Note on the asymptotic isomer count of large fullerenes

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Abstract The leading term in the large-\(N\) asymptotics of the isomer count of fullerenes with \(N\) carbon atoms is extracted from the published enumerations for \(N \leq 400\) with the help of methods of series analysis. The uncovered simple \(N^9\) scaling is distinct from isomer counts of most classes of chemical structures that conform to mixed exponential/power-law asymptotics. The second leading asymptotic term is found to be proportional to \(N^{25/3}\). A conjecture concerning isomer counts of the IPR fullerenes is also formulated.

Keywords Fullerenes · Isomer count · Series analysis

1 Introduction

Recent advances in graph-theoretical algorithms have opened new vistas for enumeration of chemical isomers. In particular, significant progress has been achieved in the case of fullerenes \(C_N\), of which all structures with \(N \leq 400\) have now been generated [1,2]. The availability of these data has prompted speculations concerning the behavior of the fullerene isomer counts at the \(N \to \infty\) limit, both the \(N^9\) [3] and \(N^{19/2}\) [4] asymptotics being inferred from crude log–log plots and supported by heuristic arguments. For the reason spelled out in the following, this simple power-law scaling appears unlikely at the first glance.
Complete information about isomer counts for a class of chemical species is encoded in the generating function \( F(t) \) given by the formal series

\[
F(t) = \sum_{k=1}^{\infty} M(k) t^k,
\]

where \( M(k) \) is the number of isomers comprising \( k \) units (such as atoms, bonds, rings, etc.). Since, in general, \( M(k + 1) \geq M(k) \) for all \( k > 0 \), the series \( (1) \) possesses a finite radius of convergence. Consequently, \( F(t) \) possesses at least one singular point, at which it behaves like \( (t_c - t) \xi_c \), where \( 0 < t_c \leq 1 \). The smallest critical point \( t_c \) and the corresponding critical exponent \( \xi_c \) determine the leading term in the large-\( k \) asymptotics of \( M(k) \), which reads

\[
M(k) = A t_c^{-k} k^{-(\xi_c + 1)} + \cdots,
\]

where \( A \) is a constant. Typically, \( t_c < 1 \) (e.g. ca. 0.35518 for alkanes \([5]\), ca. 0.20915 for polyenes \([5]\), and \( \frac{1}{5} \) for catafusenes \([5–7]\)), giving rise to the mixed exponential/power-law asymptotics \((2)\). On the other hand, the alleged power-law scaling of the fullerene isomer counts would imply \( t_c = 1 \).

In order to investigate this matter, in this note we invoke the mathematical formalism of series analysis that is commonly used in lattice statistics \([8]\). Such a formalism has been previously employed in successful extraction of the asymptotic isomer counts of several classes of chemical structures \([5]\).

2 Series analysis

Let \( M(k) \) be the number of isomers of the \( C_{2k} \) fullerene. Let \( U_0 = 1, W_0 = 0 \), and \( \{U_k, k = 1, \ldots m\}, \{V_k, k = 0, \ldots m\}, \{W_k, k = 1, \ldots m\} \) be the solution of the system of equations

\[
\sum_{j=0}^{m} \left[ U_j (k - j)^2 + V_j (k - j) + W_j \right] C_{k-j} = 0, \quad k = 1, \ldots, 3m - 2,
\]

where

\[
C_k = \begin{cases} 
M(k + n) & \text{for } k \geq 0 \\
0 & \text{for } k < 0 
\end{cases}.
\]

Let

\[
Q(z) = z \sum_{k=0}^{m} U_k z^k
\]

and

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Fig. 1  The deviations of the estimates $z_c$ from 1 versus $n$ for $1 \leq m \leq 20$ (gray), $21 \leq m \leq 40$ (red), and $41 \leq m \leq 66$ (black) (Color figure online)

$$R(z) = \sum_{k=0}^{m} (U_k + V_k) z^k. \tag{6}$$

The smallest positive root $z_c$ of $Q(x)$ and the quantity $\eta_c = 1 - R(z_c)/Q'(z_c)$ yield unbiased estimates for $t_c$ and $\zeta_c$, respectively [5,8]. In general, the accuracy of these estimates increases with both $n$ and $m$. 
3 Results and conclusions

Application of the aforedescribed formalism to the isomer counts reported in Ref. [1] produces estimates that clearly converge to $t_c = 1$ (Fig. 1) and $\zeta_c = -10$ (Fig. 2). Thus, the leading term proportional to $N^9$ in the large-$N$ asymptotics of the isomer count of fullerenes with $N$ carbon atoms is now firmly established (although not rigorously proven).
The present result imposes the same asymptotics for the isomer count $M_{IPR}(k)$ of the IPR fullerenes with $2k$ carbon atoms as $0 < M_{IPR}(k) < M(k)$ and $\lim_{k \to \infty} M_{IPR}(k)/M(k) \to 1$. Curiously, inspection of the published data [1] allows one to formulate the following conjecture (see Fig. 3):

For all $k > 53$, $M(k - 24) < M_{IPR}(k) < M(k - 25)$, i.e. for all $N > 106$, the number of the IPR fullerene isomers with $N$ carbon atoms is bracketed by the total numbers of isomers of the $C_{N-50}$ and $C_{N-48}$ fullerenes.

The second leading term in the large-$k$ asymptotics of $M(k)$ is also of interest. As revealed by the plot of $M(k)/k^9$ versus $k^{-2/3}$ (Fig. 4), this term scales simply as $k^{25/3}$ and is negative. The combination of the $N^9$ and $N^{25/3}$ asymptotics explains the apparent $N^{19/2}$ scaling deduced from a crude log–log plot [4].

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