avogadro constant]. As α_S decreases, experimental Ψ in a given good solvent increases from the asymptotic value, while theoretical Ψ decreases toward zero. Recently, Yamakawa[7] explained this discrepancy as due to effects of chain stiffness on A_2 and α_S, on the basis of the Yamakawa–Stockmayer–Shimada theory[8-10] for the wormlike chain or the helical wormlike chain. We suspect that the same is responsible for part of the above-mentioned discrepancy in g if not all. Some effect of three-segment interactions is another factor to be considered, since recent experimental work[11] clearly shows A_3 to remain positive at the Θ point. Thus, in the present work, we first carry out a first-order perturbation calculation of g on Yamakawa and Stockmayer's wormlike bead model[8] and then combine the result with the Stockmayer–Casassa theory to obtain an approximate closed expression for g of flexible chains with a finite stiffness but in the binary cluster approximation. The effect of three-segment interactions is finally incorporated in a crude approximation.

First-Order Perturbation Coefficient for *g*

In the binary cluster approximation, the first-order expansion of A_3 in the wormlike bead model[8] may be expressed as

$$A_3 = \frac{N_A^{\ 2}}{3M^3\lambda^6}B_2^{\ 3}J + O(B_2^{\ 4}) \tag{1}$$

where

$$B_2 = \beta_2/l^2 \tag{2}$$

$$J = 8\left(\frac{3}{2\pi}\right)^{3/2}\int_0^L dt_1\int_0^L dt_2\int_0^L dt_3 \times (L-t_1)(L-t_2)(L-t_3)\, f(t_1,t_2,t_3) \tag{3}$$

$$f(t_1,t_2,t_3) = \left(\frac{2\pi}{3}\right)^{3/2}\int d\mathbf{R}_1\int d\mathbf{R}_2 \times G(\mathbf{R}_1;t_1)\, G(\mathbf{R}_2;t_2)\, G(\mathbf{R}_2-\mathbf{R}_1;t_3) \tag{4}$$

In these equations, λ^{-1} is the Kuhn segment length, L the contour length of each chain, β_2 the binary cluster integral for the interaction between a pair of beads, l the bead spacing, and $G(\mathbf{R}_i;t_i)$ the distribution function of the end-to-end vector $\mathbf{R}_i$ for the contour distance t_i in chain i (i = 1, 2, 3); all the lengths except A_3 are measured in units of λ^{-1}.

Similarly, A_2 is expanded as $A_2 = N_AL^2B_2/2M^2\lambda^3 + O(B_2^2)$,[8] so that we have

$$g \equiv A_3/A_2^{\ 2}M = Cz + ... = C\bar{z} + ... \tag{5}$$

where

$$C = 4(2\pi/3)^{3/2}J/(3L^{9/2}) \tag{6}$$

$$z = (3/2\pi)^{3/2}B_2L^{1/2} \tag{7}$$

$$\bar{z} = z/\alpha_S^{\ 3} \tag{8}$$

Our task here is to evaluate the first-order coefficient C and hence J given by eq 3 with eq 4.

For $G(\mathbf{R};t)$ [$=G(\mathbf{R}_i;t_i)$] in eq 4, we use the second Daniels approximation[12] (the second-order deviation from the coil

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limit) and the second-order deviation from the rod limit;[13] i.e.,

$$G(\mathbf{R};t) = \left(\frac{3}{2\pi t}\right)^{3/2} \exp\left(-\frac{3R^2}{2t}\right) \times \left[1 - \frac{5}{8t} + \frac{2R^2}{t^2} - \frac{33R^4}{40t^3} - \frac{79}{640t^2} - \frac{329R^2}{240t^3} + \frac{6799R^4}{1600t^4} - \frac{3441R^6}{1400t^5} + \frac{1089R^8}{3200t^6} + \ldots\right] \quad \text{for } t \gg 1 \quad (9)$$

$$G(\mathbf{R};t) = \frac{1}{4\pi t^2}(1 + t/3 + t^2/15 + \ldots)\,\delta(\xi) + \frac{1}{4\pi R}(t/3 + t^2/15 + \ldots)\,\frac{\mathrm{d}\delta(\xi)}{\mathrm{d}\xi} + \frac{1}{4\pi R}(7t^3/90 - \ldots)\,\frac{\mathrm{d}^2\delta(\xi)}{\mathrm{d}\xi^2} + \ldots \quad \text{for } t \ll 1 \quad (10)$$

where

$$\xi = R - t$$

and δ denotes the Dirac delta function. Note that in the limit of $t = 0$, eq 10 reduces to the distribution function for rods

$$G(\mathbf{R};t) = \frac{1}{4\pi t^2}\,\delta(R - t) \quad (11)$$

Substitution of eqs 9 and 10 or 11 into eq 4, followed by integration, gives

$$f(t_1,t_2,t_3) = \frac{1}{(t_1 + t_2 + t_3)^{3/2}}\left\{1 + \frac{7}{8(t_1 + t_2 + t_3)} + \frac{4483}{1920(t_1 + t_2 + t_3)^2}\right\} \quad \text{for } t_1,t_2,t_3 \gg 1 \quad (12)$$

$$\lim_{t_3 \to 0} f(t_1,t_2,t_3) = \frac{1}{(t_1 + t_2)^{3/2}}\left\{1 + \frac{1}{8(t_1 + t_2)} + \frac{1223}{1920(t_1 + t_2)^2}\right\} \quad \text{for } t_1,t_2 \gg 1 \quad (13)$$

$$\lim_{t_2,t_3 \to 0} f(t_1,t_2,t_3) = \frac{1}{t_1^{3/2}}\left\{1 - \frac{5}{8t_1} - \frac{79}{640t_1^2}\right\} \quad \text{for } t_1 \gg 1 \quad (14)$$

The resulting expression of $f(t_1,t_2,t_3)$ for t_i ($i = 1, 2, 3$) $\ll 1$, denoted below as $f_0(t_1,t_2,t_3)$, is lengthy and omitted here.

Following Yamakawa and Stockmayer,[8] we assume that eq 12 is valid for t_i ($i = 1, 2, 3$) $\geq \sigma$ ($\sigma = 0.96093$) and $f_0(t_1,t_2,t_3)$ for $0 < t_i$ ($i = 1, 2, 3$) $< \sigma$. Further, building on eqs 13 and 14, we approximate $f(t_1,t_2,t_3)$ for t_1 and $t_2 \geq \sigma$ and $0 < t_3 < \sigma$ and that for $t_1 \geq \sigma$ and $0 < t_2,t_3 < \sigma$, respectively, by

$$f(t_1,t_2,t_3) = \frac{1}{(t_1 + t_2)^{3/2}}\left[a_0(x) + \frac{a_1(x)}{t_1 + t_2} + \frac{a_2(x)}{(t_1 + t_2)^2}\right] \quad (t_1,t_2 \geq \sigma \text{ and } 0 < t_3 < \sigma) \quad (15)$$

and

$$f(t_1,t_2,t_3) = \frac{1}{t_1^{3/2}}\left[b_0(y) + \frac{b_1(y)}{t_1} + \frac{b_2(y)}{t_1^2}\right] \quad (t_1 \geq \sigma \text{ and } 0 < t_2,t_3 < \sigma) \quad (16)$$

where

$$a_j(x) = a_{j0} + a_{j1}(x_0)x + a_{j2}(x_0)x^2 + a_{j3}(x_0)x^3 \quad (j = 0, 1, 2) \quad (17)$$

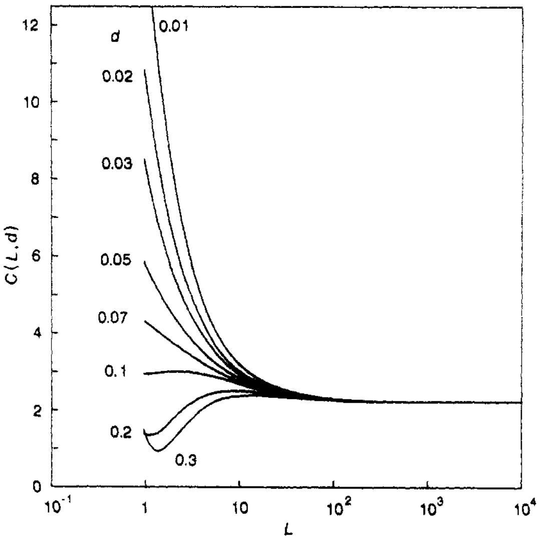

Figure 1. First-order coefficient $C(L,d)$ plotted against log L for indicated d values.

$$b_j(y) = b_{j0} + b_{j1}(y_0)y + b_{j2}(y_0)y^2 + b_{j3}(y_0)y^3 \quad (j = 0, 1, 2) \quad (18)$$

with

$$x = \frac{t_3}{t_1 + t_2}, \qquad x_0 = \frac{\sigma}{t_1 + t_2} \quad (19)$$

$$y = \frac{t_2 + t_3}{t_1}, \qquad y_0 = \frac{2\sigma}{t_1} \quad (20)$$

$$a_{00} = 1, \qquad a_{10} = \frac{1}{8}, \qquad a_{20} = \frac{1223}{1920} \quad (21)$$

$$b_{00} = 1, \qquad b_{10} = -\frac{5}{8}, \qquad b_{20} = -\frac{79}{640} \quad (22)$$

The coefficients a_{jk} and b_{jk} for $k \geq 1$ were determined as functions of x_0 and y_0 by joining the f in eq 15 or 16 and that in eq 12 at $x = x_0$ or $y = y_0$ (see ref 8 for the procedure). The difference between the values of $f(\sigma,\sigma,\sigma)$ in eq 16 and $f_0(\sigma,\sigma,\sigma)$ was no more than 3.2%.

With the f's obtained in this way, J in eq 3 was evaluated for $L \geq \sigma$. In actuality, the triple integration in this equation for $0 < t_i$ ($i = 1, 2, 3$) $< \sigma$ was carried out by introducing a cutoff parameter d, i.e., for $d < t_i < \sigma$, and the result obtained in powers of d was truncated at two leading terms.

The final expression for $C(L,d)$ ($\equiv C$) is too lengthy, and we present its expression for large L. It reads

$$C(L,d) = 2.219\{1 + 3.143L^{-1} - L^{-3/2}[6.536 + 2.790 \ln d + d(3.669 - 4.639 \ln d)] - 11.216L^{-2} + L^{-5/2}[14.427 - 0.1372 \ln d + d(20.967 - 6.958 \ln d)] - 10.215L^{-3}\} \quad (23)$$

which is accurate within an error of 2.8% for $L \geq 3$ and $d \lesssim 0.3$. The C value of 2.219 in the coil limit agrees with that obtained from the known first-order coefficient 1.664 in the z expansion of A_3 in the two-parameter theory.[1] Importantly, the first-order deviation of C from this limit is of order L^{-1}, differing from the cases of α_S and A_2 for which the corresponding deviations are of order $L^{-1/2}$.[8,10]

In Figure 1, the values of $C(L,d)$ are plotted against log L for different d values. Below $L \sim 10$, C is larger for a smaller d, i.e., for a higher stiffness; note that d is of the order 0.01 for typical stiff chains and about 0.3 for flexible chains.[7,8] As L increases above 50, C for any indicated d abruptly converges to the coil-limiting value 2.219, thus showing that the effect of chain stiffness on g itself is negligible for $L \gtrsim 50$. This may be a reflection of the fact that C in eq 23 contains no $L^{-1/2}$ term. A point to note in the figure is that for flexible chains, i.e., for $d \sim 0.3$, the stiffness effect contributes toward lowering g unless L is larger than 10.

Approximate Closed Expression for *g*

As mentioned in the Introduction, the Stockmayer–Casassa theory[4] describes fairly well our experimental g data for $\alpha_S^3 \gtrsim 2$. We therefore use it to derive an approximate closed expression for g applicable to flexible chains with finite stiffness and large excluded volume.

First, we searched for an empirical g vs $\bar{z}$ relation that gives a close agreement with the tabulated g values of Stockmayer and Casassa[4] and also the correct first-order coefficient 2.219 in the vicinity of $\bar{z} = 0$. The desired expression thus found is

$$g_2 = \frac{2.22\bar{z}}{(1 + 18\bar{z} + 12.6\bar{z}^2)^{1/2}} \tag{24}$$

where the subscript 2 attached to g indicates explicitly that g given by eq 24 is based on the binary cluster approximation. Next, the effect of chain stiffness is incorporated into this equation in the same way as that taken by Yamakawa et al.[7–9] for α_S and A_2, i.e., by replacing $\bar{z}$ with a scaled parameter $\hat{z}$ defined by

$$\hat{z} = \frac{C}{2.22}\bar{z} \tag{25}$$

Thus we have

$$g_2 = \frac{2.22\hat{z}}{(1 + 18\hat{z} + 12.6\hat{z}^2)^{1/2}} \tag{26}$$

It should be noted that, in the coil limit, $\hat{z}$ becomes equal to $\bar{z}$ and hence eq 26 reduces to eq 24.

To transform the g_2 vs $\hat{z}$ relation to a g_2 vs α_S^3 relation, we adopt the combination[9] of the Yamakawa–Stockmayer perturbation theory[8] for wormlike bead chains and the Domb–Barrett equation[14] for flexible chains just for convenience. It reads

$$\alpha_S^2 = [1 + 10\tilde{z} + (70\pi/9 + 10/3)\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3]^{2/15} \times [0.933 + 0.067 \exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \tag{27}$$

where

$$\tilde{z} = \frac{3}{4}K(L)z \tag{28}$$

with[10]

$$\begin{aligned} K(L) &= 4/3 - 2.711L^{-1/2} + 7/(6L) \qquad \text{for } L > 6 \\ &= L^{-1/2} \exp(-6.611L^{-1} + 0.9198 + 0.03516L) \qquad \text{for } L \leq 6 \end{aligned} \tag{29}$$

We note again that eq 27 reduces to the original Domb–Barrett equation in the coil limit.

With eqs 25–29, it is possible to calculate g_2 as a function of α_S^3 for a given set of B_2 and d. The solid curves in Figure 2 represent the resulting values for a fixed d of 0.3 and the indicated B_2 values. The dot–dash line refers to the coil limit. It can be seen that the solid lines considerably shift to the left from this coil line despite the fact that C for $d = 0.3$ is smaller than the coil-limiting value for $L \lesssim 10$. The shift manifests itself in the stiffness effect on α_S which leads to a considerable decrease in α_S^3 from the two-parameter theory value for a given L and surpasses the stiffness effect of lowering g_2. The positive intercept (at $\alpha_S^3 = 1$) of each solid curve implies that intramolecular excluded-volume effects diminish to zero at a nonzero L where intermolecular excluded-volume effects remain appreciable.

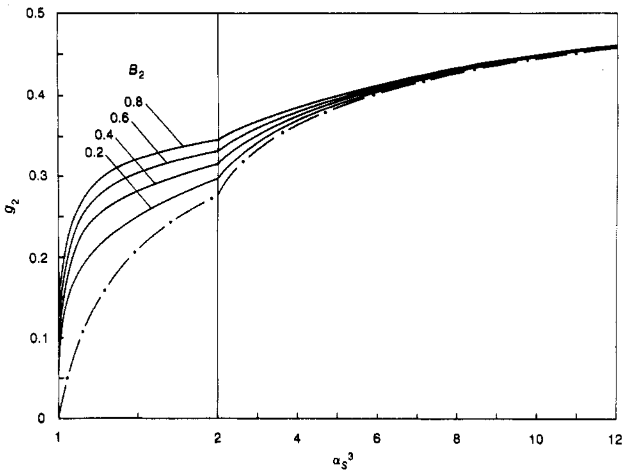

Figure 2. Values g_2 calculated from eqs 25–29 for $d = 0.3$ and indicated B_2 values. The dot–dash line represents the coil-limiting values.

Effect of Three-Segment Interactions

Since three-segment interactions do not vanish at Θ in general, A_2 and A_3 in good solvents should also contain certain contributions from such residual interactions unless binary interactions are overwhelming. According to perturbation calculations[15–17] on long flexible chains with three-segment interactions, a sum of β_2 and constant × β_3 (the reduced ternary cluster integral) appears in A_2 and the end-distance expansion factor (essentially the same as α_S) as if it were a single parameter. Thus, the binary cluster approximation may be formally valid for these properties if the sum β_2 + constant × β_3 is regarded as an effective binary cluster integral.

On the other hand, β_3 appears without the counterpart in the first-order term of A_3.[16,18] Hence, it seems reasonable to take into account three-segment interactions only for A_3 and to express g as

$$g = g_2 + g_3 \tag{30}$$

with

$$g_3 = \frac{A_3{}^*}{A_2{}^2 M} \tag{31}$$

Here, $A_3{}^*$ denotes the contribution purely from β_3 to A_3. It may be expressed in a first approximation as

$$A_3{}^* = \frac{N_A{}^2 L^3 B_3}{3M^3\lambda^6} \tag{32}$$

with B_3 defined by β_3/l^3. Since $A_3{}^*$ in this equation is independent of M, g_3 is expected to decrease rather sharply with an increase in M. If A_2 in eq 31 is approximated by the single-contact term, i.e., $A_2 = N_A L^2 B_2 / 2M^2\lambda^3$, g_3 becomes

$$g_3 = \frac{4B_3}{3B_2{}^2 L} \tag{33}$$

which contains only one additional parameter B_3.

Comparison between Theory and Experiment

The theory for g presented above contains three unknowns, B_2, B_3, and d. In its comparison with data for

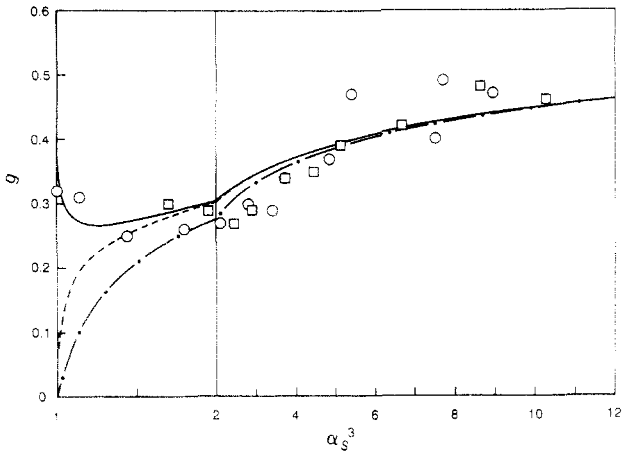

Figure 3. Comparison between theoretical and experimental g values: solid line, $g_2 + g_3$ from eq 30 with eqs 26 and 33 for $B_2 = 0.25$, $B_3 = 0.025$, and $d = 0.3$; dashed line, g_2; dot–dash line, coil limit; circles, PS in benzene;[2,19] squares, PIB in cyclohexane.[3]

polystyrene (PS) in benzene[2,19] and polyisobutylene (PIB) in cyclohexane[3] made below, we assume that $B_2 = 0.25$, $B_3 = 0.025$, and $d = 0.3$ for both systems. The last parameter value, reasonable for flexible chains, is the same as that used by Yamakawa[7] for explaining the behavior of Ψ for polystyrene in benzene. With regard to the first two parameters, the following remarks are pertinent.

When PS in the unperturbed state is modeled[20] by the wormlike chain with $\lambda^{-1} = 2$ nm and $M_L = 390$ nm^{-1}, where M_L is the shift factor defined by $M_L = \lambda M/L$, eq 27 with $B_2 = 0.23$ quantitatively describes the M dependence of $\langle S^2 \rangle$ for the polymer in benzene;[9] though according to recent work by Yamakawa and co-workers,[21] the unperturbed PS chain is better modeled by the helical wormlike chain, its helical nature is weak and ignored here. The value of B_2 for PIB in cyclohexane is estimated to be 0.25 from the previously determined M dependence[3] of $\langle S^2 \rangle$ (see ref 22 for the procedure), with λ^{-1} and M_L for the PIB chain taken to be 1.4 nm and 241 nm^{-1},[23] respectively. Thus, the B_2 of 0.25 assumed above is consistent with the available $\langle S^2 \rangle$ data for both PS and PIB. On the other hand, the B_3 value of 0.025 is a rough estimate for PS based on the assumption that the ternary cluster integral is insensitive to solvent conditions; this B_3 value is obtained from eq 32 with A_3 (at Θ) $\approx 4 \times 10^{-4}$ mol g^{-3} cm^6 (see ref 11) and the above wormlike chain parameters[20] for PS. For PIB, no precise value for A_3 (at Θ) is yet unknown. Taking A_3 (at Θ) to be 5×10^{-4} mol g^{-3} cm^6, we obtain $B_3 = 0.021$ for PIB, a value quite close to 0.025 for PS.

In Figure 3, the solid curve of g vs α_S^3 computed from eqs 26, 30, and 33 is compared with the reported data for PS in benzene[2,19] (the circles) and PIB in cyclohexane[3] (the squares). Here, the dashed and dot–dash lines refer, respectively, to g_2 and the coil-limiting g in the binary cluster approximation. It can be seen that the solid curve closely fits the data points over the entire range of α_S^3 indicated. The contribution of g_3 to g is significant in the vicinity of $\alpha_S^3 = 1$ and becomes negligible at $\alpha_S^3 \approx 1.5$, where the solid curve almost merges with the dashed line. If Yamakawa's closed expression[7] (the combination of Barrett's A_2 theory[24] for flexible chains and the Yamakawa–Stockmayer perturbation theory[8] for wormlike bead chains) is used for A_2 in eq 31, the contribution of g_3 diminishes somewhat more slowly with increasing α_S^3, but the resulting relation between g and α_S^3 does not differ much from that shown in the figure.

In conclusion, the effects of chain stiffness and three-segment interactions investigated in this work give a satisfactory explanation of the behavior of experimental g in the region of α_S^3 below 2 for PS in benzene and PIB in cyclohexane. The former effect on the g vs α_S^3 relation comes primarily from α_S, differing from the case of the interpenetration function. When α_S^3 exceeds 2, the two effects become almost insignificant and do not impair the previously observed agreement between the original Stockmayer–Casassa theory and the experimental data for α_S^3 above 2.

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